



26th ISPPCC

International Symposium on the
Photochemistry and Photophysics of
Coordination Compounds
and
y-ISPPCC 2025

7 – 12 July 2025
Trifiletti Theater and Villa Vaccarino
Milazzo (ME) - Italy

<https://isppcc2025.unime.it/>



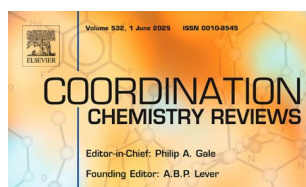
PATRONAGE



Comune di Milazzo



SPONSORS



A Note of Welcome

Dear ISPPCC 2025 participants,

It is our great pleasure to welcome you to the 26th ISPPCC in Milazzo. ISPPCC has always been the host for seminal developments of novel perspectives and research fields, and we have no doubt that it will respect the tradition even in this occasion. We are excited to hearing about the latest developments in the field, discussing research, and revitalizing and starting collaborations. And – not less important, particularly in these weird times – to offer all of us the possibility of interacting, sharing ideas and information, and reinforce and create new friendships.

We also welcome the success of the satellite Young-ISPPCC, which gather more than 60 PhD and post-docs from all over the world and testifies for the continued attraction of our favorite science. We are sure that all of them – as well as all the participants – will benefit from the friendly and rather informal atmosphere of the ISPPCC. We also would like to thank our sponsors for their unvaluable financial support and in particular the Municipality of Milazzo, who offered us its historical theater for the conferences. Finally, we hope that you will have the time to enjoy the lively city of Milazzo and to explore its very interesting surroundings, including the Eolian Islands.

We wish you all a successful and enjoyable Symposium!

The Local Organizing Committee

INTERNATIONAL SCIENTIFIC COMMITTEE

Sebastiano Campagna

Peter Ford

James McCusker

Felix Castellano

Konrad Szacilowski

Wojciech Macyk

Antonin Vlcek

Julia Weinstein

Kenneth Lo

Michael Wolf

Benjamin Dietzek-Ivanšić

Sven Rau

26th ISPPCC ORGANIZING COMMITTEE

Sebastiano Campagna

Fausto Puntoriero

Scolastica Serroni

Francesco Nastasi

Giuseppina La Ganga

Antonio Santoro

Maurilio Galletta

Ambra Maria Cancelliere

Ivana Bonaccorsi

y-ISPPCC 2025 ORGANIZING COMMITTEE

Alessandro Amadeo

Amine Assel

Salvatore Genovese

Federica Giorgianni

Claudio La Falce

Giuliana Lazzaro

Martina Mazzaferro

Arindam Saha

A Brief History of the International Symposium on the Photochemistry and Photophysics of Coordination Compounds (ISPPCC) (After Vancouver edition)



The conference started as meetings among a group of friends, mainly promoted (among others) by Vincenzo Balzani, Arnd Vogler, Nick Serpone, Morton Hoffman (sorry for disregarding other important members of the seminal group). Important roles in promoting the first meetings (and attending or organizing them) were played by David Whitten, Arthur Adamson, Peter Ford, Charles Giannotti, Thomas J. Meyer, Franco Scandola, Takeshi Ohno, Masaoki Furue. Even the same name, ISPPCC, was not used during the first editions (different names were in fact used, like “Reaction mechanism of photoinduced processes of transition metal coordination compounds”) and it was officially introduced only at the beginning of the 1980s. Some doubts remain about the exact years when the first three editions were held, but conventionally, 1974 is now considered as the year of the starting event.

- | | |
|-------------|---|
| 1974 | Mülheim, Germany (Ernst Koerner von Gustorf) |
| 1976 | Ferrara, Italy (Vittorio Carassiti, Franco Scandola, Vincenzo Balzani) |
| 1978 | Köln, Germany (H. F. Wastge) |
| 1980 | Montreal, Canada (Nick Serpone) |
| 1982 | Gif-sur-Yvette, Paris, France (Charles Giannotti) |
| 1984 | London, UK (Anthony Harriman) |
| 1987 | Elmau, Germany (Arnd Vogler, Hartmut Yersin)
<i>participants were snowed for several days in the conference hotel in the Alps (meeting was held in Spring in a Medieval Castle in mountain). ISPPCC becomes formally biennial.</i> |
| 1989 | Santa Barbara, USA (Peter Ford, Richard Watts)
<i>The logo of ISPPCC (octahedron) was introduced. Coordination Chemistry Reviews starts publishing ISPPCC proceedings, a tradition never interrupted.</i> |
| 1991 | Fribourg, Switzerland (Alexander von Zelewsky, Peter Belser) |
| 1993 | Sendai, Japan (Hiroshi Kobayashi, Takeshi Ohno, Masaoki Furue) |
| 1995 | Krakow, Poland (Zofia Stasicka, Grazyna Stochel)
<i>ISPPCC incorporates the existing “Symposium on the Photochemical and Thermal Reactions of Coordination Compounds (SPTROCC)” which took place in Europe.</i> |
| 1997 | Saint Michael’s College, Colchester, USA (Josh van Houten) |
| 1999 | Lipari, Italy (Sebastiano Campagna, Scolastica Serroni, Francesco Barigelli) |
| 2001 | Veszprém, Hungary (Attila Horwath, Otto Horwath) |
| 2004 | Hong Kong, China (Vivian W.-W. Yam, Chi-Ming Che)
<i>initially planned for 2003.</i> |

- 2005** Asilomar, CA, USA (Patrick Hoggard, Peter Ford)
- 2007** Dublin, Ireland (Han Vos, John Kelly)
- 2009** Sapporo, Japan (Moboru Kitamura, Masa-aki Haga, Osamu Ishitani)
- 2011** Strasbourg, France (Chantal Daniel, Luisa De Cola)
- 2013** Traverse City, USA (James McCusker, Felix Castellano)
- 2015** Krakow, Poland (Konrad Szacilowski, Wojciek Macyk)
- 2017** Oxford, UK (Antonin Vlcek, Julia Weinstein)
- 2019** Hong Kong, China (Kenneth K.-W. Lo)
Peter Ford is nominated honorary Chair and permanent member of the International Scientific Committee.
- 2022** Vancouver, Canada (Michael Wolf)
initially planned for 2021, moved for COVID.
- 2023** Ulm, Germany (Benjamin Dietzek-Ivansic, Sven Rau)

General Information

Venue

The 26th ISPPCC will take place in Milazzo, Italy, hosted at the historic Teatro Trifiletti and the nearby Villa Vaccarino.

The Congress venue will be in the heart of city centre, at the “**Trifiletti Theater**” built in 1911 on a project by Letterio Savoja, on the initiative of Stefano Trifiletti, an enterprising and multifaceted entrepreneur who intended to create a multipurpose structure capable of hosting the most varied forms of entertainment. Inaugurated on 29 June 1912, it covered an area of over one thousand square meters in which 47 boxes and three hundred seats were included in the beautiful exhibition hall. From 1912 to the seventies the greatest interpreters of opera, prose and light theatre passed through it. Recently the theatre has been renovated with new seats, air conditioning, and other useful facilities to meet more comfortable standards.



A short walk away lies **Villa Vaccarino**, an elegant 19th-century residence surrounded by a charming garden. Once a private villa, it now serves as a prestigious venue for institutional and cultural activities, maintaining its historical charm and architectural integrity.

Presentations

Speakers are required to give their ppt files to the ISPPCC technicians in advance of their own session and check the presentation. Please note that both PC and McIntosh computers are available.

Poster exhibition

Posters will be displayed at the backstage of Trifiletti Theater. Panels will be provided, as well materials to hung up the posters (maximum size: 100 cm height, 70 cm wide). Access to the backstage will be from the main stage and from a hallway near the stage.

Posters for the Poster Session 1 (even numbers, planned for July 9 evening) have to be hung during coffee breaks or lunch time of July 9 and must be removed before July 10, 14:50.

Posters for the Poster Session 2 (odd numbers, planned for July 11 afternoon) can be hung during lunch time of July 11 or coffee breaks of July 11 and must be removed before July 12, 16:40.

Welcome Cocktail and Coffee Breaks

Welcome cocktail and coffee breaks for ISPPCC will be offered in the garden of **Villa Vaccarino**, a nineteenth century Villa about 150 m away from Trifiletti Theater. When you exit the main entrance of the Theater, turn left and you will find Villa Vaccarino at the end of the road.

Social Excursions

The social excursions—both on foot and by boat—will take place within the **Marine Protected Area of Capo Milazzo**, a stunning natural reserve that showcases the region's exceptional marine biodiversity and scenic beauty.

This protected area encompasses dramatic coastal cliffs, hidden coves, and crystal-clear waters rich in marine life, including posidonia meadows, octopuses, groupers, and, at times, dolphins. Participants will have the opportunity to explore the “**Pool of Venus**”, a natural rock basin nestled between the sea and the cliffs, steeped in local myth and legend. The walking excursion offers breathtaking panoramic views, while the boat tour provides a unique perspective of Milazzo's coastline and the promontory's volcanic origins.

The Marine Protected Area is not only a place of ecological significance but also a site of historical and cultural interest, dotted with ancient paths, watchtowers, and traces of past civilizations.

Where to eat

Milazzo is a charming coastal town and popular tourist destination, especially during the summer season. Just steps away from the conference venue, Teatro Trifiletti, attendees will find a wide range of lunch options, including traditional Sicilian *rostiticcerie*, patisseries, and restaurants offering everything from quick snacks to full meals.

Please note that, due to the tourist season, some places may be busy during peak hours. However, it is easy to find a local café or bar where you can enjoy a quick **Sicilian granita with brioche** or a freshly made **ricotta cannolo**.

To make your stay more convenient, we have arranged **discounts** with selected restaurants and bars near the conference venues. These discounts are available upon showing your **conference badge** when ordering.

Here is a short list of participating establishments you may wish to explore while enjoying your time in Milazzo:

RESTAURANTS

RESTAURANT “RIVIERA LIDO”

Strada Panoramica Milazzo

Cell. +39 334 258 1950 – 090 928 3456

Email: info@hotelrivieralido.it

Offer: -10% on the à la carte menu and/or €35 fixed menu

RESTAURANT “MACCHIA NERA”

Via Marina Garibaldi 275, Milazzo

Tel. 090 922 3249

Offer: -15% on the à la carte menu

RESTAURANT “DA FILIPPO”

Via Marina Garibaldi 241, Milazzo

Tel. 090 928 1951 – 392 181 0381

Offer: -10% on the à la carte menu

OSTERIA “ADAGIO ADAGIO”

Via Umberto I° 181, Milazzo

Tel. 090 914 6252

Offer: -10% on the à la carte menu and/or €35 fixed menu

RESTAURANT “PETIT HOTEL”

Via Dei Mille 37, Milazzo

Tel. 090 928 6784

Email: info@petithotelmilazzo.com

Offer: -10% on the à la carte menu and/or €35 fixed menu

OSTERIA “HYCESIA”

Via Migliavacca 3, Milazzo

Tel. 090 956 0746 – 348 510 6315

Offer: -10% on the à la carte menu and/or €35 fixed menu

RESTAURANT “MILAZZO”

Via Acqueviole 78, Milazzo

Tel. 090 922 4061

Email: info@hotelmilazzo.net

Offer: €35 fixed menu

Cafés/Pastry Shops/Takeaways/Sandwich Shops

“CAFFÈ NETTUNO”

Via Luigi Rizzo 4, Milazzo

Tel. 090 928 1615

Café, Pastry, Gelato, Takeaway

Offer: -10% on all products

“CHANTILLY CAFÉ”

Via Cumbo Borgia 43, Milazzo

Tel. 090 922 9099

Email: info@chantillycafe.it

Café, Pastry, Gelato

Offer: -10% with a minimum spend of €20

“SCOTCH BAR”

Via Cassisi, Milazzo

Tel. 090 928 2106

Café, Pastry, Gelato

Offer: -10% on all products

Sandwich Shop “STUZZIKOSA”

Via Domenico Piraino 11, Milazzo

For reservations: Tel. 347 090 9657

Sandwich and 500 ml of water €5

“RED MOON CAFÉ”

Via Risorgimento 191, Milazzo

Tel. 090 958 7864

Café, Pastry, Gelato

Offer: -10% on all products

Things to Do in Milazzo

Milazzo offers a unique blend of natural beauty, historical heritage, and vibrant local culture. Whether you're staying for just a few days or exploring the area before or after the conference, here are some top recommendations:

1. Explore the Castle of Milazzo

One of the largest fortified citadels in Sicily, the **Castello di Milazzo** is a remarkable site with layers of history—from ancient Greek foundations to Arab, Norman, and Spanish influences. Enjoy panoramic views over the town and sea from its walls.

2. Visit the Old Town (Borgo Antico)

Stroll through the charming **old quarter**, with its narrow alleys, historic churches, and small artisan shops. It's a perfect place for a relaxing walk and a taste of local life.

3. Relax at the Beach

Milazzo boasts both **sandy and rocky beaches**, with crystal-clear waters ideal for swimming and sunbathing. The **Ponente Beach** is popular for sunsets, while the **Levante side** offers a quieter, more natural setting.

4. Discover the Pool of Venus (Piscina di Venere)

This natural rock pool at the tip of the Milazzo Peninsula is one of the area's most magical spots. A short hike leads to this secluded cove, perfect for a dip or a photo.

5. Take a Boat Tour

Explore the **Marine Protected Area of Capo Milazzo** by sea. Boat tours offer a chance to admire the rugged coastline, sea caves, and maybe even spot dolphins.

6. Enjoy Local Cuisine

Savor Sicilian Street food like **arancini** and **pitoni**, or sit down for fresh seafood and traditional pasta dishes. Don't miss local desserts such as **cassata**, **granita with brioche**, and the famous **cannolo**.

7. Day Trips to the Aeolian Islands

Milazzo is the main port for ferries to the **Aeolian Islands**, a UNESCO World Heritage site. Consider a day trip to Lipari, Vulcano, or Stromboli if your schedule allows.

How to arrive

The main port connecting the mainland to the Aeolian Islands is Milazzo. As for the car, not all islands have driveways and those who possess them, that is, Lipari, Vulcano, Salina, and Filicudi, may be subject to restrictions, especially in summer. Also adjacent to the port of Milazzo area is provided with a good service of guarded parking lots, for those wishing to reach the Aeolian starting from Milazzo.

LibertyLines (<http://www.libertylines.it/>). Siremar (<https://carontetourist.it/it/siremar>)

Useful Contacts and Local Services

During your stay in Milazzo, here are some essential services and emergency contacts located near the conference area:

- **Municipal Police (Polizia Municipale)**
Via XX Settembre, 98057 Milazzo (ME)
Responsible for traffic, local regulations, and public safety.
- **Milazzo Hospital (Ospedale di Milazzo)**
Via Francesco Crispi, 98057 Milazzo (ME)
The main medical facility in town, offering emergency and general care.
- **Carabinieri Station (Stazione dei Carabinieri)**
Via Giorgio Rizzo, 98057 Milazzo (ME)
National police force responsible for law enforcement and public order.
- **Post Office (Ufficio Postale)**
Via XX Settembre, 13, 98057 Milazzo (ME)
Services include mail, parcels, ATM access, and other basic utilities.

y-ISPPCC 2025

time	July 7	time	July 8
8:30	Registration y-ISPPCC	9:00-9:15	Francesca Mancini
9:40-09:50	opening	9:15-9:30	Oussama Bindech
09:50-10:05	Yoan Fréroux	9:30-9:45	Fumika Sueyoshi
10:05-10:20	Marius Müßler	9:45-10:00	Minli Zhang
10:20-10:35	Jie Ying Chen	10:00-10:15	Elkhansa Elbashier
10:35-10:50	Xiao Ma	10:15-10:30	Andrea Mantovani
10:50-11:05	Noémie Chantry	10:30-11:00	<i>Coffee break</i>
11:05-11:35	<i>Coffee break</i>	11:00-11:15	Baldeep Sidhu
11:35-11:50	Laura Duncan	11:15-11:30	Hirohisa Yanagikawa
11:50-12:05	Martin Pižl	11:30-11:45	Nicolò Quadrio
12:05-12:20	Dorothee S. Wagner	11:45-12:00	Arindam Saha
12:20-12:35	Federico Droghetti	12:00-12:15	Greta Fogar
12:35-12:50	Stefano Scoditti	12:15-12:30	Yu Hui Lin
12:50-14:00	<i>Lunch time</i>	12:30-13:45	<i>Lunch time</i>
14:00-14:15	Emily L. Race	13:45-14:00	Federica Ruani
14:15-14:30	Marta Costa Verdugo	14:00-14:15	Felix Glaser
14:30-14:45	Li-Ting Zhuo	14:15-14:30	Luis G. Alves do Nascimento
14:45-15:00	Amelia Kacperkiewicz	14:30-14:40	Closing remarks
15:00-15:15	Eleonor Windle		
15:15-15:30	Elena Dallerba		
15:30-16:00	<i>Coffee break</i>		
16:00-16:15	Chizuru Kasahara		
16:15-16:30	Sophia Lipinski		
16:30-16:45	Edoardo Marchini		
16:45-17:00	Simon Liedtke		
17:00-17:15	Ana Karem Vega Salgado		
17:15-17:30	Sergio Aranda Ruiz		
17:30-17:45	Othmane Essahili		

y-ISPPCC 2025 – Program

Monday, July 7th

8:30-9:40		ISPPCC Registration	
9:40-9:50		y-ISPPCC Opening	
Session 1			
Chair: Alessandro Amadeo (University of Messina)			
yOC-1	9:50-10:05	Yoann Fréroux (Université de Rennes, CNRS, ISCR) New antennae for photoswitchable luminescent lanthanide(III) complexes	
yOC-2	10:05-10:20	Marius Müßler (Universität Ulm) “If you like it you should put a ring on it” - Rotaxanes as supramolecular protective motifs in reductive heterodinuclear photocatalysis	
yOC-3	10:20-10:35	Jie Ying Chen (Fu Jen Catholic University) Characteristics of photoinduced quenching [Ru(tpm)(prbm)(NH ₃)] ²⁺ ions: density functional modeling and efficient metal center state quenching mechanisms	
yOC-4	10:35-10:50	Xiao Ma (University of Tokyo) Microscopic analyses of vapochromism in single particles	
yOC-5	10:50-11:05	Noémie Chantry (Université Catholique de Louvain) Exploring substituents effects on the anti-Kasha reactivity of binuclear Ru(II) photosensitizers	
11:05-11:35		Coffee Break	
Session 2			
Chair: Giuliana Lazzaro (University of Messina)			
yOC-6	11:35-11:50	Laura L. Duncan (Durham University) The development of Sulfur-containing, APTRA-derived fluorescent probes with specific Zn ²⁺ binding	
yOC-7	11:50-12:05	Martin Pižl (University of Chemistry and Technology Prague, University of Reading) Ultrafast time-resolved infrared spectroelectrochemistry of Ru(II) complexes for DNA studies	

yOC-8	12:05-12:20	Dorothee S. Wagner (<i>University of Basel</i>) Synthetic control over excited-state behavior of Nickel(II) complexes
yOC-9	12:20-12:35	Federico Droghetti (<i>University of Ferrara</i>) Light-driven CO ₂ reduction with a heptacoordinated Iron(II) polypyridine complex
yOC-10	12:35-12:50	Stefano Scoditti (<i>DIPC, University of Calabria, PMAS</i>) Exploring Ru(II) photocages for cancer therapy: a theoretical investigation of light-induced acetonitrile ligand release
12:50-14:00		Lunch Time
Session 3 Chair: Amine Assel (<i>University of Messina</i>)		
yOC-11	14:00-14:15	Emily L. Race (<i>University of Sheffield</i>) Ultrafast spectroscopic investigations into solvent and hetero-atom effects on the photophysics of Platinum(II)-based artificial photosynthetic systems
yOC-12	14:15-14:30	Marta Costa Verdugo (<i>DIPC, PMAS</i>) Photochemical behavior of Ruthenium(II) complexes in Choline Geranate (CAGE) ionic liquids
yOC-13	14:30-14:45	Li-Ting Zhuo (<i>Fu Jen Catholic University</i>) The characteristic of photo-induced ³ MLCT emission behavior for Ru-TBPZ chromophore, a Ru-(cyclometalated) chromophore
yOC-14	14:45-15:00	Amelia Kacperkiewicz (<i>University of Manitoba</i>) From rags to riches: enabling abundant metals to exhibit significant photophysical and magnetic properties using efficient ligand design
yOC-15	15:00-15:15	Eleanor R. Windle (<i>University College Dublin</i>) Contrasting excited state processes of Zn(II) and Cu(II) phthalocyanines
yOC-16	15:15-15:30	Elena Dallerba (<i>Curtin University</i>) Unveiling the potential of Iridium complexes in tissue imaging
15:30-16:00		Coffee Break

Session 4 Chair: Arindam Saha (<i>Université de Montréal</i>), Martina Mazzaferro (<i>University of Messina</i>)		
yOC-17	16:00-16:15	Chizuru Kasahara (<i>University Jena</i>) [FeFe]-H ₂ ase mimicking complex bearing two organic photosensitisers for photocatalytic H ₂ evolution
yOC-18	16:15-16:30	Sophia Lipinski (<i>Technical University of Munich</i>) Diphosphine design enables rainbow emitting Ag(I) complexes for light-emitting electrochemical cells
yOC-19	16:30-16:45	Edoardo Marchini (<i>University of Ferrara</i>) A deep insight into the role of basic additives in the charge injection of Fe(II)-based complexes
yOC-20	16:45-17:00	Simon A. Liedtke (<i>Lund University</i>) Reaction-diffusion simulations of photoredox processes in solution
yOC-21	17:00-17:15	Ana Karem Vega Salgado (<i>Université Catholique de Louvain</i>) Key factors influencing cage escape in photoinduced electron transfer
yOC-22	17:15-17:30	Sergio Aranda (<i>University of Zurich</i>) Unveiling the activation pathway of the CO ₂ reduction catalyst trans-(Cl)-[Ru(X,X'-dimethyl-2,2'-bipyridine)(CO) ₂ Cl ₂] by direct spectroscopic observation
yOC-23	17:30-17:45	Othmane Essahili (<i>Mohammed VI Polytechnic University</i>) Sustainable luminescent materials for next-generation smart building integration

Tuesday, July 8th

Session 5 Chair: Federica Giorgianni (<i>University of Messina</i>)		
yOC-24	9:00-9:15	Francesca Mancini (<i>University of Bologna</i>) Supramolecular interaction in Ru-Co and Ru-Fe complexes for efficient solar-driven hydrogen evolution and CO ₂ reduction

yOC-25	9:15-9:30	Oussama Bindech (<i>Université de Strasbourg</i>) Combining effective hamiltonians and Brillouin-Wigner approach: a step by step construction of energy states from perturbation theories
yOC-26	9:30-9:45	Fumika Sueyoshi (<i>Kyushu University</i>) Photocatalytic H ₂ evolution by pyridinium-tethered mononuclear and dinuclear Platinum complexes
yOC-27	9:45-10:00	Minli Zhang (<i>Uppsala University</i>) High-efficiency photoinduced charge separation in Iron N- heterocyclic carbenes
yOC-28	10:00-10:15	Elkhansa Elbashier (<i>University of Otago</i>) Altering the optical properties of Zn-porphyrin through β - substitutions
yOC-29	10:15-10:30	Andrea Mantovani (<i>University of Ferrara</i>) Comparison of Iridium sensitizers employed in the photoelectrochemical generation of added-value organics
10:30-11:00		Coffee Break
Session 6 Chair: Salvatore Genovese (<i>University of Messina</i>)		
yOC-30	11:00-11:15	Baldeep K. Sidhu (<i>University of Manitoba</i>) Stabilizing high spin states in Fe(II)-N _{amido} complexes to tune visible light absorption and excited state behaviour
yOC-31	11:15-11:30	Hirohisa Yanagikawa (<i>University of Tokyo</i>) Novel spectroscopic approaches to evaluate the excited triplet states of metal complexes using magnetic circular dichroism
yOC-32	11:30-11:45	Nicolò Quadrio (<i>University of Milan</i>) Plastics detection using hydrogels functionalized with switchable Iridium complexes
yOC-33	11:45-12:00	Arindam Saha (<i>Université de Montréal</i>) A bright exception: rare case of anti-Kasha ¹ ILCT emission from Co(III) complexes based on amidine-N-oxide ligands

yOC-34	12:00-12:15	Greta Fogar (<i>University of Trieste, Leiden University</i>) Sn ^{IV} -porphyrins conjugates as bio-inspired models for artificial photosynthesis
yOC-35	12:15-12:30	Yu-Hui Lin (<i>Fu Jen Catholic University</i>) Examine 77 K phosphorescence of [Os(bpy) ₂ (en)] ²⁺ : ADF modeling and spin-orbit coupling mediated intensity stealing
12:30-13:45		Lunch Time
Session 7 Chair: Claudio La Falce (<i>University of Messina</i>)		
yOC-36	13:45-14:00	Federica Ruani (<i>ISOF-CNR</i>) Solvent-controlled photoinduced processes in a bis(acridinium-Zn(II) porphyrin)-tetra(4-pyridyl) porphyrin host-guest complex
yOC-37	14:00-14:15	Felix Glaser (<i>Université Catholique de Louvain</i>) Welcome to the dark side: photoactive Iron complexes with microsecond excited-state lifetimes
yOC-38	14:15-14:30	Luis G. A. do Nascimento (<i>University of São Paulo</i>) Investigation on one-electron reduced species of Re(I)-naphthalimide photosensitizers
14:30-14:40		Closing Remarks

y-ISPPCC 2025

ABSTRACTS

New antennae for photoswitchable luminescent lanthanide(III) complexes

Y. Fréroux,^a S. Kiraev,^b A. Banyasz,^b O. Galangau,^a O. Maury,^b L. Norel^{*a} and S. Rigaut^{*a}

^a Univ Rennes, CNRS, ISCR, Université de Rennes, UMR 6226, F-35000 Rennes, France

^b Univ Lyon, CNRS, ENS de Lyon, UMR 5182, F-69007 Lyon, France

yoann.freroux@univ-rennes.fr

Lanthanide(III)-based complexes are widely used due to their original emission features such as long-lived and narrow bandwidth luminescence from the visible up to the near infrared spectral range.^[1] Photomodulation of this emission is a fundamental challenge, which has been mostly achieved with visible light emitting Eu(III) complexes, whereas our research group more recently achieved photoswitchable NIR luminescent lanthanide(III) complexes.^[2]

To this end, we have previously designed a new ligand bearing a dithienylethene (DTE) moiety, efficient for quenching the luminescence of lanthanide(III) complexes by energy transfer in only one of its two states, even in the NIR region, paving the way for applications ranging from anti-counterfeiting systems to super-resolution microscopy. However, at this stage, these systems suffer from low brightness and present only destructive readout.^[3]

Here, we present a new strategy based on new boranil-based lanthanide(III) complexes displaying (i) an improved brightness with a high on/off intensity quenching ratio, (ii) an antenna effect leading to lanthanide ion NIR emission (Ln = Yb, Er) with a non-destructive readout through selective visible light excitation in the boranil centered absorption band.

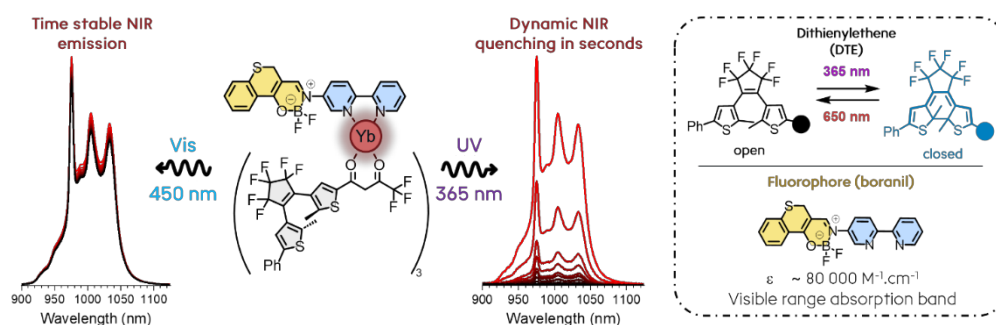


Figure 1. An Ytterbium(III) complex combining a photochromic dithienylethene ligand and a fluorophore as an antenna provides efficient luminescence switching with non-destructive readout behaviour.

Acknowledgments

We thank the Université de Rennes, the ENS de Lyon, the CNRS, the Agence Nationale de la Recherche (2LCDOR - ANR-21-CE07-0063) and LUMOMAT for support.

References

- [1] J.-C. G. Bünzli, *Coord. Chem. Rev.*, **2015**, 293-294, 19-47.
- [2] Y. Fréroux, L. Caussin, N. El Beyrouiti, S. Rigaut, L. Norel, *Handbook on the Physics and Chemistry of Rare Earths*, **2024**, 65, 35-91.
- [3] H. Al Sabea, L. Norel, O. Galangau, H. Hijazi, R. Métivier, T. Roisnel, O. Maury, C. Bucher, F. Riobé, S. Rigaut, *J. Am. Chem. Soc.* **2019**, 141, 20026-20030.

“If you like it you should put a ring on it” Rotaxanes as supramolecular protective motifs in reductive heterodinuclear photocatalysis

M. Müßler,^a M. Semwal,^c L. Blechschmidt,^c L. Zedler,^d K. Zois,^e P. Hoffmann,^b M. V. Delius,^b L. González,^e B. Dietzek-Ivanšić,^c A. K. Mengele,^a S. Rau^{*a}

^a Institute of Inorganic Chemistry I, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany,

^b Institute of Organic Chemistry I, Albert-Einstein-Allee 11, 89081 Ulm, Germany

^c Friedrich Schiller University Jena, Institute of Physical Chemistry, Helmholtzweg 4, Jena, Germany

^d Leibniz Institute of Photonic Technology, Research Department Functional Interfaces, Albert-Einstein-Str. 9, Jena, Germany

^e Institute of Theoretical Chemistry, Vienna University, Währinger Str. 17 A-1090, Vienna
marius.muessler@uni-ulm.de

Alkyne bonds offer great potential as a potent spacing group in bridging ligands for key functionalities in light-driven catalysis based on ruthenium polypyridyl complexes.^[1]

While providing great co-planarity of the polyaromatic backbone, alkynes tend to undergo hydrogenation when being exposed to reductive conditions (e.g. in presence of sacrificial electron donors), leading to a loss in efficient communication and diminished catalysis.

Herein, we present the utilization of a macrocycle (cucurbit[7]uril; CB[7]) used as a protective motif for the labile alkyne linkage and leading ultimately to the formation of a heterodinuclear rotaxane structure capable for NAD⁺ hydrogenation (**Figure 1**). The implementation of the macrocycle showed extended durability of the catalyst by shielding the alkyne moiety from being irreversibly reduced.

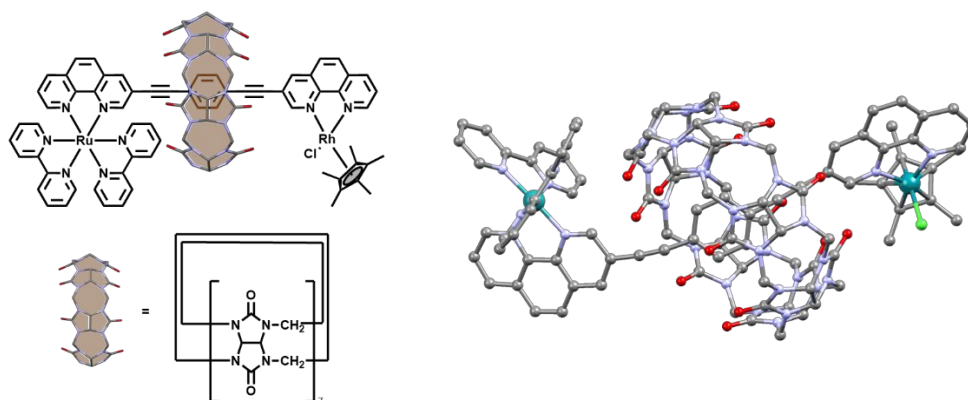


Figure 1: Molecular depiction & DFT structure of Hetero[2]Rotaxane.

Acknowledgments

Funding by the Deutsche Forschungsgemeinschaft (German Research Foundation) via the TRR CATALIGHT, Projektnummer 364549901, TRR 234, A1 & C3.

References

- [1] L. Zedler, P. Wintergerst, A.K. Mengele, S. Rau, *et al.*, Nat Commun **2022**, 13, 2538.

Characteristics of photoinduced Quenching $[\text{Ru}(\text{tpm})(\text{prbim})(\text{NH}_3)]^{2+}$ Ions: Density Functional Modeling and Efficient Metal Center State Quenching Mechanisms

Jie-Ying Chen,^a Li-Chin Yin,^a Ming-Kang Tsai^b and Yuan Jang Chen^a

^aDepartment of Chemistry, Fu Jen Catholic University, Taipei, Taiwan E-mail:

^bDepartment of Chemistry, National Taiwan Normal University, Taipei, 11677, Taiwan

411048041@mail.fju.edu.tw

We synthesized the photoinduced quenching complex, $[\text{Ru}(\text{tpm})(\text{prbim})(\text{NH}_3)]^{2+}$ to investigate the excited-state relaxations between triplet metal-to-ligand charge-transfer ($^3\text{MLCT}$) and metal-center (^3MC) states, where prbim and tpm are N,N'-propylene-protected 1H, 1'H-2,2'-biimidazole and tris-(1-pyrazolyl)methane, respectively. The complex was characterized based on its electrochemical properties and room-temperature absorption spectra, while no phosphorescence signal was observed at 77K. To further understand this behavior, we developed a computational model. Electrochemical analysis revealed that the $[\text{Ru}(\text{tpm})(\text{prbim})(\text{NH}_3)]^{2+}$ complex does not exhibit a reduction wave corresponding to the coordinated prbim moiety in the low cathodic wave region. This phenomenon is likely due to the high reduction energy of the π^* -orbitals in both the prbim and tpm ligands. Furthermore, the emission spectra at 77K were too weak to be detected, prompting an investigation into the underlying causes. Density Functional Theory (DFT) modeling of $[\text{Ru}(\text{tpm})(\text{prbim})(\text{NH}_3)]^{2+}$ suggests that the transition from $^3\text{MLCT}$ to ^3MC states occurs via modifications in metal-ligand bond lengths, providing insight into the quenching mechanism.

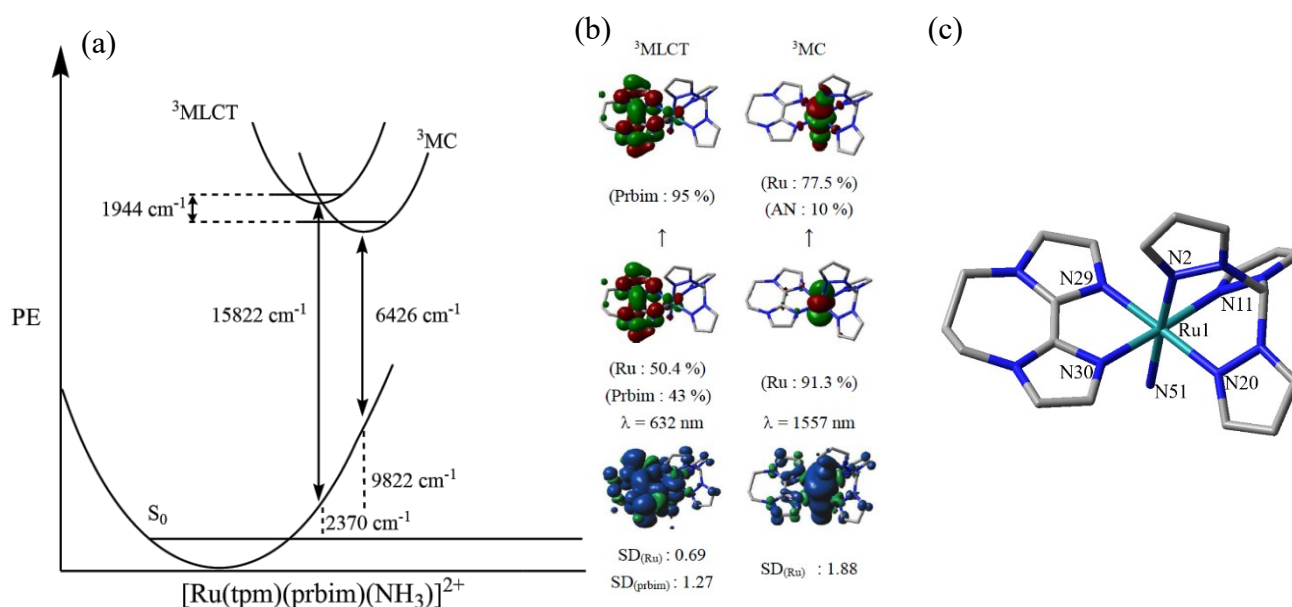


Figure 1. Illustration of the computational model for the relaxation of the $^3\text{MLCT}$ and ^3MC excited states for the target complex $[\text{Ru}(\text{tpm})(\text{prbim})(\text{NH}_3)]^{2+}$: (a) potential energy diagram illustrating the energy gap between the $^3\text{MLCT}$ and ^3MC excited states. (b) Natural Transition Orbitals (NTOs) of the $^3\text{MLCT}$ and ^3MC states, with spin density (SD) and orbital population. (c) Structural representation with labeled coordinating atoms.

Aknowlegments

This work was funded by the National Science and Technology Council (Taiwan, ROC) through Grants 112-2113-M-030-004 and 113-2113-M-030-006.

Microscopic analyses of vapochromism in single particles

X. Ma^a, K. Enomoto^a, K. Ishii^a, Y. Matsuda^b, M. Abe^b

^aInstitute of Industrial Science, The University of Tokyo, 4-6-1 Komaba Meguro-ku, 153-8505 Tokyo, Japan.

^bDepartment of Material Science, Graduate School of Science, University of Hyogo, 3-2-1, Kouto, Kamigori, Ako, Hyogo, 678-1297 Japan.
maxiao22@iis.u-tokyo.ac.jp

Vapochromism, which refers to the gaseous molecule-induced color or emission changes in materials, has drawn much attention in the view of gas sensing.^[1] Super-resolution microscopes, which have been historically developed for biological cells, would be appropriate for investigating vapochromism of solid materials, because time-dependent, three-dimensional vapochromic behaviors can be traced with meso/micro spatial resolutions.

Our laboratory has prepared the attachments for vapochromism of solid materials. Briefly, the sample was initially placed on a cover glass with a frame. After a solvent was injected into reservoirs in the frame, followed by sealing the system with a top cover. Just after closing the top, three-dimensional luminescence images and their spectra, as well as corresponding transmitted light microscopy images, were observed.

Using this system, our laboratory successfully observed the vapochromic behaviors of [Pt(CN)₂(H₂dcbpy)] (**Figure 1a**).^[2] Figure 1b shows typical confocal laser phosphorescence microscopy images overlapped with transmitted light microscopy images for [Pt(CN)₂(H₂dcbpy)] particles before and after exposure to MeOH vapor. After exposure to MeOH vapor, the phosphorescence intensities of particles obviously increased, which corresponded to the three-dimensional vapochromic behaviors. This vapochromic behaviors reflects the amorphous-to-crystal transition of [Pt(CN)₂(H₂dcbpy)] induced by MeOH vapor.

In *fac*-[Re(CO)₃Br(ppt)] (**Figure 2a**), the vapochromic single-crystal-to-single-crystal phase transitions were investigated by confocal laser microscopy. In order to observe vapochromic behaviors within several hours, the attachment was improved, and thus, the vapochromism was successfully observed. In the confocal laser phosphorescence microscopy images (**Figure 2b**) of a particle, after exposure to CHCl₃ vapor, the phosphorescence intensity initially increased in certain regions, and then, spread over other regions of the particle, which indicates the three-dimensional vapochromic behaviors.

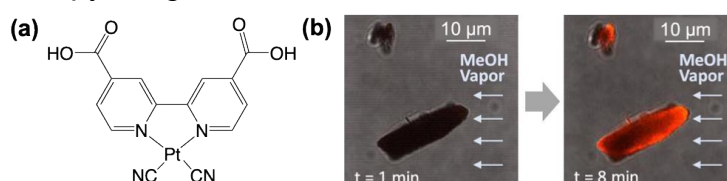


Figure 1. (a) Molecular structure of [Pt(CN)₂(H₂dcbpy)] and (b) confocal laser phosphorescence microscopy images overlapped with transmitted light microscopy images of its particle before and after exposure to MeOH vapor.

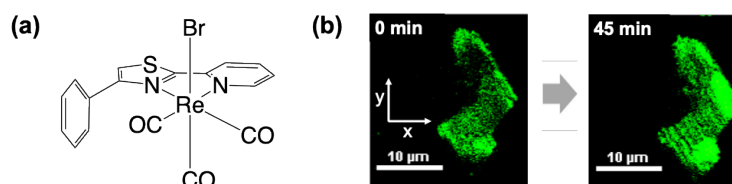


Figure 2. (a) Molecular structure of *fac*-[Re(CO)₃Br(ppt)] and (b) confocal laser phosphorescence microscopy images of its particle before and after exposure to CHCl₃ vapor.

References

- [1] E. Li, *et al.*, *Chem. Soc. Rev.*, **2020**, 49, 1517-1544.
- [2] K. Ishii, *et al.*, *J. Phys. Chem. C.*, **2021**, 125, 21055–21061.

Exploring substituents effects on the anti-Kasha reactivity of binuclear Ru(II) photosensitizers

N. Chantry,^a A. Cotic,^{b,c} S. De Kreijger,^a B. Elias,^a L. Troian-Gautier,^{a,d} * A. Cadranel^{b,c,e,f} *

^a Université catholique de Louvain (UCLouvain), Institut de la Matière Condensée et des Nanosciences (IMCN), Molecular Chemistry, Materials and Catalysis (MOST), Place Louis Pasteur 1, bte L4.01.02, 1348 Louvain-la-Neuve, Belgium,

^b Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Química Inorgánica, Analítica y Química Física, Pabellón 2, Ciudad Universitaria, C1428EHA, Buenos Aires, Argentina.

^c CONICET – Universidad de Buenos Aires, Instituto de Química-Física de Materiales, Medio Ambiente y Energía (INQUIMAE), Pabellón 2, Ciudad Universitaria, C1428EHA, Buenos Aires, Argentina.

^d Wel Research Institute, Avenue Pasteur 6, 1300 Wavre, Belgium

^e Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Physical Chemistry I, Egerlandstr. 3, 91058, Erlangen, Germany.

^f Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Interdisciplinary Center for Molecular Materials, Egerlandstr. 3, 91058, Erlangen, Germany.

noemie.chantry@uclouvain.be

Solar energy conversion is at the basis of life on Earth through natural photosynthesis. Therefore, chemists tried over the last decades to reproduce it. However, a caveat in natural or artificial photosynthesis is that excited-state population by photon absorption is often accompanied by 20-30% energy loss through vibrational relaxation (VR) and internal conversion (IC).^[1] Thus, the reactive excited state is lower in energy than the one initially formed by photon absorption. Anti-dissipative strategies were postulated to prevent these energy losses or slow down the timescale at which they take place, allowing to trap high-energy excited states useful for photoredox catalysis.

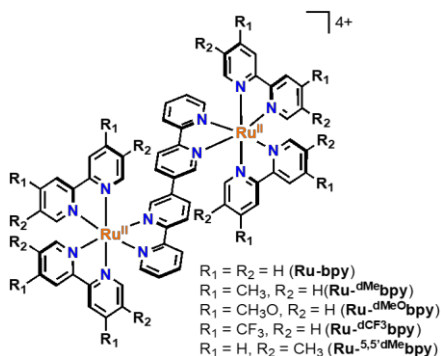


Figure 1: Structure of the complexes

To mediate those VR and IC processes, Kasha's rule needs to be circumvented by decreasing the electronic coupling between excited states. Previous work from our groups focusing on binuclear and trinuclear Ru(II) photosensitizers has highlighted that an anti-dissipative behavior could be achieved by carefully controlling the topology of the ligand bridging the different Ru(II) centers (**Figure 1**). All-*meta* (5,5') connections led to photosensitizers that exhibited an Anti-Kasha behavior while photosensitizers with *para* (4,4') connections behaved like conventional [Ru(bpy)₃]²⁺ photosensitizers.^[2]

In this study, we investigated other factors that could impact the anti-dissipative behavior while keeping the weak electronic coupling scenario provided by the bridging 2,2':5',3'':6'';2''':6'''-quaterpyridine scaffold. Substituents were added on the ancillary 2,2'-bipyridine ligands to influence the energy level of the later *vis-à-vis* the bridging ligand. These changes were investigated using classical spectroscopy methods, (spectro)electrochemistry as well as more advanced nanosecond and femtosecond transient absorption spectroscopy (nsTAS and fsTAS, respectively). This study allowed us to unambiguously identify the precise nature of high-energy excited states, and derive design guidelines for the achievement of anti-dissipative behavior in oligomeric Ru(II) polypyridines relevant for photoredox catalysis.

References

- [1] D. Gust, D. Kramer, A. Moore, T. A. Moore and W. Vermaas, *MRS Bull.*, **2008**, 33, 383-387
- [2] A. Cotic, S. Cerfontaine, L.D. Slep, B. Elias, L. Troian-Gautier and A. Cadranel, *J. Am. Chem. Soc.*, **2023**, 145, 5163-5173.

The Development of Sulfur-Containing, APTRA-Derived Fluorescent Probes with Specific Zn²⁺ Binding

L.L. Duncan, C. Hogg and J.A.G. Williams

Department of Chemistry, Durham University, South Road, Durham, DH1 3LE.

laura.l.duncan@durham.ac.uk

The divalent cations Mg²⁺, Ca²⁺ and Zn²⁺ are all essential for human life. Consequently, there is great interest in monitoring their concentrations in cells and tissues, in real time, using fluorescent probes in conjunction with fluorescence microscopy.¹ The binding unit of a given probe must be tuned to target different biologically relevant metal ions selectively. With respect to Mg²⁺ detection, *o*-aminophenol-*N,N,O*-triacetate (APTRA) is a commonly used binding unit, despite the fact it also binds to Ca²⁺ and Zn²⁺ (Figure 1).²



Figure 1. Structures of APTRA (left) and S-APTRA (right).

Work within the group has focused on new ligands related to APTRA, but which have been modified in such a way that the selectivity for different metal ions changes profoundly. We have discovered that the replacement of the phenolic oxygen atom of APTRA with sulfur gives a new ligand, *o*-aminothiophenol-*N,N,S*-triacetate (S-APTRA), that binds to Zn²⁺ very strongly, and with high selectivity over Mg²⁺ and Ca²⁺ (**Figure 1**). We have devised and implemented a synthetic route to fluorescent derivatives of S-APTRA, including a particularly exciting example in which the ligand is connected to a rosamine fluorophore. This new molecule possesses many of the desirable features of a bio-compatible fluorescent probe, including the ability to excite at long wavelengths in the visible region.

We have now shown that this probe gives a significant turn-on emission response upon Zn²⁺ binding, with no interference from either Mg²⁺ or Ca²⁺ (**Figure 2**). It also has the advantage of improved water solubility compared to many of the other reported Zn²⁺ probes, whilst the high (pentadentate) denticity prevents the formation of ternary complexes with endogenous biological molecules, allowing the sole detection of free Zn²⁺ *in vivo*. This renders S-APTRA-Rosamine a reliable and selective Zn²⁺ probe, with potential application in cellular imaging.

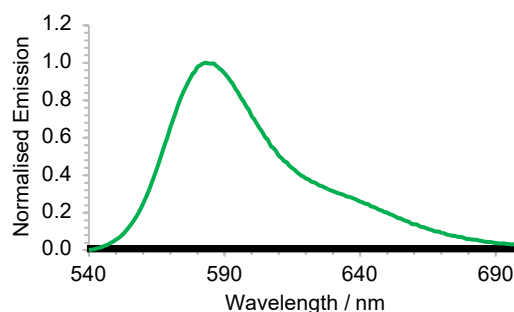


Figure 2. Emission spectrum of S-APTRA-rosamine (black) and in its Zn²⁺-bound forms (green) in aqueous buffer solution (50 mM HEPES, 100 mM KCl, pH 7.21).

References

- [1] K.P. Carter, *Chem. Rev.*, **2014**, 114, 4565-4601. E.R.H. Walter, C. Hogg, D. Parker, J.A.G. Williams, *Coord. Chem. Rev.*, **2021**, 428, 213622.
- [3] L.A. Levy, E. Murphy, B. Raju and R.E. London, *Biochemistry*, **1988**, 27, 4041-4048. M. Brady, S.D. Plombo, C. Hu and D. Buccella, *Dalton Trans.*, **2016**, 45, 12458-12464.

Ultrafast time-resolved infrared spectroelectrochemistry of Ru(II) complexes for DNA studies

M. Pižl,^{a,b} G. Greetham,^c F. Hartl^b

^a Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic

^b Department of Chemistry, University of Reading, Reading RG6 6DX, United Kingdom

^c Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 0QX, UK
martin.pizl@vscht.cz

Ruthenium(II) polypyridyl complexes keep attracting attention for their rich photophysical, photochemical and electrochemical properties. Theoretical approaches are widely used to confirm and assign the experimental data. Different types of polypyridyl ligands, substituted or non-substituted, have extensively been studied for various applications, such as the modeling of photosystems, luminescent probes for DNA, RNA or G-quadruplexes, etc.^[1] The prototype of a luminescent probe is [Ru(α -diimine)₂(dppz)]²⁺, where α -diimine = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) or 1,4,5,8-tetraazaphenanthrene (tap), and dppz = dipyrido[3,2-*a*:2',3'-*c*]phenazine. This type of complexes can intercalate into DNA grooves with the dppz phenazine part.^[1-2] A new time-resolved infrared spectroelectrochemical (TRIR SEC) technique capable of investigating the excited state dynamics of *in situ* generated redox products with ps–ns time resolution will be introduced.

In this work, CN-substituted dppz ligands (**Figure 1**) were used to lower the HOMO–LUMO energy gap. The influence of the nitrile group on the redox behavior and its IR-probe function has been determined by electrochemical and spectroelectrochemical measurements^[3] and, more importantly, pioneering TRIR SEC measurements. Theoretical calculations have been performed with Gaussian 16, Rev. C01 quantum chemical package. DFT calculations were used to characterize the localization of the first three electrochemical reduction steps.

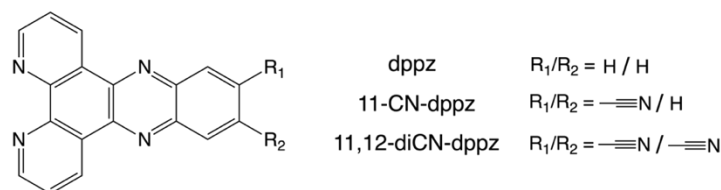


Figure 1. Structures of investigated dppz ligands in [Ru(tap)₂(dppz-R₁,R₂)]²⁺.

Acknowledgments

This work was financially supported by the Czech Science Foundation (project 23-05760O), by the project "The Energy Conversion and Storage", funded as project No. CZ.02.01.01/00/22_008/0004617 by Programme Johannes Amos Comenius, call Excellent Research and by spin-out company Spectroelectrochemistry Reading. We would like to thank Ian P. Clark, and Partha Malakar for helping us set up our measurements in Rutherford Appleton Laboratory, Central Laser Facility, Harwell Campus, Didcot, UK, and for support from the Science and Technology Facilities Council (access grants 2022-2024).

References

- [1] G. Li, L. Sun, L. Ji, H. Chao, *Dalton Trans.* **2016**, 45, 13261-13276.
- [2] K. McQuaid, J. P. Hall, J. A. Brazier, D. J. Cardin, C. J. Cardin, *Chem. Eur. J.* **2018**, 24, 15859-15867.
- [3] E. Sumner, M. Pižl, K. T. McQuaid, F. Hartl, *Inorg. Chem.* **2024**, 63 (5), 2460-2469.

Synthetic Control Over Excited-State Behavior of Nickel(II) Complexes

D. S. Wagner^{a†}, B. Lazarevski^{a†}, S. K. Banik^b, J. Wellauer^a, B. Pfund^{a,c}, T. Ogawa^{a,d}, D. Schwarzer^{2*}, O. S. Wenger^{1*}

[†] These authors contributed equally

^aDepartment of Chemistry, University of Basel, Switzerland

^bDepartment of Dynamics at Surfaces, Max-Planck-Institute, Germany

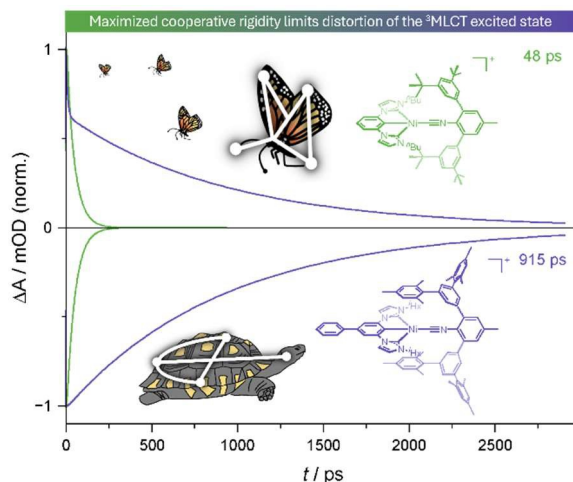
^cPresent address: Department of Chemistry, Michigan State University, United States

^dPresent address: Graduate School of Sciences Dept. of Chemistry, University of Kyushu, Japan

Conventionally, photochemical reactions occur only from the lowest excited state of the photoactive species while higher excited states relax on a ps timescale, and the additional energy is lost, limiting photochemical reactivity.^[1,2] Here we present a molecular design strategy to slow the relaxation of the higher ³MLCT excited states of Ni^{II} complexes from the sub-ps to the ns timescale.

From the excited ³MLCT state, square planar Ni^{II} complexes undergo molecular distortion and fast deactivation into low lying ³MC states. Our approach is to suppress this nonradiative deactivation by introducing cooperative rigidity. The excited-state behavior of three new Ni^{II} complexes was probed *via* UV-Vis and IR fs-TA spectroscopy. The combination of a structurally rigid tridentate chelate with a bulky mesitylene-substituted monodentate isocyanide ligand extends the photoactive ³MLCT state lifetime by three orders of magnitude: from 0.5 ps^[3] (for the sterically unhindered MeCN complex) to 48 ps^[3] (for the previously published isocyanide complex) to 915 ps, presented herein.

The elongated lifetime enables bimolecular photochemistry from this higher excited state, an unusual type of reactivity minimizing energy losses. We present triplet-triplet energy transfer quenching studies with three high energy acceptors, investigated by fs-TA spectroscopy.



References

- [1] N. J. Turro, V. Ramamurthy, W. Cherry, W. Farneth, *Chem. Rev.* **1978**, 78 (2), 125-145.
- [2] B. Pfund, O. S. Wenger, *JACS Au* **2025**, 5 (2), 426-447.
- [3] T. Ogawa, N. Sinha, B. Pfund, A. Prescimone, O. S. Wenger, *J. Am. Chem. Soc.* **2022**, 144 (48), 21948-21960.



Light-Driven CO₂ Reduction with a Heptacoordinated Iron(II) Polypyridine Complex

F. Droghetti,^a A. Ruggi,^b F. Lemken,^c L. Rulíšek,^c M. Natali^a

^aUniversity of Ferrara, Via Luigi Borsari 46, Italy

^bUniversity of Fribourg, Chemin du Musée 9, Switzerland

^cInstitute of Organic Chemistry and Biochemistry of the CAS, Flemingovo náměstí 542/2
Praha 6, Czech Republic

drgfrc@unife.it

The growing necessity to mitigate human-induced CO₂ emissions has driven research toward innovative approaches for converting them into value-added products. Recent findings in designing molecular catalysts for the CO₂ reduction reaction (CO₂RR) have focused on metal complexes with ligands that exhibit a significant degree of electronic delocalization, a feature crucial for reducing overpotential and enhancing selectivity over the competitive hydrogen evolution reaction (HER).^[1,2]

In this communication, we report the catalytic activity of a Fe(II)-based molecular catalyst for CO₂ reduction, featuring a hexadentate, redox-active DBPy-PyA ligand (1-([2,2'-bipyridin]-6-yl)-N-([2,2'-bipyridin]-6-ylmethyl)-N-(pyridin-2-ylmethyl)-methanamine), under electrochemical and photochemical conditions. We optimize the catalytic performance of the Fe(II) complex through a fine-tuning of the proton donor, photon flux, and different photosensitizers, achieving over 99% selectivity and one of the highest reported quantum efficiencies.^[3] Furthermore, time-resolved spectroscopy and DFT calculations provide a mechanistic understanding of electrochemical and photochemical behavior.^[4,5]

References

- [1] H. Takeda, C. Cometto, O. Ishitani, M. Robert, *ACS Catal* **2017**, 7, 70–88.
- [2] F. Droghetti, A. Amati, A. Ruggi, M. Natali, *ChemComm* **2023**, 60, 658–673.
- [3] F. Droghetti, L. Villa, A. Sartorel, L. Dell'Amico, A. Ruggi, M. Natali, *ChemSusChem* **2025**, 18 (11).
- [4] F. Droghetti, F. Lemken, L. Rulíšek, A. Ruggi, M. Natali, *ACS Catal* **2024**, 16920–16935.
- [5] F. Droghetti, A. Amati, F. Pascale, A. Crochet, M. Pastore, A. Ruggi, M. Natali, *ChemSusChem* **2024**, 17 (4).

Exploring Ru(II) Photocages for Cancer Therapy: A Theoretical Investigation of Light-Induced Acetonitrile Ligand Release

S. Scoditti,^{a,b,c} G. Mazzone,^b E. Sicilia,^c

^a Donostia International Physics Center, Paseo Manuel de Lardizabal 4, Donostia, 20018, Spain

^b Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Rende, 87036, Italy

^c Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia, Kimika Fakultatea, Euskal Herriko Unibertsitatea UPV/EHU, Paseo Manuel de Lardizabal 3, Donostia, 20018, Spain

stefano.scoditti@dipc.org

The fundamental discovery of the anticancer properties of metal-based drugs, such as cisplatin and its derivatives, has been crucial in advancing cancer chemotherapy. However, the side effects associated with platinum-based treatments have paved the way for the search for safer and more efficient alternatives. Photoactivated Chemotherapy (PACT) is a promising alternative therapy that uses light to activate prodrugs, converting them into potent anticancer agents.^[1] The resulting bioactivity may stem from the dissociated ligand, the metal-based product, or synergistic effects between both species.

Ru(II) polypyridyl compounds have attracted considerable attention due to their favorable photophysical properties.^[2] Understanding their excited-state dynamics is key to optimizing photodissociation efficiency and enhancing therapeutic potential. Density Functional Theory (DFT) serves as a valuable tool for studying photochemical reactions and characterizing the excited states involved.

In this contribution, we present a computational analysis of the photodissociation mechanism of **THCRuACN** (**Figure 1**), a Ru-based photocage model compound. Upon exposure to near-infrared light, **THCRuACN** undergoes a photodissociation process, releasing a nitrile group and yielding the resulting species **THCRuWAT**.^[3] DFT calculations reveal that this process is facilitated by the metal-centered triplet excited state (³MC), where the coordination environment and the tridentate ligand play a crucial role in the photodissociation pathway.

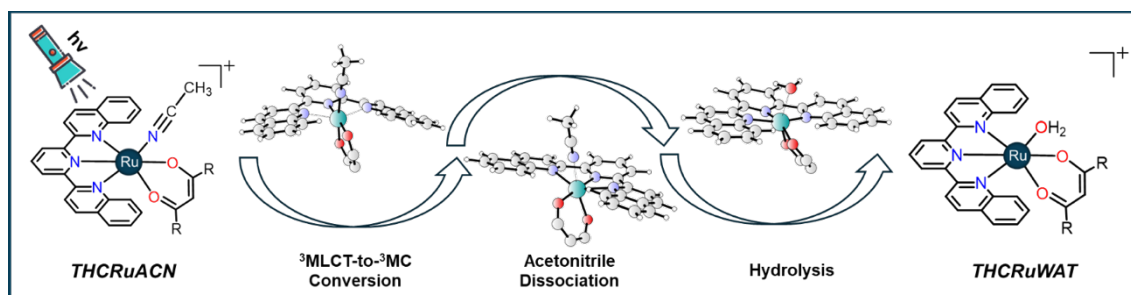


Figure 1. Mechanism of Photodissociation of THCRuACN complex.

References

- [1] S. Bonnet. *J. Am. Chem. Soc.*, **2023**, 145, 23397–23415
- [2]. N. J. Farrer, L. Salassa, P. J. Sadler, *Dalton Trans.*, **2009**, 10690-10701.
- [3] G. He, M. He, R. Wang, X. Li, H. Hu, D. Wang, Z. Wang, Y. Lu, N. Xu, J. Du, J. Fan, X. Peng, W. Sun, *Angewandte Chemie International Edition*, **2023**, 62, e202218768.

Ultrafast Spectroscopic Investigations into Solvent and Hetero-Atom Effects on the Photophysics of Platinum(II)-based Artificial Photosynthetic Systems

E. L. Race, M. D. Horbury, C. Royle, G. Wu, P. Scattergood, D. Chekulaev, J. A. Weinstein

Department of Chemistry, School of MPS, University of Sheffield

elrace1@sheffield.ac.uk

Platinum-based coordination compounds, featuring donor and acceptor moieties, demonstrate complex electronic and structural dynamics. These include formation of long-lived charge separated states which have extensive application within artificial photosynthesis and photocatalytic development. Specifically, increasing the yield of these desirable states against those of other competing pathways is a current challenge. Some success in modifying excited state lifetimes and yields has been achieved through synthetic functionalisation and the recently introduced concept of IR-control of photochemical pathways.^[1-2]

However, variation of the local environment also has extensive effects on the dynamics. Here, we demonstrate how changes in solvent polarity can induce as much as a 10-fold increase in singlet state lifetimes of some Pt(II) trans-acetylide complexes, which feature an aromatic acid anhydride or an aromatic imide as the acceptor.

Remarkably, a change from previously well-studied imides (X = N, R = alkyl) to the corresponding anhydride (X = O) dramatically changes excited state dynamics whilst preserving the population of the charge-separated state.

This dependence on the environment and the heteroatom was discovered using several ultrafast transient spectroscopy techniques including transient absorption (TA), transient infrared (TRIR), and femtosecond broadband fluorescence up-conversion spectroscopy (FLUPS).

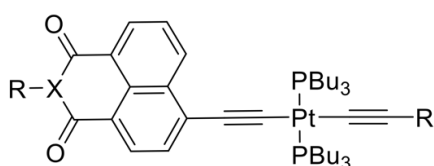


Figure 1. *trans*-(4-ethynyl-1,8-naphthalic anhydride)Pt(PBu₃)₂R.

Acknowledgments

We thank the University of Sheffield, the EPSRC Molecular Photonics Breadboards programme grant and the Lord Porter Laser Laboratory.

References

- [1] M. Delor, T. Keane, P. A. Scattergood, I. V. Sazanovich, G. M. Greetham, M. Towrie, A. J. Meijer and J. A. Weinstein, *Nature chemistry*, **2015**, 7, 689–695.
- [2] M. Delor, P. A. Scattergood, I. V. Sazanovich, A. W. Parker, G. M. Greetham, A. J. Meijer, M. Towrie and J. A. Weinstein, *Science*, **2014**, 346, 1492–1495.

Photochemical Behavior Of Ruthenium(II) Complexes In Choline Geranate (CAGE) Ionic Liquids

M. Costa Verdugo^{a,b}, V. Martínez-Martínez^c, L. Salassa^{a,b,d}

^a Donostia International Physics Center, Paseo Manuel de Lardizabal 4, Donostia, 20018, Spain

^b Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia, Kimika Fakultatea, Euskal Herriko Unibertsitatea UPV/EHU, Paseo Manuel de Lardizabal 3, Donostia, 20018, Spain

^c Departamento de Química Física, Universidad del País Vasco UPV/EHU, Apartado 644, Bilbao, 48080, Spain

^d Ikerbasque, Basque Foundation for Science, Bilbao, 48011, Spain
marta.costa@dipc.org

In this study, we investigate the photophysical and photochemical behavior of three model ruthenium(II) polypyridyl compounds: $[\text{Ru}(\text{bpy})_3]^{2+}$ (**1**), $[\text{Ru}(\text{bpy})_2(\text{py})_2]^{2+}$ (**2**), and $[\text{Ru}(\text{tpy})_2]^{2+}$ (**3**) in water^[1] and in unconventional solvents, such as the ionic liquid choline geranate (CAGE IL). CAGE ILs, composed of choline and geranic acid, have been widely studied for their ability to enhance transdermal, subcutaneous, and oral drug delivery, effectively facilitating the release of antiviral, anticancer, and antifungal drugs without exhibiting in vivo toxicity.^[2]

Herein, UV-Vis spectroscopy was employed to analyze the absorbance of **1–3** before and after irradiation with blue and green light at varying time intervals. In water, only **2** exhibited significant photoactivity, whereas in CAGE IL, both **1** and **2** underwent photoinduced ligand dissociation.^[3] Compound **3** remained photochemically inactive in both solvents. The influence of CAGE IL concentration in aqueous mixtures was also evaluated, revealing its critical role in the photoreactivity of **1**. Computational studies (DFT) indicated that photoactivity of **1** in CAGE IL originated from the stabilization of the ³MC (metal-centered) state. Additional experiments, including NMR analysis, emission spectroscopy, lifetime measurements, and quantum yield determinations completed the photophysical characterization of **1** in CAGE IL compared to water.

These findings provide insights into the impact of CAGE IL on the photoactivity and stability of ruthenium-based compounds, with potential implications for photochemotherapy and photocatalysis.

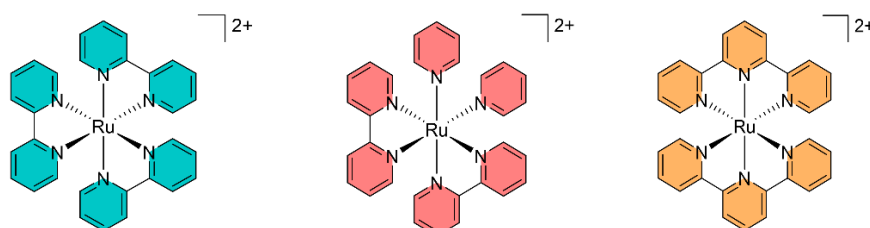


Figure 1. Structure of the ruthenium compounds used in this study

Aknowlegments

The authors thank the Spanish State Research Agency (Grant PID2022-139267OB-I00). DIPC was supported by the “Severo Ochoa” Programme for Centres of Excellence in R&D (MINECO, CEX2018-000867-S).

References

- [1] C. Garino, A. Terenzi, G. Barone, L. Salassa, *J. Chem. Educ.*, **2016**, 93, 292.
- [2] A. Banerjee, K. Ibsen, Y. Iwao, M. Zakrewsky, S. Mitragotri, *Adv. Healthc. Mater.* **2017**, 6, 1601411.
- [3] E. Borfecchia, C. Garino, L. Salassa, T. Ruii, D. Gianolio, X. Zhang, K. Attenkofer, L. X. Chen, R. Gobetto, P. J. Sadler, C. Lamberti, *Dalton Trans.*, **2013**, 42, 6564.

The Characteristic of Photo-Induced ³MLCT Emission Behavior for Ru- TBPZ Chromophore, A Ru-(Cyclometalated) Chromophore

L.-T. Zhuo,^a M.-K. Tsai,^{*b} Y.J. Chen^{*a}

^aDepartment of Chemistry, Fu-Jen Catholic University, New Taipei City 24205, Taiwan, ROC

^bDepartment of Chemistry, National Taiwan Normal University, Taipei City 11677, Taiwan, ROC
qq10120@gmail.com

This is a rare report of Ru-(Cyclometalated), Ru-CM, phosphorescent chromophore in the mixed ligand $[\text{Ru}(\text{bpy})_2(\text{CM})]^+$, type complexes for $[\text{Ru}(\text{bpy})_2(\text{TBPZ})]^+$, where bpy 2,2'-bipyridine, TBPZ = Tribenzo[a,c,i]phenazine. The $[\text{Ru}(\text{bpy})_2(\text{TBPZ})]^+$ complexes was synthesized and its electrochemical and photophysical properties were characterized. In the cyclic voltammogram scan, the first reduction potential in the negative region corresponds to the reduction of the $\text{TBPZ}^{-1/2}$. The observed absorption spectrum shows a low-energy metal-to-ligand charge transfer (MLCT) band, which is attributed to contributions from both Ru-TBPZ and Ru-bpy moieties based on the DFT modeling. The 77K MLCT phosphorescence behavior of $[\text{Ru}(\text{bpy})_2(\text{ppy})]^+$ (ppy = 2-phenylpyridine) is well-know characteristics of Ru-bpy chromophore.^[1,2] The characteristics of 77K phosphorescence observations and computational modeling in this study indicate that $[\text{Ru}(\text{bpy})_2(\text{TBPZ})]^+$ exhibits the Ru-CM phosphorescent chromophore

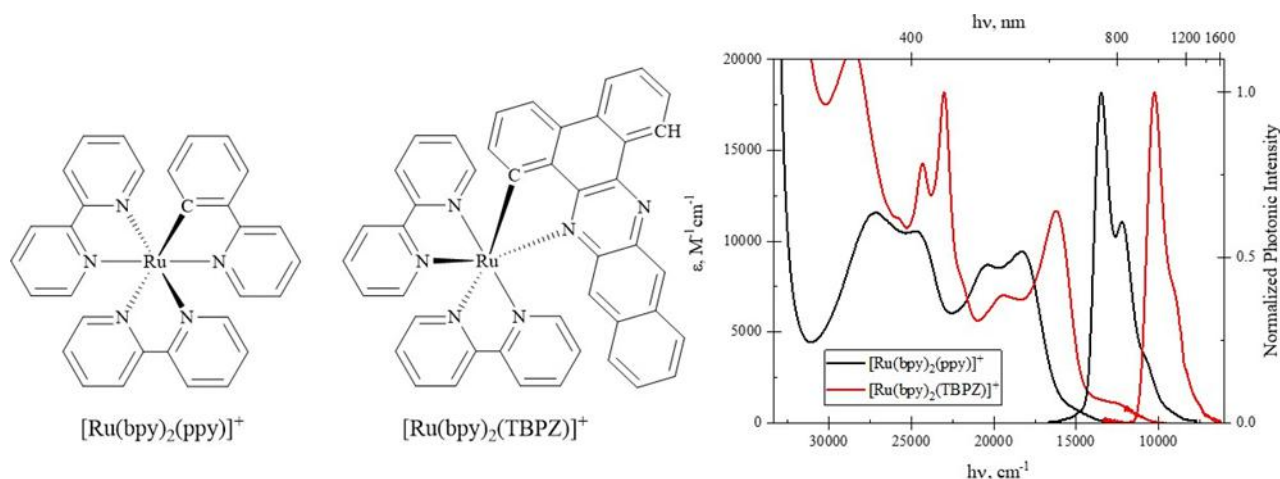


Figure 1. The 298K absorption spectra in CH_3CN and 77K emission spectra in butyronitrile glasses. (right panels), and structure of $[\text{Ru}(\text{bpy})_2(\text{ppy})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{TBPZ})]^+$ (left panels).

Acknowledgment

Thank to the Ministry of Science and Technology, R.O.C. for partial funding of this work (Yuan Jang Chen). Grants NSTC-113-2113-M-030-006.

References

- [1] X.Z. Zhang, C. C. Cheng, Y. R. Chih, Y.-T. Lin, H.-Y. Chen, Y. J. Chen, J. F. Endicott, *J. Phys. Chem. A*, **2019**, 123, 9431-9449.
- [2] M.L. Muro-Small, J. E. Yarnell, C. E. McCusker, F. N. Castellano, *Inorg. Chem.*, **2012**, 25, 4004-4011.

From Rags to Riches: Enabling Abundant Metals to Exhibit Significant Photophysical and Magnetic Properties Using Efficient Ligand Design

A. Kacperkiewicz,^a B. K. Sidhu,^a R. J. Ortiz,^a J. A. G. Williams,^b D. E. Herbert^a

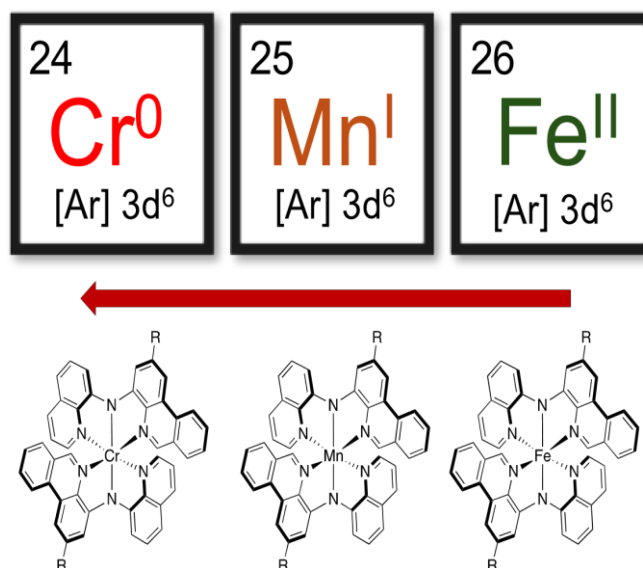
^aDepartment of Chemistry, University of Manitoba, Winnipeg, MB, R3T 2N2, Canada

^bDepartment of Chemistry, Durham University, Durham, DH1 3LE, UK

kacperka@myumanitoba.ca

Coordination chemistry allows one to combine the unique influence of metals on the physical properties of molecules with the ability to further tune these properties using ligand design. Accordingly, coordination complexes can be applied in light emitting diodes, artificial photosynthesis schemes and dye-sensitized solar cells, magnetic materials and sensors, and much more. From a sustainability perspective, the responsiveness of molecular properties to those of the ligand presents the opportunity to rationally engineer the favourable characteristics of heavier, rarer transition metal elements into complexes of more abundant, renewable 3d metals.^[1]

With this aim in mind, our group has sought to delineate the impact of nitrogen donor motifs and benzannulated C=N moieties on the photophysical, magnetic, and photochemical properties of first row transition metal coordination complexes.^[2] In this presentation, I will describe ligand motifs with amido (:NR₂) character and their remarkable influence over photophysical properties such as light absorption, excited states, and photochemistry beginning with iron and extending to earlier metals such as manganese and chromium.



Acknowledgements

I would like to thank my group members, my advisor, and our collaborators for their help throughout the years and their contributions to this project.

References

- [1] C. Wegeberg, O.S. Wenger, Luminescent First-Row Transition Metal Complexes. *JACS Au* **2021**, 1 (11), 1860–1876.
- [2] D.E. Herbert, When Is a Pyridine Not a Pyridine? Benzannulated N-Heterocyclic Ligands in Molecular Materials Chemistry. *Can. J. Chem.* **2023**.

Contrasting Excited State Processes of Zn(II) and Cu(II) Phthalocyanines

E.R. Windle,^a D. Graczyk,^a D. MacKay,^b P. Malakar,^c R.M. Edkins,^b S.J. Quinn^a

^aSchool of Chemistry, University College Dublin, Dublin 4, Ireland.

^bDepartment of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK.

^cCentral Laser Facility, STFC Rutherford Appleton Laboratory, UK

eleanor.windle@ucdconnect.ie

Phthalocyanines are promising photodynamic therapy (PDT) sensitizers with strong absorbance in the biological window and photophysical properties determined by the aggregation state.^[1] This study has monitored the excited state dynamics of a regioregular zinc(II) phthalocyanine (**1**) using transient absorbance (TA) spectroscopy in different environments from femto- to micro-second time scales. While either the fast or slow processes have been reported on related complexes,^[2] this is the first study to examine this full time range providing a full understanding of the excited state processes of **1**. This has revealed **1** to be monomeric and luminescent in DMSO with a strong ground state bleach band, stimulated emission and transient excited state absorbances. In this environment, **1** possesses an S₁ lifetime of 1.8 ns, matching the fluorescence lifetime, followed by a longer-lived triplet lifetime of 210 μs suitable for PDT. In aqueous solution, **1** forms soluble aggregates with rapid non-radiative decay with lifetime of 74 ps. This provides **1** with high photothermal therapy (PTT) activity. An isotope effect was observed for **1** with a 32% shorter lifetime observed in H₂O compared to D₂O. With good potential for both PDT and PTT, and the ability to modulate between aggregated and monomeric state using nucleic acids, **1** is a promising dual-activity photosensitizer.^[3]

These photophysical properties have been compared to the equivalent paramagnetic Cu(II) phthalocyanine (**2**) that shows phosphorescence. **2** possesses ultrafast intersystem crossing (τ = 1 ps) in both aqueous and organic environments. Following this, a lifetime of ~20 ns is observed in both environments. The effect of varying environment on the aggregation behaviour and excited state dynamics of **1** and **2** has been studied using alternative organic and deuterated solvents and organic/aqueous mixtures.

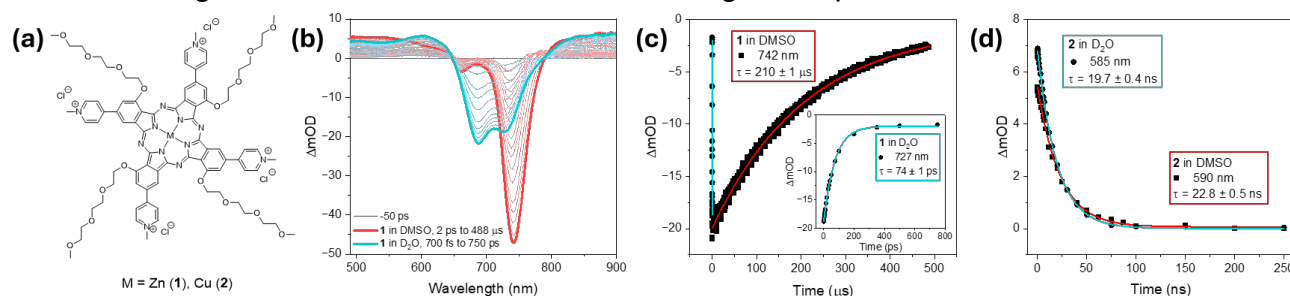


Figure 1. (a) Structure of **1** and **2**. (b) TA spectra of **1** in DMSO and D₂O. Recovery of (c) ground state bleach band of **1** and (d) transient band of **2** in DMSO and D₂O.

Acknowledgments

This project was funded by a Government of Ireland Postgraduate Scholarship (GOIPG/2022/1362) and the ultrafast studies at the CLF were funded by the STFC.

References

- [1] D.A. Bunin, A.G. Martynov, D.A. Gvozdev and Y.G. Gorbunova, *Biophys. Rev.* **2023**, 15 (5), 983-998.
- [2] J. Savolainen, D. van der Linden, N. Dijkhuizen and J.L. Herek, *J. Photochem. Photobiol. A: Chem* **2008**, 196 (1), 99-105.
- [3] E.R. Windle, C.C. Rennie, R.M. Edkins and S.J. Quinn, *Chem. Eur. J.*, **2025** 31 (2), e202403095.

Unveiling the Potential of Iridium Complexes in Tissue Imaging

E. Dallerba,^a M. J. Hackett,^a M. Massi^a

^aSchool of Molecular and Life Sciences, Curtin University, Perth, WA, Australia
elena.dallerba@curtin.edu.au

The photophysical properties of transition metal complexes can be finely tuned through chemical modifications of their ligands.^[1,2] For this reason, iridium complexes have been extensively studied for cell staining applications. Nevertheless, the application of such complexes as probes for tissue staining remains a relatively unexplored field. This presentation will showcase whether ligand modifications can further enhance the photophysical properties of these complexes, enabling the synthesis of probes suitable for biological imaging. Specifically, we assessed a series of luminescent transition metal complexes for their potential as imaging probes in brain tissue samples. Currently, the availability of fluorescent probes for *ex vivo* tissue section imaging is significantly limited compared to those designed for *in vitro* live or fixed cell imaging. This gap poses a challenge for advancing neurobiological research, which relies on fluorescence microscopy to elucidate neurological function and disease mechanisms. In this study, we utilized novel fluorescent probes to stain brain tissue and demonstrated their imaging capabilities using confocal microscopy.

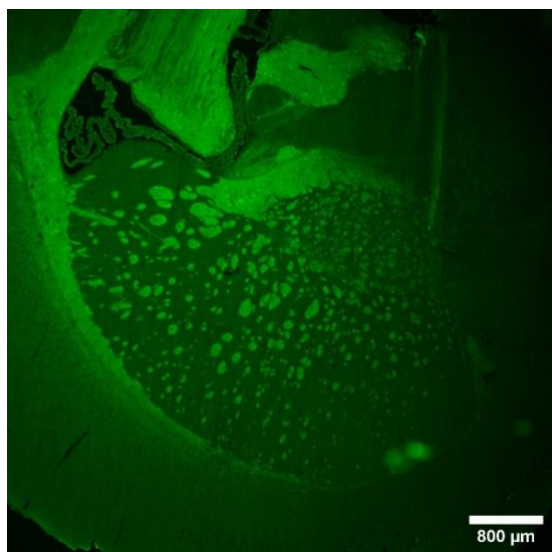


Figure 1. Microscopy image showing the staining of mouse brain tissue using an Ir(III) luminescent probe.

Aknowlegments

Confocal microscopy analysis was performed using the Curtin Health Innovation Research Institute Microscopy and Histology Shared Resources Laboratory with the assistance of Mr Michael Nesbit.

References

- [1] Li G., Nobusyasu S., Zhang B., Geng Y., Yao B., Xie Z., Zhu D., Shan G., Che W., Yan L., Su Z., Dias F., Bryce M. R., *Chemistry – A European Journal*, **2017**, 23, 11761-11766.
- [2] Fiorini V., Zandoni I., Zacchini S., Costa A. L., Hochkoepler A., Zanolini V., Ranieri A. M., Massi M., Stefan A., Stagni S., *Dalton Transactions.*, **2017**, 46, 12328-12338.

[FeFe]-H₂ase mimicking complex bearing two organic photosensitisers for photocatalytic H₂ evolution

C. Kasahara,^{a,b} M. K. Farh, K^a. Rediger,^c P. Buday,^a S. Gräfe,^b M. Micheel,^c S. Kupfer,^b M. Wächtler,^{c,d} W. Weigand^a

^aInstitute of Inorganic and Analytical Chemistry, University Jena, Humboldtstr. 8, 07743 Jena, Germany

^bInstitute of Physical Chemistry, University Jena, Lessingstr. 4, 07743 Jena, Germany

^cChemistry Department and State Research Center OPTIMAS, RPTU Kaiserslautern-Landau, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Germany

^dInstitute of Physical Chemistry and Kiel Nano, Surface and Interface Science (KiNSIS), Kiel University, Kiel, Max-Eyth-Straße 1, 24118 Kiel, Germany

chizuru.kasahara@uni-jena.de

Photocatalytic H₂ evolution has attracted interest from the scientific community, and numerous efforts have been made to modify the reaction greener and more sustainable, i.e. substitute precious metals to the earth-abundant elements. One promising compound for the noble-metal-free catalytic centre is [(μ-S)₂Fe₂(CO)₆], the mimic of [FeFe]-H₂ase's catalytic centre (**CAT**), as the enzyme is known to exhibit remarkable H₂ production.^[1] Thereby, applications of [(μ-S)₂Fe₂(CO)₆] derivatives for photocatalytic H₂ production have been investigated by combining with a photosensitiser (**PS**).^[2, 3]

In this contribution, we present a novel molecular catalyst (**PS-CAT**) which builds on our previous joint synthetic-spectroscopic-theoretical studies^[4, 5] and covalently connects two metal-free **PS**s and one **CAT** (Figure 1). The molecular triad structure can avoid diffusion control interaction between **PS** and **CAT**, and (potentially) increase the probability of accessing the excited state of **PS** which triggers photoinduced electron transfer (ET) from **PS** to **CAT**. The new **PS-CAT** was investigated in terms of the electro- and photo-reduction properties, combining experimental and computational approaches to achieve a comprehensive understanding of the (photo)reduction mechanism of the new triad.

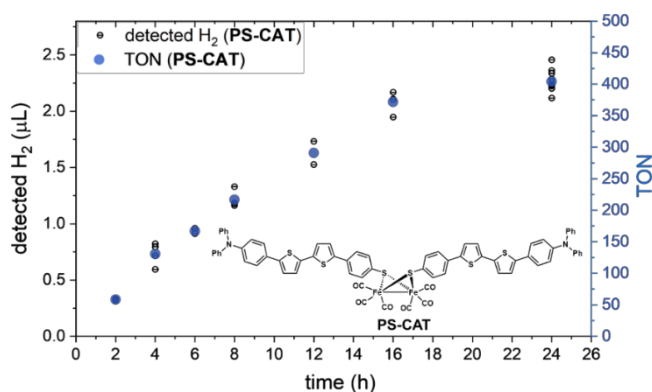


Figure 1. Molecular structure and photocatalytic activity of PS-CAT. The reactions were performed under 455 nm irradiation in the presence of 1, 3-dimethyl-2-phenylbenzimidazole in N-Methyl-2-pyrrolidone.

References

- [1] J. T. Kleinhaus, F. Wittkamp, S. Yadav, D. Siegmund, U. -P. Apfel, *Chem. Soc. Rev.* **2021**, 50 (3), 1668-1784.
- [2] J. Amaro-Gahete, M. V. Pavliuk, H. Tian, D. Esquivel, F. J. Romero-Salguero, S. Ott, *Coord. Chem. Rev.* **2021**, 448, 214172.
- [3] R. Gupta, A. K. Pal, *Sustainable Energy Fuels* **2024**, 8 (20), 4709-4751.
- [4] P. Buday, C. Kasahara, E. Hofmeister, D Kowalczyk, M. K. Farh, S. Riediger, M. Schulz, M. Wächtler, S. Furukawa, M. Saito, et al. *Angew. Chem. Int. Ed.* **2022**, 61 (20), e202202079.
- [5] C. Kasahara, K. Rediger, M. Micheel, P. Liebing, S. Gräfe, S. Kupfer, M. Wächtler, W. Weigand, *ChemCatChem* **2024**, 16, (11) e202400247.

Diphosphine Design Enables Rainbow Emitting Ag(I) Complexes for Light-Emitting Electrochemical Cells

S. Lipinski^a, Y. Atoini^a, P. B. Coto^b, R. D. Costa^a

^aTechnical University of Munich, Campus Straubing for Biotechnology and Sustainability, Schulgasse 22, 94315 Straubing, Germany.

^bNanomaterials and Nanotechnology Research Center (CINN), Spanish National Research Council (CSIC), Avda. de la Vega 4-6, 33940 El Entrego, Spain.
sophia.lipinski@tum.de.

Light-emitting electrochemical cells (LECs) are the simplest and cheapest lighting devices as they combine a single-layered device architecture, air-stable electrodes as well as lowcost and up-scalable solution-based fabrication techniques.^[1] As the demand for sustainable electroluminescent emitters is constantly increasing, d¹⁰ ionic transition metal complexes (iTMCs) have emerged as more ecologically friendly and cost-effective alternatives than their Ir(III) and Ru(II) counterparts.^[2] Over the last decades, the photo- and electroluminescent properties of heteroleptic Cu(I)-iTMCs have been widely studied, while heteroleptic and homoleptic Ag(I)-iTMCs have been neglected.^[3] This is related to the *i*) poor electrochemical stability upon reduction, *ii*) controversially discussed emission mechanisms and *iii*) lack of low-energy emitting Ag(I)-iTMCs.^[4]

Herein, we will rationalize the photo-/electroluminescent and electrochemical properties of a rainbow emitting homoleptic Ag(I) series (λ_{em} = 450-690 nm; ϕ up to 48 %) that was accessed by a subtle modification of the diphosphine ligand without dramatically affecting the steric properties (e.g. bite angle).^[5] They feature a thermally activated delayed fluorescence mechanism in crystalline powder that has rarely been observed in cationic fourcoordinated Ag(I)-iTMCs. More striking, dramatic changes in the emission properties (bathochromic shifts of up to 130 nm) from crystalline powder to thin-films were found and rationalized by PXRD and DFT/TDDFT studies. This new Ag(I) family exhibits improved electrochemical stability in solution and in LECs compared to prior art as evidenced by CV and EIS measurements. This finally resulted in LECs that can compete in terms of brightness and efficacy with the well-established Cu(I)-based LECs.

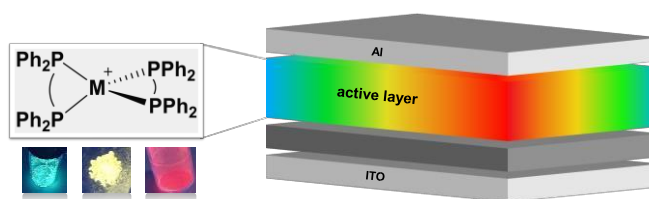


Figure 1. Diphosphine design toward rainbow emitting homoleptic cationic Ag(I) complexes for LECs.

References

- [1] E. Fresta, R. D. Costa, *J. Mater. Chem. C* **2017**, 5 (23), 5643.
- [2] G. U. Mahoro, J. Fernandez-Cestau, J.-L. Renaud, P. B. Coto, R. D. Costa, S. Gaillard, *Adv. Opt. Mater.* **2020**, 8 (16), 2000260. b) C. E. Housecroft, E. C. Constable *J. Mater. Chem. C* **2022**, 10 (12), 4456.
- [3] A. Farokhi, S. Lipinski, L. M. Cavinato, H. Shahroosvand, B. Pashaei, S. Bellani, F. Bonaccorso, S. Karimi, R. D. Costa, *Chem. Soc. Rev.* **2025**, 54 (1), 266.
- [4] E. Fresta, J. M. Carbonell-Vilar, J. Yu, D. Armentano, J. Cano, M. Viciano-Chumillas, R. D. Costa, *Adv. Funct. Mater.* **2019**, 29 (31), 1901797. b) S. Lipinski, L. M. Cavinato, T. Pickl, G. Biffi, A. Pöthig, P. B. Coto, J. Fernandez-Cestau, R. D. Costa, *Adv. Opt. Mater.* **2023**, 11 (15), 2203145.
- [5] S. Lipinski, T. Pickl, Y. Atoini, S. Sansotta, J.-L. Schmitt, L. M. Cavinato, A. Pöthig, J. Fernández-Cestau, P. B. Coto, R. D. Costa, *manuscript submitted*.

A deep insight into the role of basic additives in the charge injection of Fe(II)-based complexes

E. Marchini,^a F. Ruani,^b B. Ventura,^b N. Armaroli,^b M. Pastore,^c P. C. Gros,^c S. Caramori^a

^aUniversity of Ferrara, 44121 Ferrara, Italy,

^bIstituto per la Sintesi Organica e la Fotoreattività (ISOF), CNR, 40129 Bologna, Italy;

^cUniversité de Lorraine, CNRS, 54000 Nancy, France

edoardo.marchini@unife.it

Since the pioneering contribution of Ferrere and Gregg, iron complexes have demonstrated the ability to undergo charge injection into a semiconductor substrate, despite the low Power Conversion Efficiency (PCE) of the resulting Iron-Sensitized Solar Cells (Fe(II)-SSCs) [1]. Recently, we reported a panchromatic co-sensitization strategy based on Fe(II)-NHC complexes, achieving an exceptionally high photocurrent density of 9 mAcm⁻² [2]. Nevertheless, the PCE remains limited by the low open-circuit photovoltage (V_{oc}), which generally is typically improved by tuning the TiO₂ Fermi Level position through the addition of an electron-rich base, such as tert-butyl pyridine (TBPY), to the electrolyte. However, despite the injection driving force on the order of 1 eV, which suggests no thermodynamic limitations, the presence of these alkaline additives proves detrimental in the system's efficiency. To date, the reasons behind the photocurrent loss remains cryptic. Herein, we reported a deep investigation on the role of tert-butyl pyridine in Fe(II)-SSCs and its impact on photocurrent suppression, combining photoelectrochemical analysis with ultra-fast spectroscopy. Thermodynamics effects contribute to the performance degradation, as depicted by the Marcus parabola trend. Nevertheless, compared to well-established ruthenium complexes, it is not sufficient to outline the observed losses.

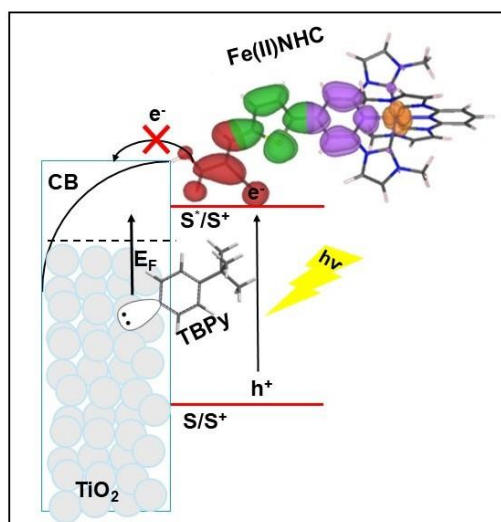


Figure 1. Schematic representation of an Fe(II)-SSC, with the absorption of TBPY onto TiO₂ also depicted.

References

- [1] S. Ferrere, B. A. Gregg, *JACS* **1998**, 120 (4), 843-844
- [2] A. Reddy-Marri, E. Marchini, V. Diez Cabanes, R. Argazzi, M. Pastore, S. Caramori, P.C. Gros, *Chem. Sci.* **2023**, 14, 4288-4301

Reaction-Diffusion Simulations of Photoredox Processes in Solution

S. A. Liedtke^a, M. Trulsson^a, P. Persson^a

^aComputational Chemistry Division, Chemistry Department, Lund University,
Box 124, SE-22100 Lund, Sweden
simon.liedtke@compchem.lu.se

A computational method to simulate bimolecular quenching reactions in solution using coarse-grained reaction-diffusion dynamics is presented and applied to quenching of molecular photosensitizers in solutions.^[1,2,3,4] The simulations are implemented to describe photoinduced reactions involving explicit excited states of light-harvesting species, that can be populated by a pulsed excitation, together with intrinsic deactivation as well as collision quenching from separate quencher species (**Figure 1**). The presented simulation methodology is applied to quenching of light-harvesting Fe(III) complexes in electron donating solvents over a wide range of quencher concentrations as a prototype system of experimental interest for the reaction-diffusion dynamics over a wide range of concentrations.^[3] The results show clear signatures for the transition from classical diffusion-limited Stern-Volmer dynamics to close-contact quencher-photosensitizer interactions at high quencher concentrations, and the simulations are used to assess physically realistic photosensitizer-quenching collision interaction parameters for photoinduced dynamics beyond the classical Stern-Volmer model.

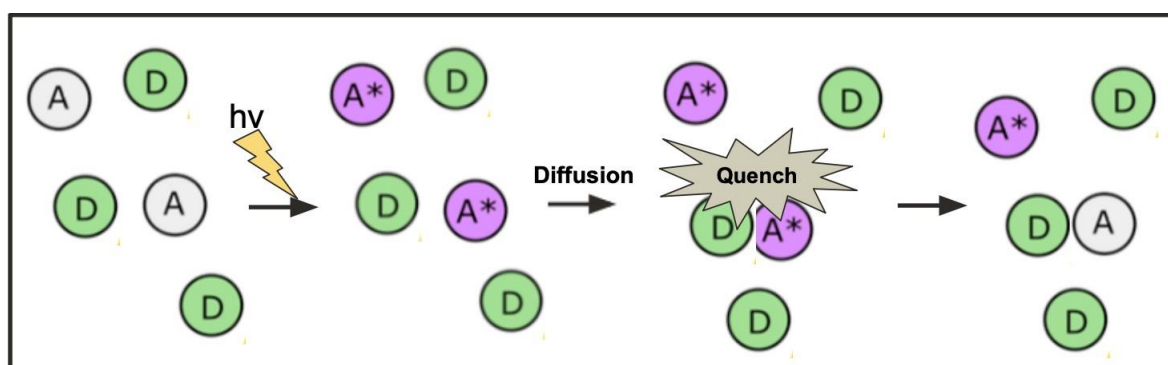


Figure 1: Collision quenching of donor and excited acceptor.

Acknowledgements:

The Swedish Research Council (VR, 2021-05313), the Knut and Alice Wallenberg (KAW, 2016.0059) foundation, the Swedish e-Science initiative eSENCE, and NanoLund are acknowledged for support. Computing resources were generously provided by the LUNARC and NSC high performance computing centers via SNIC/NAISS allocations. We thank Prof. Arkady Yartsev for valuable discussions.

References:

- [1] I. R. Gould and S. Farid, *Accounts of Chemical Research*, **1996**, 29, 522–528.
- [2] M. H. Gehlen, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, **2020**, 42, 100338.
- [3] N. W. Rosemann, P. Chábera, O. Prakash, S. Kaufhold, K. Wärnmark, A. Yartsev and P. Persson, *Journal of the American Chemical Society*, **2020**, 142, 8565–8569.
- [4] S. A. Rice, C. H. Bamford, C. F. H. Tipper and R. G. Compton, *Diffusion-limited reactions*, Elsevier, Amsterdam, **1985**.



Key factors influencing cage escape in photoinduced electron transfer.

A. K. Vega Salgado^a and L. Troian-Gautier^{a,b}

^aUCLouvain, Institut de la Matière Condensée et des Nanosciences (IMCN), Molecular Chemistry, Materials and Catalysis (MOST), Place Louis Pasteur 1/L4.01.02, B-1348 Louvain-la-Neuve, Belgium

^bWel Research Institute, Avenue Pasteur 6, 1300 Wavre, Belgium

The interaction between an excited-state photosensitizer and a quencher within an encounter complex can give rise to bimolecular electron transfer, leading to the formation of the corresponding geminate radical pair. The cage escape yield, i.e. the separation of the geminate radical pair is key for many light induced transformations. Many factors have been proposed to affect the cage escape process, such as the spin, the driving force for forward or reverse electron transfer, viscosity, etc ^[1,2]. One of the parameters that has been proposed to influence the cage escape is the driving force for forward or reverse electron transfer between a photosensitizer and a quencher ^[2,3,4].

In here, we investigated the effect of spin and driving force for forward and reverse electron transfer using 8 Ruthenium and 4 Osmium photosensitizers and using phenothiazine and tris(4-methoxyphenyl)amine as electron donors. Quenching rate constants, determined by steady-state and time-resolved spectroscopic techniques, ranged from 9×10^7 to $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile. The cage escape yields were determined through comparative actinometry method, using changes in molar absorption coefficients that were determined by spectroelectrochemistry. Clear trends with driving force as well a spin state were observed, where cage escape yields were larger for Ru(II) than Os(II) photosensitizers and were also larger when the driving force for geminate charge recombination was located furthest in the Marcus inverted region.

Acknowledgments

This work was supported by the “Action de Recherche Concertée” through the project “UNCAGED” under grant no. 23/28-135.

References

- [1] A. Ripak, A.K. Vega Salgado, D. Valverde, S. Cristofaro, O.Y. de Gary A, B. Elias, and L. Troian-Gautier. *Journal of the American Chemical Society* **2024**, *146* (32), 22818-22828.
- [2] M.J. Goodwin, J.C. Dickenson, A. Ripak, A.M. Deetz, J.S. McCarthy, G.J. Meyer, and L. Troian-Gautier, *Chemical Reviews* **2024**, *124* (11), 7379-7464.
- [3] S. De Kreijger, F. Glaser and L. Troian-Gautier, *Chem Catalysis* **2024**, *16* (11), 101110.
- [4] A. Ripak, S. De Kreijger, R.N. Sampaio, C.A. Vincent, É. Cauët, I. Jabin, U.K. Tambar, B. Elias, L. Troian-Gautier, *Chem Catalysis* **2023**, *3* (2), 100490.

Unveiling the Activation Pathway of the CO₂ reduction catalyst Trans-(Cl)-[Ru(X,X'-dimethyl-2,2'-bipyridine)(CO)₂Cl₂] by Direct Spectroscopic Observation^[1]

Sergio Aranda, Luka Tatarashvili, Kerstin Oppelt, Peter Hamm Department of Chemistry, University of Zürich, Switzerland

We report on the activation pathway (*Figure 1*) of a series of CO₂ reduction catalyst, Trans-(Cl)-[Ru(X,X'-dimethyl-2,2'-bipyridine)(CO)₂Cl₂], with a focus on Trans-(Cl)-[Ru(6,6'-dimethyl-2,2'-bipyridine)(CO)₂Cl₂ or Ru6dmb^[2], in the presence of the reductive quencher 1-{benzyl}-1,4-dihydronicotinamide or BNAH and the photosensitizer Ru(bpy)₃Cl₂. Most mechanistic studies of these types of catalytic systems use spectroelectrochemistry in the IR, where the vibrational frequencies of the carbonyl vibrations report on the electron density on the metal center. However, spectroelectrochemistry may miss short-lived intermediates, while at the same time the spectra can be dominated by accumulating side-products, which may play only a minor role in the reaction cycle. Transient IR spectroscopy on all relevant timescales, from picoseconds to 100s of milliseconds, can bridge this gap, revealing a surprisingly complex reaction pathway. That is, electron transfer from the reduced photosensitizer is followed by a loss of a first chloride ligand, a replacement of the second chloride ligand by a solvent molecule, and a ligand rearrangement that releases the strain between the equatorial carbonyl ligands and the methyl group on the bpy ligand in this catalyst. These reaction steps happen on a ten of nanoseconds to tens of microseconds timescale. In the case of Ru6dmb, the complex is then reduced a second time from the oxidized 1-{benzyl}-1,4-dihydronicotinamide on a significantly slower 10-100 ms timescale, protonated and the solvent ligand is exchanged back to a chloride. The final product hence is a hydride, trans-(Cl)-[Ru(6,6'-dimethyl-2,2'-bipyridine)(CO)₂ClH]^[3], which is stable on a minute-to-hour timescale.

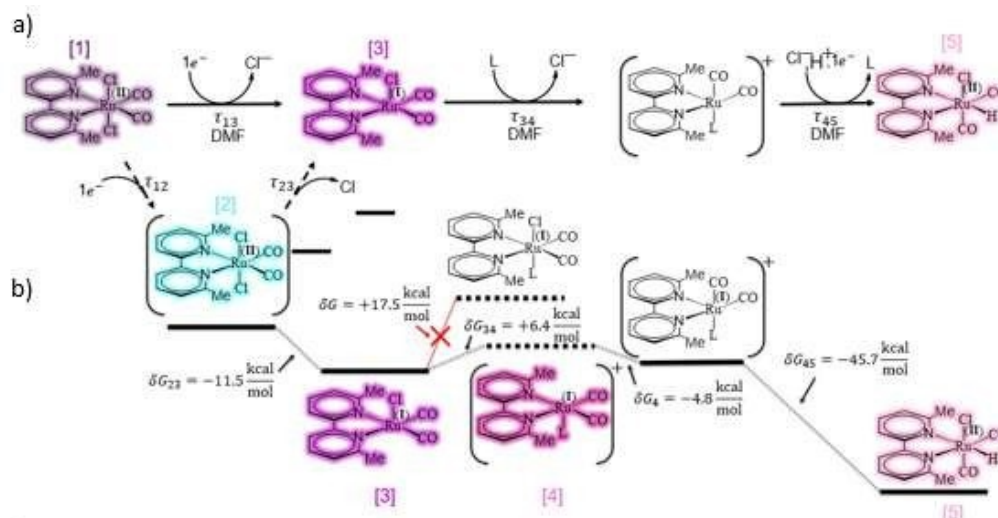


Figure 1. Proposed mechanism for Ru6dmb as a catalyst, Rubp3 and BNAH system based on a) experimental TRIR measurements and b) DFT calculations.

References

- [1] Aranda-Ruiz, S., Tatarashvili, L., Oppelt, K., & Hamm, P. (2025). *ACS Catalysis*, 15, 3023-3037.
- [2] Kuramochi, Y., Itabashi, J., Toyama, M., Ishida, H., *J. ChemPhotoChem*, **2(3)**, 314-322 (2018)b.)
- [3] Machan, C.W., Sampson, M.D., Kubiak, C.P., *J. Am. Chem. Soc.*, **137**, 8564 - 8571 (2015).



Sustainable Luminescent Materials for Next-Generation Smart Building Integration

O. Essahili,^a M. Ilsouk,^a C. Duhayon,^b O. Moudam^a

^a*Applied Chemistry and Engineering Research Centre of Excellence (ACER CoE) Mohammed VI Polytechnic University (UM6P) Lot 660, Hay Moulay Rachid, 43150 Benguerir, Morocco*

^b*Laboratoire de Chimie de Coordination du CNRS Institution 205, route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4, France
othmane.essahili@um6p.ma*

In this work, five phenanthroline derivatives substituted with different methyl groups have been selected to synthesize β diketonate-based europium complexes to check the influence of the substitutions on the degradation effect of those complexes in poly(methyl methacrylate) (PMMA) films. The photophysical properties of Eu(III) complexes, including absorbance, excitation, and emission have been carefully investigated in solution, solid-state, and doped in PMMA film. In all these states, the complexes exhibit an impressive red emission at 614 nm with a high photoluminescence quantum yield of up to 85%. The films have been exposed under outdoor, indoor, and dark storage stability lifetime conditions for 1200 hours. The photoluminescence measurements recorded every 400, 800, and 1200 hours demonstrated that the film containing europium complex with phenanthroline ligand substituted by a high number of methyl groups (Eu(TTA)₃L5) showed good photoluminescent stability in indoor and dark conditions, and exhibited better resistance to degradation in outdoor conditions compared to other complexes. This study has proved that phenanthroline ligands could be tuned chemically leading to better stability of those types of complexes in films which can be end-used for future stable optoelectronic devices such as luminescent solar concentrators.

Acknowledgment

Thanks to UM6P for funding the project * **Elaboration of sustainable luminescent materials based on rare earth complexes for solar energy conversion**.*

References

[1] O. Essahili, M. Ouafi, M. Ilsouk, O. Lakbita, C. Duhayon, L. Mahi, O. Moudam, *ChemistryOpen*, **2024**, 13, e202300192

Supramolecular interaction in Ru-Co and Ru-Fe complexes for efficient solar-driven hydrogen evolution and CO₂ reduction

F. Mancini^a, A. Bianco^a, A. Ruggi^b, G. Bergamini^a

^aDepartment of Chemistry "Giacomo Ciamician", University of Bologna, Italy

^bDepartment of Chemistry, University of Fribourg, Switzerland.

francesca.mancini27@unibo.it

Cyano (CN)-bridged ruthenium complexes, such as [Ru(bpy)_xCN_y], are known to form photoactive supramolecular assemblies via cyanide group coordination to metal ions. These complexes exhibit remarkable redox and photophysical properties, and their ability to form polynuclear structures has been well-documented.^[1,2]

In this study, we explore the potential of [Ru(bpy)₂CN₂] within the field of solar energy conversion, focusing on its application to molecular hydrogen evolution and CO₂ reduction. The primary objective is to enhance the electron transfer from the photosensitizer to the catalyst through supramolecular interaction, thereby improving the efficiency of the photoreactions.

We investigate the formation of the supramolecular adduct between [Ru(bpy)₂CN₂] and hexadentate polypyridyl cobalt and iron complexes.^[3,4]

Spectroscopic titrations were employed to monitor changes in absorbance, luminescence intensity, and lifetimes of the [Ru(bpy)₂CN₂] complex upon addition of the catalyst. Our results demonstrate the successful formation of 1:1 supramolecular adducts, exhibiting a high association constant ($K_{\text{ass}} \approx 10^5 \text{ M}^{-1}$), which results in efficient static quenching of the ruthenium complex emission. The photocatalytic system comprises the [Ru(bpy)₂CN₂] photosensitizer, the catalyst and 1,3dimethyl-2-phenylbenzimidazoline (BIH) as sacrificial electron donor, operating in an acetonitrile medium. Depending on the catalyst employed, the photocatalytic cycle promotes one of the two photoreactions with highly promising performances: hydrogen evolution in the presence of the cobalt complex and CO₂ reduction in the presence of the iron complex.

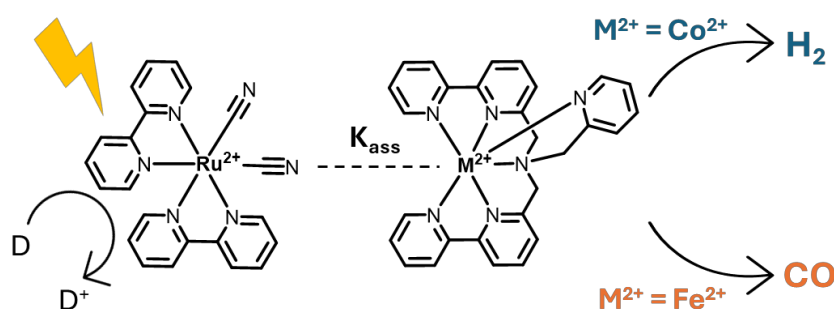


Figure 1. Schematic representation of the photo-driven hydrogen evolution and CO₂ reduction mechanisms through Ru-Co and Ru-Fe supramolecular interactions.

References

- [1] T. Lazarides et al., *Journal of the American Chemical Society*, **2007**, 129 (13), 4014-4027.
- [2] M. G. Kinnaird et al., *Chemical Physics Letters*, **1982**, 88 (3), 275-280.
- [3] F. Lucarini et al., *Chemistry—A European Journal*, **2017**, 23 (28), 6768-6771
- [4] F. Droghetti et al. *ChemSusChem*, **2024**, 17 (4), e202300737.

Combining Effective Hamiltonians and Brillouin-Wigner approach: A step by step construction of energy states from perturbation theories

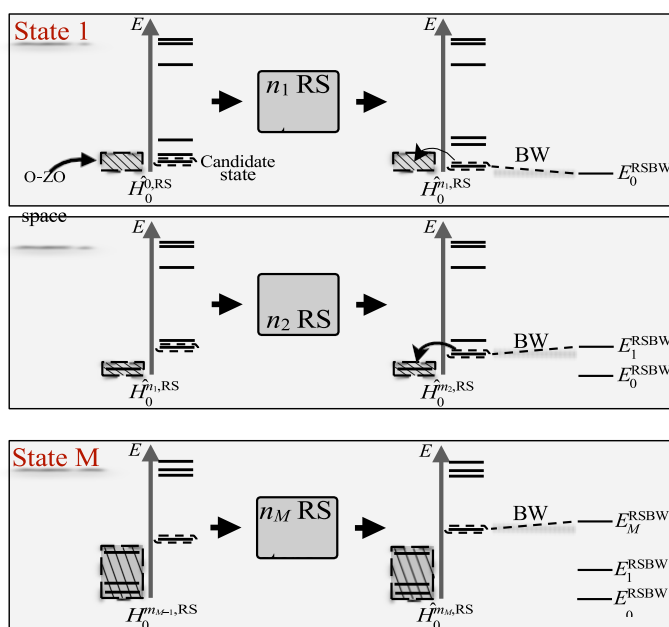
O. Bindech^a, S. Yalouz^a, V. Robert^a

^a Laboratoire de Chimie Quantique de Strasbourg, 4 rue Blaise Pascal 67000 Strasbourg-FRANCE, Institut de Chimie de Strasbourg, CNRS, Université de Strasbourg

The high computational cost of variational methods often drives the adoption of perturbative approaches for determining the electronic structure of molecular systems. A recent study^[1,2] introduced a multi-step Rayleigh-Schrödinger perturbative scheme that sequentially constructs effective Hamiltonians, providing an efficient means to approximate both model functions and their associated energies. In a subsequent step, the method takes advantage of an updated partitioning of the Hamiltonian to perform a state-specific Brillouin-Wigner energy correction, which further enhances the accuracy of the computed results. Building on this framework, the method proposed here follows a similar step-by-step approach for constructing the energy levels of a system, with a focus on reliably determining the lowest-lying state energy. This strategy offers a more refined and computationally efficient pathway for electronic structure calculations, making it especially valuable for complex molecular systems.

The construction of the energy states is exemplified through several chemical systems, highlighting its reliability in accurately capturing energy levels and its potential for practical applications in spectroscopy, where precise energy state determination is essential for understanding molecular properties and behaviors.

Figure 1. The diagram illustrates the calculation of a specific states using the RSBW approach. Initially, the Optimized Zero-Order (OZO) space is empty, and the first candidate is the lowest-energy zero-order state. After several Rayleigh-Schrödinger treatments, the candidate state becomes a reliable model for the target eigenstate. This state is then integrated into the OZO-space and processed with a Brillouin-Wigner scheme to obtain the final energy. The procedure is repeated for each subsequent state, with the next candidate chosen as the lowest-energy state outside the OZO-space.



References

- [1] Delafosse, L., Hussein, A., Yalouz, S., & Robert, V. (2024). A two-step Rayleigh-Schrödinger Brillouin-Wigner approach to transition energies. *Electronic Structure*, 6(1), 015009.
- [2] Bindech, O., Valentin, B., Yalouz, S., & Robert, V. (2024). Combining effective Hamiltonians and Brillouin-Wigner approach: a perturbative approach to spectroscopy. *Electronic Structure*, 6(4), 045009.

Photocatalytic H₂ Evolution by Pyridinium-tethered Mononuclear and Dinuclear Platinum Complexes

F. Sueyoshi, K. Yamauchi, K. Sakai

Department of Chemistry, Faculty of Science, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan.

sueyoshi.fumika.622@s.kyushu-u.ac.jp

Artificial photosynthesis has attracted much attention in recent years as one of the promising approaches to solve the energy shortage and global warming. One of the interests has also concentrated on the development of fully aqueous photocatalytic system.^[1] With this aim, Pt-based single-molecular photocatalysts for H₂ evolution reaction have been extensively studied.^[2,3] On the other hand, a recent mechanistic study revealed that dimerization of the catalyst is a key to accelerate H₂ evolution catalyzed by platinum-bipyridine type complexes.^[4] The dimerization has been considered to play a key role of stabilizing the hydride intermediate based on the metal-metal bonding.^[5]

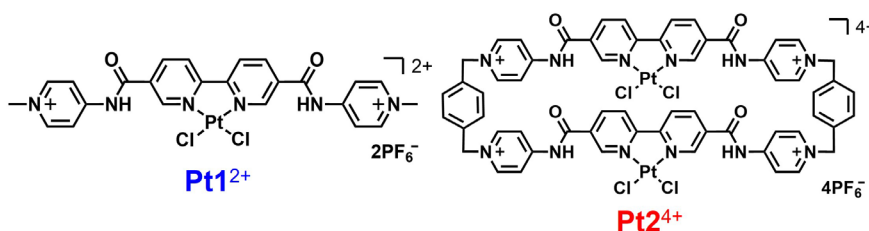


Figure 1. The structures of **Pt1²⁺** and **Pt2⁴⁺**.

In this study, we synthesized new mononuclear and dinuclear platinum photocatalysts (**Pt1²⁺**, **Pt2⁴⁺**, **Figure 1**) to evaluate the role of dinucleating ligand installed in **Pt2⁴⁺**. By adopting positively-charged pyridinium, these complexes are designed to have high water-solubility. Additionally, the rigid macrocyclic chelate ligand is expected to facilitate the Pt-Pt interaction. **Pt1²⁺** and **Pt2⁴⁺** were successfully characterized by ¹H NMR and ESI-TOF-MS and elemental analysis. It was found that **Pt1²⁺** and **Pt2⁴⁺** show photocatalytic activity for H₂ evolution in the presence of EDTA (**Figure 2**). The difference in their photocatalytic activity was investigated by photochemical and electrochemical technique.

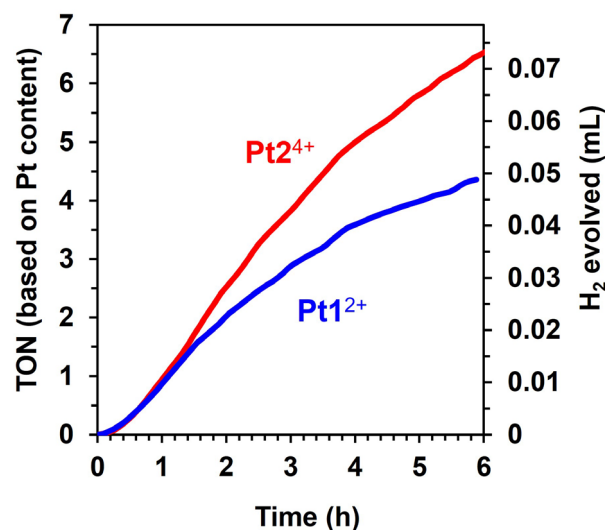


Figure 2. Photocatalytic H₂ evolution activities of **Pt1²⁺** (0.05 mM) or **Pt2⁴⁺** (0.025 mM) in an aqueous acetate buffer (pH = 5.0, 0.1 M) containing 20 vol % TFE and EDTA (30 mM) under Ar. Irradiated by Xe lamp ($\lambda > 400$ nm, 300 mW cm⁻²).

References

- [1] F. Sueyoshi, X. Zhang, K. Yamauchi, K. Sakai, *Angew. Chem. Int. Ed.* **2023**, 62 (9), e202217807.
- [2] H. Ozawa, M. Haga, K. Sakai, *J. Am. Chem. Soc.* **2006**, 128 (15), 4926-4927.
- [3] K. Yamauchi, K. Sakai, *Dalton Trans.* **2015**, 44 (18), 8685-8696.
- [4] F. Wakiyama, *Doctor thesis, Kyushu University* **2020**.
- [5] K. Sakai, H. Ozawa, *Coord. Chem. Rev.* **2007**, 251 (21-24), 2753-2766.



High-Efficiency Photoinduced Charge Separation in Iron N-Heterocyclic Carbenes

M. Zhang,^a J. Schwarz,^b O. Prakash,^b A. Ilic,^b K. Wärnmark,^b R. Lomoth^a

^aDepartment of Chemistry – Ångström Laboratory, Uppsala University, SE-75120 Uppsala, Sweden.

^bCenter for Analysis and Synthesis, Department of Chemistry, Lund University, SE-22100 Lund, Sweden
minli.zhang@kemi.uu.se

Iron N-heterocyclic carbenes (FeNHCs) have, in recent years, emerged as novel photoactive compounds and attracted tremendous attention for their potential in offering interesting excited-state reactivities.^[1] Symmetry-breaking charge separation (SBCS) in molecular systems has been widely investigated from a fundamental perspective and in view of potential applications in photovoltaics and photocatalytic applications.^[2] However, the scarcity of bimolecular SBCS cases and the demand of solvation processes to assist the SBCS in multichromophoric assemblies has limited the application of SBCS reactions. It has been proven that certain Fe(III) N-heterocyclic carbene compounds provide exceptional properties that are capable of oxidizing or reducing the complex in its ground state by its ²LMCT excited state. Bimolecular SBCS of a Fe(III)NHC complex was recently demonstrated in fluid solution^[3] and the intrinsic driving force for charge separation makes these chromophores promising candidates for SBCS in the solid state.^[4] Herein, the bimolecular SBCS study of several FeNHCs will be presented. The ultrafast spectroscopy and photoconductivity studies show that high-efficiency photoinduced charge separation can be achieved in FeNHC solids despite their differences in the excited-state lifetimes and the SBCS driving forces, which provide new insight into the consideration of the potential applications for FeNHCs.

Acknowledgments

Thanks to the Swedish Research Council (VR, 2020-05058), the Foundation for Strategic Research (SSF, EM16-0067), and the Knut and Alice Wallenberg Foundation (KAW2018.0074) for financial support on research. Thanks to C.F. Liljewalch Scholarship Foundation for financial support on traveling.

References

- [1] K. S. Kjær, N. Kaul, O. Prakash, P. Chábera, N. W. Rosemann, A. Honarfar, O. Gordivska, L. A. Fredin, K. E. Bergquist, L. Häggström, T. Ericsson, L. Lindh, A. Yartsev, S. Styring, P. Huang, J. Uhlig, J. Bendix, D. Strand, V. Sundström, P. Persson, R. Lomoth, K. Wärnmark. *Science*, **2019**, 363, 249–253. L. H. M. Groot, A. Ilic, J. Schwarz, K. Wärnmark. *J. Am. Chem. Soc.*, **2023**, 145, 9369–9388.
- [2] L. Estergreen, A. R. Mencke, D. E. Cotton, N. V. Korovina, J. Michl, S. T. Roberts, M. E. Thompson and S.E. Bradforth, *Accounts of Chemical Research*, **2022**, 55, 1561-1572; X. Zhao, R. M. Young, C. Tang, G. Wu, K. R. Peinkofer, Y. Han, S. Yang, Y.-K. Xing, H. Han, H. Wu, X. Li, Y. Feng, R. Zhang, C. L. Stern, M. R. Wasielewski and J. F. Stoddart, *Chem*, **2025**, 11, 102248.
- [3] N. Kaul and R. Lomoth, *J. Am. Chem. Soc.*, **2021**, 143, 10816-10821.
- [4] M. Zhang, C. E. Johnson, A. Ilic, J. Schwarz, M. B. Johansson and R. Lomoth, *J. Am. Chem. Soc.*, **2023**, 145, 19171-19176.

Altering the optical properties of Zn-porphyrin through β -substitutions

E. Elbasher,^a P. Wagner,^b D. L. Officer,^b K. C. Gordon^a

^a*Department of Chemistry and Dodd Walls Centre, University of Otago, Dunedin 9016, New Zealand.*

^b*Australian Institute of Innovative Materials, University of Wollongong, Wollongong, Australia.*

elbel670@student.otago.ac.nz

Zn porphyrins, recognized for their unique optical properties, play a crucial role in photonic and electronic applications. Four β -substituted Zn porphyrins were examined to determine how different substituents influence their electronic transitions. An unmodified Zn porphyrin typically features two primary absorption bands: the Soret (B) band (~ 420 nm) and the Q band (550–600 nm). However, the introduction of substituents alters the frontier orbitals and enhances state mixing, resulting in additional electronic transitions. In derivatives containing methoxy-trimethyl-3H-indolium (Ind) and diphenyl-pyrimidinetrione (Pyr), which are electron-rich/neutral substituents, the porphyrin macrocycle is stabilized, promoting localized π – π^* transitions. This expansion of the UV–Vis absorption window (400–600 nm) results from two distinct transitions (B' and T, with molar absorptivities of ~ 40 $\text{mM}^{-1}\text{cm}^{-1}$) observed between the main B and Q bands. Extended conjugation further broadens and red-shifts the Q band to above 600 nm, with the Ind derivative showing a more pronounced red shift and a lower HOMO–LUMO gap (1.86 eV) compared to Pyr. Conversely, compounds bearing (dinitrophenyl)-methylenhydrazine (Hyd) and methylnitroethen-2-yl (Nitro) substituents, which are electron-deficient and exhibit twisted conformations, display a merged, broader B band (380–500 nm). Although TD-DFT predicts a strong transition around 523.2 nm and resonance Raman spectroscopy confirms its electronic character, the UV–Vis absorption remains weak due to spectral overlap and broadening. These findings underscore how modifications induced by substituents can extend conjugation, introduce a charge-transfer character, or preserve the inherent symmetry of the porphyrin core.

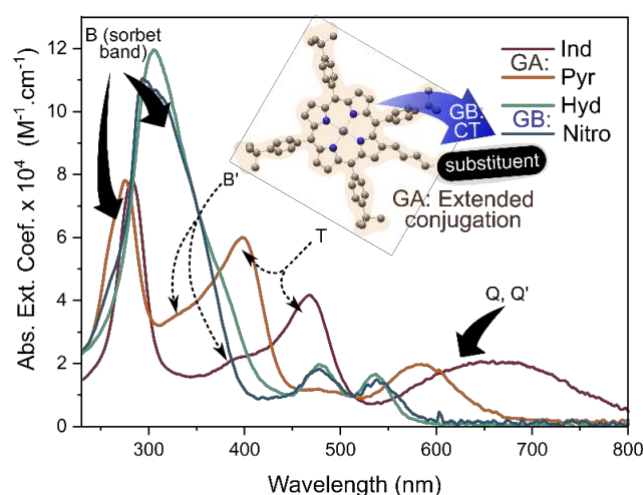


Figure 1. UV-Vis spectra of the four Zn-porphyrins, indicating the main electronic transitions.



Comparison of Iridium Sensitizers Employed in the Photoelectrochemical Generation of Added-Value Organics

Andrea Mantovani,^a Edoardo Marchini,^a Annagioia Mastrolorenzo,^b Paola Manini,^b Mirco Natali^a

^a*Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121 Ferrara, Italy.*

^b*Department of Chemical Sciences, University of Naples Federico II, Via Cintia 4, 80126 Napoli, Italy.*

andrea.mantovani@unife.it

The pressing issues of climate change need the development of sustainable technologies.^[1] Dye-sensitized photoelectrochemical cells (DSPECs) represent a promising approach to this challenge. In this regard, great attention has been paid in the last years towards the development of photoanodes for the water oxidation to dioxygen. However, this reaction still constitutes a major challenge due to its strict kinetic requirements and strategies have been recently envisioned to replace water oxidation with more favorable reactions.^[2] Within this framework, the present study targets the investigation of two different cyclometallated iridium complexes featuring highly positive oxidation potentials as sensitizers onto TiO₂ electrodes for the light-driven oxidation of organics into added-value products. In particular, two different processes have been considered, namely the oxidation of benzyl alcohol to benzaldehyde^[3] and a Diels-Alder reaction.^[4] The critical role of the sensitizer in the formation of the target products will be examined in details by combining photoelectrochemical measurements and optical spectroscopy.

References

- [1] C. Wang, M. Amiri, R. T. Endean, O. Martinez Perez, S. Varley, B. Rennie, L. Rasu, S. H. Bergens, *ACS Appl. Mater. Interfaces*, **2018**, *10*, 24533–24542.
- [2] M. Natali, A. Sartorel, A. Ruggi, *Front. Chem.*, **2022**, *10*, 1-8.
- [3] G. Di Carlo, C. Albanese, A. Molinari, S. Carli, R. Argazzi, A. Minguzzi, F. Tessore, E. Marchini, S. Caramori, *ACS Appl. Mater. Interfaces*, **2024**, *16*, 14864–14882.
- [4] M. D. Turlington, S. Ahmed, K. S. Schanze, *ACS Catal.*, **2024**, *14*, 12512–12517.

Stabilizing High Spin States in Fe(II)-N_{amido} Complexes to Tune Visible Light Absorption and Excited State Behaviour

B.K. Sidhu,^a R.J. Ortiz,^a C. Wegeberg,^{b,c} Petter Persson,^d Arkady Yartsev,^b D.E. Herbert^a

^a Department of Chemistry, University of Manitoba, Winnipeg, MB R2P 0M1, Canada

^b Division of Chemical Physics, Department of Chemistry, Lund University, 22100 Lund, Sweden

^c Current affiliation: Department of Chemistry, Physics and Pharmacy, University of Southern Denmark, 5230 Odense M, Denmark

^d Division of Computational Chemistry, Department of Chemistry, Lund University, 22100 Lund, Sweden

sidhub34@myumanitoba.ca

Iron coordination complexes have long been sought as a sustainable replacement for precious metal sensitizers in applications that exploit photo-generated excited states, from luminescent materials to photoredox catalysis to dye-sensitized solar cells. The main shortcoming of iron-based dyes is their short-lived charge transfer (CT) excited states which result from rapid relaxation to low-lying metal centered states. Photophysics of Fe(II) complexes so far have been dominated by low-spin, singlet ground states, while the photophysics originating from high spin, quintet ground states stay underexplored. This talk will shine light on ligand design strategies to stabilize high spin ground states in pseudo-octahedral Fe(II)-N_{amido} complexes while maintaining strong visible light absorption, and how that influences the excited state behaviour of these complexes compared to their low spin congeners.

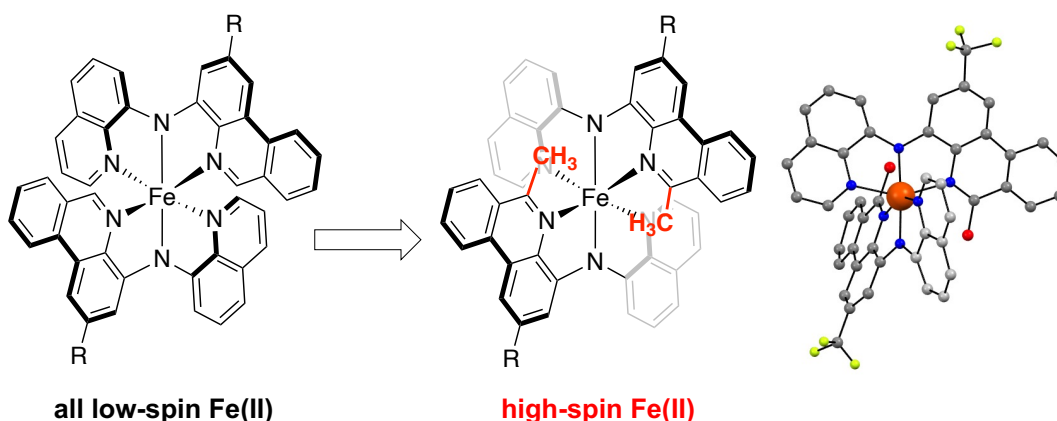


Figure 1. Stabilizing high spin, quintet ground states in pseudo-octahedral Fe(II)-N_{amido} complexes.

Acknowledgements

Thanks to my supervisor David Herbert, everyone in the Herbert group, and to our collaborators Chritina Wegeberg, Arkady Yartsev and Petter Persson from Lund University.

Novel Spectroscopic Approaches to Evaluate the Excited Triplet States of Metal Complexes using Magnetic Circular Dichroism

H. Yanagikawa,^a K. Ishii.^a

^aInstitute of Industrial Science, the University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo, 153-8505, Japan.

h-yanagi@iis.u-tokyo.ac.jp

In recent years, the photophysical or photochemical properties of the molecular photoexcited triplet states have attracted considerable attention for developing novel photofunctional materials. For example, room temperature phosphorescence is useful for developing luminescent materials, such as organic electroluminescent devices. Also, singlet oxygen produced by energy transfer from the excited triplet molecules to molecular oxygen is a fundamental approach for photodynamic therapy. Therefore, the importance of analyzing the excited triplet states of metal complexes possessing heavy atoms has increased because of their large spin-orbit coupling (SOC).^[1]

Magnetic circular dichroism (MCD) spectroscopy is to measure the difference in absorption between left and right circularly polarized light under an external magnetic field. In the degenerated excited states, the dispersion-type MCD spectral shape, called the Faraday A term, can be obtained by the Zeeman splitting owing to the orbital angular momenta between the degenerated excited states.^[2] In addition to the spin-allowed transitions, our laboratory has applied the MCD spectroscopy to probing the spin-forbidden transitions by the use of large SOC on heavy atoms and highly concentrated solutions (**Figure 1**). Firstly, in an iridium(III) phthalocyanine (IrPc) complex, which possesses the strong SOC inducing the $S_0 \rightarrow T_1$ absorption band, a Faraday A term for the $S_0 \rightarrow T_1$ transition, indicating the degeneracy of the T_{1x} and T_{1y} states.^[3] Secondly, in a platinum(II) octaethylporphyrin (PtOEP) complex, a distinct Faraday A term was observed not only for the $S_0 \rightarrow T_1$ transition but also for the $S_0 \rightarrow T_2$ transition, which allows us to directly observe the nonluminescent, short-lived T_2 state.^[4]

Based on these previous studies, we applied MCD spectroscopy to the excited triplet states of octahedral hexanuclear molybdenum(II) clusters. We successfully observed the Faraday A term of the $S_0 \rightarrow T_1$ transitions in Mo clusters for the first time and analyzed their large SOC and orbital angular momenta consisting of d-orbitals of six Mo ions. Overall, we have demonstrated the usefulness of MCD for investigating the excited triplet states of metal complexes.

References

- [1] M. A. Baldo, M. E. Thompson, S. R. Forrest, *Nature* **2000**, 403 (6771), 750-753.
- [2] E. I. Solomon, M. L. Neidig, G. Schenk, *Comprehensive Coordination Chemistry II*, Elsevier, **2003**, 339.
- [3] K. Murata, K. Ishii, *Eur. J. Inorg. Chem.* **2017**, 2017 (44), 5103-5107.
- [4] K. Ishii, J. Wada, K. Murata, *J. Phys. Chem. Lett.* **2020**, 11 (22), 9828-9833.

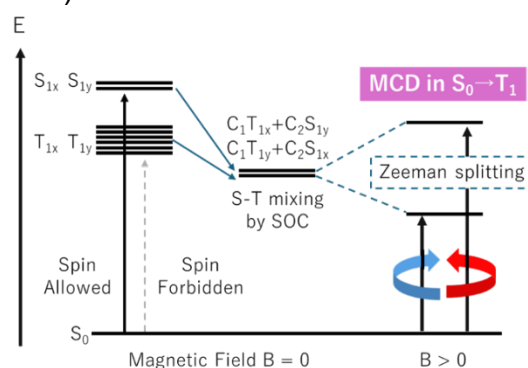


Figure 1. The mechanism of MCD Faraday A term in spin-forbidden $S_0 \rightarrow T_1$ transition.

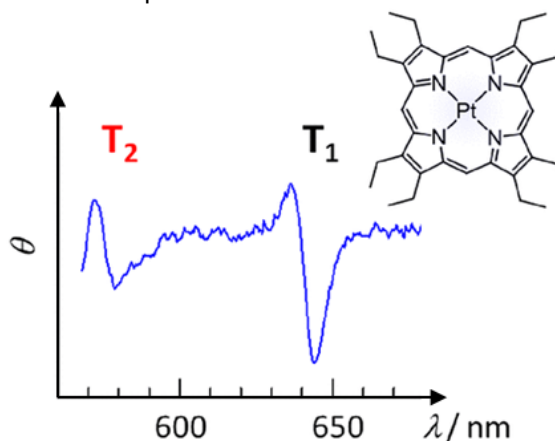


Figure 2. The MCD Faraday A term of excited triplet states in PtOEP.^[4]



Plastics detection using Hydrogels Functionalized with Switchable Iridium Complexes

N. Quadrio,^a C. Zehe,^b L. Menduti,^a N. Rossi,^b L. De Cola^{a,b}

^aDepartment of Pharmaceutical Science DISFARM Università degli Studi di Milano

^bDepartment of Molecular Biochemistry and Pharmacology, Istituto di Ricerche Farmacologiche Mario Negri IRCCS
nicolo.quadrio@unimi.it

Micro- and nanoplastics are increasingly recognized as significant environmental pollutants, with their toxicity influenced by factors such as particle size, polymer type, and exposure conditions. Among the deleterious effects of these pollutants we can count endocrine disruption, inflammation, oxidative stress and metabolic disturbances. ^[1] Hydrogels, known for their excellent water retention capacity, high adsorption, reversible swelling, and biocompatibility, are promising materials for environmental remediation. ^[2]

In the detection of nano- and microplastics, the most exploited luminescence-based strategy involves the use of fluorophores able to stain MPs. In this field, detection of the solvatochromic response of organic dyes (e.g. Nile red) to their surrounding polarity is one of the main interesting properties exploited for plastic detection. The use of hydrophobic dyes leads to their aggregation causing low emission problems, used to monitor the interaction with hydrophobic materials. ^[3] Organometallic complexes, with their color tunability and longer excited state lifetimes, can be a solution to the limitations of organic dyes.

In this contribution we report on neutral Ir(III)-complexes functionalized hydrogels able to switch on their emission upon interaction with hydrophobic plastics due to their de-aggregation, limited oxygen diffusion and increase rigidity due to the intermolecular interactions with the surrounding materials. The triplet state emission allows to monitor the switch-on of the phosphorescence by time resolved measurements. ^[4]

We show that a simple hydrogel covalently bound to Ir(III) complexes can indeed recognize and interact with PET plastics, and work is in progress to differentiate different microplastics by modulating the nature of the excited states.

References

- [1] K. Pellegrini, T.C.B. Pereira, T.G. Maraschin, *Sci. Total Environ.*, **2023**, 878, 162954
- [2] J. Yang et al., *Int J Biol Macromol*, **2021**, 189, 53-64
- [3] a) C. Capolungo, D. Genovese, M. Montalti, E. Rampazzo, N. Zaccheroni, L. Prodi, *Chem. Eur. J.* **2021**, 27, 17529–17541; b) M. Cingolani, E. Rampazzo, N. Zaccheroni, D. Genovese, L. Prodi, *Environ Sci Nano*, **2022**, 9, 582–588
- [4] F. Fiorini, E. Longhi, A. Lázaro, D. Di Prisco, G. Tamboia, G. Alonci, L. Menduti, L. De Cola *Chem. Eur. J.* **2025**, e202404572

A bright exception : Rare case of anti-Kasha $^1\text{ILCT}$ emission from Co(III) complexes based on Amidine-*N*-oxide ligands

A. Saha,^a G. Turner,^a M. Cibian,^b S. Serroni,^c S. Campagna,^c S. Genovese,^c G. S. Hanan,^a and F. Nastasi.^c

^a Dept. de Chimie, Université de Montréal, Montréal, Canada

^b Dépt. de biochimie, chimie, physique et science forensique and Institut de recherche sur l'hydrogène, Université du Québec à Trois-Rivières, Canada

^cDipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali and Interuniversity research center SOLAR-CHEM, University of Messina, Italy
arindam.saha@umontreal.ca

The photophysical properties of 3d metal complexes remain a fascinating field of study, particularly when transitioning from the rare 2nd and 3rd row metal complexes towards their abundant 1st row congeners.^[1-3] Here, we present a series of novel photoactive Co(III) metal complexes based on amidine-*N*-oxide ligands. These complexes exhibit unusual anti-Kasha type singlet emissions. Contrary to the widely accepted Kasha emitters, which emit from the lowest-lying excited state, these complexes show room temperature fluorescence from higher-lying states consisting of an admixture of $^1\pi-\pi^*$ and intra-ligand charge-transfer ($^1\text{ILCT}$) character. Detailed steady state and ultrafast spectroscopy alongside extensive theoretical calculations establish the electronic factors governing this behavior. The structural rigidity and higher lying π orbitals of the ligands render these metal complexes photoactive.^[4]

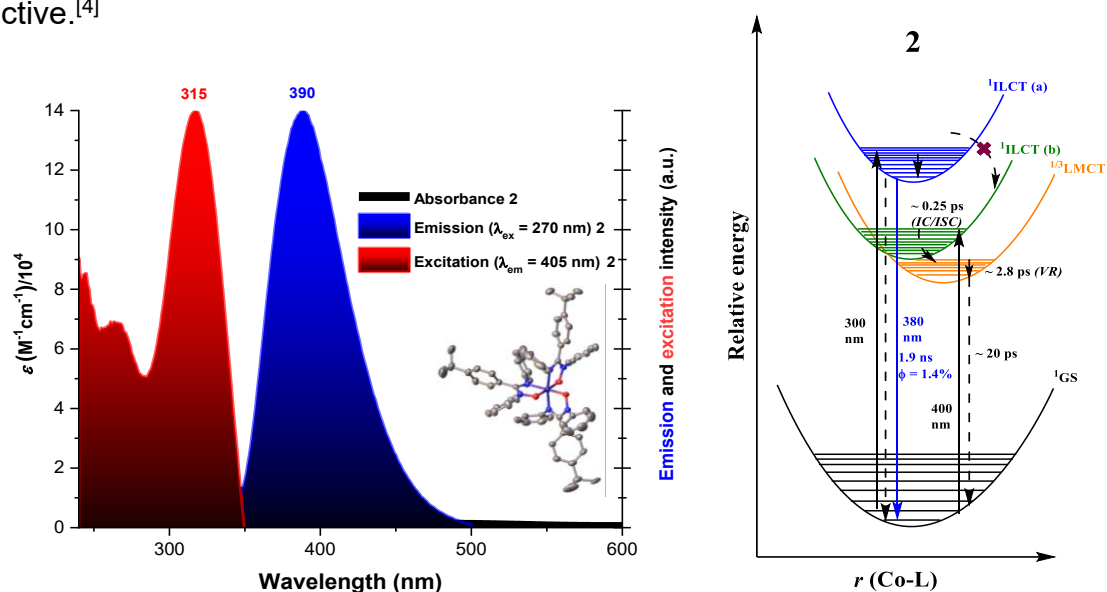


Figure 1. Graph showing the absorbance and emission spectra for one of the Anti-Kasha Co(III) complexes (left) and schematic for the decay pathway (right)

Acknowledgments

AS, GT, GSH thank FRQNT, CCVC, CQMF, NSERC and UdeM for financial support. SC, SS, SG and FN thank NextGeneration EU and European Union-FSE-REACT-EU for funding.

References

- [1] A. K. Pal, C. Li, G. S. Hanan, E. Zysman-Colman, *Angew. Chem. Int. Ed.* **2018**, 57, 8027
- [2] Y. Zhang, T. S. Lee, J. M. Favale, D. C. Leary, J. L. Petersen, G. D. Scholes, F. N. Castellano, C. Milsmann, *Nat. Chem.*, **2020**, 12, 345
- [3] N. Sinha, C. Wegeberg, D. Häussinger, A. Prescimone, O. S. Wenger, *Nat. Chem.*, **2023**, 15, 1730
- [4] A. Saha, G. Turner, M. Cibian, S. Genovese, S. Serroni, S. Campagna, F. Nastasi, G.S. Hanan, *manuscript in preparation*

Sn^{IV}-porphyrins conjugates as bio-inspired models for artificial photosynthesis

G. Fogar,^{a,c} F. Droghetti,^b M. Natali,^b F. Berti,^a D.V. Filippov,^c S. Bonnet,^c E. Iengo^a

E. Dallerba,^a M. J. Hackett,^a M. Massi^a

^aDepartment of Chemical and Pharmaceutical Sciences, University of Trieste, Italy,

^bDepartment of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Italy,

^cLeiden Institute of Chemistry, Leiden University, The Netherlands.

greta.fogar@phd.units.it; g.fogar@lic.leidenuniv.nl

Photosynthesis, a fundamental biological process, involves water oxidation reaction catalyzed by three key components: initial light absorption by the chromophore, followed by oxidation of a tyrosine donor and reduction of a quinone acceptor, coupled with a proton transfer through a *Proton Coupled Electron Transfer* mechanism (PCET). The water oxidation, which occurs in Photosystem II (PSII), is a far more difficult process than proton reduction.^[1] By taking advantage of the peculiar opto-electronic and redox properties of Sn^{IV}-porphyrins,^[2] we will here show how conjugation of these chromophores to either a simple amino acid, or a peptide sequence may provide useful models to gain insights in artificial PCET or *unidirectional electron transfer* (ET). The synthesis, characterization, and photophysical behavior of two Sn^{IV}-porphyrin/tyrosine conjugates, which differ in the relative position between the amino acid and the chromophore, will be illustrated (**Figure, left**).^[3,4] Additionally, some preliminary results on the design and preparation of a Sn^{IV}-porphyrin/YALP conjugate (YALP = hydrophobic α -helical peptide with tyrosine residues, Figure, right) will also be shown. The latter system is designed in order to achieve the more ambitious goal of photo-induced unidirectional ET across a lipid membrane, and thus may serve as a model of PSII.^[5]

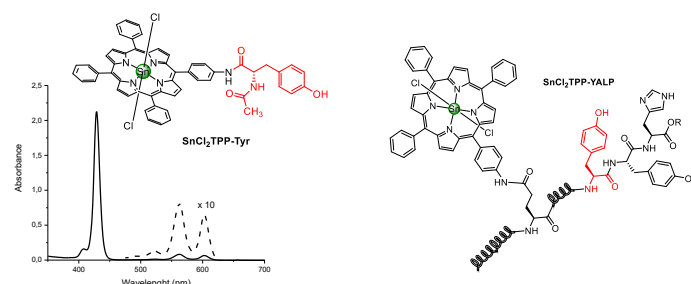


Figure 1. Example of a Sn^{IV}-porphyrin/amino acid conjugate for PCET studies (**SnCl₂TPP-Tyr**) and schematic representation of a Sn^{IV}-porphyrin/YALP conjugate for transmembrane unidirectional ET studies (**SnCl₂TPP-YALP**).

Acknowledgments

This work was supported by the European Union - Next Generation.

References

- [1] N. Nelson, C.F. Yocum, *Annu. Rev. Plant Biol.* **2006**, 57 (1), 521–565.
- [2] D.P. Arnold; J. Blok, *Coord. Chem. Rev.* **2004**, 248 (3–4), 299–319.
- [3] a) M. Natali, A. Amati, N. Demitri, E. Iengo, *Chem. Commun.* **2018**, 54 (48), 6148–6152; b) M. Natali, A. Amati, S. Merchiori, B. Ventura, E. Iengo, *J. Phys. Chem. C* **2020**, 124 (16), 8514–8525.
- [4] G. Fogar, F. Droghetti, F. Berti, M. Natali, E. Iengo, *manuscript in preparation*.
- [5] D.M. Klein, X. Li, A.L. Boyle, R. Van der Pol, A.J.A. Sevink, A.M. Brouwer, S. Bonnet, *manuscript in preparation*.

Examine 77 K Phosphorescence of $[\text{Os}(\text{bpy})_2(\text{en})]^{2+}$: ADF Modeling and Spin-Orbit Coupling Mediated Intensity Stealing

Yu-Hui Lin^a, Yuan Jang Chen^a, Ming-Kang Tsai^b

^aDepartment of Chemistry, Fu-Jen Catholic University, Taiwan R.O.C.

^bDepartment of Chemistry, National Taiwan Normal University, Taiwan R.O.C.

annlove60504@gmail.com

In early studies, the basic optical properties of the $[\text{Os}(\text{bpy})_3]^{2+}$ ion were characterized.^[1] Consequently, in this study, we report the 77 K emission spectra, the 298 K absorption spectra, and the computational results of the $[\text{Os}(\text{bpy})_2(\text{en})]^{2+}$ ion. The results of the 298 K absorption spectra indicate that there are two absorption bands in the low-energy absorption region. The singlet-to-singlet absorption transitions occur in the range of 17,000–22,000 cm^{-1} , whereas the absorption band in the range of 12,000–17,000 cm^{-1} is attributed to singlet-to-triplet transitions. Based on the properties of the $[\text{Os}(\text{bpy})_3]^{2+}$ ion and computational results,^[2] it was found that an intense singlet-to-triplet absorption band appears in the lowest absorption-energy region only when spin-orbit coupling (SOC) perturbations are included in the calculations. In this work, the low-energy absorption and emission spectra of $[\text{Os}(\text{bpy})_2(\text{en})]^{2+}$ ion were characterized as spin-forbidden metal-to-ligand charge-transfer transitions, which are attributed to the mechanics of SOC-mediated phosphorescence intensity stealing from efficient singlet states.^[3,4]

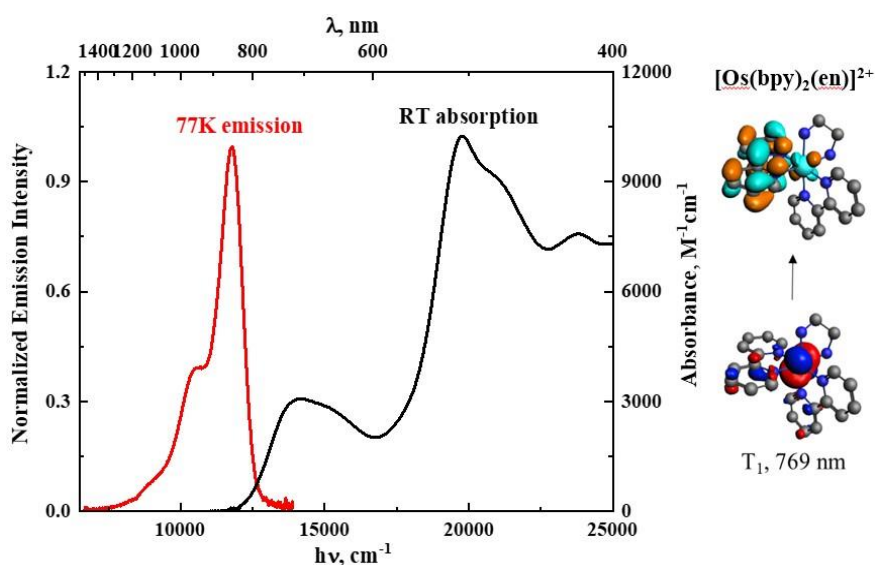


Figure 1. The 77 K emission spectra (red line, in butyronitrile) and the 298 K absorption spectra (black line, in CH_3CN) of the $[\text{Os}(\text{bpy})_2(\text{en})]^{2+}$ ion are shown in the left panel, along with the T_1 natural transition orbitals (NTOs) displayed in the right panel.

Aknowlegments

This work was funded by the National Science and Technology Council (Taiwan, ROC) through Grants NSTC 113-2113-M-030-006.

References

- [1] Crosby, G. A. et al., J. Am. Chem. Soc. **1971**, 93 (12), 2841-2847.
- [2] Ronca, E. et al., J. Phys. Chem. C **2014**, 118 (30), 17067-17078.
- [3] B. J. Powell, Coord. Chem. Rev. **2015**, 295, 46.
- [4] C. M. Marian, Comput. Mol. Sci. **2012**, 2, 187.

Solvent-Controlled Photoinduced Processes in a bis(acridinium-Zn(II) porphyrin)-tetra(4-pyridyl) porphyrin host-guest complex

F. Ruani,^a D. Veclani,^a D. Sánchez-Resa,^a A. Edo-Osagie,^b A. Barbieri,^a H.-P. Jacquot de Rouville,^b V. Heitz,^b B. Ventura,^a N. Armaroli^a

^aIstituto ISOF-CNR, Via P. Gobetti 101, 40129 Bologna, Italy

^bLaboratoire de Synthèse des Assemblages Moléculaires Multifonctionnels, Institut de Chimie de Strasbourg, CNRS/UMR 7177, 4 rue Blaise Pascal, 67000 Strasbourg, France

federica.ruani@isof.cnr.it

Metalloporphyrins, known for their rich photophysical and electrochemical properties, are widely studied as coordinating sites in supramolecular receptors.^[1] Notably, porphyrin-N-acridinium conjugates exhibit ultrafast electron transfer (eT) from the porphyrin donor to the acridinium acceptor, which quenches fluorescence in both units. Among these, a bis(acridinium-porphyrin) tweezer (**Figure 1**) stands out as a multi-responsive array with Zn(II) porphyrin coordination sites and acridinium switching units.^[2-3] Here, we explore its complexation with *meso*-(5,10,15,20-tetra(4-pyridyl)porphyrin) (**TPyP**) in two different solvents (CH₂Cl₂ and toluene) and discuss the photophysical behavior of the formed complex. Interestingly, the solvent polarity strongly affects the photophysical response of the system.

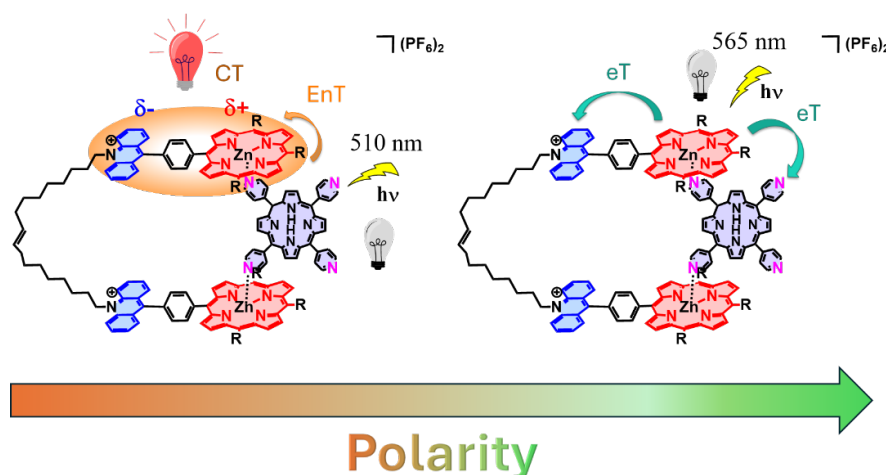


Figure 1. Effect of solvent polarity on photoinduced processes occurring in the host-guest complex.

Acknowledgments

The work is supported by the H2020-MSCA-ITN-2017-765297 project “NOAH”, by the H2020-LC-SC3-2020-RES-RIA-101006839 project “CONDOR” and by the European Union – Next Generation EU and the Italian Ministry of Environment and Energy Security (POR H2 AdP MMES/ENEA-CNR-RSE, PNRR–Mission 2, Component 2, Investment 3.5 “Ricerca e sviluppo sull’idrogeno”).

References

- [1] V. Valderrey, G. Aragay, P. Ballester *Coord. Chem. Rev.* **2014**, 258-259, 137-156.
- [2] A. Edo-Osagie, D. Sanchez-Resa, D. Serillon, E. Bandini, C. Gourlaouen, H. P. Jacquot de Rouville, B. Ventura, V. Heitz, *Cr. Chim.* **2021**, 24, 47-55;
- [3] A. Edo-Osagie, D. Serillon, F. Ruani, X. Barril, C. Gourlaouen, N. Armaroli, B. Ventura, H.-P. Jacquot de Rouville, V. Heitz, *J. Am. Chem. Soc.* **2023**, 145, 10691–10699.



Welcome to the Dark Side:

Photoactive Iron Complexes with Microsecond Excited-State Lifetimes

F. Glaser,^a S. De Kreijger,^a G. M. Beneventi,^b A. Cadranet,^{b,c} L. Troian-Gautier^{a,d}

^a UCLouvain, Place Louis Pasteur 1/L4.01.02, B-1348 Louvain-la-Neuve, Belgium

^b Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstr. 3, 91058, Erlangen, Germany.

^c Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, and CONICET INQUIMAE, Buenos Aires, Argentina.

^d Wel Research Institute, Avenue Pasteur 6, 1300 Wavre, Belgium
felix.glaser@uclouvain.be

In recent years, photosensitizer development based on earth-abundant metals or organic dyes as a replacement for precious metal complexes in photoredox catalysis has obtained significant attention.^[1] Iron-based complexes are very attractive for this due to its high abundance in the Earth crust, low toxicity and environmental impact.^[2,3] Up to now, the limited excited-state lifetimes up to a few nanoseconds represent a limiting factor to their widespread use.

One possibility to tackle this issue is the design of molecular dyads composed of a photosensitizer and an energy acceptor. Up to now, the development of dyads mostly focused on excited-state equilibrium to repopulate the iron-based emissive state exploiting a so-called reservoir effect.^[4,5] In contrast, we designed a molecular dyad composed of an energy acceptor attached to an iron-based photosensitizer that exhibited a microsecond-living non-luminescent excited state without repopulation of the iron-centered emissive state.^[6] Photophysical characterization and comparison to the unmodified iron photosensitizer highlighted the benefit of the energy acceptor present in the dyad. In addition to an improved excited-state lifetime, the energy acceptor also changed the excited-state character to triplet. This enables singlet oxygen photosensitization and led to a tenfold increase in cage escape yield for bimolecular electron transfer, in comparison to the unmodified complex. More detailed photophysical analyses uncovered that the mechanism to populate the triplet excited state is more complex than a direct doublet-triplet energy transfer. Our results clearly highlight the advantages of molecular dyads based on iron-based complexes with previously short excited-state lifetimes.

References

- [1] C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, 49, 1057–1070.
- [2] O. S. Wenger, *Chem. Eur. J.* **2019**, 25, 6043–6052.
- [3] F. Glaser, A. Aydogan, B. Elias, L. Troian-Gautier, *Coord. Chem. Rev.* **2024**, 500, 215522.
- [4] S. Campagna, S. Genovese, A. Cancelliere, A. Arrigo, F. Puntoriero *Res. Square* **2024**, DOI: 10.21203/rs.3.rs-4002627/v1.
- [5] J. Wellauer, J., B. Pfund, I. Becker, F. Meyer, A. Prescimone, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, 147 (10), 8760–8768.
- [6] F. Glaser, S. De Kreijger, L. Troian-Gautier, *J. Am. Chem. Soc.* **2025**, 147 (10), 8559–8567.

Investigation on One-Electron Reduced Species of ReI-naphthalimide photosensitizers

L. G. A. do Nascimento,^a S. Nikolaou,^a A. S. Polo^b

^aDepartment of Chemistry, FFCLRP-USP, Ribeirão Preto, Brazil

^bCenter for Natural and Human Sciences, UFABC, Santo André, Brazil

luis_nascimento@usp.br

Rhenium(I) complexes are promising candidates for artificial photosynthesis studies, mainly focused on CO₂ photoreduction.^[1] As this photoreduction requires that the complex act as catalyst and photosensitizer, it is very common that modifications in the organic ligands coordinated to the rhenium center occur to improve one of those characteristics.^[1] In this sense, 1,8-naphthalimide dyes reveal themselves as good ligands for this system, once the ability to suffer one or two consecutive reversible reductions makes their structure a powerful electron reservoir.^[2] Based on this, this work aims to investigate the use of two new rhenium compounds with general formula *fac*-[Re(CO)₃(phen)(NI)]PF₆, where phen = 1,10-phenanthroline and NI = (N)-piridil-1,8-naphthalimide (**1**) or 4-amino-(N)-piridil-1,8-naphthalimide (**2**) through its interaction with the triethanolamine (TEOA). Once the reduction of the complex by this sacrificial reagent, to form the one-electron reduced species (OERS), is a determinant step in the CO₂ photoreduction mechanism,^[1] a fluorescence titration of a deaerated solution of complexes **1** and **2** in N,N-dimethylformamide (DMF) (10⁻⁵ mol/L) with TEOA was carried out, and the data were treated using the Stern-Volmer equation, obtaining the linear fits represented in Figures 1A and 1B. The complex **1** was more sensitive to TEOA than the complex **2**, with a K_{SV} value of 142 (**1**) and 2.77 (**2**), being higher than the precursor *fac*-[Re(CO)₃(phen)(Cl)] (K_{SV} = 3.5).^[1] The reason for this high oxidizing potential of complex **1** is that on the excitation wavelength (λ_{exc} = 350 nm) we promote, simultaneously, a metal-to-ligand charge transfer (MLCT) transition from the Re(dπ) to the π* phen orbitals and a intraligand transition centered in the NI, while in complex **2**, with a λ_{exc} = 430 nm, the main transition observed is the intraligand charge transfer (ILCT) of the amino-naphthalimide. Previous cyclic voltametric studies reveal that the reduction potentials of these naphthalimides are too negative (~ -1.1 V vs NHE) to produce a driving force for the TEOA electron transfer, which explains the low quenching constant of complex **2**. However, in complex **1**, an intramolecular electron transfer from the NI^{•+} excited chromophore to the rhenium center (with the Re⁺⁰ reduction potential nearly to 2.0 V vs NHE) can also occur, as illustrated for the scheme in Figure 1C, explaining why low concentrations of TEOA are necessary to quench the observed photoluminescence, again, when compared with the precursor *fac*-[Re(CO)₃(phen)(Cl)].^[1] This indicates a possible production of a two-electron reduced specie (TERS) in one single stage, revealing a powerful photosensitizer candidate.

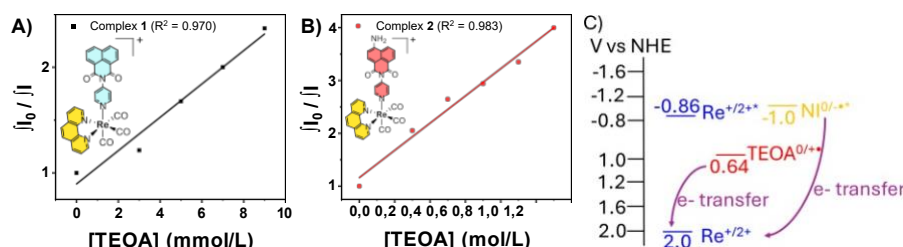


Figure 1. Stern-Volmer plots of the reductive quenching of the excited state of complexes **1** (A) and **2** (B) by TEOA in deaerated DMF at different concentrations (the complexes structures are in the figure) (B); Schematic energy diagram of the reductive quenching of the complex **1** excited state (C)

Aknowlegments: Thanks to Fundação de Amparo à Pesquisa do Estado de São Paulo (Grant number: 2022/16402-0; 2022/03478-8) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (Grant number: 305761/2021-8)

References:

- [1] A.V. Müller, W.M. Wierzbza, L.G.A. do Nascimento, J.J. Concepcion, S. Nikolaou, D.E. Polyansky, A.S. Polo, *Artificial Photosynthesis* **2025**, DOI: 10.1021/aps.4c00026.
- [2] D.R. Case, A. Spear, A.F. Henwood, M. Nanao, S. Dampf, T.M. Korter, T. Gunnlaugsson, J. Zubieta, R.P. Doyle, *Dalton Transactions* **2021**, 50, 3479.

26th ISPPCC – Program

time	July 8	time	July 9	time	July 10	time	July 11	time	July 12
		9:00-9:40	PL2: M. Thompson	9:00-9:40	PL4: A. Vloek	9:00-9:40	PL5: F. Wuerthner	9:00-9:40	PL6: K. Ishii
		9:40-10:10	KN1: J. Concepcion	9:40-10:10	KN4: B. Dietzek-Ivansik	9:40-10:10	KN7: M. Massi	9:40-10:10	KN9: K. Sakai
		10:10-10:30	IN2: L. Sun	10:10-10:30	IN6: E. Young	10:10-10:30	IN9: K. Glusac	10:10-10:30	IN12: D. Herbert
11:00		10:30-11:00	Coffee Break	10:30-11:00	Coffee Break	10:30-11:00	Coffee Break	10:30-11:00	Coffee Break
		11:00-11:30	KN2: F. Castellano	11:00-11:30	KN5: M. Wolf	11:00-11:30	KN8: S. McFarland	11:00-11:30	KN10: A. Aukauloo
		11:30-11:50	IN3: B. Ventura	11:30-11:50	IN7: O. Wenger	11:30-11:50	IN10: C. Cerretani	11:30-11:50	OR22: S. Eliseeva
		11:50-12:10	OR3: P. Persson	11:50-12:10	OR10: K. Haldrup	11:50-12:10	OR15: P. Elliott	11:50-12:10	OR23: K. Miyata
		12:10-12:30	OR4: L. Troian-Gautier	12:10-12:30	OR11: A. Aliprandi	12:10-12:30	OR16: ME Alberto	12:10-12:30	OR24: J. Dabrowski
12:50		12:30-12:50	OR5: T. Connell	12:30-12:50	OR12: C. Berlinguette	12:30-12:50	OR17: A. Cannizzo	12:30-12:50	OR25: M. Pryce
			Lunch time		Lunch time		Lunch time		Lunch time
		14:50-15:30	PL3: T. Weil	14:50-15:20	KN6: L. De Cola	14:50-15:10	IN11: J. Rack	14:50-15:10	OR26: D. Genovese
14:00		15:30-16:00	KN3: R. Van der Veen	15:20-16:00	Joint Commun. (IN8+OR13): E. Galoppini, G. Meyer	15:10-15:30	OR18: H. Yersin	15:10-15:30	OR27: S. Perruchas
		16:00-16:20	IN4: K. Gordon			15:30-15:50	OR19: P. Ceroni	15:30-15:50	OR28: M. Natali
16:00-16:20		16:20-16:40	OR6: Y. Hasegawa	16:00-16:20	OR14: Y. Pellegrin	15:50-16:10	OR20: M. Senge	15:50-16:10	OR29: T. Lazarides
16:20-17:00		16:40-17:10	Coffee Break			16:10 -16:30	OR21: S. Baitalik	16:10 -16:40	Coffee Break
17:00-17:20		17:10-17:30	IN5: O. Ishitani	17:00		16:30-17:00	Coffee Break	16:40-17:00	OR30: AK Patra
17:20-17:40		17:30-17:50	OR7: C. Wegeberg			17:00-18:30	POSTER-2 (odd)	17:00-17:20	OR31: S. Rau
17:40-18:00		17:50-18:10	OR8: A. Bossi						
		18:10 -18:30	OR9: C. Kerzig						
19:00		18:30-20:00	POSTER-1 (even)			20:30	Social Dinner		closing

Legend: **PL**: Plenary Lecture, **KN**: keynote lecture, **IN**: Invited lecture, **OR**: oral talk

26th ISPPCC PROGRAM

Tuesday July 8 2025		
11:00 – 15:30	Registration (Trifiletti Theater)	
16:00 -16:20	Opening	
Chair: Antonin Vlcek (J. Hyerovsky Institute, Prague and Queen Mary University London)		
16:20 – 17:00	PL1	James K. McCusker (Michigan State University) Probing Reaction Coordinates for Ligand Field-state Interconversion Dynamics
17:00 – 17:20	IN 1	Alejandro Cadranel (Friedrich-Alexander-Universität Erlangen-Nürnberg and Universidad de Buenos Aires) High-Energy MLCT States in Ru Polypyridines for Solar-Energy Conversion
17:20 – 17:40	OR1	Evan Moore (University of Queensland, St. Lucia, Australia) Synergistic Hetero-TTA: Fact or Fiction?
17:40 – 18:00	OR2	Julia Weinstein (The University of Sheffield) Ultrafast structural and spin dynamics in Copper(I) diimine phosphine complexes from femtosecond optical and X-ray spectroscopies
19:00	Welcome Party	

Wednesday July 9 2025

Chair: James McCusker (Michigan State University)

9:00-9:40	PL2	Mark E. Thompson (University of Southern California, Los Angeles) Achieving Short and Long Phosphorescent Lifetimes in Two-Coordinate Coinage Metal Complexes
9:40 – 10:10	KN1	Javier J. Concepcion (Brookhaven National Laboratory) Ligand-Based Oxidative and Reductive Catalysis for Water Oxidation and Fuels Generation from CO ₂
10:10 – 10:30	IN2	Licheng Sun (Westlake University, Hangzhou, China) (Photo)electrochemical water splitting and mechanisms of O-O bond formation—From natural to artificial photosynthesis
10:30 – 11:00	Coffee Break	

Chair: Frank Würthner (University of Wuerzburg)

11:00 – 11:30	KN2	Felix N. Castellano (North Carolina State University) Steric and Electronic Influence of Excited State Decay in Cu(I) MLCT Chromophores
11:30 - 11:50	IN3	Barbara Ventura (ISOF-CNR, Bologna) Insights into the photophysics of molecular and supramolecular systems based on porphyrins
11:50 – 12:10	OR3	Petter Persson (Lund University) Photoactivation Dynamics of Abundant Transition Metal Complexes
12:10 – 12:30	OR4	Ludovic Troian-Gautier (Université Catholique de Louvain) Recent Progress in the Understanding and Improvement of Cage Escape Processes using Transition Metal Photosensitizers
12:30 – 12:50	OR5	Tim Connell (Deakin University, Victoria, Australia) Maximizing Photon to Product Efficiency in Photoredox Catalysis

Lunch Time

Chair: Benjamin Dietzek-Ivansic (University of Jena)

14:50 – 15:30	PL3	Tanja Weil (Max Planck Institute for Polymer Research, Mainz) Nanodiamond Sensors to Control Cellular Function
15:30 – 16:00	KN3	Renske M. Van Der Veen (Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin and Technical Universität Berlin) Ultrafast excited-state dynamics of metal-complexes in solution revealed by soft and hard X-ray spectroscopies

16:00-16:20	IR4	Keith Gordon (University of Otago) Using metal complexes to open the door to long-lived excited states
16:20 – 16:40	OR6	Yasuchika Hasegawa (Hokkaido University) Luminescence Changeable Lanthanide-mixed Coordination Polymers for CO ₂ -storage
16:40 – 17:10	Coffee Break	
Chair: Oliver Wenger (University of Basel)		
17:10 – 17:30	IN5	Osamu Ishitani (Hiroshima University) Application of selective photo-splitting of a Mn(0)-Mn(0) bond for developing a highly durable photocatalytic CO ₂ reduction using a Mn-complex catalyst
17:30 – 17:50	OR7	Christina Wegeberg (University of Southern Denmark, Odense) Captivating Bimolecular Photoredox Dynamics of Ligand-to-Metal Charge Transfer Complexes
17:50 – 18:10	OR8	Alberto Bossi (SCITEC-CNR, Milan) Impact of Cis/Trans Geometry on the Photophysical, Electronic, and Structural Properties of Pt(II) Cyclometalated Complexes
18:10 – 18:30	OR9	Christoph Kerzig (Johannes Gutenberg University Mainz) Combining the best of organic and inorganic photochemistry with molecular and coulombic dyads
18:30 – 20:00	POSTER SESSION 1 (even numbers)	

Thursday July 10 2025

Chair: Felix Castellano (North Carolina State University)

9:00 - 9:40	PL4	Antonin Vleck (J. Heyrovský Institute of Physical Chemistry Prague and Queen Mary University of London) Vibrational dynamics of electronically excited metal complexes: relaxation, coherence, and ultrafast Raman spectroscopy
9:40-10:10	KN4	Benjamin Dietzek-Ivansic (University of Jena) Light driven molecular reactivity – electron and electron-coupled proton transfer in complex environments
10:10 – 10:30	IN6	Elizabeth R. Young (Lehigh University) Illuminating the Unexpected Excited-State Dynamics of Non-Aromatic Pd(II) Porphyrinoids
10:30 – 11:00	Coffee Break	

Chair: Osamu Ishitani (Hiroshima University)

11:00 – 11:30	KN5	Michael O. Wolf (University of British Columbia, Vancouver) Stimuli-responsive Flexible Lewis Pair Functionalized Coordination Complexes
11:30 – 11:50	IN7	Oliver Wenger (University of Basel) New metal complexes in luminescence, photocatalysis and charge accumulation
11:50 -12:10	OR10	Kristoffer Haldrup (Technical University of Denmark, Copenhagen) Structural characterization of the $\text{Fe}(\text{CN})_6 \rightarrow \text{Fe}(\text{CN})_5\text{H}_2\text{O}$ photo-aquation process
12:10 – 12:30	OR11	Alessandro Aliprandi (University of Padova) Redox-Driven Photoselective Self-Assembly
12:30 – 12:50	OR12	Curtis Berlinguette (University of British Columbia, Vancouver, and CIFAR, Toronto) π Covalency in the Halogen Bond

Lunch Time

Chair: Fausto Puntoriero (University of Messina)

14:50 – 15:20	KN6	Luisa De Cola (University of Milan and Mario Negri, Milan) Signal amplification in electrochemiluminescent biosensors
---------------	-----	---

15:20 – 16:00	Joint IN8+OR13	Elena Galoppini (Rutgers University), Gerald J. Meyer (University of North Carolina at Chapel Hill) Gated Pathway for Photoinduced Interfacial Electron Transfer
16:00 – 16:20	OR14	Yann Pellegrin (University of Nantes) Elucidating Chemical Engineering Principles for Achieving High Emission and $^1\text{O}_2$ Photogeneration Quantum Yields with Homoleptic Cu(I) Complexes
17:00	EXCURSIONS	

Friday July 11 2025

Chair: Javier Concepcion (Brokhaven National Laboratory)

9:00 – 9:40	PL5	Frank Würthner (University of Wuerzburg) Supramolecular Engineering of Ruthenium Catalysts toward High Water Oxidation Activity
9:40 – 10:10	KN7	Max Massi (Curtin University, Perth) Lanthanoid Sensitisation from Re(I) Triangular Assemblies
10:10 - 10:30	IN9	Ksenia Glusak (University of Illinois Chicago and Argonne National Laboratory) Electrochemistry of electrode/graphene nanoribbon hybrid materials
10:30 – 11:00	Coffee Break	

Chair: Luisa De Cola (University of Milan and Mario Negri Institute)

11:00 – 11:30	KN8	Sherri A. McFarland (University of Texas at Arlington) Light-Triggered Metallodrugs: Harnessing Excited State Dynamics for Phototherapy
11:30 – 11:50	IN10	Cecilia Cerretani (University of Copenhagen) Photophysical characterization and structure determination of DNA-stabilized silver nanoclusters
11:50 – 12:10	OR15	Paul Elliott (University of Huddersfield) Photophysical properties of triazolylidene ‘abnormal’ carbene complexes of Earth-abundant metal ions
12:10 – 12:30	OR16	Maria Erminia Alberto (University of Calabria) The role of computational studies in identifying the distinct features of metal-based photosensitizers for photodynamic therapy
12:30 – 12:50	OR17	Andrea Cannizzo (University of Bern) Photo-induced oxidation-enhancement in biomimetic Molybdenum photo-catalysts

Lunch Time

Chair: Elena Galoppini (Rutgers University)

14:50 – 15:10	IN11	Jeffrey J. Rack (University of New Mexico, Albuquerque) A New Look at the Magneto-Optical Activity of Metalloporphyrins
15:10 – 15:30	OR18	Hartmut Yersin (University of Regensburg) Ag(I) complexes: From extremely long-lived phosphorescence for oxygen sensing to ultra-short-lived TADF for OLEDs

15:30 – 15:50	OR19	Paola Ceroni (University of Bologna) Chiral metal complex for asymmetric photocatalysis
15:50 – 16:10	OR20	Mathias O. Senge (Trinity College Dublin) Conformational Engineering and Atropisomerism as Photosensitizer Design Principles
16:10 – 16:30	OR21	Sujoy Baitalik (Jadavpur University) Modulation of Photoisomerization Kinetics via Multi-Stage Switching in Ru(II) and Os(II)-Terpyridine Complexes
16:30 – 17:00	<i>Coffee Break</i>	
17:00 – 18:30	POSTER SESSION 2 (odd numbers)	
20:30	<i>Social Dinner</i>	

Saturday July 12 2025

Chair: Garry Hanan (University of Montreal)

9:00 – 9:40	PL6	Kazuyuki Ishii (The University of Tokyo) Excited-State Spin Dynamics, Chiroptical/Magnetooptical Properties and Soft Crystals in Metal Complexes and Supramolecules
9:40 – 10:10	KN9	Ken Sakai (Kyushu University) Molecular Catalysis of Water Splitting and CO ₂ Reduction
10:10 – 10:30	IN12	David Herbert (University of Manitoba) Beyond Donor Strength: Unconventional Ligand Designs for Optically Interesting 3d Coordination Complexes
10:30 – 11:00	Coffee Break	

Chair: Paola Ceroni (University of Bologna)

11:00 – 11:30	KN10	Ally Aukauloo (University Paris-Saclay) Photocatalytic events for CO ₂ reduction and oxygen atom transfer
11:30 – 11:50	OR22	Svetlana Eliseeva (Center for Molecular Biophysics CNRS, Orleans) Lanthanide(III)-based metallacrowns functionalized with ruthenium(II) complexes for multiplex imaging and oxygen sensing in the NIR-II
11:50 – 12:10	OR23	Kiyoshi Miyata (Kyushu University) Dynamic Excited-State Jahn-Teller Distortion in the Al(III) Dinuclear Metal Complexes Observed by Coherent Vibrational Spectroscopy
12:10 – 12:30	OR24	Janusz M. Dabrowski (Jagellonian University) Illuminating new pathways in antimicrobial photodynamic therapy: coordination metal complexes and functional materials for enhanced selectivity and efficiency
12:30 – 12:50	OR25	Mary Pryce (Trinity College Dublin) Photocatalytic Reduction of CO ₂ to HCOOH using a Porphyrin-Rhenium Dyad

Lunch Time

Chair: Ken Sakai (Kyushu University)

14:50 – 15:10	OR26	Damiano Genovese (University of Bologna) Understanding mechanochromism in CuX-L hybrid coordination polymers
---------------	------	--

15:10 – 15:30	OR27	Sandrine Perruchas (IMN-CNRS, Nantes) Luminescence mechanochromism of copper-based materials
15:30 – 15:50	OR28	Mirco Natali (University of Ferrara) Light-driven Catalysis of the CO ₂ Reduction Reaction using Heptacoordinated Cobalt and Iron Complexes
15:50 – 16:10	OR29	Theodore Lazarides (Aristotle University of Thessaloniki) Estrogen-conjugated [Ru(bpy) ₃] ²⁺ complexes exhibit selective phototoxicity against breast cancer cells
16:10 – 16:40	Coffee Break	
Chair: Sebastiano Campagna (University of Messina)		
16:40 -17:00	OR30	Ashis K. Patra (Indian Institute of Technology Kanpur) Modulation of Energy Transfer Pathways in Time-Gated Luminescent Eu(III) and Tb(III) Probes for Sensing and Discrimination of Physiological Phosphates and Biochemical Hazards
17:00 – 17:20	OR31	Sven Rau (Ulm University) Highly efficient artificial photocatalysts mimicking Photosystem I
17:20 – 18:00	Closing	

26th ISPPCC

**ORAL
*ABSTRACTS***



Probing Reaction Coordinates for Ligand Field-state Interconversion Dynamics

A. Ghosh, Y.-J. Lien, and J.K. McCusker*

Department of Chemistry, Michigan State University, 578 South Shaw Lane, East Lansing, Michigan USA 48824 (jkm@chemistry.msu.edu)

Our research program focuses on the development of chromophores based on first-row transition metal ions for use as light harvesting components in light-to-chemical energy conversion. The underlying motivation stems from the question of scalability and the limited potential of traditional second- and third-row chromophores to fill this void due to their elemental scarcity. A key scientific issue concerns the rapid deactivation of charge-transfer states to lower-lying, metal-centered ligand-field states, presenting distinct challenges for the development of the use of these earth-abundant analogs for a range of potential applications.

The presentation will highlight two of the research threads currently being pursued. The first focuses on spin-state interconversion in a Fe(II)-based polypyridyl complex that was synthetically tailored to operate in the so-called “spin-crossover” regime. This approach allowed the free energy change associated with high-spin to low-spin conversion to be determined using variable-temperature solution-phase magnetic susceptibility, thereby affording values for ΔG_0 as a function of temperature from an independent measurement. The photo-induced non-radiative decay dynamics acquired for the chromophore could then

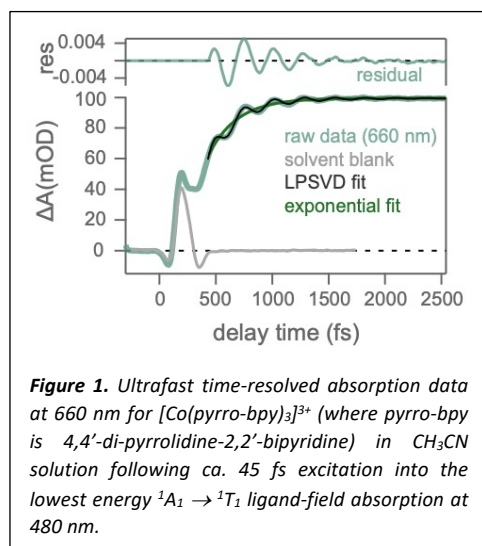


Figure 1. Ultrafast time-resolved absorption data at 660 nm for $[\text{Co}(\text{pyrro-bpy})_3]^{3+}$ (where pyrro-bpy is 4,4'-di-pyrrolidine-2,2'-bipyridine) in CH_3CN solution following ca. 45 fs excitation into the lowest energy $^1A_1 \rightarrow ^1T_1$ ligand-field absorption at 480 nm.

be fit to semi-classical Marcus theory to yield analytically precise values for the reorganization energy (λ) and the electronic coupling between the two states (H_{ab}).

The second project concerns the use of femtosecond time-resolved absorption spectroscopy on Co(III)-based complexes to leverage excited-state vibronic coherences for the identification of degree(s) of freedom that are coupled to ultrafast intersystem crossing dynamics (Figure 1). The data reveal that, following $^1A_1 \rightarrow ^1T_1$ excitation, intersystem crossing to the lowest energy excited state of the compound (3T_1) is driven by symmetry-breaking, low-frequency torsional degree(s) of freedom of the molecule (as opposed to a metal-

ligand Jahn-Teller mode that presents as the dominant feature in the experimental data). The implications of this finding as it relates to the prospect of inducing reactivity from excited states other than the lowest energy excited state of the system will be presented.

Acknowledgements

This project was generously supported by the Chemical Sciences, Geosciences, and Biosciences Program within the Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy through Grant no. DE-FG01-01ER15282.



Achieving Short and Long Phosphorescent Lifetimes in Two-Coordinate Coinage Metal Complexes

M.E. Thompson, K. Biv, T.A.N. Kallungal, N. Baluyot-Reyes, P.I. Djurovich, S.E. Bradforth

Department of Chemistry, University of Southern California, Los Angeles, CA

met@usc.edu

In my talk I will discuss our research toward developing emitters for organic LEDs (OLEDs) and sensitizers for photo-electrocatalytic reactions with two-coordinate carbene-metal-amide (cMa, M = Cu(I) and Au(I)) complexes.[1, 2] I will begin with a discussion of how the absorption/emission energy and lifetime can be tuned by ligand choice in cMa complexes of Cu and Au. Our initial efforts were aimed at achieving very short lifetimes (and high F_{PL}). [3, 4] The cMa complexes studied here emit via thermally assisted delayed fluorescence (TADF) and the TADF lifetime are tied directly to the S_1 decay rate (k_{S1}) and the equilibrium constant for $T_1 \rightleftharpoons S_1$ (K_{eq}) and K_{eq} is tied to the energy difference between S_1 and T_1 (ΔE_{ST}). [5] Achieving fast phosphorescence involved designing cMa complexes with small ΔE_{ST} (20-40 meV) while maintaining a k_{S1} in the 10^8 s^{-1} regime. I will discuss how ligand and metal ion choices impact these parameters and the application to OLEDs.

In addition to very short lifetimes, a long excited state lifetime could be beneficial, for application as sensitizers for photoelectrocatalytic processes for example. I will discuss our efforts to shift the absorption profile of the cMa complexes to better cover the visible part of the solar spectrum and increase the lifetime into the 100s of ms regime. Shifting from an interligand charge transfer (ICT) excited state to one that has mixed ICT and ligand excited (LE) character markedly increases the lifetimes of these materials, pushing them as long as 250 ms in polar solvents. I will discuss the design and physical and photophysical properties and these ultralong lived sensitizers.

The last topic in my talk explores the role of spin-orbit coupling (SOC) in facilitating intersystem crossing (ISC) in cMa complexes. Prior studies have shown that ISC rates in these systems span a wide range (10^9 - 10^{11} s^{-1}). [1] However, the precise contribution of SOC to ISC, and its interplay with TADF, is not well understood. Using a combination of transient absorption spectroscopy, lifetime measurements, and theoretical modeling, we investigate how structural modifications in cMa influences SOC constants (SOCCs). Through Arrhenius and Marcus-Hush theories, we experimentally determined that substituting Cu with Au increases the SOCC from $\sim 1 \text{ cm}^{-1}$ to $\sim 3 \text{ cm}^{-1}$, in agreement with the enhanced ISC rates. Further modifications to the ligands also lead to notable changes in SOCC values. I will tie these SOC studies back to the observed photophysical properties of both long and short lived cMa complexes.

References

1. Michael S. Kellogg, et al., *The Journal of Physical Chemistry C*, (2024). 128, 6621–6635.
2. T. Y. Li, et al., *Chem Rev*, (2024). 124, 4332–4392.
3. Collin N. Muniz, et al., *Journal of American Chemical Society*, (2022). 144, 17916–17928.
4. Rasha Hamze, et al., *Journal of the American Chemical Society*, (2019). 141, 8616–8626.
5. Daniel M. R. Sylvinson and Mark E. Thompson, *Materials Horizons*, (2020). 7, 1210–1217.

Nanodiamond Sensors to Control Cellular Function

Y. Wu, C. Ender, T. Weil

Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz

weil@mpip-mainz.mpg.de

Nanodiamonds with lattice defects have emerged as photostable emitters and nanoscale sensors in cell biology. However, nanodiamonds with narrow size distributions and defined lattice defects are still challenging to synthesize. We report the preparation of narrowly dispersed nanodiamonds with different lattice defects and their surface functionalization, which is essential for cellular experiments. Our strategy is to equip nanodiamonds with a functional shell that allows the stimulation and nanoscale sensing of physical parameters and reactive species inside living cells.

In living cells, a multitude of biological reactions occur in a concurrent manner, giving rise to an inhomogeneous distribution of different species, temperatures, radicals, and pH at the nanoscale. The local and quantitative detection of these intracellular signals and molecules, including transient reactive structures with limited lifetimes, is of paramount importance. Current methodologies that allow quantification at the nanoscale are frequently constrained to strict conditions such as low temperature or vacuum and are not suitable for living systems. We propose surface-functionalized nanodiamond sensors capable of manipulating and probing critical parameters in situ within the living cell. This approach offers a novel means to elucidate cellular responses to intracellular changes, which could facilitate deeper insights of cell-based diseases and treatments.

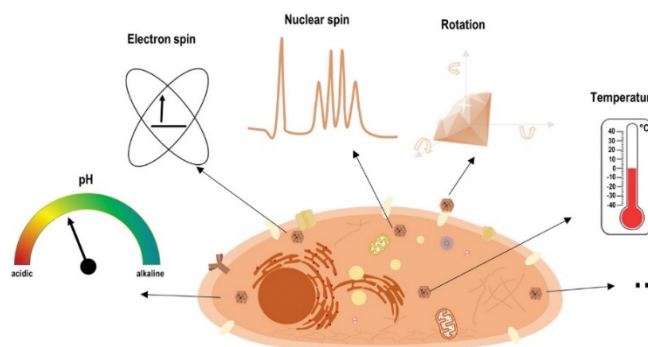


Figure 1. Detecting and manipulating intracellular signals[1]

Acknowledgments

Thanks to the Carl Zeiss Foundation for funding the project Ultrasense-Vir

References

- [1] Y. Wu, T. Weil, *Advance Science* **2022**, 9, (19), 2200059
- [2] Y. Wu, P. Balasubramanian, Z. Wang, J. A. S. Coelho, M. Prslja, M.B. Plenio, R. Siebert, F. Jelezko, T. Weil. *J. Amer. Chem. Soc.* **2022**, 144, (28), 12642–12651
- [3] Y. Wu, M. N. A. Alam, P. Balasubramanian, A. Ermakova, S. Fischer, H. Barth, M. Wagner, M. Raabe, F. Jelezko, T. Weil, *Nano Letters* **2021**, 21, (9), 3780–3788



Vibrational dynamics of electronically excited metal complexes: relaxation, coherence, and ultrafast Raman spectroscopy

M. Kloz^a and A. Vlček^b

^a *Extreme Light Infrastructure ERIC, ELI Beamlines Facility, 252 41 Dolní Břežany, Czechia*

^b *J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, 182 23 Prague, Czechia, and Queen Mary University of London, E1 4NS London, UK.*

a.vlcek@qmul.ac.uk

Outcomes of photochemical reactions are often determined very early after light absorption when excited-state evolution branches between different pathways such as conversion to other electronic states, charge separation, bond dissociation or, rarely, bond formation. These processes are largely determined by dynamics of Franck-Condon-active vibrations together with anharmonically coupled modes, and by their coupling with electronic dynamics. While state-of-the-art ultrafast X-ray techniques can directly follow evolution of molecular structures and solvation after electronic excitation, time-resolved vibrational spectroscopy provides deep insights into the behavior of individual vibrational modes, unravelling specific structural changes and vibrational (vibronic) activation of photophysical processes. This information and understanding are best gathered by combining ultrafast infrared absorption (TRIR) and Raman spectroscopies, together with coherent spectroscopy of oscillating transient absorption signals. In addition, quantum-chemical calculations aid assigning spectral features and visualize vibrational motions.

In this contribution, we will demonstrate several important aspects of excited-state vibrational dynamics as unraveled by ultrafast Raman spectroscopy – technique so far applied much more to biophysical and organic systems than to transition-metal complexes. We will show how femtosecond stimulated Raman spectroscopy (FSRS) detects short-lived MLCT excited states ($[\text{Fe}(\text{bpy})_3]^{2+}$) and, in combination with TRIR, their initial evolution ($\text{ReCl}(\text{CO})_3(\text{bpy})$ and $\text{W}(\text{C}\equiv\text{NAr}(\text{yl}))_6$). Finally, we will discuss in a greater detail the Ir–Ir bond formation upon $^1(\text{d}\sigma^* \rightarrow \text{p}\sigma)$ excitation of a di-iridium complex with bridging isocyanide ligands. The latter system showed stimulated emission and FSRS signals whose coherent intensity oscillations and periodic spectral shifts revealed how the Ir–Ir bond forms through repeated weakening and strengthening facilitated by a network of anharmonically coupled deformation vibrations.

Aknowlegments

This work was supported by the Czech Science Foundation grant 21-05180S and the “Energy Conversion and Storage” project of the Johannes Amos Comenius program, grant CZ.02.01.01/00/22_008/0004617.

References

- [1] M. Pižl, et al. *J. Phys. Chem. A* **2020**, 124, 1253–1265.
- [2] M. Kloz, et al. *J. Am. Chem. Soc.* **2025**, 147, 9810–9824.

Supramolecular Engineering of Ruthenium Catalysts toward High Water Oxidation Activity

F. Würthner

Universität Würzburg, Center for Nanosystems Chemistry, 97074 Würzburg, Germany

(wuerthner@uni-wuerzburg.de)

Water oxidation catalysis (WOC) represents one of the key steps for the ambitious goal of artificial photosynthesis and the replacement of fossil fuels by alternative energy carriers. Ruthenium complexes have shown excellent performance for the kinetically sluggish proton-coupled four-electron transfer process required for oxygen generation and recently enabled the first “all-in-one” nanoparticle system for water splitting into hydrogen and oxygen without sacrificial reagents.[1] Accordingly, a plethora of different frameworks based on mono- and multinuclear ruthenium complexes have been reported in recent years leading to significant enhancement of catalyst efficiency.

Herein, we present our research on multinuclear ruthenium 6,6'-dicarboxylate-2,2'-bipyridine (bda) complexes including macrocycles,[2] linear oligomers[3] and covalent organic frameworks[4] that are employed for chemical, electrochemical and photochemical WOC. Our research shows how the desirable mechanistic switch towards water nucleophilic attack can be accomplished by the organization of water networks, leading to significant rate enhancements for proton-coupled electron transfer steps. These systematic studies for a variety of metallosupramolecular arrays recently culminated in a mononuclear Ru(bda) complex endowed with a suitable pocket for water organization in front of the ruthenium center. This enzyme mimic affords turn-over frequencies comparable to those found for the natural manganese cluster in photosynthesis.[5]

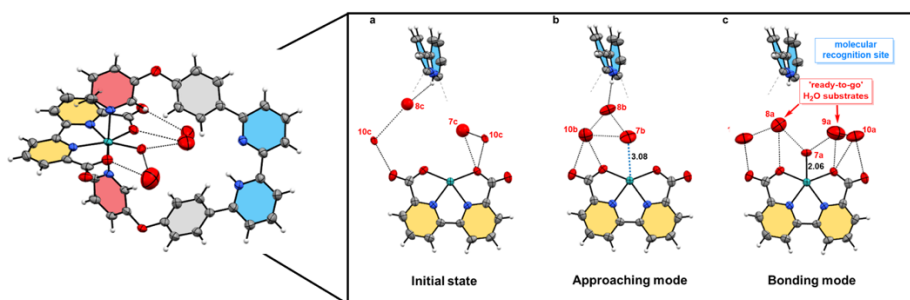


Figure 2. Single crystal “snapshot” of Ru(bda) catalyst with pocket of organized water molecules.

References

- [1] C. M. Wolff, P. D. Frischmann, M. Schulze, B. J. Bohn, R. Wein, P. Livadas, M. T. Carlson, F. Jäckel, J. Feldmann, F. Würthner, J. K. Stolarczyk, *Nat. Energy* **2018**, 3, 862.
- [2] M. Schulze, V. Kunz, P. D. Frischmann, F. Würthner, *Nat. Chem.* **2016**, 8, 576.
- [3] T. Schlossarek, V. Stepanenko, F. Beuerle, F. Würthner, *Angew. Chem. Int. Ed.* **2022**, 61, e202211445.
- [4] S. Karak, V. Stepanenko, M. A. Addicoat, P. Keßler, S. Moser, F. Beuerle, F. Würthner, *J. Am. Chem. Soc.* **2022**, 144, 17661.
- [5] N. Noll, A.-M. Krause, F. Beuerle, F. Würthner, *Nat. Cat.* **2022**, 5, 867.

Excited-State Spin Dynamics, Chiroptical/Magnetoptical Properties and Soft Crystals in Metal Complexes and Supramolecules

K. Ishii

Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba Meguro-ku, 153-8505 Tokyo, Japan. k-ishii@iis.u-tokyo.ac.jp

In this talk, I'll present the characteristic photophysical/photochemical properties of metal complexes and supramolecules in terms of excited-state spin dynamics, chiroptical/magnetoptical properties and flexible molecular crystals, i.e., Soft Crystals. Firstly, since we investigated the excited-state spin dynamics of ZnTPP-nitpy and R2c (Fig. 1) by time-resolved electron paramagnetic resonance (TREPR), the excited multiplet state properties will be presented.¹⁻³ Next, based on our studies on circular dichroism (CD), magnetic circular dichroism (MCD), and magneto-chiral dichroism (MChD, Fig. 2), some attractive examples, such as the first MChD of organic compounds, the highly reproducible rotary-evaporation induced chirality, and the direct MCD observation of the $S_0 \rightarrow T_2$ transition will be delivered.⁴⁻⁷ Finally, we proposed the concept of "Soft Crystals" for flexible molecular crystals,^{8,9} and thus, vapochromism studies using super-resolution spectroscopy will be introduced.¹⁰ Further, I'll show you some photobiological applications of metal complexes.^{11,12}

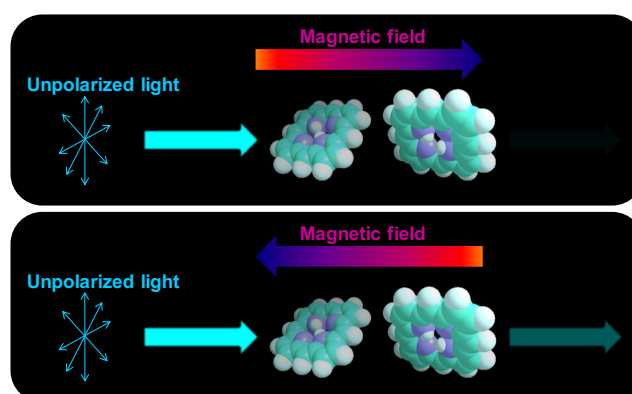
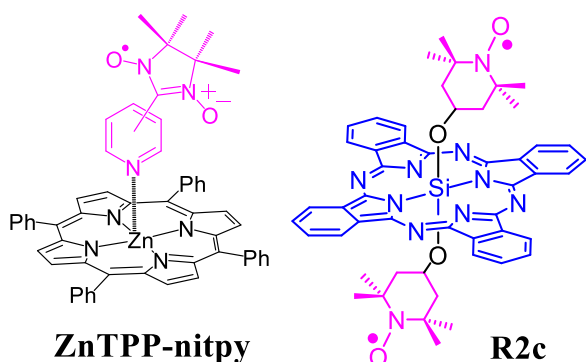


Figure 3. Molecular structures of ZnTPP-nitpy and R2c

Figure 2. Magneto-chiral dichroism (MChD)

References

- [1] K. Ishii, J. Fujisawa, Y. Ohba, S. Yamauchi, *J. Am. Chem. Soc.*, **1996**, *118*, 13079.
- [2] K. Ishii, J. Fujisawa, A. Adachi, S. Yamauchi, N. Kobayashi, *J. Am. Chem. Soc.*, **1998**, *120*, 3152.
- [3] K. Ishii, Y. Hirose, M. Fujitsuka, O. Ito, N. Kobayashi, *J. Am. Chem. Soc.*, **2001**, *123*, 702.
- [4] Y. Kitagawa, H. Segawa, K. Ishii, *Angew. Chem. Int. Ed.*, **2011**, *50*, 9133.
- [5] Y. Kitagawa, T. Miyatake, K. Ishii, *Chem. Commun.*, **2012**, *48*, 5091.
- [6] M. Kuroha, et al., *Angew. Chem. Int. Ed.*, **2019**, *58*, 18454.
- [7] K. Ishii, J. Wada, K. Murata, *J. Phys. Chem. Lett.*, **2020**, *11*, 9828.
- [8] M. Kato, H. Ito, M. Hasegawa, K. Ishii, *Chem. Eur. J.*, **2019**, *25*, 5105.
- [9] "Soft Crystals Flexible Response Systems with High Structural Order", Eds. M. Kato, K. Ishii, Springer, **2023** (Open access <https://link.springer.com/book/10.1007/978-981-99-0260-6>).
- [10] K. Ishii, et al., *J. Phys. Chem. C*, **2021**, *125*, 21055.
- [11] K. Ishii, K. Kubo, T. Sakurada, K. Komori, Y. Sakai, *Chem. Commun.*, **2011**, *47*, 4932.
- [12] T. Yokoi, T. Otani, K. Ishii, *Sci. Rep.*, **2018**, *8*, 1560

Ligand-Based Oxidative and Reductive Catalysis for Water Oxidation and Fuels Generation From CO₂

S. Desai, A. Müller, C. Cappuccino, D. Polyansky, D. Grills, M. Ertem, J. Concepcion

Affiliations: Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973-5000, USA

jconcepc@bnl.gov

Small molecule activation is at the heart of many important challenges for humanity in the 21st century. These include water oxidation to dioxygen and hydrogen peroxide, CO₂ reduction to fuels and dinitrogen reduction to ammonia and other commodity chemicals. In this presentation, the use of ligand-based catalysis for small molecule activation as a strategy that enables the transition to earth-abundant, first-row transition metals will be discussed. The photochemical reduction of CO₂ to formate with high selectivity using metal formyl and dihydroquinoxalinide intermediates as hydride donors will be demonstrated. The development of synthetic procedures, as well as the initial mechanistic studies using ruthenium complexes have been key to understanding the behavior of these systems before transitioning to the first-row analogues.

These complexes are highly active and 100% selective in the photochemical CO₂ reduction to formate. The formyl and dihydroquinoxalinide intermediates, generated by an ET-PCET mechanism, are the culprits in the hydride transfer to CO₂. The fact that the coordination environment remains saturated during the catalytic cycle (ligand-based) is very encouraging in transitioning to first-row transition metals. The role of formyl intermediates in the reduction of CO to methanol will be discussed as well.

A ligand-based approach to water oxidation catalysis based on [M(bpy)₂(bi-bimH₂)]ⁿ⁺ will also be presented. This platform includes self-healing capabilities and because it is ligand-based, is amenable to first-row transition metals, a feature that we have demonstrated with cobalt- and iron-based catalysts.

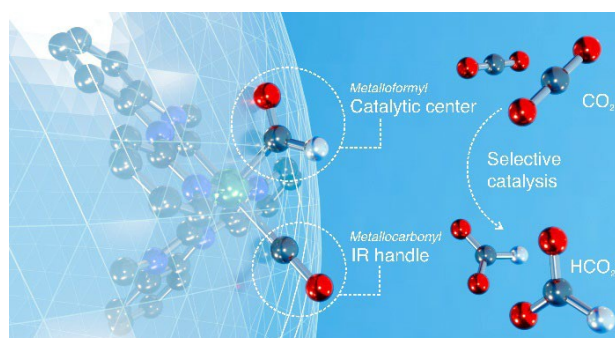


Figure 1. Ligand-Based CO₂ Reduction to Formate.

Aknowlegments

This work was carried out at Brookhaven National Laboratory and supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, & Biosciences, under contract DE-SC0012704 and by the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE), an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0021173.



Steric and Electronic Influence of Excited State Decay in Cu(I) MLCT Chromophores

F. N. Castellano*

North Carolina State University, Department of Chemistry, Raleigh, NC 27695-8204, USA

E-mail: fncastel@ncsu.edu

Since 2013, we have continuously developed new classes of visible-light absorbing Cu^I MLCT-based 1,10-phenanthroline-containing photosensitizers to facilitate excited-state chemistry. Our initial work leveraged ligand structural motifs featuring cooperative steric influence that ultimately achieved an unprecedented excited state lifetime in homoleptic Cu(I) MLCT complexes, realizing a seven-fold increase relative to its predecessor.¹ This led to a thorough investigation of their ultrafast dynamics, which were shown to inform the resultant photophysical properties and vice versa.² Computationally assisted molecular designs generated chromophores with cooperative steric influence to maintain long excited state lifetimes, with charge transfer bands featuring markedly enhanced visible light absorption properties.³ Exploiting combinations of cooperative steric influence and inductive electronic effects within the ligand structures ultimately achieved three record-setting excited state lifetimes and photoluminescence quantum yields in Cu(I) *bis*(phenanthrolines) with variable excited state redox properties.⁴ Adopting the lessons learned from a decade of research in Cu(I) homoleptics, heteroleptic Cu^I-based photosensitizers have been designed using the HETPHEN strategy to promote panchromatic light absorption⁵ and to independently possess excited state lifetimes suitable for engaging in bimolecular excited state reactions (hundreds of nanoseconds) while exhibiting measurable photoluminescence emission at room temperature. Our research in this area has recently been summarized.⁶

References

- (1) McCusker, C. E.; Castellano, F. N. Design of a Long-Lifetime, Earth-Abundant, Aqueous Compatible Cu(I) Photosensitizer Using Cooperative Steric Effects. *Inorg. Chem.* **2013**, 52 (14), 8114-8120. DOI: 10.1021/ic401213p.
- (2) Garakyaraghi, S.; Danilov, E. O.; McCusker, C. E.; Castellano, F. N. Transient Absorption Dynamics of Sterically Congested Cu(I) MLCT Excited States. *J. Phys. Chem. A* **2015**, 119 (13), 3181-3193. DOI: 10.1021/acs.jpca.5b00901.
- (3) Garakyaraghi, S.; McCusker, C. E.; Khan, S.; Koutnik, P.; Bui, A. T.; Castellano, F. N. Enhancing the Visible-Light Absorption and Excited-State Properties of Cu(I) MLCT Excited States. *Inorg. Chem.* **2018**, 57 (4), 2296-2307. DOI: 10.1021/acs.inorgchem.7b03169.
- (4) Rosko, M. C.; Espinoza, E. M.; Arteta, S.; Kromer, S.; Wheeler, J. P.; Castellano, F. N. Employing Long-Range Inductive Effects to Modulate Metal-to-Ligand Charge Transfer Photoluminescence in Homoleptic Cu(I) Complexes. *Inorg. Chem.* **2023**, 62 (7), 3248-3259. DOI: 10.1021/acs.inorgchem.2c04315.
- (5) Rosko, M. C.; Wheeler, J. P.; Alameh, R.; Faulkner, A. P.; Durand, N.; Castellano, F. N. Enhanced Visible Light Absorption in Heteroleptic Cuprous Phenanthrolines. *Inorg. Chem.* **2024**, 63 (3), 1692-1701. DOI: 10.1021/acs.inorgchem.3c04024.
- (6) Steric and Electronic Influence of Excited-State Decay in Cu(I) Chromophores. Castellano, F.N., Rosko, M.C. *Acc. Chem. Res.* **2024**, 57, 2872-2886. DOI: [10.1021/acs.accounts.4c00476](https://doi.org/10.1021/acs.accounts.4c00476).



Ultrafast excited-state dynamics of metal-complexes in solution revealed by soft and hard X-ray spectroscopies

Renske M. van der Veen¹

¹*Department of Atomic-Scale Dynamics in Light-Energy Conversion, Helmholtz Center Berlin for Materials and Energy, 14109 Berlin, Germany; Institute of Optics and Atomic Physics, Technical University of Berlin, 10623 Berlin, Germany*

The conversion of light energy into other forms of energy is of uttermost importance in a vast range of fields, such as natural and artificial photosynthesis, photoelectrochemistry, or optoelectronic device development. Excited-state energy dissipates by a variety of mechanisms, including intersystem crossing, electron-phonon coupling, luminescence, charge/energy transfer, or non-radiative decay in the form of heat. Depending on the specific application, the aim is to optimize one or several of these relaxation pathways, while avoiding others. A fundamental atomic-scale and microscopic understanding of the dynamics after photon absorption is thus important to uncover the mechanisms of bond-breaking and -making in photochemical reactions, to derive intricate structure-property-photoactivity relationships, and to enhance the predictive ability of theoretical atomic-scale models in photovoltaics, photocatalysis, and optoelectronics.

While ultrafast optical spectroscopies are very powerful for probing the electronic population of excited states with attosecond (as) to nanosecond (ns) temporal resolution, they often lack the spatial resolution necessary to resolve individual atoms. Our research group at the Helmholtz Center Berlin specializes in the development and application of time-resolved pump-probe techniques based on X-ray and fast-electron probes. The Å-nm-scale de Broglie wavelength of these probe pulses renders them directly sensitive to the atomic-scale structure. In this talk I will present our recent results on ultrafast soft and hard X-ray spectroscopy on metal complexes in solution. These include Ni-based photoredox complexes and mixed-valence Fe-Co complexes. We'll show that the combined knowledge from two X-ray regions (soft and hard) can deliver powerful complementary information on spin-state, charge, and structural dynamics. This enables us to unambiguously confirm the nature of excited states that have been implied by ultrafast optical spectroscopies and density functional theories.

References

- [1] J.H. Burke, D.Y. Bae, R.F. Wallick, C.P. Dykstra, T.C. Rossi, L.E. Smith, C.A. Leahy, R.D. Schaller, L.M. Mirica, J. Vura-Weis, R.M. van der Veen, *J. Am. Chem. Soc.* **2024**, 146, 21651–21663; <https://doi.org/10.1021/jacs.4c05646>
- [2] R.F. Wallick, S. Chakrabarti, J.H. Burke, R. Gnewkow, J.B. Chae, T.C. Rossi, I. Mantouvalou, B. Kanngießner, M. Fondell, S. Eckert, C. Dykstra, L.E. Smith, J. Vura-Weis, L.M. Mirica, R.M. van der Veen, *J. Phys. Chem. Lett.* **2024**, 15, 4976–4982; <https://doi.org/10.1021/acs.jpcllett.4c00226>



Light driven molecular reactivity – electron and electron-coupled proton transfer in complex environments

B. Dietzek-Ivanšić

Leibniz Institute of Surface Engineering, Permoserstraße 15, 04318 Leipzig, Germany

This contribution will discuss various aspects of studying the light driven molecular reactivity of transition metal compounds in complex environments, in which the specific function of the compounds is envisioned to happen. The talk will consider in-situ time-resolved spectroscopy to follow the fate of electronically excited states of a molecular photocatalysts during photocatalysis. We will discuss the light-induced processes in a binuclear photocatalyst operating in homogeneous solution^{1,2} and the activation of a Co-catalyst for hydrogen evolution anchored to a NiO electrode.³⁻⁵ Going beyond transition metal complexes as photoredox catalysts, we will consider the opportunity of utilizing novel Ru(II) and Fe(II) complexes as visible-light activated photobases.^{6,7}

Aknowlegments

Financial support by the German Science Foundation via the CRC/TRR 234 CataLight, the CRC 1278 PolyTarget and the SPP 2104 is greatly acknowledged.

References

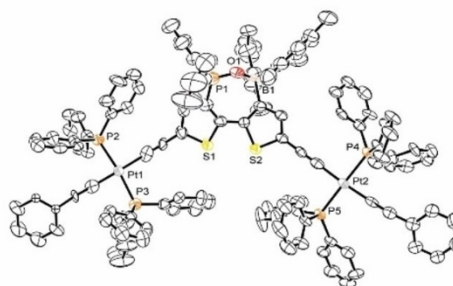
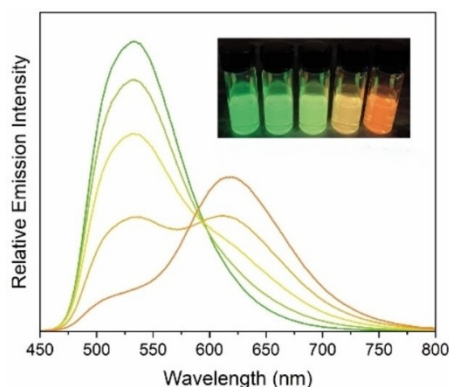
- [1] M.G. Pfeffer et al., *Nature Chemistry* **2022**, 14 (5), 500.
- [2] L. Zedler et al., *Angew. Chem. Int. Ed.* **2019**, 58 (37), 13140-13148.
- [3] E. Giannoudis et al., *ACS AMI* **2021**, 13 (42), 492802-498015.
- [4] S. Bold et al., *ACS Catalysis* **2021**, 11(6), 3662-3678.
- [5] S. Bold et al., *Catalyst* **2019**, 10(11), 1340.
- [6] N. Klosterhalfen et al., *Chem. Eur. J.* **2025**, DOI10.1002/chem.202404033
- [7] S.S. Nair et al., *ACS Omega*, **2024**, 9 (11), 13427-13439.
- [8] O. Bysewski et al., *Coord. Chem. Rev.* **2024**, 498, 215441.

Stimuli-responsive Flexible Lewis Pair Functionalized Coordination Complexes

K.-M. Tong,¹ N.E. Arsenault,¹ X. Zu,¹ M.O. Wolf¹

1. Department of Chemistry, University of British Columbia, Vancouver, BC, V6T 1Z1, Canada. mwolf@chem.ubc.ca

Coupling photo- and electroactive metal complexes to stimuli-responsive organic molecules results in intriguing new properties in these systems which can be leveraged for diverse applications in chemical sensing, bioimaging, and photopatterning. Flexible Lewis pair (FlexLPs) are systems that encompass phosphine oxide Lewis bases and dimesitylborane Lewis acids attached to a bithiophene scaffold, which can switch between an “open” unbound Lewis pair and a “closed” bound Lewis adduct depending on the hydrogen bond-donating (HBD) strength of the solvent.^[1] Functionalization of photoactive metal complexes with FlexLP-based ligands allows control of photophysical behavior via switching of the ligand state.^[2,3] In this talk, the photophysical and photochemical properties of these novel complexes will be discussed.



References

- [1] Y. Cao, N.E. Arsenault, M.O. Wolf, *J. Org. Chem.* **2019**, 84 (9), 5394-5403
- [2] N.E. Arsenault, Xu, Z., M.O. Wolf, *Inorg. Chem.* **2022**, 61, (6), 2804-2812
- [3] K.-M. Tong, J. Toigo, S. Kamal, B.O. Patrick, M.O. Wolf, *Chem. Eur. J.* **2024**, 30 (53), e202401657



Signal amplification in electrochemiluminescent biosensors

L. De Cola^{a,b}, I. Rimoldi^a, G. Facchetti^a, G. Valentini^c, L. Prodi^c

^a*Department of Pharmaceutical Science, Università degli Studi di Milano, Milan 20133, Italy*

^b*Istituto di Ricerche Farmacologiche Mario Negri IRCCS, Milan 20156, Italy*

^c*Department of Chemistry "G. Ciamician" Università degli Studi di Bologna, 40126 Bologna, Italy*

Electrogenerated chemiluminescence, also called electrochemiluminescence (ECL), is the generation of excited states upon recombination of oxidized/reduced species generated at the electrode and reduced/oxidized species produced by a chemical reaction.

In the past decades, ECL-active molecules have been employed in many applications such in systems for the detection of viruses/bacteria.^[1] However, despite the increasing demands for accuracy in diagnostics, the sensitivity of ECL in immunoassays, already in the picomolar range, can still be improved by designing emitters with higher emission quantum yields or by thinking of multiple emitter for a single analyte. The replacement of the commercial ECL emitter $[\text{Ru}(\text{bpy})_3]^{2+}$ with more efficient^[2] and easily-color tunable emitters such as water soluble Ir(III)-complexes,^[3] represents a promising tool to further improve the signal-to-noise ratio.

The strategy to increase the sensitivity of bioassays by constructing multi-labeled systems, such as the one developed by Roche, PolyRu, consisting of 8 units connected to the same antibody, did not achieve the desired sensitivity. Indeed, increasing the number of emitters does not increase the ECL signal proportionally. The reason for such lack of linear response is related to the quenching of the excited luminophore by the neighbouring oxidized or reduced species.

In this contribution we describe a shift in the paradigm of the research: from chasing a longer-lasting signal from the luminescent species to developing cleavable emitting labels. In order to realize such system, we designed and synthesized $[\text{Ru}(\text{bpy})_2(\text{bpy-S-S-R})]^{2+}$, a $[\text{Ru}(\text{bpy})_3]^{2+}$ derivative incorporating a disulfide moiety on the lateral chain of the ancillary ligand. The disulfide bridge is purposely designed to be cleaved by electrogenerated coreactant radicals, thereby releasing the luminophores into the solution, avoiding the quenching and activating the homogeneous ECL mechanism.

Acknowledgments

This project as received funding from the European Union's Horizon Europe EIC Pathfinder Open programme under Grant Agreement N. 101046787 (ECLIPSE).

References

- [1] Sobhanie, E.; Salehnia F.; Xu G.; Hamidipناه Y.; Arshian S.; Firoozbakhtian A.; Hosseini M.; Ganjali, M. R.; Hanif, S. *Trends Analyt. Chem.* **2022**, 157, 116727.
- [2] Fernandez-Hernandez, et al. *Anal. Chem.* **2016**, 88, 4174–4178.
- [3] Bergmann, F. et al. **2013**, PCT/EP2013/992325

Lanthanoid Sensitisation from Re(I) Triangular Assemblies

M. Massi¹

¹ School of Molecular and Life Sciences – Curtin University, Perth WA, Australia
m.massi@curtin.edu.au

The antenna effect is the strategy of choice for the synthesis of highly luminescent lanthanoid complexes with emission in the visible or near-infrared region.^[1] The most common approach to sensitise lanthanoid luminescence is the use of π -conjugated organic chromophores. However, energy transfer to lanthanoid excited states can also be achieved from transition metal complexes, which has been particularly investigated for the sensitisation of near-infrared lanthanoids such as Yb(III) and Nd(III).^[2] We have recently encountered a triangular assembly featuring three Re(I) tricarbonyl tetrazolato complexes that has proven to be a very efficient sensitiser for both Yb(III) and Eu(III) (figure 1). Sensitisation of the red-emission of Eu(III) is particularly surprising given the energy mismatch between the donor and acceptor excited states.^[3] This presentation will showcase our investigation on the mechanism of energy transfer in these triangular assemblies.

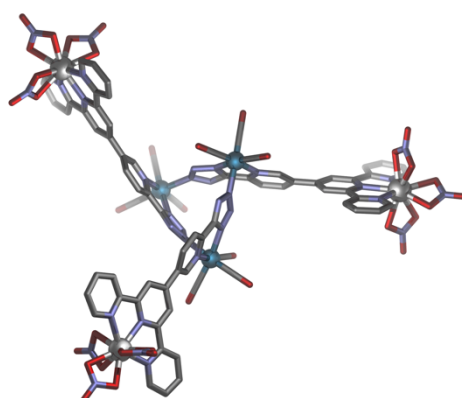


Figure 1. DFT model structure for the Re(I) tricarbonyl tetrazolato triangular assembly, featuring Eu(III) cations bound to the external terpyridine ligands.

Aknowlegments

The Australian Research Council is kindly acknowledged for funding (DP240103097).

References

- [1] D. Parker, J. D. Fradgley, K. -L. Wong, *Chem. Soc. Rev.* **2021**, 50, 8193.
- [2] T. Lazarides, D. Sykes, S. Faulkner, A. Barbieri, M. D. Ward, *Chem. Eur. J.* **2008**, 14, 9389.
- [3] P. J. Wright, L. J. Cameron M. I. Ogden, E. G. Moore, M. Massi *et al*, *Chem. Eur. J.* **2024**, 30, e202401233.



Light-Triggered Metallodrugs: Harnessing Excited State Dynamics for Phototherapy

Sherri A. McFarland

The University of Texas at Arlington

Photodynamic therapy (PDT) represents a targeted approach in photomedicine, utilizing photosensitizing agents, light, and oxygen to selectively eliminate cancer cells. While traditional PDT agents have predominantly been organic porphyrins and their tetrapyrrole derivatives, recent advancements have highlighted the therapeutic potential of metal-based complexes. Among these, ruthenium-based photosensitizers have emerged as promising candidates due to their unique photophysical properties. Notably, TLD1433, a ruthenium complex developed in our laboratory, has achieved a significant milestone as the first compound of its class to enter clinical trials for bladder cancer PDT. This presentation will explore ongoing research directions inspired by the design and clinical application of TLD1433, with a focus on understanding some of the mechanistic underpinnings of TLD1433 that complement the known PDT pathways. This knowledge can be exploited in novel strategies for enhancing the efficacy of metal-based phototherapy agents.



Molecular Catalysis of Water Splitting and CO₂ Reduction

K. Sakai

Department of Chemistry, Faculty of Science, Kyushu University, Motooka 744, Nishiku, Fukuoka 819-0395, Japan. E-mail: ksakai@chem.kyushu-univ.jp

Besides our extended studies on photocatalytic hydrogen evolution by Pt(II)-based molecular catalysts [1], mechanistic studies on single-site water oxidation catalysts (WOCs) of Ru, Fe, Co, and Cu have been advanced [2,3]. Recently, the O-O coupling by a cobalt polyoxomolybdate (CoPOM) was shown to proceed among the preinstalled oxygen atoms in the cluster [4]. We also showed that both CoPOM and cobalt tetraphenylporphyrin (CoTPP) WOCs effectively promote photocatalytic WO when they are physisorbed over the photosensitizing carbon nitrides (C₃N₄) [5]. Our molecular-based TiO₂ photoanode fabricated by chemisorption of Ru-based polypyridyl photosensitizer and WOC (Ru-bda catalyst) were also shown to drive photocatalytic WO at an interface [6].

Another important issue has been to fabricate artificial photosynthetic systems enabling photocatalytic carbon dioxide (CO₂) reduction into value-added fuels. By insisting in the use of aqueous reaction platforms, our initial challenge was to gain a sufficiently high CO₂ reduction selectivity versus water reduction even in fully aqueous media. A high selectivity in CO₂ reduction versus water reduction (Sel_{CO₂}=90 %) with a high turnover number (TON_{CO}=4000, 12 h) was successfully achieved by us [7-9]. The high selectivity was rationalized by the mismatch in frontier MO association of the metal nucleophile with a 1s(H⁺) orbital [9]. The lifetime of our water-soluble copper(I) diphosphine-diimine photosensitizer was shown to be drastically elongated by the hydrophobic coverage of alkylammonium ions, leading to demonstrate a new technique to improve the reductive quenching efficiency [10].

Although formate is an attractive alternative to fossil fuels due to its potential application in reversible hydrogen storage, selective catalysts for CO₂-to-HCOOH conversion are still limited, especially when photo-driven in aqueous media. Our recent studies successfully unveiled the mechanism of CO₂ reduction to formate which undergoes via the M-H attack on CO₂, directly ends up with the release of formate [11,12]. Remarkably, the water-soluble [Rh^{III}Cp*(dihydroxy-bpy)Cl]⁺ family was found to be the first example showing the water-induced switching in selectivity for the CO₂-to-HCOOH conversion [12].

References

- [1] T. Kunikubo, R. Castañeda, M. Murugesu, J. L. Brusso, K. Yamauchi, H. Ozawa, K. Sakai, *Angew. Chem. Int. Ed.* **2025**, 64, e202418884N.
- [2] Y. Aimoto, A. Parent, K. Yamauchi, K. Sakai, *J. Am. Chem. Soc.* **2024**, 146, 16866-16877.
- [3] A. Parent, T. Nakazono, Y. Tsubonouchi, N. Taira, K. Sakai, *Adv. Inorg. Chem.* **2019**, 74, 197-240.
- [4] N. Taira, K. Yamauchi, K. Sakai, *ACS Catal.* **2023**, 13, 3211-3223.
- [5] Y. Tomita, N. Taira, K. Sakai, H. Ozawa, *ACS Catal.* **2024**, 14, 5788-5794.
- [6] X. Yan, K. Sakai, H. Ozawa, *ACS Catal.* **2023**, 13, 13456-13465.
- [7] A. Call, M. Cibian, K. Yamamoto, T. Nakazono, K. Yamauchi, K. Sakai, *ACS Catal.* **2019**, 9, 4867-4874.
- [8] X. Zhang, M. Cibian, A. Call, K. Yamauchi, K. Sakai, *ACS Catal.* **2019**, 9, 11263-11273.
- [9] X. Zhang, K. Yamauchi, K. Sakai, *ACS Catal.* **2021**, 11, 10436-10449.
- [10] F. Sueyoshi, X. Zhang, K. Yamauchi, K. Sakai, *Angew. Chem. Int. Ed.* **2023**, 62, e202217807.
- [11] C. Liao, K. Yamauchi, K. Sakai, *ACS Catal.* **2024**, 14, 11131-11137.
- [12] D. Lee, K. Yamauchi, K. Sakai, *J. Am. Chem. Soc.* **2024**, 146, 31597-31611.

Photocatalytic events for CO₂ reduction and Oxygen Atom Transfer

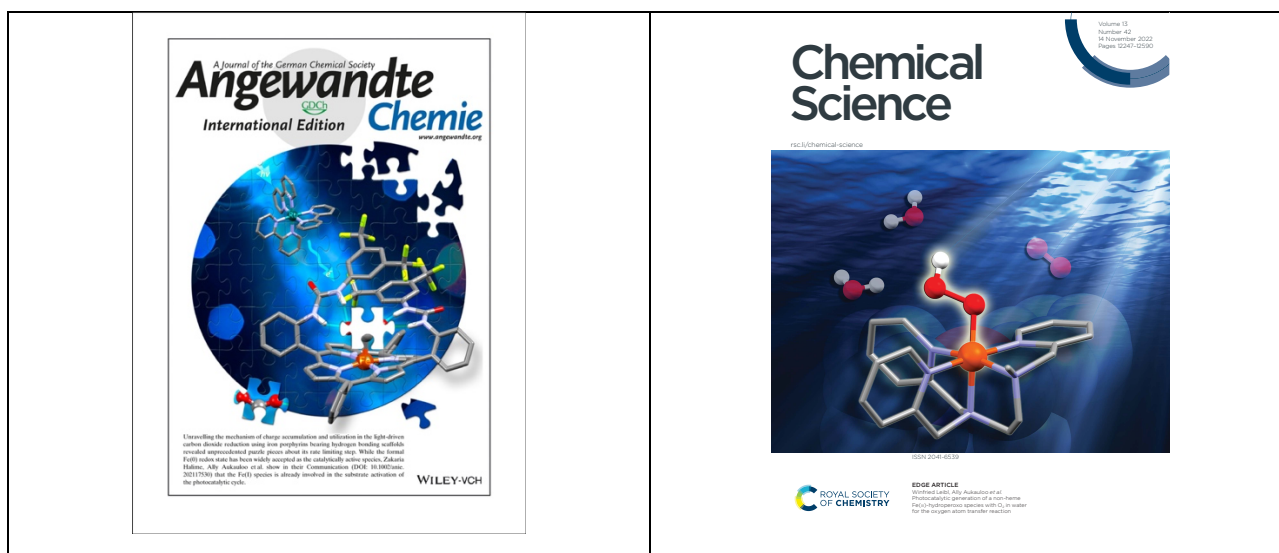
A. Aukauloo

ICMMO, Université Paris-Saclay.

ally.aukauloo@universite-paris-saclay.fr

We found that the light-driven CO₂ reduction using an iron porphyrin holding urea groups as hydrogen bonding donor in the second coordination sphere of the catalyst lead to a multifold increase in TON and TOF compared to both non-substituted **TPPFe**, reaching one of the highest values in molecular photocatalysis and importantly with water as proton source. In contrast to the classic photocatalytic scheme where Fe⁰ is argued to be the species to react with CO₂, we evidenced that the RDS herein resides in the formation of the **[UrFe^I-CO₂]** adduct. The added urea functionality plays an important role in the binding and activation of CO₂ at the Fe^I state enabling the faster photocatalytic conversion.¹

Coupling a photoredox module and a bio-inspired non-heme model to activate O₂ for the oxygen atom transfer (OAT) reaction is under We found that the efficient oxidative quenching mechanism between a [Ru(bpy)₃]²⁺ chromophore and a reversible electron mediator, methyl viologen (MV²⁺), to form the reducing species methyl viologen radical (MV^{•+}) can convey an electron to O₂ to form the superoxide radical and reset an Fe(III) species in a catalytic cycle to the Fe(II) state in an aqueous solution. The formation of the Fe(III)-hydroperoxo (Fe^{III}-OOH) intermediate can evolve to a highly oxidized iron-oxo species to perform the OAT reaction to an alkene substrate.²



Acknowledgments

Thanks to ANR LOCO, CNRS, Université Paris-Saclay, CEA-Saclay and Institut Universitaire de France

References

- [1] E. Pugliese et al. *Angew. Chem. Int. Ed.* 2022, 61, e202117530
- [2] E. Pugliese et al. *Chem. Sci.*, 2022, 13, 12332



High-Energy MLCT States in Ru Polypyridines for Solar-Energy Conversion

Alejandro Cadranel^{1,2,3}

¹ Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Physical Chemistry I, and Interdisciplinary Center for Molecular Materials, Egerlandstr. 3, 91058, Erlangen, Germany

² Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Química Inorgánica, Analítica y Química Física, Pabellón 2, Ciudad Universitaria, C1428EHA, Buenos Aires, Argentina

³ CONICET – Universidad de Buenos Aires, Instituto de Química-Física de Materiales, Medio Ambiente y Energía (INQUIMAE), Pabellón 2, Ciudad Universitaria, C1428EHA, Buenos Aires, Argentina.

ale.cadranel@fau.de

Important fractions of the solar energy absorbed in natural and artificial photosynthetic schemes are dissipated via fast internal conversion (IC) processes which, in line with Kasha's rule, populate the lowest-energy excited state. In contrast, chromophores that undergo internal conversion in slow timescales allow high-energy excited states to engage in bimolecular or long-range reactivity, outcompeting dissipation. This provides opportunities to improve solar-energy conversion efficiencies and perform energy-demanding photochemistry.^[1]

In Ru polypyridines, the challenge is to trap either the excited hole in Ru-based orbitals below the HOMO, or the excited electron in ligand-based orbitals above the LUMO. This talk will address both strategies. On one hand, the focus will be on monometallic {Ru(bpy)} complexes, where the presence of only one acceptor ligand fixed the fate of the excited electron, and slow hole-reconfiguration (HR) dynamics were observed due to a 1000 cm⁻¹ barrier.^[2] There, theoretical calculations revealed the geometrical changes related to this reaction coordinate, which was exploited to tune HR-IC barriers by synthetic modifications.^[3,4] On the other hand, bimetallic {Ru(qpy)Ru} (qpy = quaterpyridine) complexes will be shown, where slow intra-ligand electron transfer (ILET) allowed a high-energy MLCT state to undergo photoinduced electron transfer, producing a high-energy photo-reductant which prevented the dissipation of around 140 meV.^[5] Temperature-dependent ultrafast transient absorption studies were at the forefront, revealing ILET-IC barriers of around 2000 cm⁻¹.

Acknowledgments

All colleagues that participated in this research are acknowledged

References

- [1] A. Cotic, I. Ramírez-Wierzbicki, A. Cadranel, *Coord. Chem. Rev.* **2024**, 514, 215878.
- [2] A. Cotic, K. Veys, D. Escudero, A. Cadranel, *Phys. Chem. Chem. Phys.* **2022**, 24, 26428–26437.
- [3] A. Cotic, F. W. Heinemann, L. D. Slep, A. Cadranel, *ChemPhysChem* **2024**, 25, e202400246.
- [4] A. Cotic, A. Cadranel, *Unpublished*.
- [5] A. Cotic, S. Cerfontaine, L. D. Slep, B. Elias, L. Troian-Gautier, A. Cadranel, *J. Am. Chem. Soc.* **2023**, 145, 5163–5173.



(Photo)electrochemical water splitting and mechanisms of O-O bond formation—From natural to artificial photosynthesis

Licheng Sun

Center of Artificial Photosynthesis for Solar Fuels and Department of Chemistry, Westlake University, Dunyu Road 600, 310030 Hangzhou, China.

sunlicheng@westlake.edu.cn

To generate solar fuels, such as green H₂, green MeOH, or green NH₃ by the reduction of respective H₂O, CO₂, or N₂, we need green electrons and green protons, which can be obtained through water splitting driven directly or indirectly by sustainable energy sources such as sunlight. In photosystem II, nature uses a Mn₄CaO₅ cluster as the water oxidation catalyst to generate green electrons and green protons in the form of NAD(P)H and ATP, which in turn drive the reduction of CO₂, producing biomass. In this presentation, our recent studies on water oxidation mechanisms in photosystem II and the missing steps in the catalytic cycle will be discussed. Our efforts of several decades on the design and synthesis of transition metal complex-based molecular catalysts for water oxidation, O-O bond formation mechanisms and their assemblies in functional devices like photoelectrochemical (PEC) cells, anion exchange membrane water electrolyzers (AEM-WE) will be presented.

References (recent publications)

- Y. Guo et al, *Angew. Chem. Int. Ed.* **2025**, e202421383.
L. Yin et al, *Angew. Chem. Int. Ed.*, **2025**, e202503715.
S. Sun et al, *J. Am. Chem. Soc.* **2025**, doi.org/10.1021/jacs.5c04431
Z. Hu et al, *Angew. Chem. Int. Ed.* **2024**, e202415645.
Z. Li et al, *Nat. Catal.* **2024**, 7, 944-952.
X. Cao et al, *J. Am. Chem. Soc.* **2024**, 146, 25125–25136.



Insights into the photophysics of molecular and supramolecular systems based on porphyrins

B. Ventura

*Institute for Organic Synthesis and Photoreactivity (ISOF) – National Research Council (CNR)
Via P. Gobetti 101, Bologna (Italy)
barbara.ventura@isof.cnr.it*

Porphyrins are key components for the construction of molecular and supramolecular systems with light-induced functions, since they possess unique photophysical and electrochemical properties that can be finely tuned by proper functionalization. Their combination with organic or organometallic components leads to the exploration of a variety of photoactive systems, with applications ranging from energy collection and conversion to photocatalysis [1, 2].

Our interest in the study of multicomponent arrays based on porphyrins stems from the complex interplay of photoinduced processes that can come into play and lead to the final exploitable function. Ultrafast transient absorption spectroscopy is one of the most useful tools to gain information on the formation and deactivation of excited states and transient species, such as ions and radicals, formed within photoinduced reactions.

Here we will present some of our recent studies on molecular and supramolecular multicomponent systems where porphyrins have been combined with organic units or transition metal complexes [3, 4]. These architectures present intricate and unusual photophysical behaviors, that have been elucidated by means of steady-state and time-resolved luminescence techniques and ultrafast transient absorption spectroscopy. They find application in energy collection, charge separation and photocatalytic processes such as CO₂ reduction.

Aknowlegments

Thanks to 2022FWAF2M_PE4_PRIN2022-CADIVAPE “CARbon Dioxide VALorization by chemical, Photo- and Electro-chemical processes” and to H2020-MSCA-ITN-2017-765297-NOAH “Network of Functional Molecular Containers with Controlled Switchable Abilities”

References

- [1] P. D. Frischmann, K. Mahata, F. Würthner, *Chem. Soc. Rev.* **2013**, 42, 1847-1870.
- [1] E. Nikoloudakis, I. López-Duarte, G. Charalambidis, K. Ladomenou, M. Ince, A. G. Coutsolelos, *Chem. Soc. Rev.* **2022**, 51, 6965-7045.
- [2] A. Edo-Osagie, D. Serillon, F. Ruani, X. Barril, C. Gourlaouen, N. Armaroli, B. Ventura, H.-P. Jacquot de Rouville, V. Heitz, *J. Am. Chem. Soc.* **2023**, 145, 10691-10699.
- [3] S. L. Pons Alles, D. Veclani, A. Barbieri, B. Therrien, B. Ventura, *Dalton Trans.* **2025**, DOI: 10.1039/d4dt03154g

Using metal complexes to open the door to long-lived excited states

Keith C. Gordon¹

University of Otago, Department of Chemistry, Union Place West, Dunedin, NEW ZEALAND.
keith.gordon@otago.ac.nz

Creating long-lived excited states that have the potential to act as catalytic centres is an important research goal. One way to achieve this is to use metal complexes in which the ligand has a triplet charge-transfer (³ILCT) state that can easily be accessed because of the presence of the metal centre. A number of these systems have been reported based on rhenium(I) with polypyridyl ligands. The complexity of the photophysics of these systems is challenging in terms of designing compounds. For example, we have recently demonstrated that solvent effects can tune between differing excited states (Figure 1)¹ and that modest peripheral changes to compounds can result in dramatic changes in excited state lifetime^{2,3}.

Rhenium(I) and ruthenium(II) complexes with polypyridyl ligands with donor group ((triphenylamine, TPA) can have long-lived excited states. We report how these can be characterised and what design features we can learn from these studies. The challenge of using earth abundant metals to achieve these same types of states will also be introduced.

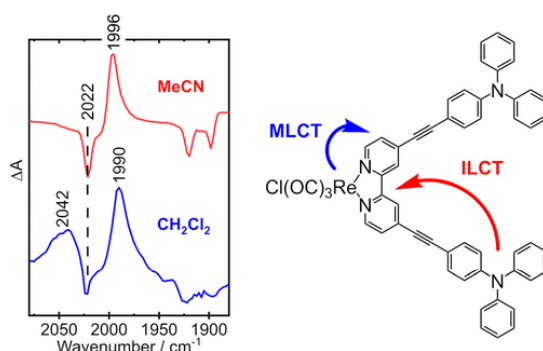


Figure 1. Switching the excited state for a metal complex using solvent as probed by time-resolved infrared spectroscopy.

References

- [1] J. J. Sutton, D. Preston, P. Trabber, J. Steinmetzer, S Kayal, X-Z Sun, J. D. Crowley, M. W. George, S. Kupfer *J. Am. Chem. Soc.* **2021**, *143*, 9082-9093.
- [2] G. E. Shillito T.B. J. Hall, D. Preston, P. Traber, L. Wu, K. E. A. Reynolds, R. Horvath, X. Z. Sun, N. T. Lucas, J. D. Crowley, M. W. George, S. Kupfer, K. C. Gordon, *J. Am. Chem. Soc.* **2018**, *140*, 4534-4542
- [3] G. E. Shillito, D. Preston, J. D. Crowley, P. Wagner, S. J. Harris, K. C. Gordon, S. Kupfer, *Inorg. Chem.* **2024**, *63*, 4947-4956

Application of selective photo-splitting of a Mn(0)-Mn(0) bond for developing a highly durable photocatalytic CO₂ reduction using a Mn-complex catalyst

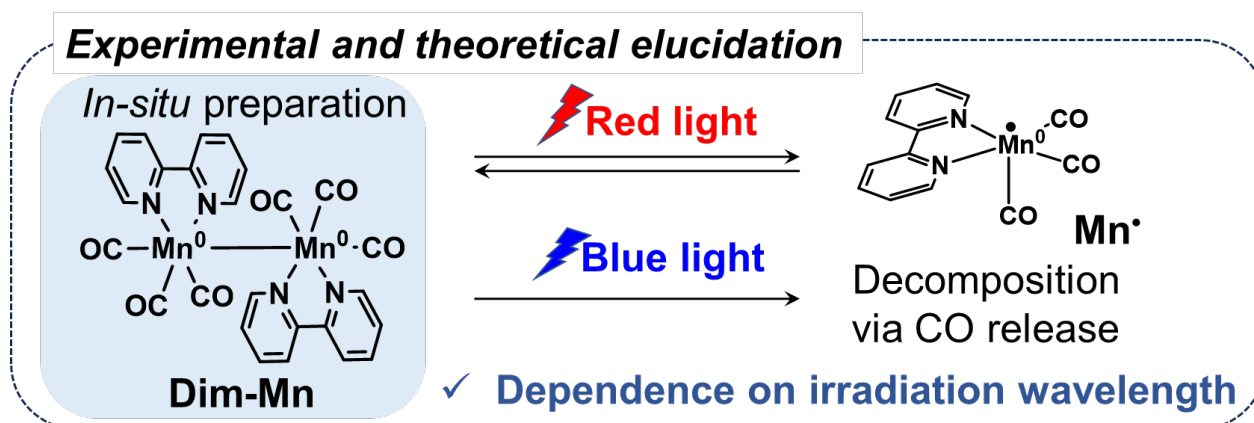
O. Ishitani

Graduate School of Advanced Science and Engineering, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739 8526, Japan. iosamu@hiroshima-u.ac.jp

$fac-[Mn^I(diimine)(CO)_3(L)]^{0/+}$ has attracted significant attention as a catalyst for the photocatalytic reduction of CO₂.^[1] However, in such photocatalytic systems, the photoexcitation of Mn complexes and reaction intermediates induces their decomposition, which lowers the durability of these systems.^[2]

In this study,^[3] we clarified the primary process whereby the Mn complex catalyst decomposes during the photocatalytic reaction. Based thereupon, we successfully constructed a highly durable photocatalytic system, of which the turnover number of formate (TON_{HCOO-}) exceeded 1700 when $fac-[Mn^I(bpy)(CO)_3((OC(O)OC_2H_5N(C_2H_5OH)_2)]$ (**Mn-CO₂-TEOA**) as the catalyst, [Os^{II}(4,4'-dimethyl-bpy)(5,5'-dimethyl-bpy)₂]²⁺ (**Os**) as the photosensitizer, and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (**BIH**) as the reductant were used in conjunction with irradiation at $\lambda_{ex} \geq 620$ nm. In contrast, for the same photocatalytic system, irradiation at $\lambda_{ex} \geq 480$ nm lowered the TON_{HCOO-} to less than 60. The significant difference in the durability of the photocatalytic system arises from the dependence of the Mn(0)-Mn(0) dimer [Mn⁰₂(bpy)₂(CO)₆] (**Dim-Mn**), an intermediate produced during the photocatalytic reaction, on the wavelength of the irradiated light for its photoreactivity as shown in Figure 1.

Figure 1. Photochemistry of [Mn⁰₂(bpy)₂(CO)₆] (**Dim-Mn**)



References

- [1] D. C. Fabry, O. Ishitani, in *Springer Handbook of Inorganic Photochemistry* (Eds.: D. Bahnemann, A. O. T. Patrocínio), Springer International Publishing, Cham, **2022**, pp. 1429-1452.
- [2] H. Takeda, H. Koizumi, K. Okamoto, O. Ishitani, *Chem. Commun.* **2014**, 50, 1491-1493.
- [3] H. Koizumi, Y. Tamaki, K. Kamogawa, M. Nicaso, Y. Suzuki, Y. Yamazaki, H. Takeda, O. Ishitani, *J. Am. Chem. Soc.* **2025**, 147, 6236-6248.

Illuminating the Unexpected Excited-State Dynamics of Non-Aromatic Pd(II) Porphyrinoids

E. R. Young¹, A. R. Dorsa¹, K. N. Ward², J. Rosenthal²

1. Lehigh University, Bethlehem, PA 18015, USA ery317@lehigh.edu

2. University of Delaware, Newark, DE, 19711, USA

Solar light harvesting and interconversion of solar energy into either electricity or driving force for small molecule activation reactions are critical to the production of energy and other processes that our society requires to function. In this talk, I will discuss the photochemistry of two non-aromatic porphyrinoid complexes: a Pd(II)biladiene and a Pd(II)isocorrole that were designed for use as photosensitizer drugs for photodynamic therapy. Up until this point, the excited-state dynamics of these new non-aromatic tetrapyrrole complexes have been virtually unexplored. During our work on the Pd(II)biladiene moiety, we discovered that while excitation into the lowest-energy absorption feature of the Pd(II)biladiene complexes produces expected photophysics, interestingly, excitation into higher-lying excited states resulted in an additional, unexpected lifetime. I will discuss our work to propose the cause of this unexpected behavior. Further our work with two Pd(II)isocorrole moieties reveals how the substitution pattern on the ring has a profound impact on the photophysics to the point that one complex is capable of producing cancer-killing reactive oxygen species, while the other moiety does not.

Pd(II) Biladiene Complexes



Pd(II) Isocorrole Complexes

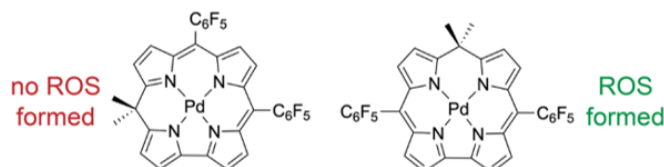


Figure 2. Molecular structures of the non-aromatic designer tetrapyrroles presented in this talk.



New metal complexes in luminescence, photocatalysis and charge accumulation

Oliver S. Wenger

Department of Chemistry, University of Basel, oliver.wenger@unibas.ch

Iron, manganese, chromium, nickel, and molybdenum offer promising alternatives to platinum group metals in photoactive coordination complexes. The first part of this presentation will highlight recent advancements in utilizing these metals in photoactive complexes featuring isocyanide and carbene ligands. Emphasis will be placed on how synthetic strategies can be employed to enhance photophysical properties, such as photoluminescence quantum yields and excited state lifetimes, aiming to achieve performance comparable to commercial complexes of noble metals. The second part will delve into the use of these metal complexes in photoredox catalysis and light-driven charge accumulation.

Gated Pathway for Photoinduced Interfacial Electron Transfer

E. Galoppini¹, M. Heidari¹, Q. Loague², H. Mann² and G. Meyer²

¹Department of Chemistry, Rutgers University, 73 Warren Street, Newark, NJ, 07102

²Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC, 27599

galoppin@rutgers.edu and gjmeyer@email.unc.edu

The talk will illustrate how careful synthetic bridge design (Galoppini) can be used to control interfacial electron injection and recombination (Meyer) between a transition metal photosensitizer and an oxide electrode via “structural gating.” Structural gating provides a

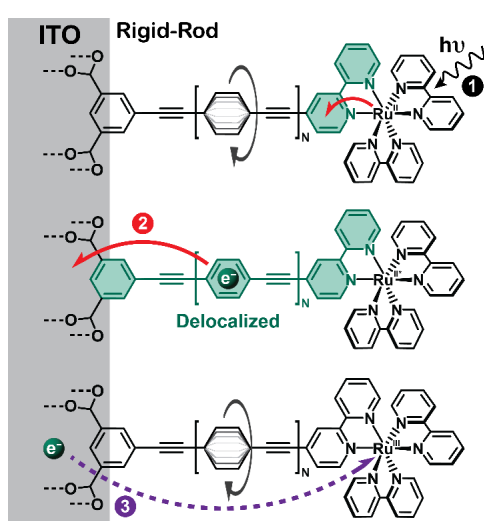


Figure 3. Mechanism for light initiated (1) “gated” electron transfer (2) that promotes long distance transfer to an oxide surface while inhibiting the unwanted charge recombination reaction (3).

molecular means to preferentially transfer electrons in one desired vectorial direction, behavior needed for applications in solar energy conversion. At the interfaces utilized, visible light absorption by a transition metal complex *opens* a ‘structural gate’ by planarization of otherwise rotating phenyl rings in *p*-phenylene ethynylene (PE) bridge units. Planarization provides a conjugated pathway for electron flow toward a conductive oxide surface. Excited state electron injection to the oxide restores rotation and *closes* the gate for the unwanted recombination reaction. This structural gating results in quantitative long-distance (> 20 Å) interfacial electron transfer that occurs about one thousand times faster than transfer in the opposite direction. Marcus-Gerischer analysis of kinetic data measured as a function of the thermodynamic driving force provided the reorganization energy and the electronic coupling matrix element for these interfacial electron transfers. Electronic coupling with the

conductive oxide surface was weak and consistent with non-adiabatic electron transfer. Smaller coupling was evident for the PE bridge units relative to insulating ionic bridges. An approximately 0.7 eV smaller reorganization energy was responsible for the enhanced vectorial electron injection through the conjugated aromatic bridge units. More broadly, a small distance-dependent reorganization energy with weak electronic coupling underlies the success of this bridge design that enables efficient long-distance electron transfer with slow recombination.

Acknowledgments

The UNC authors gratefully acknowledge support from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy (DE-SC0013461). The RU authors gratefully acknowledge support from the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (DE-FG02-01ER15256)

References

- [1] Loague, Q.; Heidari, M.; Mann, H.; Danilov, E.; Castellano, F.N.; Galoppini, E.; Meyer, G.J. *ACS Central Science* **2024**, *11*, 2132-2144.

Electrochemistry of electrode/graphene nanoribbon hybrid materials

K. D Glusac

Department of Chemistry, University of Illinois Chicago, Chicago, Illinois 60607, United States
Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, Illinois 60439,
United States

glusac@uic.edu; glusac@anl.gov

Modification of conductive electrodes with chemically tunable molecular catalysts represents an interesting and relatively unexplored area of photoelectrocatalysis research. Here, we investigated the coordination of Rh-based hydrogen evolution reaction catalyst onto the edges of graphene nanoribbons (GNRs) to form metal-nanoribbon catalyst (Rh-GNR).² The electrocatalytic hydrogen evolution reaction was observed when glassy carbon electrode is modified by Rh-GNR to form Rh-GNR@GC. The catalytic activity is maintained throughout the entire pH region, which contrasts the behavior of the homogeneous (molecular) analog catalyst, which becomes inactive in the basic pH. The Rh K-edge X-ray absorption spectroscopy reveals that the molecular analog and Rh-GNR exhibit identical coordination environment, indicating that the differences in electrochemical behavior do not arise due to functional group differences between the two catalysts. The results of this work indicate that the catalytic sites are located outside the electric double layer and that the observed catalytic enhancements are not associated with field-driven chemistry. The observed improvements for the immobilized catalyst are instead assigned to the prevention of undesired catalyst aggregation when it is attached to the electrode surface.

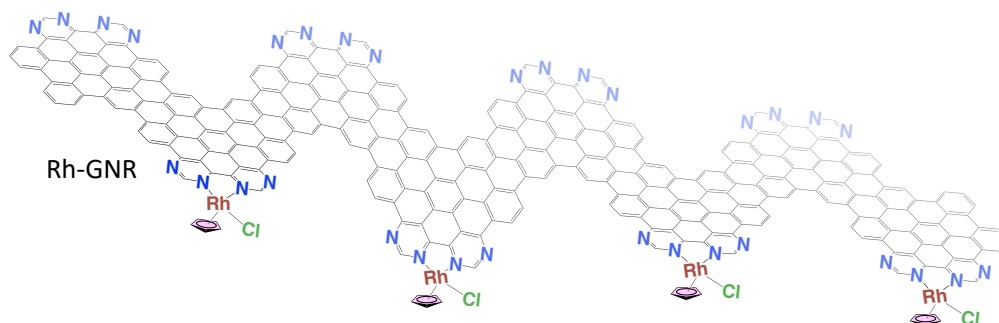


Figure 4. Structure of Rh-coordinated graphene nanoribbons.

Aknowlegments

Thanks to NSF for support.

References

- [1] Zoric, M. R.; Askins, E. J.; Qiao, X.; Glusac, K. D. Strong Electronic Coupling of Graphene Nanoribbons onto Basal Plane of a Glassy Carbon Electrode, *ACS Appl. Electron. Mater.* **2021**, 3 (2), 854-860.
- [2] Askins, E. J.; Navabi, P.; Kumar, K.; Finkelmeyer, S. J.; Presselt, M.; Cabana, J.; Glusac, K. D. Interfacial Electrochemistry of Catalyst-Coordinated Graphene Nanoribbons, *J. Am. Chem Soc.* **2024**, 146, 32, 22360.



Photophysical characterization and structure determination of DNA-stabilized silver nanoclusters

G. Romolini,^a H. Kanazawa,^b C. B. Møllerup,^c M. B. Liisberg,^a V. Rück,^a C. Cerretani,^{a,*} J. Kondo,^b T. Vosch^a

^a Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark.

^b Department of Materials and Life Sciences, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, 102-8554 Tokyo, Japan.

^c Department of Forensic Medicine, University of Copenhagen, Frederik V's Vej 11, DK-2100 Copenhagen, Denmark.

cece@chem.ku.dk

In the past twenty years, DNA has been used as a scaffold to stabilize atomically monodisperse silver nanoclusters. Thanks to their size below 2 nm, DNA-embedded silver nanoclusters (DNA-AgNCs) are characterized by discrete energy levels, allowing them to absorb and emit visible and near-infrared (NIR) light.[1]

However, the relationship between spectroscopic properties and structure is largely unknown. Such information is not only relevant to design new DNA-AgNCs with tailored properties, but it is also important for bio-conjugation experiments and essential for electronic structure calculations.

The combination of mass spectrometry and single crystal X-ray diffraction of HPLC-purified DNA-AgNCs is a powerful tool to gain insight into the atomic arrangement of silvers, the charge of the clusters, the coordinate bonds to the DNA and the overall DNA conformation. However, every step in the crystallization and structure determination process is neither trivial nor guaranteed to succeed.

The structures of two different emitters are presented, along with their steady-state and time-resolved photophysical characterization. One structure and seven mutations thereof are related to a 730-nm emitter formed by 16 Ag atoms encapsulated by two DNA decamers that take on a horse-shoe-like conformation. Mass spectrometry also revealed that two chlorido ligands are present in the structure, and the overall charge of the nanocluster is 8+. [2][3] The second structure corresponds to the longest atomically precise silver nanorod that has been solved so far. It consists of 28 silvers, of which 12 are metallic, resulting in bright emission at 960 nm. When in the crystalline state, two chlorides are also bound to the silver core, similarly to the previous structure.[4]

The integration of single-crystal X-ray diffraction measurements, mass spectrometry and spectroscopic investigation is thus paramount to advancing our understanding of these novel emitters.

References

- [1] González-Rosell, A.; Cerretani, C.; Mastracco, P.; Vosch, T.; Copp, S. M., *Nanoscale Advances* **2021**, 3 (5), 1230-1260.
- [2] Cerretani, C.; Kanazawa, H.; Vosch, T.; Kondo, J., *Angewandte Chemie International Edition* **2019**, 58 (48), 17153-17157.
- [3] González-Rosell, A.; Malola, S.; Guha, R.; Arevalos, N. R.; Matus, M. F.; Goulet, M. E.; Haapaniemi, E.; Katz, B. B.; Vosch, T.; Kondo, J.; Häkkinen, H.; Copp, S. M., *Journal of the American Chemical Society* **2023**, 145 (19), 10721-10729.
- [4] Romolini, G.; Kanazawa, H.; Møllerup, C. B.; Liisberg, M. B.; Lind, S. W.; Huang, Z.; Cerretani, C.; Kondo, J.; Vosch, T., *Small Structure* **2025**, 2500022.



A New Look at the Magneto-Optical Activity of Metalloporphyrins

J. J. Rack

Affiliations: Laboratory for Magneto-Optical Spectroscopy, Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque, NM 87131. E-mail: jrack@unm.edu

New materials featuring optimized magneto-optical activity are needed for the emergent quantum revolution as well as for existing telecommunications and photonics technologies. Current materials rely upon metal oxide materials, which limit their application due to difficulties in processing. In this talk, we will investigate the magneto-optical activity of metalloporphyrins. We will describe how to optimize the Faraday $\mathcal{A}$ -, $\mathcal{B}$ - and $\mathcal{C}$ -terms for a particular material and we will show that high symmetry pentafluorophenyl substituted metalloporphyrins show remarkable magneto-optic effects. These effects will be described within the Gouterman four-orbital model.

Beyond Donor Strength: Unconventional Ligand Designs for Optically Interesting 3d Coordination Complexes

David E. Herbert

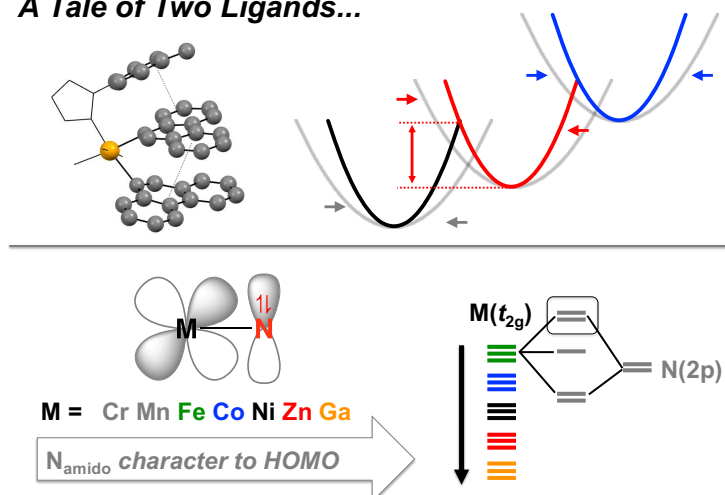
University of Manitoba – Department of Chemistry | Manitoba Institute for Materials
144 Dysart Road, Winnipeg, Manitoba, R3T 2N2 Canada

david.herbert@umanitoba.ca

Photoactive transition metal coordination complexes play an outsized role in modern photochemistry, owing primarily to their ability to absorb visible light and generate useful, long-lived excited states. Ligand design is key to efforts to control both light absorption and the properties of excited states—including their lifetimes—through manipulation of a molecule's electronic structure, with 'strong field' donors prized for their ability to destabilize metal-centered 'ligand field' states in favour of more useful charge-transfer excited states.

In this presentation, two less conventional approaches to improving the photophysical properties of coordination complexes will be discussed. First, the use of benzannulated ligands will be introduced as a means to accessing unconventional excited states in abundant element chromophores through controlling molecular rigidity.^[1] Second, molecular architectures that allow amido donors to exert favorable influence on light absorption or temper undesirable impacts on emission will be discussed.^[2] The characterization of excited states^[3] and their application in bimolecular photochemical reactions will also be presented.

A Tale of Two Ligands...



References

- [1] *J. Am. Chem. Soc.* **2025**, 147, 1694-1708
- [2] *Chem. Commun.* **2024**, 60, 3515-3518
- [3] *J. Am. Chem. Soc.* **2024**, 146, 17908-17916

Synergistic Hetero-TTA: Fact or Fiction?

E. G. Moore¹

School of Chemistry and Molecular Biosciences, The University of Queensland, St Lucia, 4072, Australia. E-mail: egmoore@uq.edu.au

Photochemical upconversion (UC) involving Triplet-Triplet Annihilation (TTA) is a fascinating process, enabling the formation of a single high-energy photon from two non-coherent low energy photons, and has attracted a myriad of applications ranging from biological sensing and imaging to improved efficiency of photocatalytic reactions and photovoltaic devices.^[1,2]

TTA-UC systems often rely on efficient triplet-triplet energy transfer (TTET) between long-lived phosphorescent metal complexes as photosensitisers (PS) and highly fluorescent organic molecules as acceptors (A), yielding photon upconversion efficiencies >30% under intense illumination. Methods to improve the lower efficiencies observed under low intensity illumination have included preorganisation of organic chromophores using supramolecular and/or Coulombic approaches and the use of mediators for energy transfer to improve the annihilator performance, allowing lower concentrations to be used, which can in turn limit parasitic losses by reabsorption.^[3]

In recent years, improvements in the overall upconversion efficiency obtained by using two (or more) chemically different annihilators has been reported, both in solution and the solid state, facilitated by hetero-TTA which it has been argued can also be synergistic.^[4,5] A consideration of the relative kinetics involved can reveal whether the higher energy organic triplet state will preferentially participate in upconversion, or more simply act as an energy shuttle to the lower energy annihilator. Herein, we report our analysis for one of these systems using steady state and time-resolved transient absorption techniques, and provide a kinetic model to explain our observations.

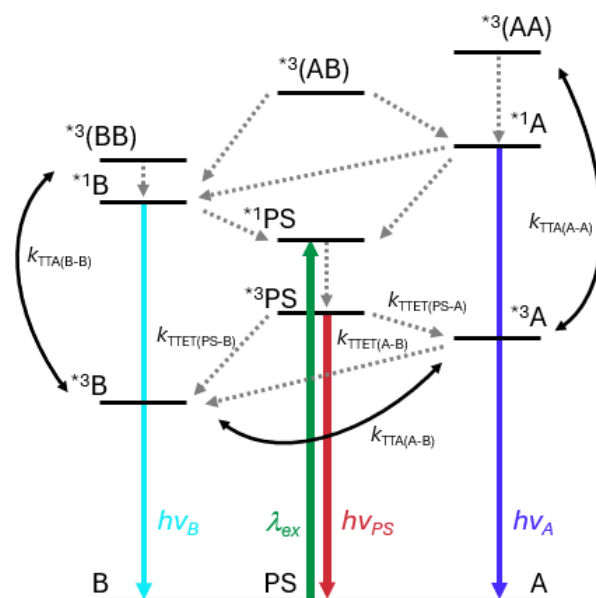


Figure 1. A simplified Jablonski diagram showing the different excited states and processes involved in homo- and hetero-TTA. S = sensitizer, A = annihilator (or mediator), B = annihilator.

Acknowledgments

Financial support by the Australian Research Council (ARC) is gratefully acknowledged.

References

- [1] Singh-Rachford, T. N., Castellano, F., *Coord. Chem. Rev.*, **2010**, 254, 2560-2573.
- [2] Seo, S. E., Choe, H-S., Cho, H., Kim, H-i, Kim, J-H., Kwon, O. S., *J. Mat. Chem. C.*, **2022**, 10, 4483-4496.
- [3] Glaser, F., Schmitz, M., Kerzig, C., *Nanoscale*, **2023**, 16, 123-137.
- [4] Cao, X., Hu, B., Zhang, P., *J. Phys. Chem. Lett.*, **2013**, 4, 2334-2338.
- [5] Turshatov, A., Busko, D., Avlasevich, Y., Miteva, T., Landfester, K., Balushev, S., *Chem. Phys. Chem.*, **2012**, 13, 3112-3115.

Ultrafast structural and spin dynamics in Copper(I) diimine phosphine complexes from femtosecond optical and X-ray spectroscopies

R. Cowin,¹ M. Appleby,² I. Meikle,¹ G. Williams,¹ E. Race,¹ I. Ivalo,¹ D. Chekulaev,¹ G. Wu,¹ C. Bacellar,² Y. Uemura,³ M. Biednov,³ D. Khakhulin,³ C. Milne,³ J. A. Weinstein¹

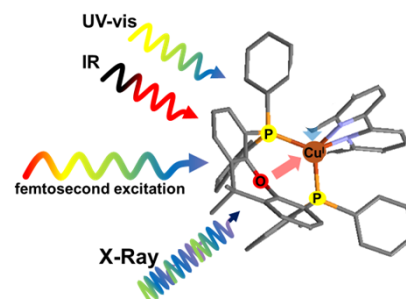
¹Chemistry, University of Sheffield, Sheffield, United Kingdom; ² Swiss FEL, Paul Scherrer Institut PSI, Villigen, Switzerland; ³ EU XFEL, Germany. E-mail: Julia.Weinstein@sheffield.ac.uk

Transition metal complexes have been used in a plethora of light-driven processes and applications for decades. In the quest for cheaper, scalable photosensitizers and photocatalysts, much recent research turned toward complexes of 1st or 2nd row transition metals. To this end, (bis)diimine complexes of Cu(I) have attracted considerable interest, owing to their intense Metal-to-Ligand charge transfer absorption in the visible region.

The drawback of such MLCT states is that pseudo-tetrahedral Cu(I) complexes undergo ultrafast Jahn-Teller distortion associated with the change from d^{10} to d^9 configuration of the metal center. As was first demonstrated by McMillin and co-workers, an introduction of bulky substituents in the diimine ligands can be used as the means to preclude such a distortion, and control the lifetime of the excited state(s).

Here, we will discuss the results of recent investigations of Cu(I) diimine diphosphine complexes, whereby an MLCT transition Cu-to-diimine is present, whilst additional steric bulk is provided by the phosphine ligand.

Specifically, we investigate the interplay between intersystem crossing and structural changes in a series of such complexes, in solution, on femto-to-picosecond time-scale. The talk will discuss the results of ultrafast broadband fluorescence upconversion (FLUPs) investigation into the rate of intersystem crossing. The structural and electronic changes are investigated by Cu K-edge X-ray absorption spectroscopy (XANES) and X-ray emission spectroscopy (XES), and P K-edge X-ray absorption spectroscopy. The results, in tandem with quantum-chemical calculations, identify Cu-P as a likely major contributor to the reaction coordinate driving the ISC; and the likely concerted mechanism for spin and structural change.



Aknowlegments

We thank the EPSRC, the Grantham Center for Sustainable Futures at TuoS, the Diamond Light Source and UK XFEL Physical Sciences hub for co-funding PhD students. Awards of beamtime from EU XFEL, Swiss FEL and Diamond Light Source are gratefully acknowledged. The EPSRC support for the Lord Porter Laser Laboratory at Sheffield is gratefully acknowledged.

References

- [1] D. R. McMillin, J. R. Kirchhoff and K. V. Goodwin, *Coord Chem Rev*, **1985**, 64, 83–92.
- [2] M. W. Mara, K. A. Fransted, L. X. Chen, *Coord. Chem. Rev.* **2015**, 282–283, 2–18.
- [3] M. Iwamura et al., *J. Am. Chem. Soc.* **2007**, 129, 5248–5256.
- [4] T. Katayama et al., *Chem. Sci.* **2023**, 14, 2572–2584.
- [5] M. V. Appleby et al., *Mater. Adv.* **2020**, 1(9), 3417–3427; *Faraday Disc.*, **2023**, 244, 391–410.

Photoactivation Dynamics of Abundant Transition Metal Complexes

Iria Bolano Losada^a, Simon Liedtke^a, Linnea Lindh^{a,b}, Arkady Yartsev^b, Petter Persson^a

^aComputational Chemistry Division, Lund University, Box 118, Lund 22100 Sweden

^bChemical Physics Division, Lund University, Box 118, Lund 22100 Sweden

Petter.Persson@compchem.lu.se

Photoactivation of transition metal complexes is key to a number of light-harvesting and photocatalytic applications, and often involves rich excited state dynamics down to ultrafast timescales.[1] We have explored a number of innovative molecular systems where molecular excited state dynamics and intermolecular charge transfer reactions play key roles for emerging photochemical applications using a combination of ultrafast spectroscopy and computational photochemistry approaches.[2-5] Here we present recent insights into the photoactivation and complex dynamics of several different transition metal complexes that highlight both common problems and emerging opportunities to drive photochemical reactions using light-harvesting transition metal complexes.

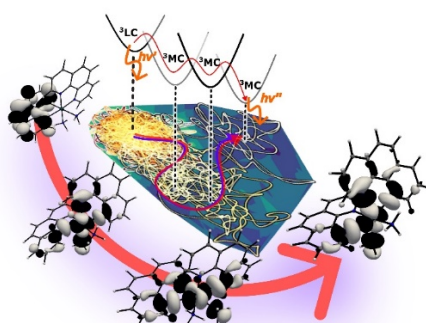


Figure 2. Photoactivation dynamics of transition metal complexes involve multidimensional motion to activate internal conversion and intersystem crossing paths.

Aknowlegments

We thank the Swedish Research Council (VR) and supercomputing facilities at LUNARC and NSC through NAISS allocations for support.

References

- [1] Ultrafast laser spectroscopy uncovers mechanisms of light energy conversion in photosynthesis and sustainable energy materials, D. Zigmantas, T. Polivka, P. Persson, V. Sundström, *Chem. Phys. Rev.* 3, 041303 (2022) [2] Microsecond photoluminescence and photoreactivity of a metal-centered excited state in a hexacarbene-Co(III) complex, S. Kaufhold et al, *J. Am. Chem. Soc.* 143, 1307 (2021) [3] Ligand-centered to metal-centered activation of a Rh(III) photosensitizer revealed by ab initio molecular dynamics simulations, I. Bolano Losada, P. Persson, *Chem. Sci.* 14, 3569 (2023) [4] Side-group switching between metal-to-ligand charge-transfer and metal-centered excited state properties in iron(II) N-heterocyclic carbene complexes, L. Lindh et al, *Coord. Chem. Rev.* 506, 215709 (2024) [5] Photoinduced hydrogen evolution catalyzed by Co(II) Complexes of N5-donor ligands, C. Li et al, *Chemistry - Euro J.* 000, 0000 (2025)



Recent Progress in the Understanding and Improvement of Cage Escape Processes using Transition Metal Photosensitizers

Ludovic Troian-Gautier^{1,2}

¹UCLouvain, Institute of Condensed Matter and Nanosciences (IMCN), Molecular Chemistry, Materials and Catalysis (MOST), Place Louis Pasteur 1/L4.01.02, 1348 Louvain-la-Neuve, Belgium

²Wel Research Institute, Avenue Pasteur 6, 1300 Wavre, Belgium

Ludovic.Troian@uclouvain.be

In natural and artificial photosynthesis, light absorption and catalysis are separate processes linked together by exergonic electron transfer. Light is commonly used to drive a plethora of organic transformations, but the corresponding reaction mechanisms are not always straightforward. A central aspect that governs excited-state electron transfer is the cage escape process, i.e. the physical separation and solvation of the geminate radical pair formed after excited-state electron transfer. Here, I will present our recent advances in the understanding of the cage escape process using coordination compounds based on rare and earth abundant transition-metal based coordination compounds. I will present our recent findings in the understanding of the cage escape process and correlated it to parameters that include spin, driving force, dielectric constants and temperature to show how these factors can be tuned to modulate the cage escape yields and thus the reaction yields.

Aknowlegments

The work presented herein benefited from support from the Fonds de la Recherche Scientifique (F.R.S.-FNRS); the Walloon Region as part of the financing of the FRFS-WEL-T strategic axis and the "Action de Recherche Concertée" through the project "UNCAGED".

References

- [1] Aydogan, A.; Bangle, R. E.; Cadranel, A.; Turlington, M. D.; Conroy, D. T.; Cauët, E.; Singleton, M. L.; Meyer, G. J.; Sampaio, R. N.; Elias, B.; Troian-Gautier, L., *J. Am. Chem. Soc.* **2021**, *143*, 15661-15673.
- [2] Aydogan, A.; Bangle, R. E.; De Kreijger, S.; Dickenson, J. C.; Singleton, M. L.; Cauët, E.; Cadranel, A.; Meyer, G. J.; Elias, B.; Sampaio, R. N.; Troian-Gautier, L., *Catal. Sci. Technol.* **2021**, *11*, 8037-8051.
- [3] Ripak, A.; De Kreijger, S.; Sampaio, R. N.; Vincent, C.; Cauët, E.; Jabin, I.; Tambar, U. K.; Elias, B.; Troian-Gautier, L., *Chem Catalysis* **2023**, *3*, 100490.
- [4] A. Ripak, A. K. Vega Salgado, D. Pires Valverde, S. Cristofaro, A. de Gary, Y. Olivier, B. Elias, L. Troian-Gautier, *J. Am. Chem. Soc.*, **2024**, *146*, 22818-22828.
- [5] M. J. Goodwin, J. C. Dickenson, A. Ripak; J. S. MacCarthy, A. M. Deetz, G. J. Meyer, L. Troian-Gautier, *Chem. Rev.*, **2024**, *124*, 7379-7464.
- [6] S. De Kreijger, A. Ripak, B. Elias, L. Troian-Gautier, *J. Am. Chem. Soc.*, **2024**, *146*, 10286-10292.
- [7] F. Glaser, S. De Kreijger, L. Troian-Gautier, *J. Am. Chem. Soc.*, **2025**, Accepted



Maximizing Photon to Product Efficiency in Photoredox Catalysis

Timothy Connell,^a

School of Life and Environmental Sciences, Deakin University, Waurn Ponds, VIC, Australia.

t.connell@deakin.edu.au

Visible light photoredox catalysis promises a sustainable approach for tackling challenging synthetic problems, including carbon-carbon bond formation, late-stage functionalization and solar fuels. The predominantly transition metal catalysts that power these reactions absorb light to form an excited state, followed by electron-transfer with a suitable donor or acceptor to produce potent single electron reductants and oxidants. Whilst primarily selected based on ground and excited state properties, catalyst activity is intrinsically tied to the nature of these redox intermediates.¹

Sacrificial additives are commonly employed in photoredox catalysis as a convenient source of electrons, but what occurs after electron-transfer is often overlooked. Productive reactions require dissociation of a charge-separated encounter complex, in a reductive quenching cycle this comprises reduced photocatalyst and oxidized electron donor (e.g. [PC^{•-}:D^{•+}]), however charge recombination offers a favourable but non-productive process. While both the electron donor and catalyst are regenerated, efficient charge recombination drastically lowers the photochemical quantum yield.

In this work, we use *in situ* spectroscopic techniques to study the kinetics of charge recombination and demonstrate how the choice of sacrificial donor plays a critical role in controlling the productive and non-productive pathways following electron transfer. Optimizing dissociation of the charge-transfer encounter complex significantly improves reaction rate, yield and atom economy. These results will direct the design of improved photocatalytic systems that exhibit higher efficiencies whilst requiring decreased energy inputs.

References

- [1] J. C. Bawden, P. S. Francis, S. DiLuzio, D. J. Hayne, E. H. Doeven, J. Truong, R. Alexander, L. C. Henderson, D. E. Gómez, M. Massi, B. I. Armstrong, F. A. Draper, S. Bernhard, T. U. Connell, *J. Am. Chem. Soc.* **2022**, *144* (25), 11189–11202

Luminescence Changeable Lanthanide-mixed Coordination Polymers for CO₂-storage

Y. Hasegawa ¹

¹Faculty of Engineering, Hokkaido University, Kita-13 Nishi-8, Kita-ku, Sapporo, Japan

hasegaway@eng.hokudai.ac.jp

The one, two-, and three-dimensional lanthanide coordination polymers alternating sequence of lanthanide(III) ions and organic linker ligands exhibits remarkable characteristics as novel organic materials with various structural and unique photophysical properties. The organic linker ligands provide formation of their polymeric and network structures. We have reported on luminescent Eu(III)/Tb(III) mixed coordination polymers. The Eu(III)/Tb(III) mixed coordination polymers show luminescent color changeable phenomena for temperature and mechano sensors.^[1, 2] Ratiometric analysis of two lanthanide luminophores is a potential method for sensing applications. Recently, we also presented Dy(III)/Tb(III) mixed coordination polymers under single crystal connections.^[3]

In this presentation, luminescent Eu(III)/Tb(III) mixed coordination polymer with inner cylindrical channels for CO₂ storage and detection is reported. Effective CO₂ gas capture from air has been now focused of photosynthesis, modern environmental and industrial chemistry. The cylindrical channels are composed of characteristic amido linker, dpa (4-(diphenylphosphoryl)-N-(4-(diphenylphosphoryl)phenyl)benzamide). This study demonstrates a luminescence changeable CO₂-storage cylinder composed of a triple-stranded helical Eu(III)/Tb(III) coordination polymer, [Eu_{0.1}Tb_{0.9}(hfa)₃(dpa)]_n.^[4]

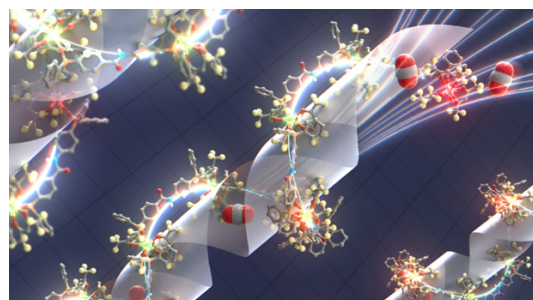
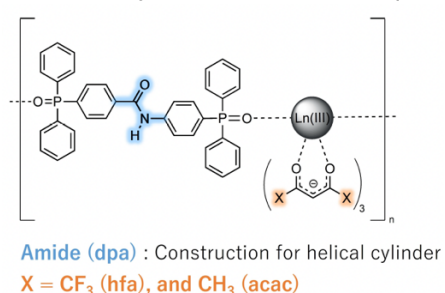


Figure 3. Chemical structure and CO₂ capture image of Eu(III)/Tb(III) mixed coordination polymer

Aknowlegments

Thanks to JSPS KAKENHI, Grant Numbers JP23 K17925 and JP23 K23420.

References

- [1] K. Miyata, Y. Hasegawa, et al, *Angew. Chem. Int. Ed.* **2013**, 52, 6413, DOI: 10.1002/anie.201301448.
- [2] Y. Hirai, Y. Hasegawa, et al, *Angew. Chem. Int. Ed.* **2017**, 56, 7171, DOI: 10.1002/anie.201703638.
- [3] P. P. Ferreira da Rosa, Y. Hasegawa; et al, *Nature Commun.* **2022**, 13; 3660, DOI: 10.1038/s41467-022-31164-z.
- [4] J. Hayashi, Y. Hasegawa et al, *Chem. Eur. J.* **2024**, e202403224, DOI: 10.1002/chem.202403224.



Captivating Bimolecular Photoredox Dynamics of Ligand-to-Metal Charge Transfer Complexes

C. Wegeberg,^{a,b} N. A. Calvet,^a M. Krafft,^{a,b} P. Chábera,^a A. Yartsev,^a and P. Persson^c

Affiliations: ^aDivision of Chemical Physics, Department of Chemistry, Lund University, 22100 Lund, Sweden; ^bDepartment of Physics, Chemistry and Pharmacy, University of Southern Denmark, 5230 Odense M, Denmark. ^cDivision of Computational Chemistry, Department of Chemistry, Lund University, 22100 Lund, Sweden. wegeberg@sdu.dk

An efficient photocatalytic bimolecular system (Figure 1) requires that 1) photo-induced charge separation (CS) is faster than charge recombination (CR) of the separated charges, and 2) CR is slower than their spatial separation via cage escape (CE). In this work, we investigate this competitive sequence of processes by the photocycles of rhenium(II) complexes featuring strongly oxidizing doublet ligand-to-metal charge transfer (²LMCT) excited states.^[1-3] Intrinsic CS and CR rates were measured up to multimolar concentrations for several electron donors to elucidate both the diffusion-controlled and close-contact regimes over a wide range of thermodynamic driving forces. The ratio between CS and CR rates was altered systematically by the thermodynamic driving force of electron transfer, utilizing the fact that the processes lie in the Marcus normal and inverted regions, respectively, and with deviations from classical Marcus behavior accounted for by using Marcus-Jortner-Levich theory. Our study provides unique insights on the dynamics of the charge separated pair because we *directly monitor* the generation and depletion of {[Re^I]⁺ + D^{•+}} and it highlights the complex competition between kinetic factors controlling the fundamental dynamics of the charge separated pairs inside the solvent cage.

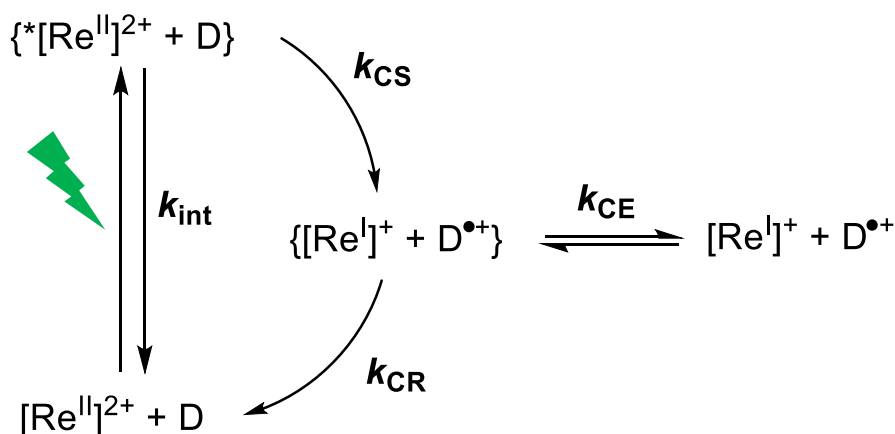


Figure 4. Photocycle between a rhenium(II) complex, $[\text{Re}]^{2+}$, and the electron donor, D. k_{int} = intrinsic decay rate of excited $[\text{Re}]^{2+}$; k_{CS} = rate of charge separation; k_{CR} = rate of charge recombination; k_{CE} = rate of cage escape.

References

- [1] Y. F. Lee, J. R. Kirchhoff. *J. Am. Chem. Soc.* **1994**, *116*, 3599–3600
- [2] A. S. Del Negro, C. J. Seliskar, W. R. Heineman, S. E. Hightower, S. A. Bryan. B. P. Sullivan. *J. Am. Chem. Soc.* **2006**, *128*, 16494–16495
- [3] J. J. Adams, N. Arulsamy, B. P. Sullivan, D. M. Roddick, A. Neuberger, R. H. Schmehl. *Inorg. Chem.* **2015**, *54*, 11136 – 11149.

Impact of Cis/Trans Geometry on the Photophysical, Electronic, and Structural Properties of Pt(II) Cyclometalated Complexes

M. Penconi,^a D. Marinotto,^a A. Poma,^{a,b} C. Baldoli,^a P. Mussini,^b A. Bossi^a

^a *Consiglio Nazionale delle Ricerche, Istituto di Scienze e Tecnologie Chimiche “Giulio Natta” SCITEC-CNR, via Fantoli 16/15, 20138 Milan, Italy;* ^b *Università degli Studi di Milano, Department of Chemistry, v. Golgi 19, 20133 Milan, Italy. Email: alberto.bossi@cnr.it*

Research on organometallic platinum complexes is still vibrant, as it continues to deepen the understanding of fundamental reactivity, electronic properties, and photophysical behavior of transition metals. These insights pave the way for innovations in areas such as optical sensors, visualization devices, catalysis, and photodynamic therapy. Pt(II) complexes, characterized by square planar coordination, can exhibit cis-trans isomerism when coordinated with bidentate or monodentate ligands. This feature can be further exploited to design molecules with tailored properties. In this context, we previously reported the first stable pair of Pt(II) complex characterized by the different stereochemical arrangement of two monoanionic bidentate ligands, the widely used 1-phenyl-pyrazole (Hppz, as the HC[^]N one) and a ortho-hydroxy Schiff-base (the HO[^]N one).[1] Herein, we extend our study on *cis-trans* isomers by tailoring the HO[^]N ligand structure expanding the π -system either at the chelating N terminus or at the O one. As the ancillary HC[^]N ligand, in addition to Hppz, we employed Hppy, leading to the formation of the corresponding complexes exclusively as single trans isomers. The optical, electronic and structural properties of the studied systems (depicted in figure 1) reveal that complexes with the same trans pattern show analogue behavior; however, those with different geometry display distinct photophysical properties until the triplet emissive state shift from a mostly MLCT type (**5a-c/6a-c**) to a IL one (**5d/6d**).

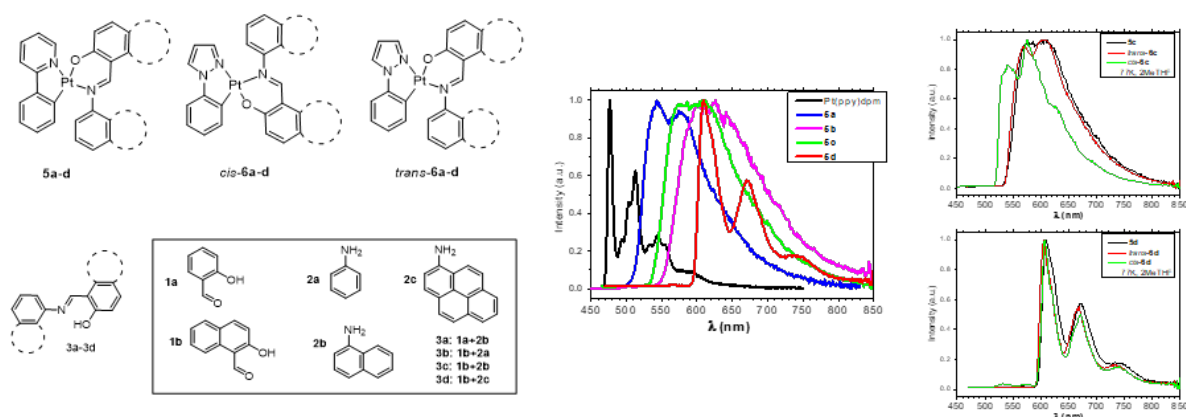


Figure 5. Structure of the studied Pt(C[^]N)(O[^]N) complexes; summary of the optical emissions

Aknowlegments

Thanks to PRIN2022 Mechanism Enhanced ECL Technology “MEET”. Prot. 20225P4EJC.

References

[1] A. Poma, A. Forni, C. Baldoli, P. R. Mussini, A. Bossi, *Dalton Trans.*, **2017**, 46, 12500–12506.

Combining the best of organic and inorganic photochemistry with molecular and coulombic dyads

M. Schmitz, Arne C. Sell, F. Glaser, M.-S. Bertrams, C. Kerzig

Affiliations: Department of Chemistry, Johannes Gutenberg University Mainz, 55128 Mainz, Germany, Email: ckertzig@uni-mainz.de

Dyads or bichromophores can be designed such that unique properties for photochemical energy and electron transfer reactions result. These properties are based on the interplay of an inorganic chromophore, enabling quantitative intersystem crossing as well as visible light absorption, and a covalently linked organic moiety with a long-lived triplet state. We synthesized ruthenium complex-based molecular dyads decorated with a covalently attached pyrene chromophore and used them for efficient photooxygenations in water, which is a challenging solvent for such reactions.^[1] The long-lived pyrene triplets in these dyads are relatively redox-inert compared to the MLCT triplets of the parent metal complexes. Hence, these dyads provide an efficient access to acceptor triplet states that are otherwise very tricky to obtain, which allowed us to establish a triplet quenching pathway control approach with molecular dyads.^[2] Guided by our recent study on coulomb effects on the energy transfer kinetics,^[3] we have developed a novel strategy for obtaining the advantages of molecular dyads without the time- and resource-consuming synthesis of these tailored photocatalysts. Simply by mixing a cationic ruthenium complex with an anionic pyrene derivative in water, a salt bichromophore is produced owing to electrostatic interactions (Fig. 1). We exploited this so-called coulombic dyad for several photoreactions in the context of light-to-energy conversion with outstanding reaction quantum yields and turnover numbers.^[4] Currently, we are about to establish that the coulombic dyad strategy can be used for versatile applications following a toolbox approach.

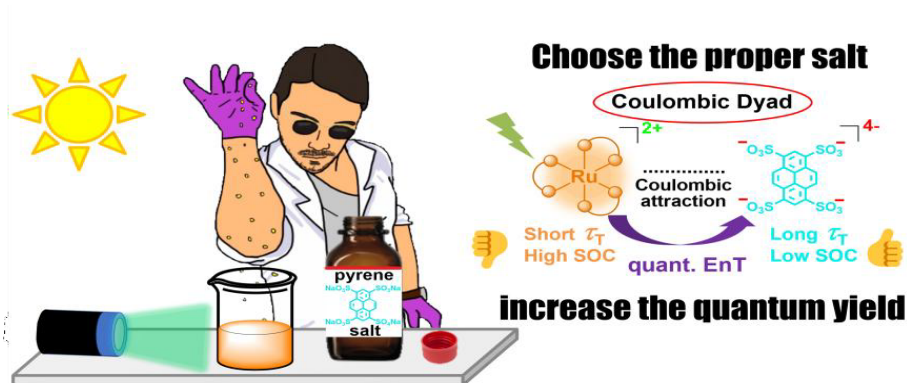


Figure 1. Straightforward preparation of a coulombic dyad for more efficient photocatalytic reactions.

References

- [1] A. C. Sell, J. C. Wetzel, M. Schmitz, A. W. Maijenburg, G. Woltersdorf, R. Naumann, C. Kerzig, *Dalton Trans.* **2022**, 51, 10799–10808.
- [2] M.-S. Bertrams, K. Hermainski, J.-M. Mörsdorf, J. Ballmann, C. Kerzig, *Chem. Sci.* **2023**, 14, 8583–8591.
- [3] F. Glaser, M. Schmitz, C. Kerzig, *Nanoscale* **2024**, 16, 123–137.
- [4] M. Schmitz, M.-S. Bertrams, A. C. Sell, F. Glaser, C. Kerzig, *J. Am. Chem. Soc.* **2024**, 146, 25799–25812.

Structural characterization of the $\text{Fe}(\text{CN})_6 \rightarrow \text{Fe}(\text{CN})_5\text{H}_2\text{O}$ photo-aquation process

K. Haldrup^{*1}, O. Ohlson¹, V. Markmann¹ *et al.*

1: Technical University of Denmark, Physics Department, 2800 Kngs. Lyngby, Denmark.

**hald@fysik.dtu.dk*

This talk will present very recent XFEL and synchrotron Time-Resolved X-ray Solution Scattering (TR-XSS) studies of the photo-aquation reaction of aqueous $[\text{Fe}(\text{CN})_6]^{4-}$ following photoexcitation at 320 nm: $[\text{Fe}(\text{CN})_6]^{4-} + h\nu \rightarrow [\text{Fe}(\text{CN})_6]^{4-*} \rightarrow [\text{Fe}(\text{CN})_5]^{3-} + \text{CN}^- \rightarrow [\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-} + \text{CN}^-$, where the characteristic time scale of the photo-aquation reaction is

~20 ps. Particular focus will be on the analysis of TR-XSS data, $\Delta S(Q, \Delta t)$, which yields a structural characterization of all the hexa- and penta-coordinated species involved in the reaction, with special emphasis on the role of the aqueous solvent.

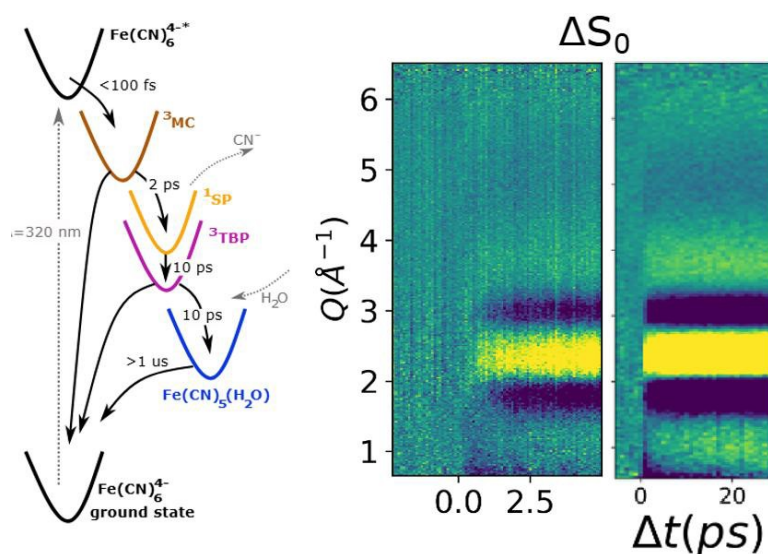


Figure 1. Schematic reaction scheme for the $[\text{Fe}(\text{CN})_6]^{4-} + h\nu \rightarrow [\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ photo-aquation reaction (left) and a 2D representation of the acquired TR-XSS data ($\Delta S(Q, \Delta t)$, right) showing how the reaction progresses on several different time scales with a concordant change in the X-ray scattering as the molecular structures change.

Acknowledgments

The authors gratefully acknowledge DANSCATT for supporting the beamtime activities and the Novo Nordisk Foundation for funding the project under grant number NNF20OC0061740

Redox-Driven Photoselective Self-Assembly

Dario Alessi¹, Luca Morgan¹, Elisa Pelorosso¹, Claudia Graiff², Piermaria Pinter³,
Alessandro Aliprandi^{1*}

¹Dipartimento di Scienze Chimiche, Università degli Studi di Padova; Via Marzolo 1, Padova, 35131, Italy; ²Department of Chemistry, Life Sciences and Environmental Sustainability, Università degli Studi di Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy; ³Novald GmbH, Elisabeth-Boer-Straße 9, 01099 Dresden, Germany

* Alessandro Aliprandi: alessandro.aliprandi@unipd.it

Self-assembly via non-covalent interactions is key to complex architectures with advanced functions.¹ Here, we couple Pt(II) self-assembly with redox reactions. Oxidation to Pt(IV) creates a non-emissive monomer, reducible to Pt(II) to trigger self-assembly, forming luminescent gels with unique pathways. UV irradiation reduces Pt(IV), generating metastable fibers with Pt···Pt interactions, enhancing photophysical properties. These fibers absorb visible light (up to 550 nm), enabling photoselective growth by converting surrounding Pt(IV) to Pt(II), promoting fiber elongation over new nuclei formation, as observed by real-time fluorescence microscopy.²

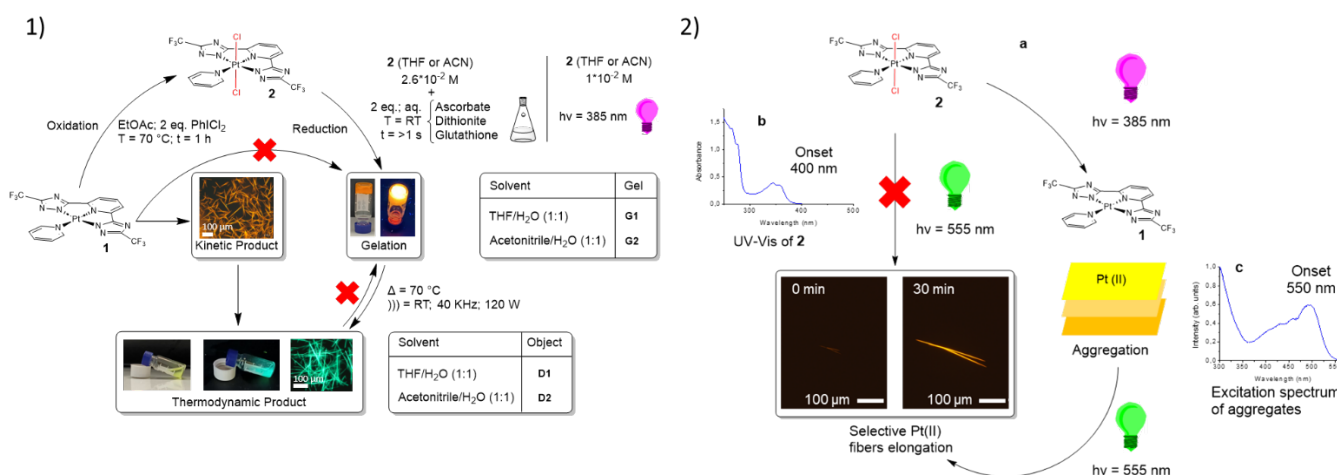


Figure 6. 1) Self-assembly pathway selection by photo or chemical reduction. 2) Photoselective elongation of Pt(II) fibers

Aknowlegments

The authors are grateful to the financial support from European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (grant agreement no. 949087)

References

- [1] J.-M. Lehn, *Angew. Chemie Int. Ed.* **2013**, 52 (10), 2836-2850
- [2] *Accepted Manuscript*



π Covalency in the Halogen Bond

C. P. Berlinguette^{1,2,3,4}

¹*Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, V6T 1Z1, Canada*

²*Department of Chemical & Biological Engineering, University of British Columbia, 2360 E Mall, Vancouver, BC, V6T 1Z3, Canada*

³*Stewart Blusson Quantum Matter Institute, University of British Columbia, 2355 East Mall, Vancouver, BC, V6T 1Z4, Canada*

⁴*Canadian Institute for Advanced Research (CIFAR), 661 University Avenue, Toronto, ON, M5G 1M1, Canada*

cberling@chem.ubc.ca

Halogen bonds are a highly directional class of intermolecular interactions widely used in chemistry and chemical biology. This linear interaction is commonly viewed to be analogous to the hydrogen bond because all hydrogen bonding models also intuitively describe the σ -symmetric component of halogen bonding. The possibility of π -covalency in a halogen bond is not contemplated in any known models. We provide herein clear evidence of π -covalency being operative in a halogen bond formed between chloride and halogenated triphenylamine-based radical cations. This conclusion was reached through computational analysis of chlorine K-edge X-ray absorption spectra recorded on these halogen bonded pairs. In light of this result, we contend that halogen bonding is better described by analogy to metal coordination bonds rather than hydrogen bonds. Our revised description of the halogen bond suggests that these interactions could be employed to influence the electronic properties of conjugated molecules in unique ways.

Gated Pathway for Photoinduced Interfacial Electron Transfer

E. Galoppini¹, M. Heidari¹, Q. Loague², H. Mann² and G. Meyer²

¹Department of Chemistry, Rutgers University, 73 Warren Street, Newark, NJ, 07102

²Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC, 27599

galoppin@rutgers.edu and gjmeyer@email.unc.edu

The talk will illustrate how careful synthetic bridge design (Galoppini) can be used to control interfacial electron injection and recombination (Meyer) between a transition metal photosensitizer and an oxide electrode via “structural gating.” Structural gating provides a

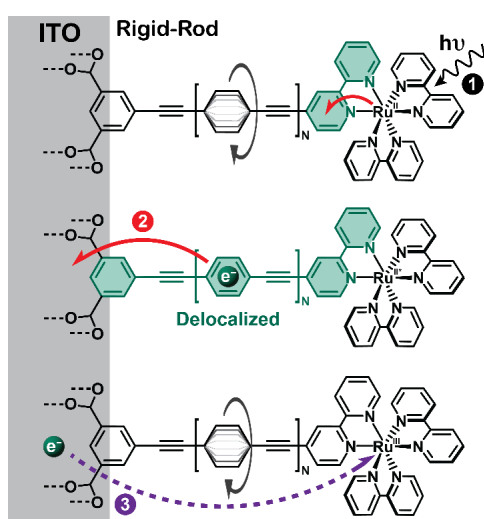


Figure 7. Mechanism for light initiated (1) “gated” electron transfer (2) that promotes long distance transfer to an oxide surface while inhibiting the unwanted charge recombination reaction (3).

molecular means to preferentially transfer electrons in one desired vectorial direction, behavior needed for applications in solar energy conversion. At the interfaces utilized, visible light absorption by a transition metal complex *opens* a ‘structural gate’ by planarization of otherwise rotating phenyl rings in *p*-phenylene ethynylene (PE) bridge units. Planarization provides a conjugated pathway for electron flow toward a conductive oxide surface. Excited state electron injection to the oxide restores rotation and *closes* the gate for the unwanted recombination reaction. This structural gating results in quantitative long-distance (> 20 Å) interfacial electron transfer that occurs about one thousand times faster than transfer in the opposite direction. Marcus-Gerischer analysis of kinetic data measured as a function of the thermodynamic driving force provided the reorganization energy and the electronic coupling matrix element for these interfacial electron transfers. Electronic coupling with the

conductive oxide surface was weak and consistent with non-adiabatic electron transfer. Smaller coupling was evident for the PE bridge units relative to insulating ionic bridges. An approximately 0.7 eV smaller reorganization energy was responsible for the enhanced vectorial electron injection through the conjugated aromatic bridge units. More broadly, a small distance-dependent reorganization energy with weak electronic coupling underlies the success of this bridge design that enables efficient long-distance electron transfer with slow recombination.

Acknowledgments

The UNC authors gratefully acknowledge support from the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, US Department of Energy (DE-SC0013461). The RU authors gratefully acknowledge support from the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (DE-FG02-01ER15256)

References

- [1] Loague, Q.; Heidari, M.; Mann, H.; Danilov, E.; Castellano, F.N.; Galoppini, E.; Meyer, G.J. *ACS Central Science* **2024**, *11*, 2132-2144.

Elucidating Chemical Engineering Principles for Achieving High Emission and ¹O₂ Photogeneration Quantum Yields with Homoleptic Cu(I) Complexes

N. Oppe,¹ T. Haddock,² O. Baffroy,¹ L. Burmeister,³ C. Monnereau,⁴ E. Blart,¹ C. Queffelec,¹ M. Karnahl,³ L. X. Chen,² Y. Pellegrin¹

¹Nantes Université, CNRS, CEISAM, UMR 6230, F-44000 Nantes, France

²Chemical Science and Engineering Division, Argonne National Laboratory, Lemont 60439, USA

³Technische Universität Braunschweig, Rebenring 31, 38106 Braunschweig, Germany ⁴Laboratoire de Chimie, ENS de Lyon, Université de Lyon, F69342 Lyon, France

McMillin and colleagues elucidated the photochemical properties of homoleptic copper(I) complexes with the general formula CuL₂⁺ in the late 1970s.^[1] By utilizing the sterically constrained neocuproine (ncup, Figure 1) as a ligand, they demonstrated that it was possible to enhance the excited-state properties of Cu(ncup)₂⁺ by limiting the flattening of the coordination sphere that typically occurs upon excitation. Since then, significant progress has been made in improving their photophysical properties and applying them to photochemical processes. One of the challenges in improving and controlling CuL₂⁺ photophysical properties is that the relationships between substituent positions on the phenanthroline core and their effects on the corresponding copper complex properties remain underexplored and poorly understood.^[2] To elucidate these relationships, we designed three new copper(I) complexes: **C1**, **C2**, and **C3** (Figure 1). We varied both the nature of substituents (methoxy vs. thiomethoxy in **C1** vs. **C2**) and their positions (3,8 vs. 4,7 in **C1** vs. **C3**). As anticipated, both the position and nature of the substituents significantly influence the overall photophysical properties of the complexes: very subtle change determine the luminescence mechanism (TADF vs. anti-TADF) and lead to either modest (below 0.1%) or high (6.7%) emission quantum yields. Notably, complex **C1** exhibits one of the highest emission quantum yields ever reported for such simple structures and demonstrates an exceptional ¹O₂ generation quantum yield (ca. 65%) for a homoleptic copper(I) complex. Using DFT calculations and ultrafast transient absorption spectroscopy, we rationalize how appropriate functionalization of positions 3, 4, 7, and 8 of phenanthroline impacts the electronic properties of the associated copper(I) complexes, endowing them with superior photophysical characteristics.

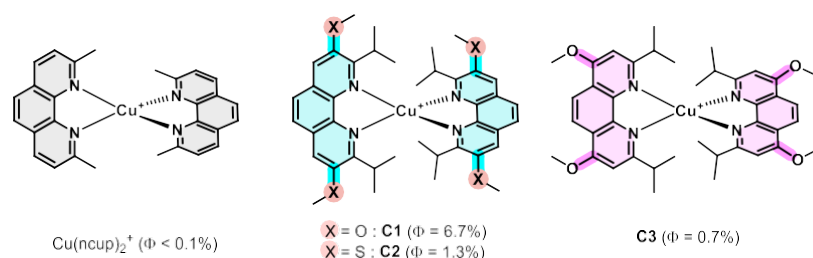


Figure 1. Structures of the seminal Cu(ncup)₂⁺ complex and of the new complexes developed.

Acknowledgement

The authors wish to thank the ANR for funding, and the CEISAM, ENS Lyon and ANL analytical platforms

References

- [1] M. W. Blaskie, D. R. McMillin, *Inorg Chem* **1980**, 19, 3519.
- [2] C. Queffelec, P. B. Pati and Y. Pellegrin, *Chem. Rev.* **2024**, 124, 6700

Photophysical properties of triazolylidene ‘abnormal’ carbene complexes of Earth-abundant metal ions

Mary E. White,^a Daniel A.W. Ross,^a Samuel Francis,^a Robert W. Jones,^a Isabelle M. Dixon,^b Louise Natrajan,^c Zehan Yao,^d Paul A. Scattergood,^a Pavel Chabera,^d Arkady Yartsev,^d Petter Persson^d & Paul I.P. Elliott^{*a}

a University of Huddersfield, UK; *b* Toulouse University, France; *c* University of Manchester, UK; *d* Lund University, Sweden. p.i.elliott@hud.ac.uk

Recent years have seen significant breakthroughs and advancements in the development of novel photosensitiser complexes based on sustainable, Earth-abundant first-row transition metal elements.^[1] This work seizes upon the opportunities afforded by alternative electron configurations and excited state paradigms that exist beyond the historical ‘standard model’ represented by complexes of d⁶ Ru(II) & Ir(III) ions with their emissive and photoreactive ³MLCT states. This includes the exploitation of microsecond lifetime ²MC states of Cr(III) complexes^[2] and the previously overlooked and remarkably long-lived highly photooxidising ³MC states of cobalt(III) ions.^[3] The now famous d⁵ Fe(III) imidazolylidene-based N-heterocyclic carbene complex [Fe(PhB{Im}₃)₂]⁺ exhibits spin-allowed fluorescence and photoinduced electron transfer reactivity stemming from a ²LMCT excited state.^[4] Triazolylidene ‘abnormal’ carbenes are less well explored for their application as ligands for photoactive metal complexes,^[5] but offer significant opportunities for the modulation of metal d-orbital energies, through their superior σ-donation, as well as modulation of ligand orbital energies. This therefore enables considerable tuning of the optoelectronic properties of resultant photosensitiser complexes. This talk will focus on results from recent work in our laboratories on the photophysical properties triazolylidene-based complexes of iron, cobalt and chromium.

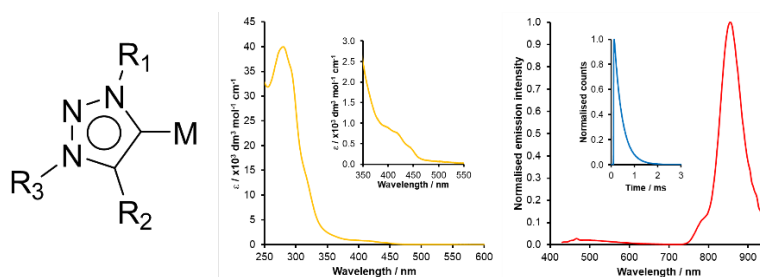


Figure 8. Generic structure of a 1,2,3-triazolylidene donor complex and absorption and emission data for a first transition series metal ion triazolylidene complex.

Acknowledgements

The authors thank the Leverhulme Trust for funding this research (grant number RPG-2022-128).

References

- [1] (a) C. Wegeberg, O. S. Wenger, *JACS Au* **2021**, 1, 1860-1876; (b) C. Förster, K. Heinze, *Chemical Society Reviews* **2020**, 49, 1057-1070.
- [2] S. Otto, *et al.*, *Angewandte Chemie International Edition* **2015**, 54, 11572-11576.
- [3] A. Y. Chan, *et al.*, *Science* **2023**, 382, 191-197.
- [4] K. S. Kjær, N. Kaul, O. Prakash, P. Chábera, N. W. Rosemann, A. Honarfar, O. Gordivska, L. A. Fredin, K.-E. Bergquist, *et al.*, *Science* **2019**, 363, 249.
- [5] P. Chábera, *et al.*, *Nature* **2017**, 543, 695-699.

The role of computational studies in identifying the distinct features of metal-based photosensitizers for Photodynamic Therapy

M. E. Alberto

Chemistry and Chemical Technologies Department, University of Calabria.

marta.alberto@unical.it

Ru(II), Os(II) and even Ir(II) are garnering rising interest as potential candidates for several light-mediated approaches, including Photodynamic Therapy (PDT). The unprecedented hypoxia activity displayed by new Os(II)- and Ru(II)-compounds bearing thiophene chains proposed and characterized in joint experimental and theoretical studies^[1,2] are herein presented, along with recent outcomes obtained on Ru(II)- and Ir(III)-coumarin-derivatives complexes.^[3,4] In all these cases, DFT and TDDFT analysis were crucial to provide fundamental insights into their dual normoxia/hypoxia activity, demonstrating that it does not rely on a photoinduced ligand loss mechanism as the better-known photoactivated cancer therapy (PACT or PCT) hence questioning the generally accepted correlation between the hypoxia phototoxicity and the population of ³MC dissociative states.

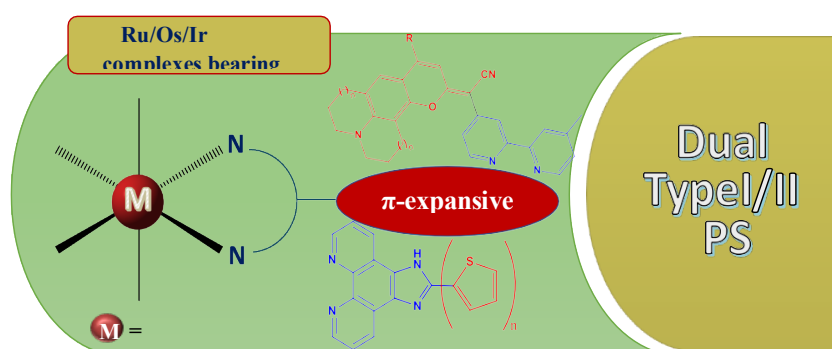


Figure 1.

Acknowledgments

PRIN D.D. 104/2022 PNRR M4.C2.1.1. – Project Code: 2022AN47CA – CUP: H53D23003820001, funded by the European Union – NextGenerationEU – Project Title “LA-G4-DACA” – Grant Assignment DD 862, 16/06/2023 is acknowledged.

References

- [1] J. A. Roque III, H. D. Cole, P. C. Barrett, L. M. Lifshits, R. O. Hodges, S. Kim, G. Deep, A. Francés-Monerris, M. E. Alberto, C. G. Cameron, S. A. McFarland, *J Am Chem Soc* **2022**, *144*, 8317–8336.
- [2] J. A. Roque, P. C. Barrett, H. D. Cole, L. M. Lifshits, G. Shi, S. Monro, D. von Dohlen, S. Kim, N. Russo, G. Deep, C. G. Cameron, M. E. Alberto, S. A. McFarland, *Chem Sci* **2020**, *11*, 9784–9806.
- [3] E. Ortega-Forte, A. Rovira, P. Ashoo, E. Izquierdo-García, C. Hally, D. Abad-Montero, M. Jordà-Redondo, G. Viguera, A. Deyà, J. L. Hernández, J. Galino, M. Bosch, M. E. Alberto, A. Francés-Monerris, S. Nonell, J. Ruiz, V. Marchán, *Inorg Chem Front* **2025**, DOI 10.1039/D4QI03369H.
- [4] D. Abad-Montero, A. Gandioso, E. Izquierdo-García, S. Chumillas, A. Rovira, M. Bosch, M. Jordà-Redondo, D. Castaño, J. Bonelli, V. V. Novikov, A. Deyà, J. L. Hernández, J. Galino, M. E. Alberto, A. Francés-Monerris, S. Nonell, G. Gasser, V. Marchán, *J Am Chem Soc* **2025**, *147*, 7360–7376



Photo-induced oxidation-enhancement in biomimetic Molybdenum photo-catalysts

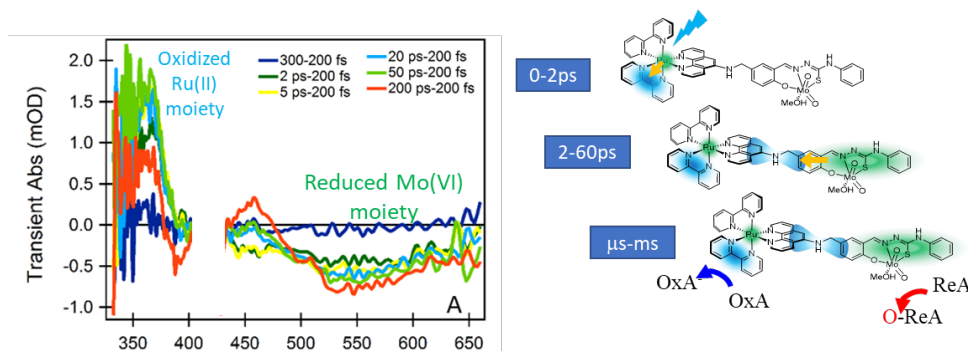
Nazari Haghighi Pashaki, M.;^(a) Choi, T.-K.;^(b) Burgos-Caminal, A.;^(c) Duhme-Klair, A.-K.;^(d) Gawelda, W.;^(c,e,f) Cannizzo, A.^(a)

^(a) Institute of Applied Physics, University of Bern, Sidlerstrasse 5, CH-3012, Bern, Switzerland; ^(b)

European XFEL, Holzkoppel 4, 22869 Schenefeld, Germany; ^(c) Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA-Nanociencia), Campus Cantoblanco, 28049 Madrid, Spain; ^(d) Department of Chemistry, University of York, Heslington, York YO10 5DD, UK.; ^(e) Departamento de Química, Facultad de Ciencias, Universidad Autónoma de Madrid, Campus Cantoblanco, 28049 Madrid, Spain; ^(f) Faculty of Physics, Adam Mickiewicz University, ul. Uniwersytetu Poznań'skiego 2, 61-614 Poznań, Poland;

andrea.cannizzo@unibe.ch

In this study we shed light on the underlying mechanisms of photo-induced oxidation-enhancement (PIOE) in biomimetic mono- and bi-metallic molybdenum photo-catalysts. In particular Ru(II)-Mo(VI) dyads show enhanced photo-activation of oxidative catalysis of Mo(VI), with respect to isolated Mo(VI) complexes.¹



Based on femtosecond transient absorption measurements, we revealed that the PIOE of Mo(VI) is due to intramolecular processes only occurring in ultrafast regime and it is not preceded or accompanied by any oxidation of the Ru(II) unit.² Instead, we observed the coexistence of both moieties in the dyad activated. Our finding has an important impact on modelling photocatalytic processes in bimetallic dyads not only in ultrafast timescales but on μ s and even ms timescales, since the competition between the oxidizing and reducing agents at the Ru(II) and Mo(VI) units, respectively, will eventually determine the effective catalytic activity of the dyad.

Our results substantially advance our insights into the photochemistry of Mo(VI) catalysts and define a new paradigm to describe oxo-transfer reactions in such biomimetic molybdenum dyads. This study advances our understanding of photo-induced electron transfer mechanisms that are of relevance to oxo-molybdoenzymes and, in perspective, in developing biomimetic oxo-transfer catalysts.

References

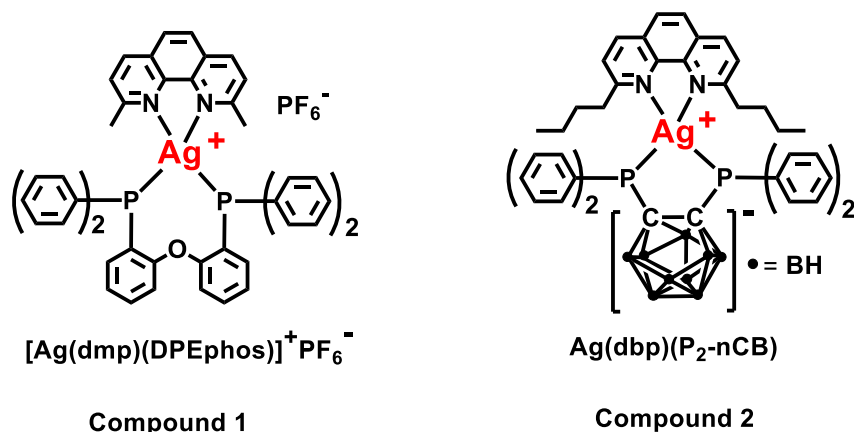
1. Ducrot, A. B.; Coulson, B. A.; Perutz, R. N.; Duhme-Klair, A.-K., Light-Induced Activation of a Molybdenum Oxotransferase Model within a Ru(II)-Mo(VI) Dyad. *Inorg Chem* **2016**, 55 (24), 12583-12594.
2. Nazari Haghighi Pashaki, M.; Choi, T.-K.; Rohwer, E. J.; Feurer, T.; Duhme-Klair, A.-K.; Gawelda, W.; Cannizzo, A., Unveiling the origin of photo-induced enhancement of oxidation catalysis at Mo(VI) centres of Ru(II)-Mo(VI) dyads. *Chem Commun (Camb)* **2021**, 57 (34), 4142-4145.

Ag(I) complexes: From extremely long-lived phosphorescence for oxygen sensing to ultra-short-lived TADF for OLEDs.

H. Yersin¹, M. Z. Shafikov¹, R. Czerwieniec¹, U. Monkowius², R. Ramazanov³, R. Valiev³

1. Institute of Physical Chemistry, University of Regensburg, 93053 Regensburg, Germany
hartmut.yersin@ur.de; 2. School of Education, Johannes Kepler University Linz, 4040 Linz, Austria;
3. Department of Chemistry, University of Helsinki, 00014 Helsinki, Finland

Photophysical properties of Ag(I) complexes can be modified drastically by ligand variation. By designing compound **1**, a heteroleptic Ag(I) complex of 2,9-dimethylphenanthroline (dmp) and a neutral diphosphine (DPEphos), an extremely long-lived phosphorescence of $\tau(\text{phos}) = 110$ ms (PMMA doped 1 wt%, $\Phi_{\text{PL}}(\text{phos}) \approx 50$ %, $\lambda_{\text{max}} = 490$ nm) assigned as phenanthroline centered $T_1 \rightarrow S_0$ transition at large S_1-T_1 gap (>1 eV, >8000 cm^{-1}) is obtained. By replacing the DPEphos ligand with the strongly electron donating di-phosphine ligand ($\text{P}_2\text{-nCB}$), comprising a negatively charged nido-carborane cage (compound **2**), the characteristics of the lowest excited singlet and triplet states are altered to $^1,^3\text{LL}'\text{MCT}$ character, involving both ligands and the metal. Accordingly, the singlet-triplet gap becomes small (0.08 eV, 650 cm^{-1}), affording efficient thermally activated delayed fluorescence (TADF).[1] Indeed, **2** shows ultra-short TADF decay of 1.4 μs at ambient-temperature with $\Phi_{\text{PL}}(\text{TADF}) = 100$ % (neat powder, $\lambda_{\text{max}} = 526$ nm). Both compounds show milestone properties as compared to other pseudo-tetrahedrally coordinated metal complexes. They are both investigated by TD-DFT calculations including SOC. It is suggested to investigate **1** as highly sensitive oxygen sensor and **2** as OLED emitter.



Reference

[1] H. Yersin, U. Monkowius, Thermally activated delayed fluorescence (TADF) and beyond. Photophysics and material design strategies. (Review) Adv. Photonics Res. **2024**, 2400111 (1-44).



Chiral metal complex for asymmetric photocatalysis

M. Villa,¹ S.-Y. Yao,^{2,3} B. Ventura,⁴ E. Meggers,² P. Ceroni¹

¹Department of Chemistry "Giacomo Ciamician", University of Bologna, Via Selmi 2, 40126 Bologna, Italy, paola.ceroni@unibo.it

²Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, 35043 Marburg, Germany

³School of Chemistry and Materials Science, Guangdong University of Education, Guangzhou 510303, P. R. China

⁴Institute for Organic Synthesis and Photoreactivity (ISOF), National Research Council (CNR), Via P. Gobetti 101, 40129 Bologna, Italy

The use of light to accelerate chemical reactions or drive chemical transformations that are endergonic in the dark has been recognized since the early days of photochemistry.^[1] Over the past decade, there has been a remarkable increase in studies utilizing visible light to promote organic reactions. Photocatalysts facilitate electron transfer processes, as electronically excited states serve as both stronger oxidants and reductants and might be involved in energy transfer processes.

This contribution will present chiral metal complexes containing Ir(III)^[2,3] or Co(III),^[4] highlighting their applications in photoredox catalysis and artificial photosynthesis. The contribution will focus on the photochemical mechanism and the discussion of the experiments performed to shed light on it. A particular emphasis will be devoted to time-resolved emission and absorption spectroscopy as a tool for investigating the photochemical mechanism.

Acknowledgments

Thanks to funding by the project SUN-SPOT - MIUR Progetti di Ricerca di Rilevante Interesse Nazionale (PRIN) Bando 2022 - grant 2022JA3PSC.

References

- [1] *Photochemistry and Photophysics: Concepts, Research, Applications*, V. Balzani, P. Ceroni, A. Juris, 2nd edition, Wiley-VCH, 2024, ISBN: 978-3-527-35276-0
- [2] H. Jung, M. Hong, M. Marchini, M. Villa, P. S. Steinlandt, X. Huang, M. Hemming, E. Meggers, P. Ceroni, J. Park, M.-H. Baik, *Chem. Sci.* **2021**, 12, 9673.
- [3] X. Huang, J. Lin, T. Shen, K. Harms, M. Marchini, P. Ceroni, E. Meggers, *Angew. Chem. Int. Ed.* **2018**, 57, 5454.
- [4] S.-Y. Yao, M. Villa, Y. Zheng, A. Fiorentino, B. Ventura, S. I. Ivlev, P. Ceroni, E. Meggers, manuscript submitted to *Nat. Commun.*



Conformational Engineering and Atropisomerism as Photosensitizer Design Principles

M. O. Senge^{1,2}

¹ Trinity College Dublin, The University of Dublin, School of Chemistry, Trinity Biomedical Sciences Institute, 152-160 Pearse Street, Dublin 2, Ireland

² Institute for Advanced Study, Technical University Munich, Lichtenbergstr. 2a, 85748 Garching, Germany. sengem@tcd.ie

The chemical and photophysical properties of porphyrins can be easily modulated through variation of the macrocycle conformation [1]. Next to fine-tuning of the photoexcited properties, appropriate manipulation of the π -conjugated macrocycle conformation allows access to core nitrogen atoms in free base porphyrins. Likewise, atropisomerism presents an intriguing, but often neglected, source of structural variety in molecular systems. While the photo- and physicochemical properties of rotamers are mostly similar, atropisomerism offers a unique design principle for novel receptors, photoactive drugs, and sensors [2].

Using atropisomeric dodecasubstituted, conformationally designed nonplanar porphyrins we have shown that they can serve as excellent hosts for various substrates and analytes with highly tuneable basicity for diverse applications including organocatalysis and optical sensing [3]. The remarkable flexibility of the porphyrin macrocycle continues to drive the search for novel ways to impose greater complexity in deformations which allows fine tuning of the chemical and photophysical properties. Atropisomerism provided an excellent molecular engineering toolbox to control symmetry elements [4] and gave rise to a case study where the inner N–H units respond to a chiral guest [5].

These concepts can also be used to enhance photosensitizer development for photodynamic therapy and related drug developments. For the preclinical photosensitizer redaporfin the four atropisomers could be separated and shown to exert dramatically different therapeutic efficacies. *In vitro* and *in vivo* studies showed a significant variability of the atropisomer phototoxicity and cellular internalization indicating that atropisomerism is a viable design principle in medicinal chemistry to enhance drug uptake [6].

Acknowledgments

This project has received funding from Taighde Éireann – Research Ireland (21/FFP-A/9469, PORPHYSHAPE) and was supported by TU Munich – Institute for Advanced Study through a Hans Fischer Senior Fellowship.

References

- [1] T. Ishizuka, N. Grover, C. J. Kingsbury, H. Kotani, M. O. Senge, T. Kojima, *Chem. Soc. Rev.* **2022**, 51, 7560–7630; b) M. Kielmann, M. O. Senge, *Angew. Chem. Int. Ed.* **2019**, 58, 418–441.
- [2] S. Maguire, G. Strachan, K. Norvaiša, C. Donohoe, L. C. Gomes-da-Silva, M. O. Senge, *Chem. Eur. J.* **2024**, 30, e202401559.
- [3] K. Norvaiša, K. J. Flanagan, D. Gibbons, M. O. Senge, *Angew. Chem. Int. Ed.* **2019**, 58, 16553–16557.
- [4] K. Norvaiša, J. O'Brien, D. Gibbons, M. O. Senge, *Chem. Eur. J.* **2020**, 27, 331–339.
- [5] a) K. Norvaiša, J. E. O'Brien, I. Osadshuk, B. Twamley, V. Borovkov, M. O. Senge, *Chem. Commun.* **2022**, 58, 5423–5456; b) I. Osadchuk, H.-E. Luts, K. Norvaiša, V. Borovkov, M. O. Senge, *Chem. Eur. J.* **2023**, 29, e202301408.
- [6] a) C. Donohoe, F. A. Schaberle, F. M. S. Rodrigues, N. P. F. Goncalves, C. J. Kingsbury, M. M. Pereira, M. O. Senge, L. A. Arnaut, *J. Am. Chem. Soc.* **2022**, 144, 15252–15265; b) C. Donohoe, A. Charisiadis, S. Maguire, B. Twamley, F. A. Schaberle, L. C. Gomes-da-Silva, M. O. Senge, *Eur. J. Org. Chem.* **2023**, e202201453.

Modulation of Photoisomerization Kinetics via Multi-Stage Switching in Ru(II) and Os(II)-Terpyridine Complexes

S. Baitalik¹

¹Department of Chemistry, Jadavpur University, Kolkata 700032, India.

sbaitalik@hotmail.com, sujoy.baitalik@jadavpuruniversity.in

Design of chromophores that can harvest light across the visible and near-infrared domain for sensitization of effective photochemical reactions is an area of present-day research.¹ It has been realized that rational design of molecular architectures is crucial to accomplish complicated functions.¹ To this end, we designed a new array of mono- and bimetallic Ru(II) and Os(II) complexes based on stilbene-appended terpyridine ligands.²⁻⁶ All the complexes exhibit strong absorption and emission across the visible to NIR domain with reasonably long room temperature excited state lifetimes. They also display sequential reversible metal-centered oxidations and ligand-centered reduction waves. The stilbene motifs facilitate reversible trans-cis photoisomerization under alternative treatment with visible and UV light, enabling the complexes to function as photo-molecular switches. Interestingly, remarkable increase in the rate of photo-isomerization has been achieved via the use of suitable external stimuli, viz. chemical oxidants, reductants, acid and base as well as light of appropriate wavelengths. In essence, the complexes display multi-steps photo-switching which in turn could open up the possibility towards the development of molecular based photonic devices.

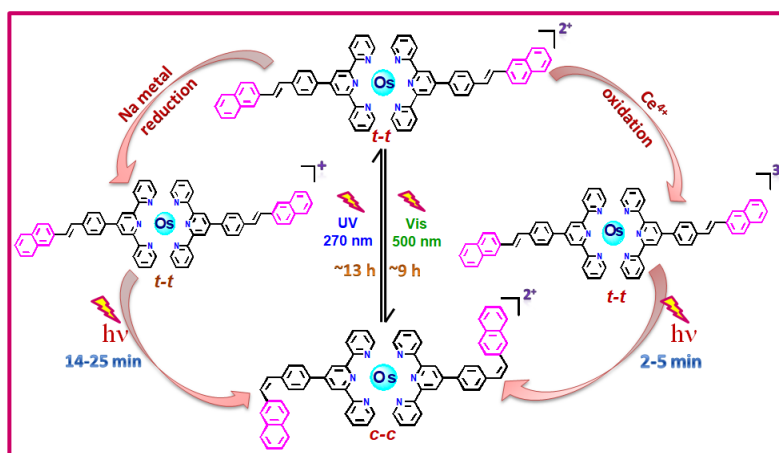


Figure 1. Multistep switching via oxidation-reduction and reversible $t\text{-}t \rightleftharpoons c\text{-}c$ isomerization.

References

- [1] V. Balzani, A. Juris, M. Venturi, *Chem. Rev.* 1996, **96**, 759.
- [2] S. Das, M. Bar, T. Ganguly, S. Baitalik, *Inorg. Chem.* 2024, **63**, 6600-6615.
- [3] T. Ganguly, S. Das, D. Maity, S. Baitalik, *Inorg. Chem.* 2024, **63**, 6883-6897.
- [4] S. Das, A. Sahoo, S. Baitalik, *Inorg. Chem.* 2024, **63**, 14933-14942.
- [5] S. Das, P. Pal, R. Biswas, S. Baitalik, *Inorg. Chem.* 2024, **63**, 23725-23741.
- [6] T. Ganguly, T. Abedin, D. Maity, S. Baitalik, *Inorg. Chem.* 2025, **64**, 4415-4430



Lanthanide(III)-based metallocrowns functionalized with ruthenium(II) complexes for multiplex imaging and oxygen sensing in the NIR-II

S. V. Eliseeva,^a C. C. Bădescu-Singureanu,^a A. Nizovtsev,^b V. L. Pecoraro,^c S. Petoud^a

^a Centre de Biophysique Moléculaire, CNRS UPR 4301, Orléans, France

^b Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia

^c Department of Chemistry, University of Michigan, Ann Arbor, Michigan, United States

E-mail: svetlana.eliseeva@cnrs-orleans.fr

Oxygen is one of the key metabolites in aerobic organisms. Oxygen deprivation (hypoxia) is connected to various diseases, including cancers, cardiovascular diseases and strokes.^[1] Therefore, it is essential to quantify oxygen levels in biological systems in real-time to ensure an early diagnosis of dysfunction. Multiplex imaging in the second near-infrared window (NIR-II, 1000–1700 nm) opens new perspectives for the comprehensive understanding of complex biological processes and for more accurate diagnosis of diseases by enabling real-time acquisition of images with improved contrast and spatial resolution in deeper tissues.^[2] However, today, the number of suitable NIR-II imaging agents remains highly limited. Lanthanide(III)-based metallocrowns (MCs) belong to a class of metal complexes that have demonstrated unique luminescence properties and perspectives to be used as NIR-II imaging agents.^[3–6] In this work, we present synthetic pathways to generate two families of Ln(III)/Ga(III) MCs functionalized with Ru(II) complexes. Detailed photophysical studies have been performed in air- and N₂-saturated solutions. We have shown that the characteristic emissions of Yb(III), Nd(III) and Er(III) in the NIR-II range can be sensitized upon excitation in the visible range, through Ru(II)-centered metal-to-ligand charge transfer states. In contrast to many fluorescent oxygen sensors for which the presence of the analyte induces a decrease of the emission signal, the presence of oxygen leads to the enhancement of Ln(III)-centered emission in studied Ln(III)/Ga(III) MCs. NIR-II imaging experiments using capillaries and biological tissue-mimicking phantoms have shown that signals arising from different Ln(III) can be detected and discriminated unambiguously.

Acknowledgments

This research was supported by EMERGENCE@INC2022 program, as well as, in part, by La Ligue Régionale contre le Cancer (comités du Loiret, d'Eure-et-Loir, du Loir-et-Cher et de la Sarthe), the network "Molécules marines, métabolisme et cancer" from the Canceropôle Grand Ouest, and la Région Centre Val-de-Loire. S.P. and C.C.B.-S. acknowledge support from the Institut National de la Santé et de la Recherche Médicale (Inserm) and the University of Orléans, respectively. The authors thank the platforms MOV2ING-NMR for the access to NMR facilities and MOV2ING-MS for mass-spectrometry analyses.

References

- [1] X. Wang, Q. Ding, R. R. Groleau, L. Wu, Y. Mao, F. Che, O. Kotova, E. M. Scanlan, S. E. Lewis, P. Li, B. Tang, T. D. James, T. Gunnlaugsson, *Chem. Rev.* **2024**, 124, 7106.
- [2] F. Wang, Y. Zhong, O. Bruns, Y. Liang, H. Dai, *Nat. Photonics* **2024**, 1.
- [2] J. C. Lutter, S. V. Eliseeva, G. Collet, I. Martinić, J. W. Kampf, B. L. Schneider, A. Carichner, J. Sobilo, S. Lerondel, S. Petoud, V. L. Pecoraro, *Chem. – Eur. J.* **2020**, 26, 1274.
- [3] I. Martinić, S.V. Eliseeva, T.N. Nguyen, V.L. Pecoraro, S. Petoud, *J. Am. Chem. Soc.* **2017**, 139, 8388.
- [4] I. Martinić, S.V. Eliseeva, T.N. Nguyen, F. Foucher, D. Gosset, F. Westall, V.L. Pecoraro, S. Petoud, *Chem. Sci.* **2017**, 8, 6042.
- [5] C. C. Bădescu-Singureanu, A. S. Nizovtsev, V. L. Pecoraro, S. Petoud, S. V. Eliseeva, *Angew. Chem. Int. Ed.* **2025**, 64, e202416101.

Dynamic Excited-State Jahn-Teller Distortion in the Al(III) Dinuclear Metal Complexes Observed by Coherent Vibrational Spectroscopy

K. Miyata,^a T. Ehara,^a Y. Yoneda,^{b,c} T. Yoshida,^a T. Ogawa,^a Y. Konishi,^a T. Ono,^a
A. Muranaka,^d H. Kuramochi,^{b,c} and K. Onda^a

^a Kyushu University. ^b Institute for Molecular Science. ^c Graduate Institute for Advanced Studies, SOKENDAI. ^d RIKEN Center for Sustainable Resource Science.

E-mail: miyata.kiyoshi.197@m.kyushu-u.ac.jp

Molecular symmetry is a fundamental determinant of optoelectronic properties, yet the dynamic interplay between symmetry and excited-state behavior remains largely unexplored, particularly in p-block element metal complexes. We try to bridge the critical knowledge gap by investigating novel Al(III) dinuclear triple-helical complexes, which combine high symmetry with twisted π -conjugated systems to achieve exceptional optical properties (ALPHY).¹ Employing transient absorption spectroscopy with a 10 femtosecond pump pulse, we observed the ultrafast dynamics of photoexcitation-triggered Jahn-Teller distortions in these high-symmetry p-block element complexes.

Figure 1a shows the transient absorption spectra of the ALPHY. Immediately after excitation, excited-state absorption centered at 570 nm was observed to rise, and then converted into the second spectral component centered at 550 nm with a time constant of approximately 200 fs. Furthermore, stimulated emission was observed around 600 nm, indicating the formation of an emissive state. In addition, beat signals originating from nuclear wavepacket motion in the excited state were observed (Fig. 1b, c). Fourier transformation of this oscillatory component (Fig. 1d) and comparison with vibrational analysis of the Franck–Condon state suggested that the motion includes a vibration that flattens the dihedral angle of one of the three ligands.

Structural optimization calculation in the S_1 state revealed the dihedral angle flattening, lowering the symmetry from D_3 to C_2 . Our research paves the way for developing high-performance, environmentally friendly materials for diverse optoelectronic applications, offering a fresh perspective on utilizing p-block elements and symmetry control in advanced material design.²

References

- [1] Y. Konishi, T. Ehara, **KM***, T. Ono*, et al, *Inorg. Chem.* **2024**, 63, 11716.
- [2] T. Ehara, T. Ono, H. Kuramochi*, **KM***, K. Onda* et al, under revision.

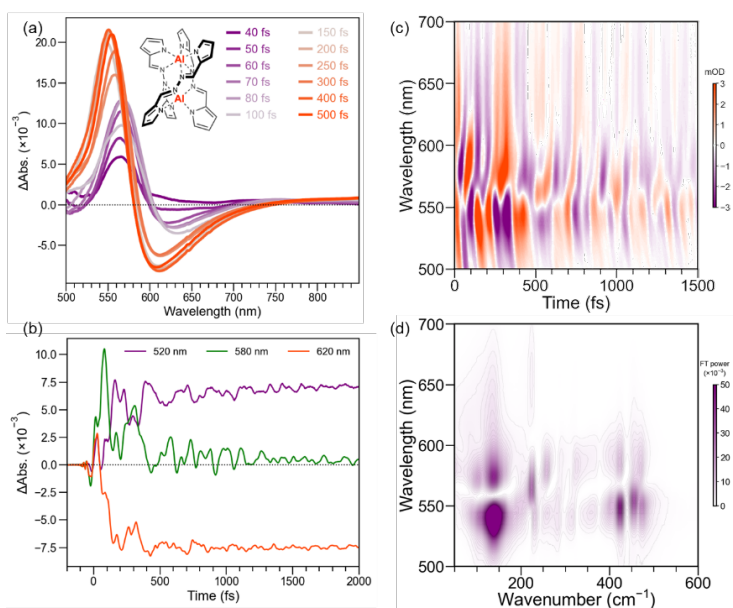


Figure 9. (a) Transient absorption with 10-fs pump pulse centered at 400 nm. (inset) The chemical structure of the Al complex (ALPHY), (b) beat signal observed at each wavelength, (c) beat signal obtained by population change subtraction, (d) beat map of the observed coherent oscillations as a function of probe wavelength.

Illuminating New Pathways in Antimicrobial Photodynamic Therapy: Coordination Metal Complexes and Functional Materials for Enhanced Selectivity and Efficiency

Janusz M. Dąbrowski

Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Krakow, Poland.
jdabrows@chemia.uj.edu.pl

The rapid rise of multidrug-resistant (MDR) microorganisms presents a significant challenge to modern medicine. Photodynamic inactivation (PDI) offers a promising alternative to conventional antibiotics by utilizing light-activated coordination compounds to generate reactive oxygen species (ROS).¹⁻² This study explores the impact of various metal coordination on the photophysical and photochemical properties of porphyrin and phthalocyanine complexes, aiming to optimize their antimicrobial efficacy.

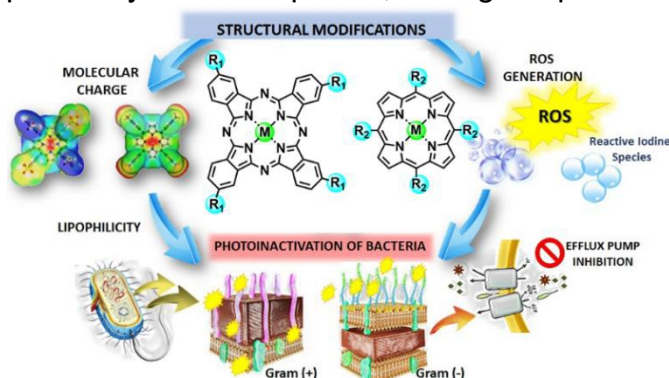


Figure 10 Schematic representation of PDI using the aforementioned families of photosensitizers.

A series of novel porphyrins and phthalocyanines, incorporating transition metal ions such as Pd²⁺ and Zn²⁺ (Fig. 1), were synthesized and characterized using advanced spectroscopic techniques, including transient absorption spectroscopy and time-resolved singlet oxygen phosphorescence. The study evaluates how variations in ligand environment, axial substitution, and metal center affect key parameters such as singlet oxygen quantum yields, triplet excited-state lifetimes, and photostability.

Our results demonstrate that Pd²⁺-based complexes exhibit superior singlet oxygen generation ($\Phi\Delta$ up to 0.93) and long triplet-state lifetimes, enhancing their bactericidal efficiency. Structural modifications, such as axial ligands and peripheral halogenation, further influence ROS production and bacterial membrane interactions, as confirmed by confocal fluorescence imaging and electron microscopy studies.³ Moreover, integration with nanocarriers and the modification of TiO₂ surfaces with selected metalloporphyrins significantly improve antimicrobial performance against MDR Gram-positive and Gram-negative strains.⁴ In vivo studies using murine wound infection models validate the translational potential of these systems, demonstrating rapid bacterial clearance and minimal cytotoxic effects. These findings provide valuable insights into the structure-activity relationships of coordination complexes, paving the way for rational design of next-generation photosensitizers for antimicrobial photodynamic therapy.

Aknowlegments

Thanks to National Science Centre (NCN) for grants no. 2016/22/E/NZ7/00420 and 2020/37/B/NZ7/04157.

References

- [1] B. Pucelik, J.M. Dąbrowski, *Adv. Inorg. Chem.* 2022, 79, 65–108.
- [2] B. Pucelik, A. Sulek, J.M. Dąbrowski, *Coord. Chem. Rev.* 2020, 416, 213340.
- [3] R.T. Aroso, M. Calvete, B. Pucelik, L.G. Arnaut, M.Pereira, J.M. Dąbrowski, *Eur. J. Med. Chem.* 2019, 184, 111740.
- [4] A. Sulek, B. Pucelik, J. Kunciewicz, J. M. Dąbrowski, *Catalysis Today* 2019, 335, 538-549.



Photocatalytic Reduction of CO₂ to HCOOH using a Porphyrin-Rhenium Dyad

J. S. O'Neill^a, A. Murphy^b, M. V. Appleby^c, M. D. Horbury^c, James D. Shipp^c, Dimitri Chekulaev^c, L. O'Reilly^a, Patrick Loftus,^a J. A. Weinstein^c, Jonathan Rochford^b, Mary T. Pryce^a

^aSchool of Chemical Sciences, Dublin City University, Dublin 9, Ireland

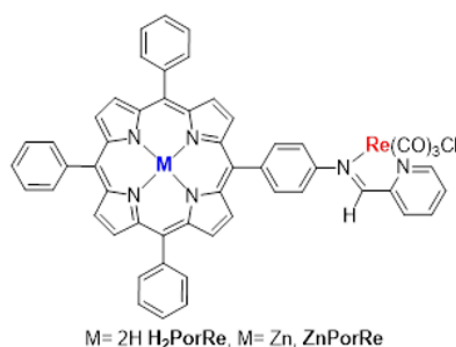
^bDepartment of Chemistry, University of Massachusetts Boston, MA, US

^cDepartment of Chemistry, University of Sheffield, Sheffield, UK

mary.pryce@dcu.ie

One approach to address increasing greenhouse gas emissions is photocatalytic carbon dioxide (CO₂) reduction into valuable C1 chemicals. Porphyrins, which absorb in the visible region of the spectrum are promising materials for photocatalytic CO₂ reduction. While a number of organometallic – porphyrin dyads have been reported for selective photocatalytic reduction of CO₂ to CO, the production of formic acid is less well known for these systems. We have assessed a range of porphyrins, including the free base porphyrin dyad (H₂PorRe) and zinc porphyrin-rhenium tricarbonyl (ZnPorRe) dyad (shown below) for intramolecular photocatalytic CO₂ reduction. Time resolved infrared and transient absorption spectroscopy were employed to probe the photophysical properties of these assemblies, and identify the excited states populated. The fluorescence of both porphyrin-rhenium dyads was significantly quenched compared to the porphyrin photosensitiser.

When photocatalysis studies were performed, formic acid was the predominant product, with negligible amounts of CO detected. Photocatalysis in this dyad lead to the formation of formic acid is proposed to occur by a hydrogen atom transfer pathway from the one-electron oxidised sacrificial electron donor.



M= 2H H₂PorRe, M= Zn, ZnPorRe

Acknowledgements: Sustainable Energy Authority of Ireland, National Energy Research, Development & Demonstration Funding Programme 2024, Grant number 24/RDD/1186 and EPSRC Programme Grant Molecular Photonics Breadboards.

References

1. Windle et al *Chem Sci*, 2015, **6** (12), 6847–6864.
2. Kou et al . *J Catal*, 2014, **310**, 57–66.
3. Kuramochi et al, *Chemistry – A European Journal*, **2020**, **6** (69), 16365–16373.

Understanding mechanochromism in CuX-L hybrid coordination polymers

E. Contini, L. Gatti, C. Corapi, M. Cingolani, S. Varol, C. Zuffa, C. Gualandi, L. Maini, D. Fazzi and D. Genovese

Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Bologna, Italy.

damiano.genovese2@unibo.it

The quest for smart and responsive materials to self-diagnose damage arising from mechanical or thermal stress is a challenge for fundamental and applied scientists. Among many active materials, hybrid coordination polymers (HCPs) emerge as a smart alternative since they can be obtained from inexpensive reagents and with sustainable methods such as mechanochemistry, and because their photophysics show novel emerging properties respect to analogous monomer-to-oligomer structures.[1]

We report the synthesis, characterization and inclusion in functional polymer coatings of an HCP based on 1-dimensional Cu(I)-halogen ladder structure complexed with pyridinic ligands, that presents a rich and responsive photophysical behavior. Its emission displays a prominent triplet character with a marked thermally-activated delayed fluorescence (TADF); interestingly, such emission is highly and irreversibly sensitive to mechanical forces. The dependence on controlled mechanical stresses has been carefully analyzed and the effects on the photophysics are here shown and discussed, highlighting discrepancies with previous reports on structurally similar systems.[2,3] Finally, first-principles modelling of model systems based on repeating units of the HCP crystals suggest a possible two-minima triplet potential energy surface (PES) to explain the observed rich photochemistry.

In conclusion, an in-depth photophysical investigation on solid-state smart materials based on a coordination polymer, accompanied by a carefully designed computational atomistic model, is here presented to propose a novel photo-chemical framework to account for the mechano-responsiveness of this class of materials.

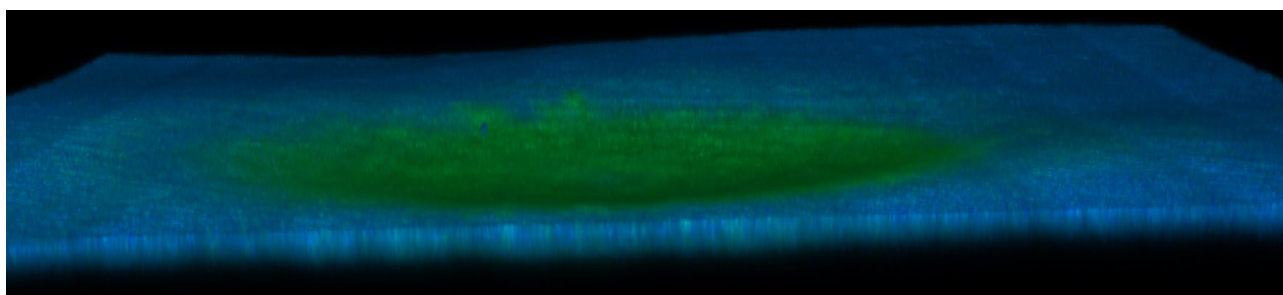


Figure 11. Confocal image of mechanically stressed polymer coating containing CuX-L HCP

Aknowlegments

This work was supported by PRIN-2022-PNRR "Piezochromic smart auto-diagnostic polymeric coatings", proposal code MUR P20223WB9K - CUP J53D23014670001 and by the NATO Science for Peace and Security Programme, Project COLORaDO – a new Chromogenic technology foR on-field Damage detection.

References

- [1] J. Conesa-Egea et al., *Coordination Chemistry Reviews*, 2019, 381, 65
- [2] S. Perruchas, *Dalton Trans.*, **2021**, 50, 12031.
- [2] R. Hamze, *J. Am. Chem. Soc.* **2019**, 141, 8616.

Luminescence mechanochromism of copper-based materials

J. Delafoulhouze,^a M. Cordier,^b J.-Y. Mevellec,^a F. Massuyeau,^a O. Hernandez,^a
C. Latouche^a and S. Perruchas^{*a}

^aNantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel (IMN),
F-44322 Nantes, France.

^bUniv. Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - F-
35000 Rennes, France.

sandrine.perruchas@cnrs-imn.fr

Achieving mechanoresponsive luminescent materials exhibiting high-contrast luminescence response to mechanical forces, is required for the development of technological applications.¹ At the same time, stimuli-responsive materials based on copper element are of great interest for developing cost-effective and efficient luminescent materials.² In this context, we report here our investigations on the study of luminescent mechanochromic materials based on copper(I) complexes.³ In particular, we have recently synthesized a copper iodide compound that exhibits a dramatic switching in emission intensity and color, from red to bright green, upon liquid-to-crystal transition, triggered by mechanical stimulations.⁴ This reversible phase transition taking place at room temperature, relies on the intriguing ability of the studied copper complex to form a supercooled metastable liquid state, as illustrated in Figure 1.

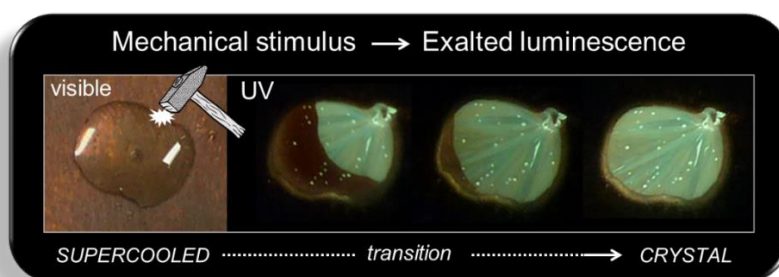


Figure 1. Photos of the supercooled liquid phase at room temperature under visible light and after mechanical stimulation (hammer) under UV showing the progressive photoluminescence switching.

In addition to the contrasted emission color changes, a 20-fold increase in the photoluminescence quantum yield is measured, reaching the high value of 87 %. The mechanism at the origin of the photoluminescence switching was investigated through X- ray diffraction experiments and Raman analyses of the metastable liquid state, combined with DFT calculations. The important luminescence changes can be attributed to modifications of the molecular structure of the complex in the different phases.

References

- [1] (a) Y. Sagara, T. Kato, *Nat. Chem.* **2009**, *1*, 605. (b) A. L. Balch, *Angew. Chem. Int. Ed.* **2009**, *48*, 2641. (c) Y. Ai, Y. Li, M. H.-Y. Chan, G. Xiao, B. Zou and V. W.-W. Yam, *J. Am. Chem. Soc.*, **2021**, *143*, 10659.
- [2] H. Takeda, A. Kobayashi and K. Tsuge, *Coord. Chem. Rev.*, **2022**, *470*, 214700.
- [3] (a) R. Utrera-Melero, B. Huitorel, M. Cordier, F. Massuyeau, J.-Y. Mévellec, N. Stephant, P. Deniard, C. Latouche, C. Martineau-Corcus, S. Perruchas, *J. Mater. Chem. C*, **2021**, *9*, 7991. (b) S. Perruchas, *Dalton Trans.* **2021**, *50*, 12031.
- [4] J. Delafoulhouze, M. Cordier, J.-Y. Mevellec, F. Massuyeau, OI. Hernandez, C. Latouche and S. Perruchas, *Chem. Commun.* **2024**, *60*, 5278.



Light-driven Catalysis of the CO₂ Reduction Reaction using Heptacoordinated Cobalt and Iron Complexes

Mirco Natali,^a Federico Droghetti,^a Albert Ruggi^b

^a Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121 Ferrara, Italy. E-mail: mirco.natali@unife.it

^b Department of Chemistry, University of Fribourg, Chemin du Musée 9, 1700 Fribourg, Switzerland.

Conversion of solar energy into chemical fuels, via the CO₂ reduction reaction (CO₂RR), represents a promising solution to the global energy problem. Direct conversion of CO₂ into carbon-based products in protic environments is, however, not a trivial task, mainly ascribed to the selectivity issues ensuing from the kinetic competition among different processes and the parallel hydrogen evolving reaction (HER).

In this communication we report on the electrochemical and light-driven catalytic activity towards the CO₂RR by the Co(II) and Fe(II) complexes of a hexadentate polypyridine ligand, both displaying a characteristic heptacoordinated structure, uncommon for 3d metal ions.[1,2] In particular we will show how the selectivity towards CO vs. H₂ formation can be properly modulated by changing the metal ion or playing on the electronic effects. Furthermore, taking advantage of the information gained by time-resolved spectroscopy, we show how the Fe(II) catalyst can be employed to achieve CO formation with high quantum efficiency,[2,3] showcasing the strong (but often underestimated) potential of molecular catalysis.

Aknowlegments

Financial support from the European Union – Next Generation EU (PRIN2022 PNRR, project PHOTOCORE, P2022ZSPWF) is gratefully acknowledged.

References

- [1] F. Droghetti, A. Amati, F. Pascale, A. Crochet, M. Pastore, A. Ruggi, M. Natali, *ChemSusChem* **2024**, 17, e202300737.
- [2] F. Droghetti, F. Lemken, L. Rulisek, A. Ruggi, M. Natali, *ACS Catal.* **2024**, 14, 16920-16935.
- [3] F. Droghetti, L. Villa, A. Sartorel, L. Dell'Amico, A. Ruggi, M. Natali, *ChemSusChem* **2025**, 18, e202402627.

Estrogen-conjugated $[\text{Ru}(\text{bpy})_3]^{2+}$ complexes exhibit selective phototoxicity against breast cancer cells

S. A. Tsoni,^a T. Kench,^b R. Vilar^b and T. Lazarides^a

^a Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece, email: tlazarides@chem.auth.gr

^b Department of Chemistry, Imperial College London, White City Campus, W120BZ London, UK

Photodynamic therapy (PDT) is a promising cancer treatment that uses photosensitizers administered in the tumor site to generate cytotoxic reactive oxygen species (ROS) under visible light excitation. This approach minimizes damage to healthy tissue and avoids the use of ionizing radiation.^[1] However, most currently used photosensitizers lack inherent selectivity for cancer cells, leading to undesirable accumulation in healthy tissues. Ru(II) polypyridyl complexes are suitable candidates for PDT due to their readily formed triplet excited states and kinetic inertness.^[2] We synthesized a series of estrogen-functionalized Ru(II) polypyridyl complexes using click chemistry and characterized their photophysical properties and biological activity. Dynamic light scattering (DLS) studies revealed that these complexes self-assemble into micelle-like structures due to their amphiphilic nature. Remarkably, two of these complexes exhibited substantially higher light-induced cytotoxicity towards estrogen-receptor-positive (ER+) breast cancer cells (MCF-7) compared to estrogen-receptor-negative (ER-) cells (MDA-MB-453) reaching up to 9.6-fold selectivity. Overall, this study underscores the potential of estrogen-conjugated Ru(II) complexes for PDT, particularly in selectively targeting ER+ cancer cells.^[3]

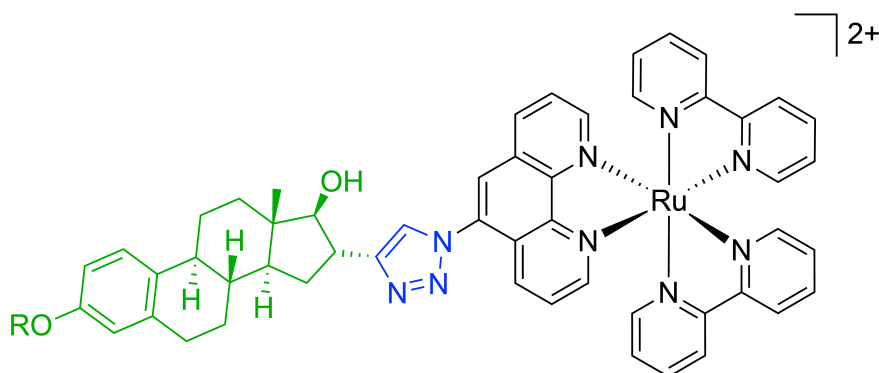


Figure 1. The estrogen-Ru(bpy)₃ conjugates described in this study.

References

- [1] M. M. Ankathatti, A. Manalac, M. Weersink, S. A. McFarland and L. Lilge, *Coord. Chem. Rev.* **2022**, 470, 214712.
- [2] J. Shum, P. K. K. Leung and K. K. W. Lo, *Inorg. Chem.* **2019**, 58 (4), 2231–2247.
- [3] S. A. Tsoni, T. Kench, R. Vilar and T. Lazarides, *Submitted*, **2025**.

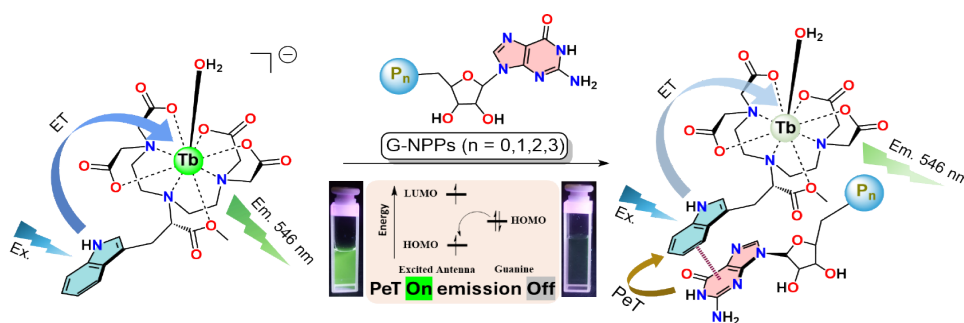
Modulation of Energy Transfer Pathways in Time-Gated Luminescent Eu(III) and Tb(III) Probes for Sensing and Discrimination of Physiological Phosphates and Biochemical Hazards

A. K. Patra^a

^aDepartment of Chemistry, Indian Institute of Technology Kanpur, Kanpur, U.P. 208016, India E-mail:

akpatra@iitk.ac.in

The nucleoside phosphates (NPP) are important physiological phosphates that are vital in energy storage, transfer and consumption, DNA synthesis, phosphorylation, molecular recognition, cellular transduction, and regulation in crucial enzyme activities, etc.^{1,2} Therefore, designing sensitive and selective responsive receptors to monitor the level of various NPPs and differentiating them in physiological conditions is of immense importance in drug discovery, diagnostic medicine, and disease management.¹ Further, developing reliable optical sensors for extremely toxic organophosphorus nerve agents is critical to mitigate and counter the resurgence of any public health and national security threats.³ Emissive Ln(III) probes have great potential as optical probes due to their long luminescence lifetime, allowing time-gated luminescence measurements thereby avoiding autofluorescence, sharp emission bands, large pseudo-Stokes' shift, etc., which are valuable prerequisites for highly sensitive bioresponsive luminescent probes. We purposefully designed luminescent Eu(III)/Tb(III)-based molecular receptors conjugated to the functional antenna capable of interacting with such critical analytes and studied their structures and photophysics with optimized modulation of sensitization pathways for desired applications.⁴⁻⁸ Herein, I will present the bottom-up approach and key strategies adopted to modulate the $4f \rightarrow 4f$ luminescence from the Ln(III) probes via perturbing the energy-transfer (EnT) pathways upon interactions with NPPs and nerve agents, EnT mechanism for sensitization, and the involvement of the optimized excited-state photophysics using a rational synthetic coordination chemistry approach.



References

- [1] S. E. Bodman and S. J. Butler, *Chem. Sci.* **2021**, 12, 2716-2734.
- [2] M. V. Ramakrishnam Raju, S. M. Harris and V. C. Pierre, *Chem. Soc. Rev.* **2020**, 49, 1090-1108.
- [3] G. H. Dennison, M. R. Johnston, *Chem. Eur. J.* **2015**, 21, 6328-6338
- [4] K. Gupta, A. K. Patra, *ACS Sensors* **2020**, 5, 1268-1272.
- [5] Z. Abbas, U. Yadav, R. J. Butcher, A. K. Patra, *J. Mater. Chem. C* **2021**, 9, 10037-10051.
- [6] U. Yadav, Z. Abbas, R. J. Butcher, A. K. Patra, *Sens. Actuators B Chem.* **2022**, 132938.
- [7] N. Shukla, V. Singhmar, J. Sayala, A. K. Patra, *Inorg. Chem.* **2025**, 64, 1287-1301.
- [8] S. Pradhan, N. Shukla, G. Panigrahi, A. K. Patra, *Chem. Commun.* **2025**, 61, 1886-1889.

Highly efficient artificial photocatalysts mimicking Photosystem 1

S.Rau^a, M. von Delius,^b L. Gonzalez,^c D. Ziegenbalg,^d B. Dietzek-Ivanšić^e

^a Institute of Inorganic Chemistry I, ^b Institute of Organic Chemistry I, ^d Institute of Chemical Engineering, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany, sven.rau@uni-ulm.de

^c Institute of Theoretical Chemistry, Vienna University, Währinger Str. 17 A-1090, Vienna

^e Friedrich Schiller University Jena, Institute of Physical Chemistry, Helmholtzweg 4, Jena, Germany; Leibniz Institute of Photonic Technology, Research Department Functional Interfaces, Albert-Einstein-Str. 9, Jena, Germany; Leibniz Institute of Surface Engineering (IOM) Permoserstraße 15, Leipzig, Germany

Biological photosynthesis has evolved to a highly efficient molecular apparatus where light induced electron transfer processes are precisely tuned with regard to sequence and direction by optimal positioning of functional units.¹ Photosystem 1 is generating a directional electron flow from the P700 to the FNR-catalysis center for NADH₂⁺ formation over a bridge of several spatially fixed FeS clusters. These highly reactive intermediates are protected by protein environments. A functional mimic of nature's example are multinuclear metal complexes containing a photosensitizing Ru-polypyridyl unit, a catalytically active Rh(III)Cp* unit and a bridging ligand, if containing an alkynyl linkage providing for very efficient electronic coupling already in the ¹MLCT state and highly efficient photocatalysis.² However, chemical instability of this linkage lead to a search of optimal linking units, which proved futile.^{3, 4} Inspired by the design of the natural system we those developed a supramolecular protection of the alkynyl link in from of a rotaxane. We present here the synthesis, photophysical and theoretical characterization and the outstanding photocatalytic activities which support the novel concept of supramolecular protection of the Achilles' heel.

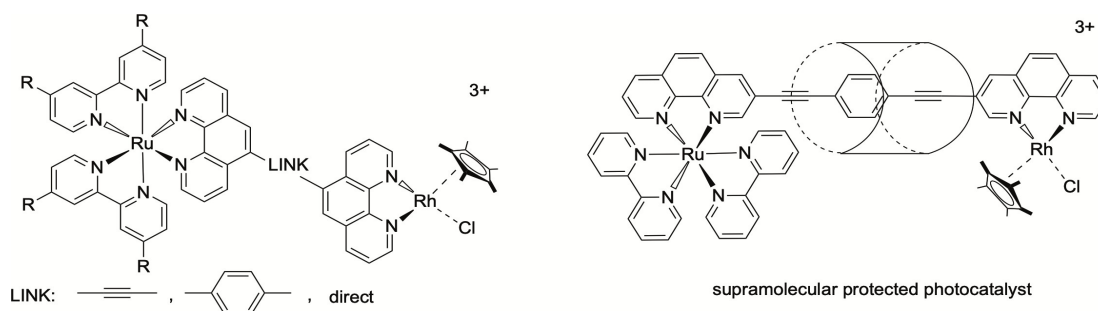


Figure 1. Photocatalysts for visible light driven formation of NADH₂⁺ and efficient protected novel catalyst

Acknowledgments

Deutsche Forschungsgemeinschaft DFG, CRC 234 Catalight, 364549901, A1, B7, C3, C6

References

- [1] R. Blankenship, Molecular Mechanisms of Photosynthesis, 3rd ed. Wiley-Blackwell, **2021**
- [2] L. Zedler, P. Wintergerst, A. K. Mengele, C. Müller, C. Li, B. Dietzek-Ivanšić, S. Rau, *Nat. Commun.*, **2022**, 13, 2538
- [3] L. Zedler, A. K. Mengele, K. M. Ziems, Y. Zhang, M. Wächter, S. Gräfe, T. Pascher, S. Rau, S. Kupfer, B. Dietzek, *Angew. Chem. Int. Ed.* **2019**, 58, 13140-13148
- [4] M. Semwal, M. Laemmle, E.M. Brohmer, S. Volk, L. Zedler, S. Kupfer, A. Mengele, G. Shillito, S. Rau, B. Dietzek-Ivanšić, *Inorg. Chem.*, **2025** accepted

List of Poster Presentations

"**Even**-numbered posters will be presented during the poster session on **July 9th**, whereas **odd**-numbered posters will be discussed during the session on **July 11th**."

#	First name	Surname	Poster Title
P1	Jibin Alex	Abraham	<i>Design, Synthesis, and Photophysical Properties of ABAC-Type Low-Symmetry Zinc Phthalocyanine</i>
P2	Mary Angela	Alfred	<i>If Yes, Activate; Else Stay Quenched - PET Controlled Switchable Silicon Phthalocyanines for Photodynamic Therapy of Cancer</i>
P3	Alessandro	Amadeo	<i>GelOx: The breathing gel</i>
P4	Sergio	Aranda	<i>Mechanistic Insights into Solvent and Structural Variations of a Homogeneous Catalyst Ni(bppe)(SCN)₂ for CO₂ Reduction</i>
P5	Amine	Assel	<i>Exploring Coumarin–Boron Monofluoride Complexes: Synthetic Approaches, Fluorescence Properties, and In Silico Medicinal Chemistry Insights</i>
P6	Maria Vittoria	Balli	<i>Ruthenium complexes as electrochemiluminescent labels for advancing PCR-free nucleic acids detection</i>
P7	Andrea	Barbieri	<i>Design and Characterization of Lanthanide complexes for Down-Shifting Luminescent Conversion Layers in Perovskite Solar Cells</i>
P8	Martyna	Bartusiak	<i>TAS and TRIR Spectro-Electrochemical Studies of a Ruthenium–Naphthalene Diimide Ester Complex: Charge Transfer Dynamics and Excited States Populated in Solution and on a NiO Surface</i>
P9	Filippo Piero	Battaglia	<i>Synthesis of cobalt complexes catalytic for visible light-assisted hydrogen production with innovative molecular-based hybrid photoelectrodes design</i>
P10	Stefan	Bednarik	<i>Self-assembly of tetrapyrroloporphyrines into J-aggregates</i>

P11	Elisabetta	Benazzi	<i>On the Mechanism of Photodriven Hydrogenations of N₂ and other substrates by Hantzsch Ester: Photoinduced generation of weak N–H pyridinyl bonds in the presence of a suitable buffer.</i>
P12	Anagha R.	Bidarahalli	<i>Developing Copper Vanadate for Enhanced Photoelectrochemical Performance</i>
P13	Jack	Biddulph	<i>Time-resolved infrared spectroelectrochemical studies of two rhenium naphthalimide complexes</i>
P14	Claudia	Bizzarri	<i>Diimine Ligands in Heteroleptic Cu(I) Complexes: A Path to Efficient Solar Energy Utilization</i>
P15	Sergey	Bokarev	<i>Theoretical X-ray spectroscopy and ultrafast dynamics in transition metal complexes</i>
P16	Olga	Bokareva	<i>Excited-State Dynamics in Cobalt(III) Polypyridyl Complexes</i>
P17	Jakob T.	Casanova	<i>Investigating Anti-Kasha dynamics with quantum-mechanically derived force-fields and non-adiabatic molecular dynamics.</i>
P18	Noémie	Chantry	<i>Exploring substituents effects on the anti-Kasha reactivity of binuclear Ru(II) photosensitizers</i>
P19	Pritha	Chatterjee	<i>Dual Photoreactive Ternary Ruthenium(II) Terpyridyl Complexes: A Comparative Study on Visible Light-induced Single-step Dissociation of Bidentate Ligands and Generation of Singlet Oxygen</i>
P20	Jie Ying	Chen	<i>Characteristics of Relaxations for Low-Energy Triplet Excited States of [Ru(tpm)(prbm)(L)]²⁺ Ions (L= NH₃ and CH₃CN): Density Functional Modeling and Efficient Metal Center State Quenching Mechanisms</i>
P21	Yuan Jang	Chen	<i>The Extremely Slow Radiative-Rate Constant of Phosphorescent Ru-(Monodentate Aromatic-Ligand) Chromophore: ADF Modeling and Spin-Orbit Coupling Mediated Intensity Stealing Mechanics</i>
P22	Mihaela	Cibian	<i>Structure – Properties Relationships in Coordination Complexes of N,N'-Disubstituted Amidine Oxide (AMOX) Ligands</i>
P23	Simon	Clausing	<i>Efficient Ferredoxin Reduction by Red-Light Generated Silicon Phthalocyanine Radicals</i>

P24	Nicolas	Issot	<i>Multiple Photoinduced Charge Separation in Covalent Molecular Triads: Insights from DFT</i>
P25	Marta	Costa Verdugo	<i>Photochemical Behavior Of Ruthenium(II) Complexes In Choline Geranate (CAGE) Ionic Liquids</i>
P26	Laura	Cuevas	<i>"CrIII Complex–DNA Interaction as a Source of Induced Circularly Polarized Luminescence and Photodamage"</i>
P27	Samira	Dabelstein	<i>Femtosecond-spectroscopy of novel Fe(III)-complexes demonstrating a reservoir effect</i>
P28	Elena	Dallerba	<i>Unveiling the Potential of Iridium Complexes in Tissue Imaging</i>
P29	Jiri	Demuth	<i>J-dimers of phthalocyanine analogues and how to use them</i>
P30	Emily	Derham	<i>Photodegradation of Herbicides Using Boron Dipyrromethane (BODIPY) Polymers</i>
P31	Jesús	Díaz-Burruenco	<i>Pyrazole-based IrIII complexes as effective antennas to sensitize EuIII-based emission in ultrasmall NaGdF4:Eu nanoparticles</i>
P32	Luis G. Alves	do Nascimento	<i>Investigation on One-Electron Reduced Species of Rel-naphthalimide photosensitizers</i>
P33	Florian	Doettinger	<i>Efficiency and Distance Dependency of Doublet-Triplet Energy Transfer Processes</i>
P34	Conor	Doran	<i>Mn(I) isocyanide complexes with benzothiadiazole motifs: unravelling the excited-state manifold using RIXS</i>
P35	Federico	Droghetti	<i>Light-Driven CO2 Reduction with a Heptacoordinated Iron(II) Polypyridine Complex</i>
P36	Laura	Duncan	<i>The Development of Sulfur-Containing, APTRA-Derived Fluorescent Probes with Specific Zn(II) Binding</i>

P37	Nils	Düsterhues	<i>Accessing the reservoir effect in Iron(III)-complexes via electron withdrawing linker-groups</i>
P38	Alexander	Eith	<i>Understanding multi-timescale effects in a light-driven overall water splitting system</i>
P39	Othmane	Essahili	<i>Sustainable Luminescent Materials for Next-Generation Smart Building Integration</i>
P40	Mona	Farhadi Rodbari	<i>Photophysical Characterization of Ru and Os Phenazine-Based Polypyridine Complexes as Potential Photosensitizers for Photodynamic Therapy</i>
P41	Mikhail	Filatov	<i>Enhancement of Intersystem Crossing in Asymmetrically Substituted BODIPY Dyes</i>
P42	Greta	Fogar	<i>SnIV-porphyrins conjugates as bio-inspired models for artificial photosynthesis</i>
P43	Antonio	Francés-Monerris	<i>A Computational Approach to Emergent Photoactivated Anticancer Therapies Based on Transition Metal Complexes</i>
P44	Paul	Francis	<i>Electrochemiluminescence of Earth Abundant Transition Metal Complexes</i>
P45	Yoann	Fréroux	<i>New antennae for photoswitchable luminescent lanthanide(III) complexes</i>
P46	Daniel	Friedewald	<i>Harnessing an Oxide Relay Pathway in a Molecular Cleft for Light-Driven Water Oxidation</i>
P47	Dennis	Fritzler	<i>Antenna effects on the photophysics of luminescent dinuclear chromium(III) complexes</i>
P48	Salvatore	Genovese	<i>Molecular deactivation dynamics of two photoactive Iron (III) complexes</i>
P49	Federica	Giorgianni	<i>Towards biohybrid systems for water photo-oxidation: design and synthesis of photo- and redox-active molecular components</i>

P50	Felix	Glaser	<i>Welcome to the Dark Side: Photoactive Iron Complexes with Microsecond Excited-State Lifetimes</i>
P51	Rebeca	Gomez Castillo	<i>Resolving Mechanistic Pathways in Bioinorganic Catalysis via Ultrafast X-ray Spectroscopy</i>
P52	Iván	González-Pavez	<i>Heteroleptic Copper(I) and Silver(I) Complexes with Me-dpa/Xantphos Ligands as Promising Materials for Light-Emitting Devices</i>
P53	Daniel	Graczyk	<i>Synthesis, DNA Binding Interactions & Time Resolved Spectroscopy of Ru(II) – Pteridinyl Complexes</i>
P54	Véronique	Guerchais	<i>Highly luminescent 1,3-bis(4-phenylpyridin-2-yl)-4,6-difluorobenzene platinum(II) complexes: Exploring the effect of substituents on the 4-phenylpyridine unit</i>
P55	Kristoffer	Haldrup	<i>X-ray Scattering From Molecular Dynamics Simulations of Photoactivated Molecules in Aqueous Solution</i>
P56	Maximilian	Henning	<i>Low-Temperature Emission of Cyclometalated Cobalt(III) Complexes Linked to Organic Chromophores</i>
P57	Masanari	Hirahara	<i>Light- and Redox-Controlled ON/OFF Switching in PCET</i>
P58	Teruyuki	Honda	<i>Excited-State Characterization of Novel Iron (II) Isocyanide Complexes Using Ultrafast Spectroscopy</i>
P59	Shota	Hosoya	<i>Energy Loop-Induced Nonlinear Emission in a Eu(III) Complex via the 7F1 State Generated through a Radiative Pathway</i>
P60	Ren	Itagaki	<i>Phase-Migrating Z-Scheme Charge Transportation Enables Photocatalytic Molecular Conversions Harnessing Water as an Electron Source</i>
P61	Munetaka	Iwamura	<i>CPL inducement and energy transfer in Eu(III) complexes by chiral transition metal complexes observed by steady-state and time-resolved CPL spectroscopy</i>
P62	Moritz	Jahn	<i>Organic Functionalization of Thiomolybdates for HER – Enabling the Design of Photocatalytic Dyads</i>

P63	Pengyue	Jin	<i>Luminescent Fe (III) Complex Sensitizes Triplet-Triplet Annihilation Upconversion and Catalyzes Photopolymerization</i>
P64	Tao	Jin	<i>Making Mo(0) a Competitive Alternative to Ir(III) in Phosphors and Photocatalysts</i>
P65	Amelia	Kacperkiewicz	<i>From Rags to Riches: Enabling Abundant Metals to Exhibit Significant Photophysical and Magnetic Properties Using Efficient Ligand Design</i>
P66	Hajime	Kamebuchi	<i>Control of emission wavelength by pH and proton conductivity of cis-Pt(II)-NHC bis(pyridylacetylide) complexes loaded in highly proton- conductive membrane</i>
P67	Michael	Karnahl	<i>Dye-sensitized solar cells based on Cu(I) complexes containing catechol anchor groups that operate with aqueous electrolytes</i>
P68	Chizuru	Kasahara	<i>[FeFe]-H₂ase mimicking complex bearing two organic photosensitisers for photocatalytic H₂ evolution</i>
P69	Alina	Koba	<i>Cell and reactor design for space and time resolved operando multi-spectroscopic analysis integration</i>
P70	Henriette	Kolbinger	<i>How to get 200% H₂ with 25% less energy input using molybdenumsulfide clusters as photocatalysts for HER</i>
P71	Athul	Krishna	<i>Light Induced Cobalt Stabilized Highly Delocalized Radical for Hydrogen Production</i>
P72	Sandra	Kronenberger	<i>Novel Manganese(II) Complex with a 190 ns Metal-to-Ligand Charge Transfer Lifetime</i>
P73	Prashant	Kumar	<i>Photoproduction of carbon monoxide and singlet oxygen by visible-light-driven Re(I)-based PhotoCORMs</i>
P74	Stephan	Kupfer	<i>Towards photoactive 3d transition metal complexes – A computational perspective</i>
P75	Claudio	La Falce	<i>Design and study of new photo-electrochemical cells for H₂ production</i>

P76	Jana	Lapesova	<i>Improved Photoinduced Electron Transfer in Azaphthalocyanine-Ferrocene System upon Formation of a Charge-Transfer Complex</i>
P77	Theodore	Lazarides	<i>Fluorescent metal-organic frameworks as an effective alternative for heavy metal detection in aqueous environment</i>
P78	Giuliana	Lazzaro	<i>Shaping light-driven reactivity: from heteroleptic to homoleptic Ru(II) bisamide complexes for H2 evolution</i>
P79	Simon	Liedtke	<i>Reaction-Diffusion Simulations of Photoredox Processes in Solution</i>
P80	Yu Hui	Lin	<i>Characteristics of 77 K Emission for Phosphorescent Os-bpy Chromophore: ADF Modeling and Spin-Orbit Coupling Mediated Intensity Stealing</i>
P81	Sophia	Lipinski	<i>Structure-Property Relationships for Heteroleptic Ag(I) Complexes for Light-Emitting Electrochemical Cells</i>
P82	Khaoula	Lmcharrag	<i>Fluorescent J-dimers of Phthalocyanines</i>
P83	Patrick	Loftus	<i>Investigating the Photophysical Properties and Activity of a Zinc Porphyrin Appended Polyethylenimine Polymer Towards Solar Driven Water Splitting</i>
P84	Jannik	Löseke	<i>Effect of electronic parameters and distortion on the inverted Marcus behavior of bidentate CoIII photocatalysts</i>
P85	Franziska	Lux	<i>Photocatalytical Reactions using Co^{III}(ImP)- and Fe^{II}(ImP)-complexes</i>
P86	Xiao	Ma	<i>Microscopic studies of vapochromic behaviors in molecular crystals of [Re(CO)₃Br(ppt)]</i>
P87	David	Magri	<i>Ferrocene-based molecular logic gates based on photoinduced electron transfer</i>
P88	Tamar	Maisuradze	<i>Theoretical Insights and Struggles on The Series of 3d₆ Metal Complexes</i>

P89	Francesca	Mancini	<i>Supramolecular interaction in Ru-Co and Ru-Fe complexes for efficient solar-driven hydrogen evolution and CO₂ reduction</i>
P90	Andrea	Mantovani	<i>Comparison of Iridium Sensitizers Employed in the Photoelectrochemical Generation of Added-Value Organics</i>
P91	Edoardo	Marchini	<i>A deep insight into the role of basic additives in the charge injection of Fe(II)-based complexes</i>
P92	Martina	Mazzaferro	<i>A novel water-dispersible microemulsion of a supramolecular copolymer for drug delivery systems</i>
P93	Nathan	McClenaghan	<i>Dynamic processes in photoactive metal-containing rotaxanes</i>
P94	Isobel	Meikle	<i>Photochemistry, electron transfer and catalysis mapped by a combination of ultrafast laser and X-ray spectroscopies</i>
P95	Martina	Milani	<i>Charge transfer dynamics in molecular-based photoanodes for solar fuels production</i>
P96	Pablo	Msellem	<i>Red and NIR emitting Zn(II)-salen complexes for sensing and biological applications</i>
P97	Marius	Müßler	<i>“If you like it you should put a ring on it” - Rotaxanes as supramolecular protective motifs in reductive heterodinuclear photocatalysis</i>
P98	Sandra Anila	Nair	<i>Tuning the photophysical properties of p-extended Cu-benzimidazole complexes</i>
P99	Akinobu	Nakada	<i>Conjugated polymer photocatalysts with a built-in metal complex for CO₂ reduction</i>
P100	Nidhi	Nehra	<i>Benzothiazole-Quinoline based sensor for selective detection of Fe³⁺ ions and its applications</i>
P101	Veronika	Novakova	<i>Tuning Electron-Accepting Properties of Phthalocyanines for Charge Transfer Processes</i>

P102	Tomohiro	Ogawa	<i>Exploration of Molecular Design to Achieve Nanosecond Excited States in Fe(II) Complexes Towards Long-Lived Triplet States</i>
P103	Ken	Onda	<i>Time-Resolved Spectroscopic Studies on Reaction Mechanism in Complex Artificial Photosynthesis Systems</i>
P104	Kerstin	Oppelt	<i>Full ThrOTTLE tr-IR: Time resolved IR Spectroscopy in Combination with Electrochemistry for Photochemical and Photophysical Investigation of Transition Metal Complexes and (Catalytic) Redox Intermediates</i>
P105	Stephen	O'Sullivan	<i>Boron Dipyrromethenes (BODIPYs) for Antimicrobial Photodynamic Therapy (aPDT)</i>
P106	Chandrani	Pal	<i>Conformational Switching of a Nano-Size Urea-bridged Zn(II)Porphyrin Dimer by External Stimuli</i>
P107	Michael	Pattuwage	<i>Near-Infrared Electrochemiluminescence from Chromium(III) Complexes in Mixed Annihilation Systems</i>
P108	Teresa	Paviglianiti	<i>Disaggregation Kinetics of TPPS J-Aggregates under Mild Acidic to Neutral pH: The Synergistic Role of Albumin and Gold Nanoclusters</i>
P109	Marta	Penconi	<i>Single Active Ligand in Iridium Complexes for Near Infrared Phosphorescent OLEDs</i>
P110	Waldemar	Pichór	<i>3D printed hybrid photocatalytic cement composites</i>
P111	Martin	Pižl	<i>Ultrafast time-resolved infrared spectroelectrochemistry</i>
P112	Mariet Sibi	Puthanagady	<i>Molecular dyad immobilised in soft matter for HER</i>
P113	Nicolò	Quadrio	<i>Plastics detection using hydrogels functionalized with switchable iridium complexes</i>
P114	Emily Louise	Race	<i>Ultrafast Laser Control of Photochemical Reactions in Light-Harvesting Transition Metal Complexes</i>

P115	Enrico	Rampazzo	<i>Prolonging Ru(bpy)₃²⁺ Luminescence Lifetime in Silica Nanoparticles via Energy Reservoir Mechanism</i>
P116	Vincent	Robert	<i>Spectroscopies from perturbation theories</i>
P117	Jonathan	Rochford	<i>Pulse Radiolysis Time-Resolved Infrared Spectroscopic Studies of Mn(II) and Re(II) Tricarbonyl CO₂ Reduction Catalysts</i>
P118	Leon David	Rodriguez	<i>Synthesis Of Low-Symmetrical Silica-Phthalocyanines With Axial Modification For Photodynamic Therapy</i>
P119	Evgenia	Ryndin	<i>From ruthenium to iron: New perspectives on DNA-intercalating metal complexes</i>
P120	Abhijit	Saha	<i>Fine-tuning the Excited State Dynamics of Ruthenium(II) Polypyridyl Complexes with Benzazole-Substituted 8-Hydroxyquinolines</i>
P121	Arindam	Saha	<i>Anti- Kasha emission from Co(III)-Amidine-N-oxide complexes: photophysics and reactivity</i>
P122	Luca Timo	Schleicher	<i>Light-driven Catalytic Activity and Deactivation Processes of Thio(oxo)molybdate Hydrogen Evolution Reaction Catalysis</i>
P123	Till	Schmidt-Raentsch	<i>Metallonitrenes as Key Intermediates in C-N Bond Formation</i>
P124	Stefano	Scoditti	<i>Computational Insights into the Photodissociation Mechanism of Terpyridine-Based Ruthenium(II) Complexes</i>
P125	Kaito	Segawa	<i>Control of Emission Efficiency and Color by Mixed Crystals of Platinum(II) and Palladium(II) Complexes in One-dimensional Chain</i>
P126	Mohini	Semwal	<i>Unraveling Solvent Polarity Effects in Thermally Activated Delayed Fluorescence Through Time-Resolved Spectroscopy</i>
P127	Indranil	Sen	<i>Conformation Dependent Emission and Circularly Polarized TADF in Linear CDP Copper (I) Complexes</i>

P128	Luis Antonio	Senz	<i>Temperature Dependency of the Light-Driven Hydrogen Evolution Reaction using Thiomolybdate Clusters</i>
P129	Georgina	Shillito	<i>Excited state processes in a supramolecular photocatalyst – a quantum computational investigation</i>
P130	Kazuteru	Shinozaki	<i>Sequential H/D exchanges and Rh-H/Rh-C s bond formations resulting from auto cyclometallation during photoirradiation of bis(6,6'-dimethyl-2,2'-bipyridine)(oxalato)rhodium(III) complex in methanol-d4</i>
P131	Baldeep	Sidhu	<i>Stabilizing High Spin States in Fe(II)-N(amido) Complexes to Tune Visible Light Absorption and Excited State Behaviour</i>
P132	Alessandro	Sinopoli	<i>Plasmon-Enhanced CO₂ Reduction to Liquid Fuel via Modified UiO-66 Photocatalysts</i>
P133	Simon Nicholas	Smith	<i>Synthesis and Resolution of tris-Heteroleptic Ruthenium Polypyridyl Complexes as Chiral DNA Binding Luminescent Probes</i>
P134	Simon	Soldner	<i>Room-Temperature Phosphorescence of Cocrystals of Aromatic Bisimides and Triplet Sensitizer Pt(acac)₂</i>
P135	Fumika	Sueyoshi	<i>Photocatalytic CO₂ Reduction and H₂ Evolution in Aqueous Media with Water-soluble Complexes</i>
P136	Paulina	Szoldra	<i>Photocatalytic degradation of nitrogen oxides (NOx) in photoreactor with granulated regolith with TiO₂</i>
P137	Kazuma	Takahara	<i>Thermochromic circularly polarized luminescence for homochiral tetracopper(I) clusters</i>
P138	Alexander	Tarnovsky	<i>Ultrafast Photophysical and Photochemical Dynamics of Hexahalobismuthates(III)</i>
P139	Luise	Thomisch	<i>Photodriven charge accumulation on Cu(I) 4H-imidazolate complexes</i>
P140	Toranosuke	Tomikawa	<i>Doublet charge transfer emission of Ce(III) complex with β-diketonate ligand</i>

P141	Simon	Torres Gonzalez	<i>Synthesis, Characterization and Study of a novel Fe(II)-complex as potential photosensitizer</i>
P142	Stefanie	Tschierlei	<i>Three-Coordinate Cu(I) Complexes of Anionic N-Heterocyclic Carbenes</i>
P143	Kiyoshi	Tsuge	<i>Synthesis of highly luminescent, isomorphous AgI and CuI complexes; Effect of halogenido ligands on emission and relaxation</i>
P144	Florent	Urbain	<i>Heteroleptic copper (I) complexes as suitable photosensitizers for new photo-induced organic transformations</i>
P145	Abha	Valavalkar	<i>in cellulo investigation of the excited state dynamics of biologically relevant photoactive compounds</i>
P146	Benjamin	Van Kuiken	<i>Identification of Metal-Centered Excited States Using Ultrafast Soft X-ray Spectroscopy</i>
P147	Ana Karem	Vega Salgado	<i>Key factors influencing cage escape in photoinduced electron transfer.</i>
P148	Marco	Villa	<i>NHC-GOLD(I)-AMIDO COMPLEXES FOR PHOTOCATALYSIS</i>
P149	Dorothee S.	Wagner	<i>Long-lived terphenyl radical anion super-reductant for photocatalysis formed via upconversion</i>
P150	Jiahao	Wang	<i>Luminescent Cyclometalated Iridium(III) Polypyridine Complexes Modified with Dendritic Guanidinium Moieties as Molecular Glues for Combined Chemo-photodynamic Therapy</i>
P151	Joël	Wellauer	<i>Iron(III) Complexes with Luminescence Lifetimes of up to 100 Nanoseconds</i>
P152	Mary	White	<i>A novel cyclometalated Co(III) triazolyldiene photosensitiser complex displaying low-temperature emission and improved light harvesting</i>
P153	Mary	White	<i>Exploring the photophysical behaviours of imidazolyldiene vs. triazolyldiene Fe(III) 'abnormal' carbene complexes</i>

P154	Eleanor	Windle	<i>Selectively Targeting DNA Structure with Regio-pure Phthalocyanines: A Photophysical Study</i>
P155	Masayuki	Yagi	<i>Transparent WO₃ Films with Organized Mesopores and Oriented Crystallinity as a Robust Photoanode for Visible-Light-Driven Water Oxidation at Neutral pH</i>
P156	Kotaro	Yakuwa	<i>Dimensionally-Controlled Coordination Polymer Eu(III) Complexes</i>
P157	Hirohisa	Yanagikawa	<i>MCD and MCPL Studies on Octahedral [Mo₆l₈Y₆]²⁻ Clusters in the Excited Triplet States</i>
P158	Borys	Zakharchenko	<i>Luminescent gold nanoparticles decorated with photoactive metal complexes for cellular imaging and photodynamic therapy</i>
P159	Clara	Zehe	<i>Put a cage on it: Luminescent metal complexes in confined space</i>
P160	Minli	Zhang	<i>High-Efficiency Photoinduced Charge Separation in Iron N-Heterocyclic Carbenes</i>
P161	Li-Ting	Zhuo	<i>The Characteristic of Photo-Induced ³MLCT Emission Behavior for Ru-(Cyclometalated) Chromophores</i>
P162	Konstantinos P.	Zois	<i>Quantum Chemical Studies on a Heterodinuclear Rotaxane: Towards Biomimetic Photocatalysis</i>

26th ISPPCC

**POSTER
*ABSTRACTS***

Design, Synthesis, and Photophysical Properties of ABAC-Type Low-Symmetry Zinc Phthalocyanine

J. A. Abraham, P. Zimcik

Faculty of Pharmacy in Hradec Kralove, Charles University, Ak. Heyrovskeho 1203, Hradec Kralove, 500 03, Czech Republic (E-mail: abrahamji@faf.cuni.cz)

Phthalocyanines (Pc) are a class of π -conjugated heteroaromatic macrocycles, consisting of four isoindole rings linked by nitrogen bridges. Upon introducing asymmetry, the molecular structure gets perturbed electronically, allowing a fine-tuning of the physical properties. The mixed condensation reactions using multiple precursors limit the feasibility of forming low-symmetric Pc's owing to the identical molecular weight and properties of the product formed.[1] Controlled formation of target Pc with a minimal amount of side products could be achieved by a [3 + 1] approach *i.e.*, a base-promoted condensation of pre-linked trisphthalonitrile (ABA-trimer) and a free phthalonitrile (C) in the presence of a metal template (M).[2] (Figure 1).

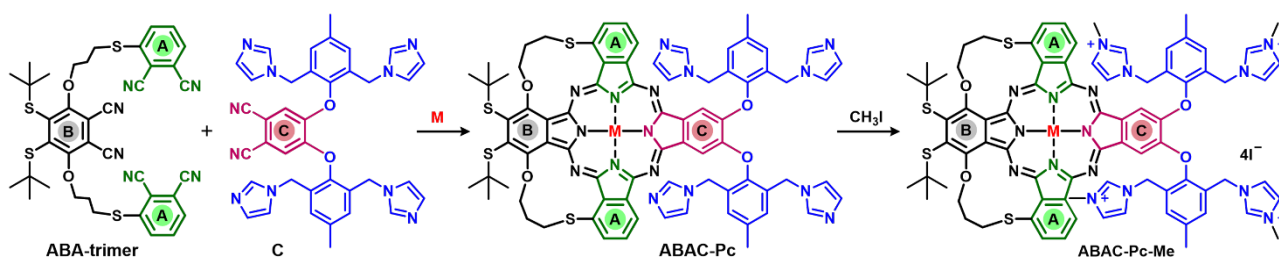


Figure 1. Synthesis of ABAC-Pc via cyclisation of an ABA-trimer with phthalonitrile (C) in the presence of a metal template (M), followed by quaternization to yield ABAC-Pc-Me.

We have successfully synthesised the designed asymmetrical ABAC-type phthalocyanine (ABAC-Pc) derivative, functionalized at the peripheral positions with 2,6-bis((1H-imidazol-1-yl)methyl)-4-methylphenoxy and *tert*-butylsulfanyl substituents. The incorporation of these electron-donating and heteroatom-containing moieties was aimed at enhancing the solubility, electronic properties, and coordination potential of the phthalocyanine core. Furthermore, the imidazole-functionalized periphery was subjected to quaternization under controlled conditions to afford the corresponding cationic phthalocyanine derivatives. This modification enhances solubility in polar media and introduces cationic charges, facilitating encapsulation within liposomes and promoting efficient cellular uptake. These features were found advantageous for photodynamic therapy applications, as the cationic nature of the compounds enhances their interaction with negatively charged cellular membranes, thereby improving localisation and phototoxic efficacy.

This work was supported by the ERC-CZ project (*Project No. LL2318*).

References

- [1] J. Mack, N. Kobayashi, *Chem. Rev.* **2011**, 111, 281.
- [2] J. Y. M. Chan, D. K. P. Ng, *J. Org. Chem.* **2022**, 87, 7213.

If Yes, Activate; Else Stay Quenched - PET Controlled Switchable Silicon Phthalocyanines for Photodynamic Therapy of Cancer

Alfred, M. A., Cavdarbasha, N., Novakova, V.

Faculty of Pharmacy in Hradec Králové, Charles University, Akademika Heyrovského 1203,
Hradec Králové 500 03, Czech Republic.
e-mail: alfredm@faf.cuni.cz.

Conventional chemotherapeutic treatment of cancer poses a threat to healthy cells, presenting the need for selective cell death. Although photodynamic therapy¹ of cancer is an efficient non-invasive therapy, an ideal photosensitizer (PS) is still on the lookout. Silicon phthalocyanines (SiPcs) are macrocyclic tetramers with interesting photophysical properties and highly applicative singlet oxygen production capabilities which can be fine-tuned. Cathepsin B is a lysosomal cysteine protease that plays a pivotal role in tumour development and its overexpression is associated with tumour environments. Its dicarboxypeptidase activity makes it cleave a valine-citrulline labile bridge² at the C-terminus.

In this work we develop an optimized photosensitizer for precision medicine, possessing desired water solubility, absorption in the biological window of tissues and high singlet oxygen production. It is modified further with ferrocene to make the PS a photoinduced electron transfer (PET)-controlled switch for in-cell activation. Two controls are included in the project, namely a SiPc with non-cleavable alkyl linker (still-OFF) and a SiPc with quaternized amine at axial positions of SiPc (still-ON).

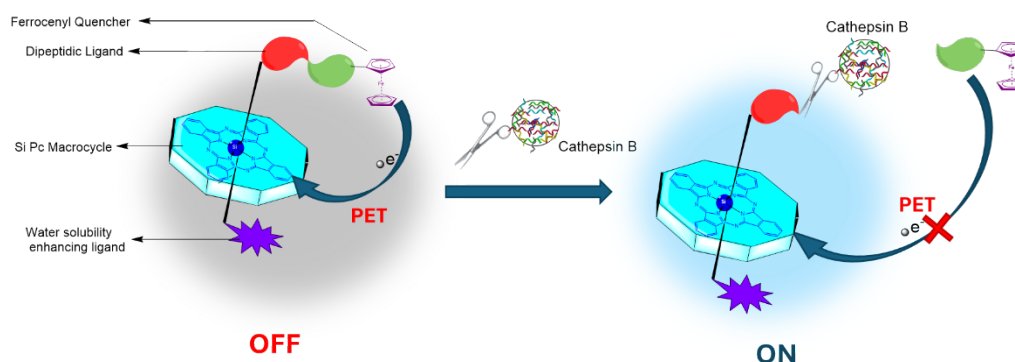


Figure 2. Schematic functioning of the antibody-drug conjugate with the cleavable Valine-Citrulline ligand.

Acknowledgments

This work was supported by the Ministry of Education, Youth and Sports under the ERC CZ programme (LL2318).

References

- [1] Claessens, C. G., *et al.*, *Chemical Record*, **2008**, 8(2), 75-97.
- [2] Bargh, J. D., *et al.*, *Chemical Society Reviews*, **2019**, 48(16), 4361-4374.

GelOx: The breathing gel

A. Amadeo,^{a,b} A. M. Cancelliere,^a F. Puntoriero,^a F. Nastasi,^a S. Campagna,^a G. La Ganga^a

^a Department of Chemical, Biological, Pharmaceutical and Environmental Science, University of Messina, via F. Stagno d'Alcontres 31, Messina, Italy

^b Department of Chemistry, Biology and Biotechnology, University of Perugia, 06123 Perugia (Italy)

One of the pivotal aspects to optimize with the aim of improving light driven water splitting performances is the oxygen production. The photocatalytic system^[1,2] employed for this reaction needs to absorb UV-visible light and exploit this energy to store four positive charges without undergo oxidative degradation. Different strategies can be used to make the photocatalytic system more robust to perform an high number of catalytic cycles and subsequently to increase oxygen production. The strategy showed here consists in functionalize an assembled photocatalyst with vinyl groups in order to use it as crosslinking units to build up an hydrogel matrix. Shining light on the precursor is enough to trigger both the formation of the hydrogel and the photocatalysis.

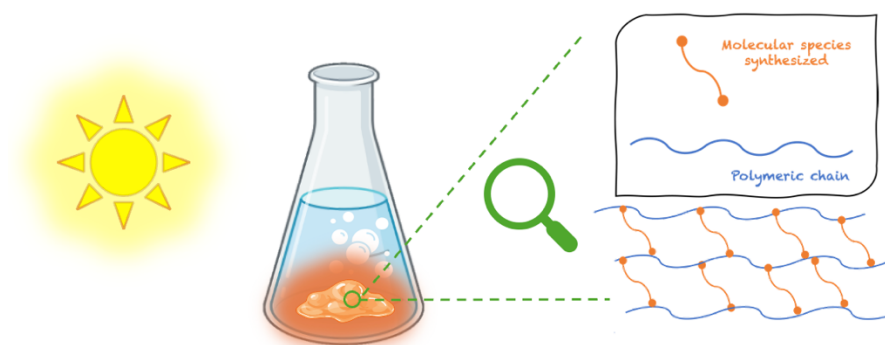


Figure 3. Scheme of photosynthetic system embedded in an hydrogel matrix.

References

- [1] A. M. Cancelliere, A. Arrigo, M. Galletta, F. Nastasi, S. Campagna, G. La Ganga, *J. Chem. Phys.* **2024**, 160, 084709
- [2] L. Duan, A. Fischer, Y. Xu, L. Sun, *J. Am. Chem. Soc.* **2009**, 131, 10397–10399.

Mechanistic Insights into Solvent and Structural Variations of a Homogeneous Catalyst Ni(bpet)(SCN)₂ for CO₂ Reduction

Sergio Aranda, C.K. Omlin and Peter Hamm
Department of Chemistry, University of Zurich, Switzerland

In the field of catalytic organometallic chemistry, complexes such as Ni(bpet)X₂ [1] have demonstrated promising activity as reductants for CO₂ and H⁺. However, mechanistic studies often underemphasize the crucial influence of labile ligands and solvent coordination, despite their potential to shape the reactivity and identity of key catalytic intermediates. To address these limitations, we have expanded the investigation to include both alternative metal centers and anchoring ligands—specifically, substituting **bppt** [2] for **bpet**—with the goal of disentangling hydrogen evolution from CO₂ reduction pathways. The flexibility of bppt may promote more defined catalytic behavior and improve vibrational coupling, enabling the spectral resolution for the symmetric and antisymmetric modes of the IR markers.

As part of this effort, we employed thiocyanate (SCN⁻) ligands in place of MeCN [3], chosen for their stronger IR absorbance and good lability, enabling real-time tracking of transient coordination events via time-resolved infrared spectroscopy. Our results underscore the necessity of thoroughly characterizing the initial state of the catalyst upon dissolution, which is often overlooked but crucial for accurate mechanistic interpretation. Solvent role emerged as a critical parameter (see Fig. 1), with marked differences in coordination behavior and redox response observed across solvents of varying donor ability.

To further investigate whether hydride intermediates are general features of H₂ evolution from CO₂ reduction or specific to certain mechanistic routes, we introduced the sterically hindered, non-nucleophilic base di-tert-butylpyridine. This strategy allowed us to suppress Hydride formation, choosing more selectively one single pathway (see Fig. 2).

Overall, our findings highlight the importance of a multifaceted approach that integrates ligand design, metal center variation, and solvent effects to resolve competing pathways and improve the interpretability of time-resolved spectroscopic data in complex catalytic systems.

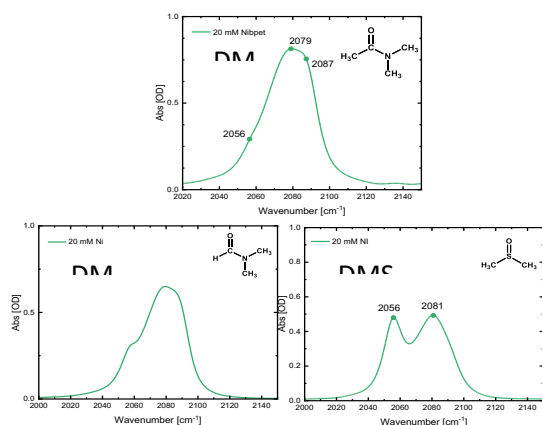


Fig 1. Metal-NCS vibration dependent on solvent.

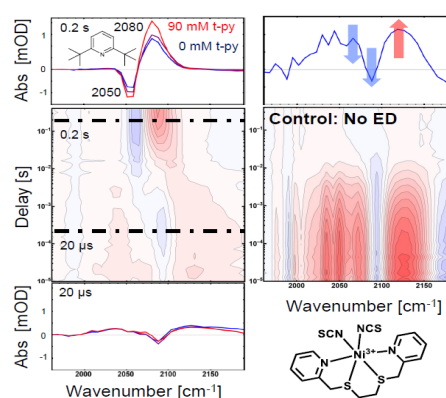


Fig 2. Left panel is a TRIR base dependence, right panel is a back electron transfer.

[1] Hong, D., Tsukakoshi, Y., Kotani, H., *JACS* **139**, 6538-6541 (2017).

[2] Hong, D., Tsukakoshi, Y., ..., Kojima, T., *Inorg. Chem.* **57**, 7180-7190 (2018).

[3] Lei, J-M., Luo, S-P., Zhan, S-Z., Wu, S-P., *Inorg. Chem. Commun.* **95**, 158-162 (2018).



Exploring Coumarin–Boron Monofluoride Complexes: Synthetic Approaches, Fluorescence Properties, and *In Silico* Medicinal Chemistry Insights

Amine Assel,^{a,b} Fausto Puntoriero,^a Mayssa Zayene,^b Scolastica Serroni,^a Sebastiano Campagna^a and Hichem Ben Jannet^b

^a *Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina- via F. Stagno d'Alcontres 31, 98166 Messina, Italy.*

^b *Laboratory of Heterocyclic Chemistry, Natural Products and Reactivity (LR11ES39), Team: Medicinal Chemistry and Natural Products, Faculty of Science of Monastir, University of Monastir- Avenue of Environment, 5019 Monastir- Tunisia.*

amine.assel@unime.it

Assel.amine@gmail.com

Four coumarin-based boron complexes (4a-d) were designed and synthesized with the objective of developing novel luminogenic bioactive molecular architectures.

We investigated the photophysical properties of the complexes in different solvents and in the solid state. Results showed that despite the absence of emission in solution in various solvents, all compounds displayed a notable solid-state luminescence. In particular, it was found that boron-coumarin complexes were almost non-emissive in THF, and the emission could be significantly intensified when a large amount of H₂O was added, illustrating the AIE (aggregation-induced emission) property.

Inspired by drug design strategy and recognizing the valuable role of computational methods, the pharmaceutical potential of novel boron-containing compounds was explored through *in silico* approaches. Specifically, *in silico* molecular docking studies were conducted, and ADMETox parameters were predicted to assess and simulate the pharmacological properties of these promising structures.

These results demonstrate the distinctive photophysical properties of boron-coumarin complexes and provide important information for creating scaffolds with specific photophysical characteristics for use in medicinal chemistry and medicine.

Aknowlegments

This work was funded by the European Union, Next Generation EU, M4, C2, investimento 1.1, PRIN 20225NSHZ5_001, CUPJ53D23007370006 and the Ministry of High Education and Scientific Research of Tunisia (LCHPN Lab : Team medicinal chemistry and natural products)

Ruthenium complexes as electrochemiluminescent labels for advancing PCR-free nucleic acids detection

M. V. Balli,^a F. Ferraresi,^a M. Jana,^a E. L. Sciuto,^b S. Conoci,^{a,b} M. Calvaresi,^a G. Valenti,^a P. Garagnani,^{c,d} L. De Cola,^{e,f} and L. Prodi^a

^a Department of Chemistry “G. Ciamician”, University of Bologna, Bologna (IT); ^b Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, Messina (IT); ^c Department of Medical and Surgical Sciences (DIMEC), University of Bologna, Bologna (IT); ^d IRCCS Azienda Ospedaliero-Universitaria di Bologna, Bologna (IT); ^e Department of Biochemistry and Molecular Pharmacology, Istituto di Ricerche Farmacologiche Mario Negri (IRCCS), Milan (IT); ^f Department of Pharmaceutical Science (DISFARM), Università degli Studi di Milano, Milan (IT)

Contact: mariavittoria.balli2@unibo.it

Accurate *in vitro* diagnostic tests are currently based on pathogens' nucleic acid (NA) detection by real-time PCR assays (LoD 1.15 aM), endowed with high sensitivity but lacking in simplicity and time effectiveness. Herein, we aim to present a novel electrochemiluminescence (ECL)-based biosensor (**Fig. 1**) for sensitive, selective, and PCR-free NA detection. ECL is a highly sensitive technique exploiting light emission from the excited state of suitable luminescent labels upon application of a proper potential. By exploiting ECL as transduction technique, we aim to obtain a faster and cost-effective process, upon optimization of a previously developed Hepatitis B Virus detection system,¹ through which we had already reached PCR-comparable LoD (1.25 aM) for some pathogenic NAs. In our assay, the use of two different ECL-active ruthenium complexes² is combined with a recognition strategy based on surface cooperative hybridization to selectively detect, e.g., SARS-CoV-2 RNA and microRNAs, without any NA amplification. The effectiveness of this strategy was further confirmed through electrochemical impedance spectroscopy analysis.^{2,3} Our biosensor design thus opens up the possibility to obtain point of care devices for a simple, fast and efficient detection of various infectious pathogens.

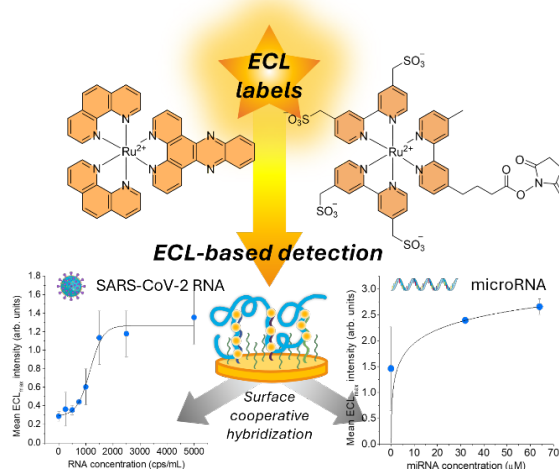


Figure 4. Schematic representation of the ECL biosensor detection approach.

Acknowledgments

The European Union's Horizon Europe EIC Pathfinder Open program “ECLIPSE” (Grant Agreement No. 101046787) is acknowledged for financial support.

References

- [1] P. Nikolaou, E. L. Sciuto, A. Zanùt, S. Petralia, G. Valenti, F. Paolucci, L. Prodi, S. Conoci, *Biosens. Bioelectron.*, **2022**, 209, 114-165.
- [2] A. E. Friedman, J. C. Chambron, J. P. Sauvage, N. J. Turro, J. K. Barton, *J. Am. Chem. Soc.*, **1990**, 112, 4960-4962.
- [3] P. Calorenni, G. Bella, M. S. Nicolò, E. L. Sciuto, M. V. Balli, G. Valenti, T. Gritti, S. Varani, L. Prodi, S. Conoci, *Adv. Mater. Interfaces*, **2024**, 2400642.

Design and Characterization of Lanthanide complexes for Down-Shifting Luminescent Conversion Layers in Perovskite Solar Cells

C. De Petra, A. Barbieri, E. Bandini

Istituto per la Sintesi Organica e la Fotoreattività (ISOF), Consiglio Nazionale delle Ricerche (CNR), Via Gobetti 101, 40129 Bologna BO, Italy. andrea.barbieri@isof.cnr.it

The efficient harvesting of solar energy using low-cost devices is vital for accelerating the transition from fossil fuels to renewable energy sources. A major limitation of current photovoltaic (PV) technologies is their restricted spectral response, which results in significant energy losses through thermalization and non-absorption of high- and low-energy photons. To overcome this, passive luminescent spectral conversion strategies – such as down-conversion (DC), up-conversion (UC), and down-shifting (DS) – are being actively investigated to enhance PV performance.[1] Among these, DS systems offer a promising route by converting ultraviolet (UV) radiation into visible light more effectively absorbed by PV cells.[2]

In this work, we report the synthesis and preliminary photophysical characterization of a series of lanthanide(III) β -diketonate complexes ($\text{Ln} = \text{Eu}^{3+}$, Tb^{3+}), with and without polypyridine ancillary ligands, as potential DS materials. These complexes exhibit high photoluminescence intensity and narrow emission bands, making them ideal candidates for integration into a luminescent down-shifting layer (LDL). The LDL is designed to be applied atop a perovskite-based solar cell (PSC), with the goal of improving both the device's power conversion efficiency and long-term stability by spectrally converting incident UV photons to energies better matched to the perovskite band gap.[3]

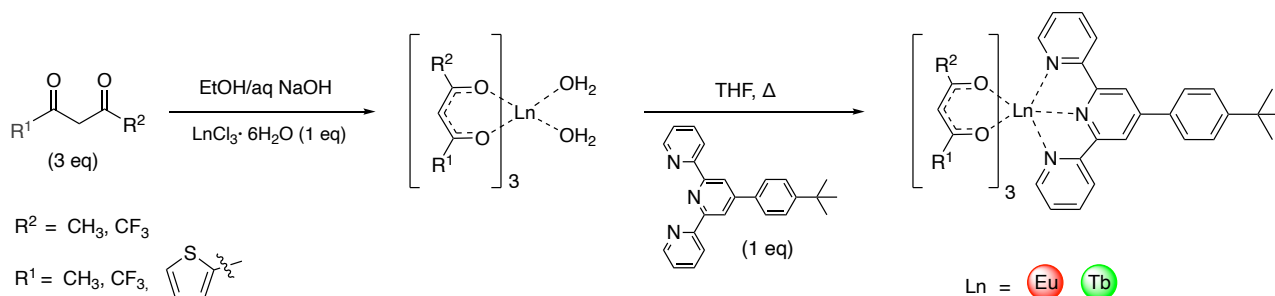


Figure 5. General synthetic procedure for the preparation of the luminescent lanthanide complexes.

Aknowlegments

This research was partially funded by the European Union – NextGeneration EU NRRP M4, C2, I1.1 MUR–PRIN P2022ACY8P “A Multicomponent Solar Energy Conversion System with Extended Spectral Collection and Improved Efficiency (MUSES)” – CUP B53D23025280001; NRRP M2, C2, I3.5 MASE–AdP “Research and development of technologies for the hydrogen supply chain” (POR H2) – CUP B93C22000630006.

References

- [1] X. Huang, S. Han, W. Huang, X. Liu, *Chem. Soc. Rev.* **2013**, 42, 173–201.
- [2] D. Yu, T. Yu, H. Lin, S. Zhuang, D. Zhang, *Adv. Optical Mater.* **2022**, 10, 2200014.
- [3] A.K. Singh, *Coord. Chem. Rev.* **2022**, 455, 214365.

TAS and TRIR Spectro-Electrochemical Studies of a Ruthenium–Naphthalene Diimide Ester Complex: Charge Transfer Dynamics and Excited States Populated in Solution and on a NiO Surface

Martyna Z. Bartusiak¹, Martin Pižl^{2,4}, Florian Cerpentier¹, Partha Malakar³, Owen Woodford⁵, František Hartl⁴, Elizabeth A. Gibson⁵, Mary T. Pryce¹

¹School of Chemical Sciences, Dublin City University, Ireland

²Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 16628 Prague, Czech Republic

³Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 0QX, UK

⁴Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6DX, UK

⁵Energy Materials Laboratory, Department of Chemistry, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK

martyna.bartusiak2@mail.dcu.ie

Abstract

Time-resolved infrared spectroscopy (TRIR) on the ps–ns timescale serves as an excellent technique for probing intermediates in photocatalytic assemblies and excited states populated by optical excitation. In this study, the complex **[Ru(dceb)₂(phen-NDI)]²⁺** (dceb = 4,4'-di-carboxyethyl-2,2'-bipyridine; phen = 1,10-phenanthroline, NDI = naphthalene diimide), further as **Ru(dceb)-NDI²⁺**, was assessed as a photosensitiser in photocatalytic hydrogen evolution. Incorporation of the peripheral ester groups at dceb significantly impacts the photophysical, electrochemical and spectroelectrochemical properties, as well as hydrogen evolution efficiency. Following excitation at 420 nm (Figure 1A, a bleach of the IR parent ester $\nu(\text{C}=\text{O})$ vibration at 1729 cm^{-1} is accompanied with an uprising new band at 1706 cm^{-1} . This behaviour is assigned to population of a triplet $\text{Ru} \rightarrow \text{dceb}$ charge transfer excited state [1]. With the pump excitation energy increased to 365 nm, the TRIR spectra are significantly different (Figure 1B). The stretching vibrations associated with the NDI $\text{C}=\text{O}$ groups at 1721, 1700 and 1686 cm^{-1} deplete, together with the ester carbonyl at 1729 cm^{-1} . New transient $\nu(\text{C}=\text{O})$ bands appear at 1677 and 1650 cm^{-1} , assigned to the NDI excited state [2]. Their red shift compared to the ground state indicates an increase in electron density on the acceptor NDI moiety. Simultaneously a transient band grows in at 1718 cm^{-1} and is attributed to the carbonyl groups at the dceb ligands. As in the 420 nm studies, the transient band at 1718 cm^{-1} is attributed to population a triplet $\text{Ru} \rightarrow \text{dceb}$ charge transfer excited state [1, 3]. Additionally, picosecond transient absorption (ps-TAS) spectroscopy was carried out both in solution and on a nickel oxide surface, with significant differences observed in solution versus on NiO. Nanosecond transient absorption spectroscopy (ns-TAS) studies were carried out at 355 nm to determine the lifetimes of the triplet states populated. Hydrogen studies were performed using solutions containing **Ru(dceb)-NDI²⁺** and **[Pt(DMSO)₂]₂]** in the presence of triethylamine (TEA) as a sacrificial electron donor and a $\text{TON}_{\text{H}_2} = 100$ obtained.

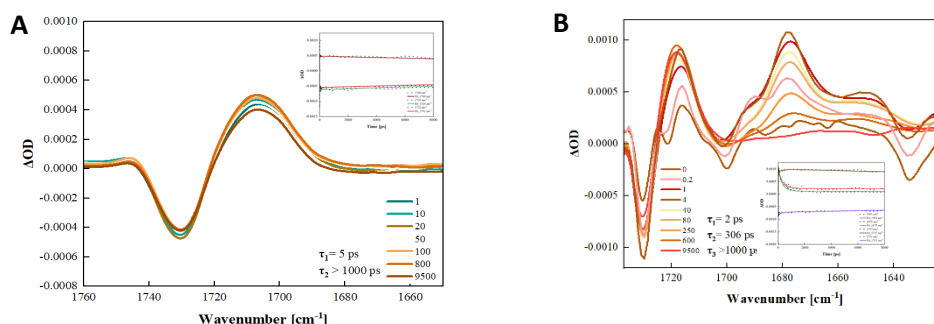


Figure 1 (A) TRIR spectrum of **Ru(dceb)-NDI²⁺** upon excitation at 420 nm and (inset) decay trace obtained in the TRIR. (B) TRIR spectrum of **Ru(dceb)-NDI²⁺** upon excitation at 365 nm and (inset) decay trace obtained in the TRIR.

Acknowledgments

Funding was provided by RI (12/RC/2302_P2, 19/FFP/6882, and 22/NCF/TF/10998), SEAI and the Czech Science Foundation (GAČR grant No. 23-057600)

References:

- [1]. Cerpentier, F. J. et al, (2021). *Frontiers in Chemistry*, 9. <https://doi.org/10.3389/fchem.2021.795877>
- [2]. Auty, A. J. et al, (2023b). *Chemical Science*, 14(41), 11417–11428. <https://doi.org/10.1039/d2sc06409j>
- [3]. Pan, Q. et al, (2016). *Chemical Communications*, 52(60), 9371–9374. <https://doi.org/10.1039/c6cc05222c>



SYNTHESIS OF COBALT COMPLEXES CATALYTIC FOR VISIBLE LIGHT-ASSISTED HYDROGEN PRODUCTION WITH INNOVATIVE MOLECULAR-BASED HYBRID PHOTOELECTRODES DESIGN

Filippo Piero Battaglia,¹ Andrea Fermi¹

*Department of Chemistry "G. Ciamician", Alma Mater Studiorum – University of Bologna – Via
Selmi 2, Bologna - Italy*

filippo.battaglia2@unibo.it

In the last decades the world energy demand increased exponentially, and, among the energy sources studied to replace the massive use of fossil fuels, solar energy has been the target of intensive research.¹ Among its applications, of particular interest is its use in photo-electrochemical devices (PEC) for water splitting (WS).¹ The research presented falls within this field: specifically, the focus is on the synthesis and the electrochemical and photocatalytic characterisation of cobalt complexes catalytically active for the hydrogen evolution reaction. Within this project, cobalt complexes will be incorporated into molecular-based hybrid photocathodes, forming the cathodic compartment of a standalone PEC for the overall WS. In addition to the intrinsic advantages brought by the use of molecular vs. material-based catalysts, the most innovative aspect of the project is represented by the incorporation of the catalysts into a super-aerophobic hydrogel, which will allow an easier release of the gas bubbles produced at the electrode surfaces.² The synthesised cobalt complexes can then be suitably functionalised, via ligand modification, in order to be cross-linked to the polymeric gel. In the wide range of cobalt complexes, cobaloximes have been identified as most interesting, as they have high efficiency in proton reduction, both electrochemically and photoelectrochemically when combined with suitable photosensitizers for visible light absorption.³

Aknowlegments

Thanks to the project financed with PNRR funds, within - Mission 4 Education and Research - entitled PHOTOGEN (PHOTOactive aerophobic hydroGels for hydrogEN generation in molecular-based photoelectrosynthetic cells, PRIN-2022AWXS83 "Photogen")

References

- [1] L. Clarizia, M. N. Nadagouda, D. D. Dionysiou, Curr. Opin. Green Sustain. Chem., **2023**, 41, 100825
- [2] Y. Kang, S. Lee, S. Han, D. Jeon, M. Bae, Y. Choi, D. Woong Lee, J. Ryu, Adv. Funct. Mater., **2023**, 2308827, 1-9
- [3] R. W. Hogue, O. Schott, G. S. Hanan, S. Brooker, Chemistry A European J, **2018**, 24 (39), 9820-9832

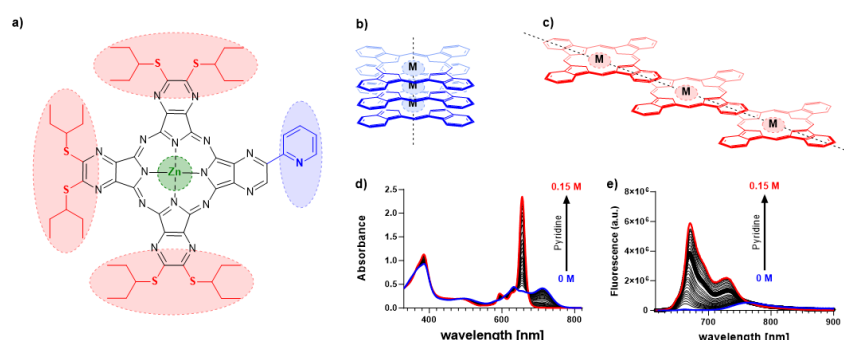
Self-assembly of tetrapyrazinoporphyrazines into J-aggregates

BEDNARIK, S.¹, DEMUTH, J.¹, NOVAKOVA, V.¹, ZIMCIK, P.¹,

¹ Department of Pharmaceutical Chemistry and Pharmaceutical Analysis, Faculty of Pharmacy
in Hradec Králové, Charles University, Czech Republic

e-mail: bednaris@faf.cuni.cz

Phthalocyanines (Pcs) are synthetic macrocyclic dyes composed of four isoindoline units linked by azomethine bridges, structurally close to porphyrins. Their extended 18 π -conjugated system endows them with unique photophysical properties, making them valuable in various applications such as fluorescence sensors and photosensitizers in photodynamic therapy (PDT).¹ However, these properties are primarily associated with the monomeric form of Pcs. Aggregation of Pcs is usually undesirable, as the planar Pc core tends to aggregate through π - π stacking interactions. The most common H-type aggregates (Figure b) align molecules in a sandwich-like arrangement, leading to increased absorption at blue-shifted wavelengths and significantly reduced fluorescence emission. In contrast, the unique J-aggregates (Figure c) result in red-shifted absorption bands and retain fluorescent properties.² In this study, we synthesized unsymmetrical Pc derivatives – tetrapyrazinoporphyrazines (Figure a) bearing one coordinating ligand (coordinating moiety, e.g., pyridyl) that formed slipped J-dimers upon coordination to the central cation of another Pc molecule in non-coordinating solvents (Figure d and e).



Aknowlegments

The study was supported by Charles University (GA UK 230723).

References

- [1] NOVAKOVA, V., *et al.*: Coord. Chem. Rev., 361, **2018**, 1-73.
- [2] DEMUTH, J., *et al.*: Inorg. Chem. Front., 12, **2025**, 1590-1608.

On the Mechanism of Photodriven Hydrogenations of N₂ and other substrates by Hantzsch Ester: Photoinduced generation of weak N–H pyridinyl bonds in the presence of a suitable buffer.

Elisabetta Benazzi^a, Christian Johansen^b, Jonas Peters^b

^a Department of Chemical Sciences, University of Padova, 35131 Padova, Italy

^b Division of Chemistry and Chemical Engineering, California Institute of Technology (Caltech), Pasadena, California 91125, United States

Hantzsch ester (HEH₂) has emerged as a valuable photoreductant in synthetic methodologies, but photodriven transfer hydrogenation reactions are generally limited to activated substrates. It was previously demonstrated that the addition of an organic buffer system comprising collidinium triflate ([ColH]OTf) and collidine (Col) enables photodriven transfer hydrogenation from HEH₂ to reduce N₂ to NH₃ (N₂R) in the presence of a Mo-catalyst.¹ This finding highlighted the significant driving force for proton-coupled electron transfer (PCET) generated by irradiating HEH₂ in the presence of Col-buffer (Figure 1).

Here, we expand on our initial findings, exploring the mechanistic and practical implications of Col-buffer in activating HEH₂ for efficient proton-coupled reductions. We show that varying the irradiation wavelength during N₂R confirms the necessity of HEH₂ excitation for NH₃ production. Additionally, while other buffer systems and dihydropyridines can support N₂R, the HEH₂ and Col-buffer combination is particularly privileged. Mechanistic studies reveal that HEH₂ forms a pre-complex with [ColH]OTf via hydrogen bonding, facilitating static quenching through electron transfer. Transient absorbance and EPR studies demonstrate that the resulting HEH₂^{•+} is rapidly deprotonated by Col to generate HEH[•]. Net irradiation of HEH₂ in the presence of Col/[ColH]OTf produces HEH[•] and ColH[•], both potent hydrogen-atom donors (Figure 1).

We further highlight the utility of this reagent combination in the photoreduction of diverse C=O and N=O π-bonds, where the presence of Col-buffer significantly enhances rates and yields. The observed reactivity aligns with ColH[•] being a highly potent PCET donor, characterized by a BDFEN–H of 28 kcal mol^{–1}. These findings pave the way for new strategies in photoreductions employing HEH₂ and Col-buffer systems.

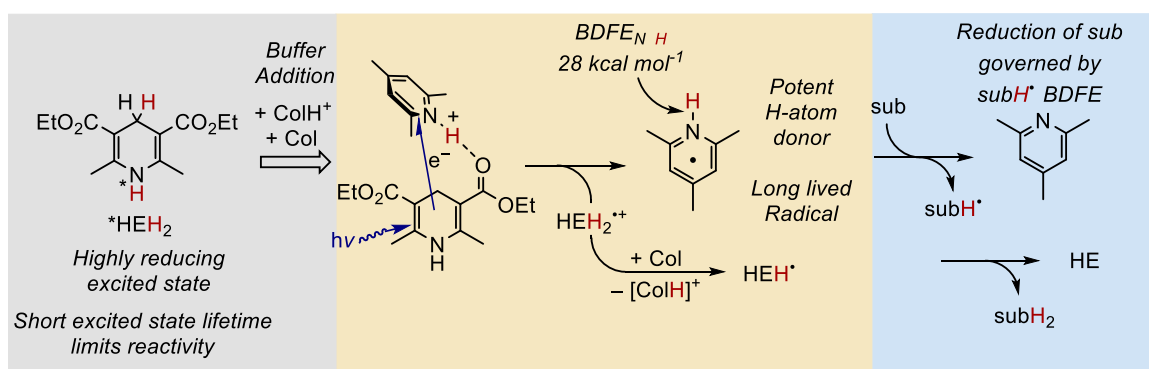


Figure 6. Mechanism behind production of HEH[•] and ColH[•], both potent hydrogen-atom donors functional for small molecule reduction, after net irradiation of HEH₂ in the presence of Col/[ColH]OTf.

References

- [1] J. Peters et al., *Science Advances*, **2022**, 8, 43: eade3510.

Developing Copper Vanadate for Enhanced Photoelectrochemical Performance

A. Bidarahalli¹, K. Berent¹, A. Podborska¹, K. Szaciłowski¹

¹Academic Centre for Materials and Nanotechnology, AGH University of Krakow, Mickiewicza 30, Krakow, 30–059 Poland. anagha@agh.edu.pl

Photoelectrochemical (PEC) studies on copper vanadate, a semiconductor material with unique optoelectronic properties [1, 2] is recently being explored for their potential applications in neuromorphic computing and synaptic. This study presents the synthesis, structural characterization (FTIR DRS, SEM) and photoelectrochemical characterization (KP, CA with light pulses) of different ratios of copper vanadate thin films. Optical and electrochemical analyses revealed a band gap about 2.3 eV, facilitating visible-light absorption. The best-performing films showed a photocurrent density of up to 4 $\mu\text{A cm}^{-2}$ under monochromatic light beam. The material demonstrates key synaptic behaviors such as paired pulses facilitation (PPF), spike-timing dependent plasticity (STDP), excitatory post-synaptic current (EPSC), driven by both electrical and optical stimuli.

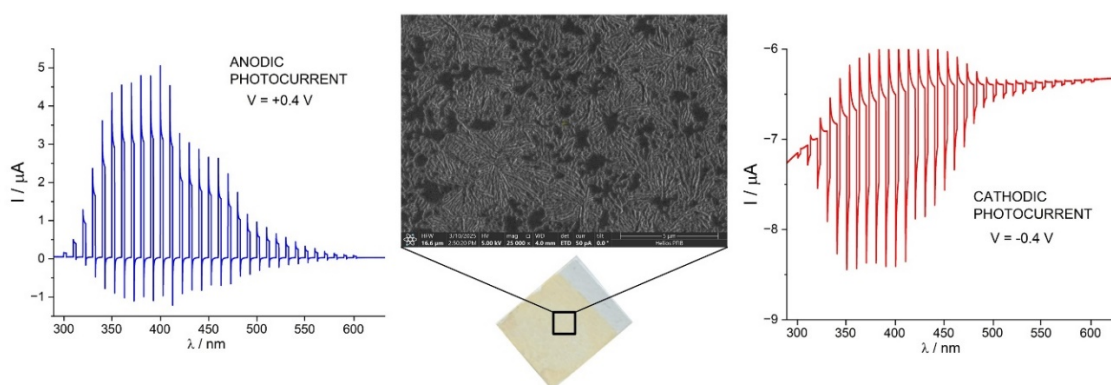


Figure 1. The layer of copper vanadate on ITO and its photocurrent spectra recorded on different potentials.

We have proven that our foils exhibit a photocurrent response over a wide potential range (900 to -500 mV) and for various wavelengths of incident light (300 to 600 nm) with PEPS (Photoelectrochemical Photocurrent Switching) effect. At positive potential, we observed an anodic photocurrent, whereas at a lower potential, a cathodic photocurrent which is characteristic of n-type and p-type semiconductors respectively. Our findings suggest that copper vanadate offers a robust platform for the development of next-generation, energy-efficient neuromorphic devices, capable of processing and storing information like our brain.

Acknowledgements: This research are supported by National Science Centre (Poland) with OPUS grant no. 2022/47/B/ST4/01420

References:

- [1] A. Hassan, T. Iqbal, M.B. Tahir, S. Afsheen, “A review on copper vanadate-based nanostructures for photocatalysis energy production”, *Int J Energy Res.* 2018; 1–20.
- [2] Jason A. Seabold and Nathan R. Neale, “All First Row Transition Metal Oxide Photoanode for Water Splitting Based on $\text{Cu}_3\text{V}_2\text{O}_8$ ”, *Chem. Mater.* 2015, 27, 1005–1013

Time-resolved infrared spectroelectrochemical studies of two rhenium naphthalimide complexes

J. Biddulph¹, M. Pižl^{2,3}, S. Bhattacharya⁴, P. Malakar⁴, F. Hartl³, M. T. Pryce¹

¹ School of Chemical Sciences, Dublin City University, Glasnevin, Dublin, D09 V289, Ireland

² Department of Inorganic Chemistry, UCT Prague, Technicka 5, Prague 6, 166 28, Czech Republic

³ Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6DX, UK

⁴ Central Laser Facility, Science & Technology Facilities Council, Research Complex at Harwell, Rutherford Appleton Laboratory, Didcot, OX11 0QX, UK

Presenting author e-mail: jack.biddulph3@mail.dcu.ie

Photocatalysis is the process by which a compound (photocatalyst) uses the energy absorbed from incident light to catalyse a reaction, CO₂ reduction for instance. Photocatalytic CO₂ reduction into its C1 synthons, widely reported for Re(α -diimine) tricarbonyl complexes, requires multiple electron transfer steps.¹ Time-resolved infrared (TRIR) spectroscopy can provide key structural and electronic insights into the excited-state(s) populated in these photocatalytic reduction processes. TRIR combined with spectroelectrochemistry (TRIR-SEC) was used to study the excited-state dynamics of the reduced species that are important intermediates in the electron transfer pathway for photocatalytic CO₂ reduction.^{2,3} The results of the TRIR-SEC studies will be presented, focusing on two Re(I) naphthalimide complexes, **Re-H** and **Re-EB** (Fig. 1), as the neutral photocatalyst precursors for photocatalytic CO₂ reduction.

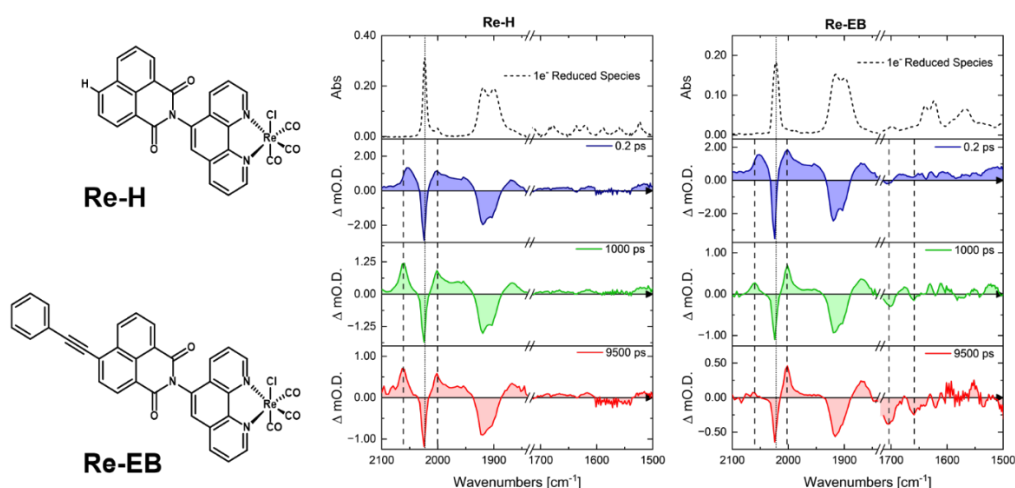


Figure 7. TRIR-SEC spectra of the 1e⁻ reduced species of **Re-H** and **Re-EB** in DCM following 420 nm excitation. The signals marked by the dashed lines indicate the concurrent population of MLCT-like (blue-shifted) and ILCT-like (red-shifted) excited-states.

References

- 1 H. Takeda, K. Koike, T. Morimoto, H. Inumaru and O. Ishitani, in *Advances in Inorganic Chemistry*, eds. R. van Eldik and G. Stochel, Academic Press, 2011, vol. 63, pp. 137–186.
- 2 J. J. A. Lozeman, P. Führer, W. Olthuis and M. Odijk, *Analyst*, 2020, **145**, 2482–2509.
- 3 J. E. Yarnell, J. C. Deaton, C. E. McCusker and F. N. Castellano, *Inorg. Chem.*, 2011, **50**, 7820–7830.

Diimine Ligands in Heteroleptic Cu(I) Complexes: A Path to Efficient Solar Energy Utilization

Claudia Bizzarri

Department of Chemical Science and Technologies, University of Rome "Tor Vergata"
Via della Ricerca Scientifica, 00133 Rome, Italy. Claudia.bizzarri@uniroma2.it

The modern challenge of harnessing solar light as a primary energy source is of great importance in the quest for sustainable energy solutions. Developing novel and efficient molecules that facilitate the conversion of solar energy to chemical energy is crucial.^[1] In this context, compounds based on earth-abundant materials are particularly valuable. Copper(I) complexes are highly appealing due to the abundance and low cost of copper.^[2] Heteroleptic Cu(I) complexes, which incorporate both diphosphine and diimine ligands, offer a promising approach to overcoming the Jahn-Teller distortion in the excited state. This excited state is primarily characterized by metal-to-ligand charge-transfer (MLCT) transitions. Our research focuses on chelating diimine ligands based on 1,2,3-triazoles and nitrogen-containing six-membered heterocycles. By varying the chromophoric part of the diimine ligand from pyridine to benzoquinoxaline, including quinoline and quinoxaline derivatives, we can cover the entire visible light spectrum for absorption. This versatility enables the fine-tuning of the photophysical and electrochemical properties of the complexes, optimizing them for various photochemical applications. These Cu(I) complexes have demonstrated their utility as light-antennae^[3a] and photosensitizers in photocatalytic CO₂ reduction.^[3b-d] Additionally, they serve as effective photocatalysts in atom-transfer radical addition (ATRA) reactions and in photoelectrochemical processes.^[4] Let us delve into the world of these heteroleptic Cu(I) complexes.

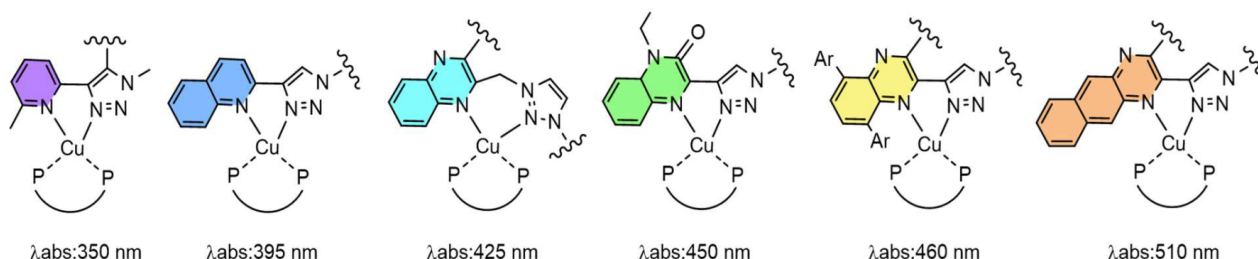


Figure 8. Schematic structures of the heteroleptic Cu(I) complexes and the influence of the diimine on the UV-vis absorption.

References

- [1] N. S. Lewis, *Science* **2016**, 351, aad1920 ; b) C. Bizzarri, *Eur. J. Org. Chem.* **2022**, e202200185;
- [2] (a) Y. Zhang, M. Schulz, M. Wächter, M. Karnahl B. Dietzek, *Coord. Chem. Rev.*, **2018**, 356, 127–146; (b) J. Beaudelot, S. Oger, S. Peruško, T.-A. Phan, T. Teunens, C. Moucheron G. Evano, *Chem. Rev.*, **2022**, 122(22), 16365–16609.
- [3] (a) Bruschi, C.; Gui, X.; Fuhr, O.; Kloppe, W.; Bizzarri, C. *Dalton Trans.*, **2023**, 52, 7809-7818 (b) L.-L., Gracia, Luci, L.; Bruschi, C.; Sambri, L.; Weis, P.; Fuhr, O.; Bizzarri, C. *Chem. Eur. J.*, **2020**, 26, 9929-9937; (c) Gracia, L.-L.; Barani, E.; Braun, J.; Carter, A. B.; Fuhr, O.; Powell, A. K.; Fink, K.; Bizzarri, C. *ChemCatChem*. **2022**, 14, e202201163; (d) Gracia, L.-L.; Henkel, P.; Fuhr, O.; Bizzarri, C. *Beilstein J. Org. Chem.* **2023**, 19, 1766-1775.
- [4] (a) Bruschi, C.; Gui, X.; Salaeh-arae, N.; Barchi, T.; Fuhr, O.; Lebedkin, S.; Kloppe, W.; Bizzarri, C. *Eur. J. Inorg. Chem.* **2021**, 4074; (b) Bruschi, C.; Gui, X.; Rauthe, P.; Fuhr, O.; Unterreiner, A.-N.; Kloppe, W.; Bizzarri, C. *Chem. Eur. J.*, **2024**, e202400765; (c) in preparation.



Theoretical X-ray spectroscopy and ultrafast dynamics in transition metal complexes

S.I. Bokarev^{a,b}

*Chemistry Department, School of Natural Sciences, Technical University of Munich, Lichtenbergstr. 4,
Garching 85748, Germany*

Institute of Physics, Rostock University, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany E-

mail: sergey.bokarev@tum.de

Transition metal complexes play an important role as catalysts and photoactive materials. Due to their complicated electronic structure, the interpretation of experiments often requires aid from the theoretical side. In my contribution, I will describe theoretical tools for the interpretation of various kinds of spectroscopic experiments: photon-in/photon-out (photon absorption, emission, and inelastic scattering) [1], as well as photon-in/electron-out (photoelectron [2,3] and Auger emission [4-6]) in XUV and X-ray photon energy ranges both in time and frequency domains. The list of systems and problems treated with these methods, among others, includes electron relay in photocatalytic water splitting systems [7], solvation and ion-ligand interactions, redox reactions, and aggregation effects in catalytically and biologically active transition metal complexes [1], as well as nuclear and electron dynamics triggered by light absorption [8-10].

References

1. S.I. Bokarev, O. Kühn, *WIREs Comp. Mol. Sci.* **2020**, 10, e1433.
2. T. Marx, S.I. Bokarev *Phys. Rev. A* **2022**, 106, 032806.
3. T. Marx, S.I. Bokarev *J. Chem. Phys.* **2025**, 162.
4. G. Grell, S.I. Bokarev *J. Chem. Phys.* **2020**, 152, 074108.
5. B. Tenorio et al. *J. Chem. Theory Comput.* **2022**, 18, 4387.
6. E. Pelimanni, A.E.A. Fouda, P.J. Ho, T.M. Baumann, S.I. Bokarev, A. De Fanis, S. Dold, G. Grell, I. Ismail, D. Koulentianos, T. Mazza, M. Meyer, M. N. Piancastelli, R. Püttner, D.E. Rivas, B. Senfftleben, M. Simon, L. Young, G. Doumy, *Commun. Phys.* **2024**, 7, 341.
7. A. Britz, S.I. Bokarev, T.A. Assefa, É. Bajnóczi, Z. Németh, G. Vankó, N. Rockstroh, H. Junge, M. Beller, G. Doumy, A.M. March, S.H. Southworth, S. Lochbrunner, O. Kühn, C. Bressler, W. Gawelda *ChemPhysChem* **2021**, 22, 693–700.
8. V. Kochetov, S.I. Bokarev *J. Chem. Theory Comput.* **2022**, 18, 46.
9. T. Romig, V. Kochetov, S.I. Bokarev *J. Chem. Phys.* **2023**, 159, 114108.
10. X. Mi, M. Zhang, L. Zhao, Zh. Liang, R. Peng, Zh. Guo, S.I. Bokarev, Zh. Li *J. Chem. Theory Comput.* **2025**, 21, 549-559.



Excited-State Dynamics in Cobalt(III) Polypyridyl Complexes

Olga B. Bokareva^{a,b}, Sebastian Mai^c, Leticia González^{c,d}

^a Leibniz Institute for Catalysis (LIKAT), Albert-Einstein-Str. 29A, 18057 Rostock, Germany

^b Institute of Chemistry and Department of Life, Light and Matter, University of Rostock, Albert-Einstein-Str. 27 and 25, 18057 Rostock, Germany

^c Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger Str. 17, 1090 Vienna, Austria

^d Research Platform on Accelerating Photoreaction Discovery (ViRAPID), University of Vienna, Währinger Strasse 17, 1090 Vienna, Austria

E-Mail: olga.bokareva@catalysis.de

Recent advances in ligand-field photocatalysis, especially with cobalt(III) polypyridyl complexes, have revealed unprecedented excited-state reactivity. Notably, ground-state recovery dynamics in these systems operate within the Marcus inverted region [1,2], a significant deviation from behavior typically observed in other first-row transition metal complexes, such as isoelectronic iron(II) systems. Iron complexes show normal Marcus behavior, where the increase in excited-state energy leads to a faster rate of excited-state decay. In contrast, cobalt(III) polypyridyl complexes follow inverted Marcus behavior, with the driving force exceeding the reorganization energy. This regime allows simultaneous enhancement of redox potential and excited-state lifetime, opening opportunities for light-to-chemical energy conversion, such as activation of oxidatively resistant substrates in photoredox catalysis.

Here, we investigate the early evolution of excited electronic states in the prototypical cobalt(III) tris(2,2'-bipyridine) complex, a model for broader studies in this area. We recapitulate key aspects of constructing a diabatic Hamiltonian (3) using the linear vibronic coupling model to describe excited-state dynamics within the ligand-field manifold. Next, we assess how accurately long-timescale behavior can be extrapolated from short-time nonadiabatic simulations. Finally, we compare deactivation mechanisms of excited states in the cobalt complex with those of its better-studied noble-metal analog, ruthenium(II) tris(2,2'-bipyridine), and evaluate ground-state recovery times against available experimental data. These results offer theoretical insight into ultrafast dynamics in cobalt complexes and support their future development in sustainable photochemistry.

Acknowledgments

O.S.B. gratefully acknowledge financial support through SPP 2102 (KU 952/12-2), project no. 404479188, and GRK 2943 "Spectroscopic Tools for Challenging Reduction Reactions: Catalytic Coupling of CO₂", project no. 507189291.

References

- [1] A. Y. Chan, A. Ghosh, J. T. Yarranton, J. Twilton, J. Jin, D. M. Arias-Rotondo, H. A. Sakai, J. K. McCusker, D. W. C. MacMillan. *Science* **2023**, 382, 191–197.
- [2] A. Ghosh, J. T. Yarranton, J. K. McCusker. *Nature Chemistry* **2024**, 16, 1665–1672.
- [3] D. Farkhutdinova, S. Polonius, P. Karrer, S. Mai, L. González. *J. Phys. Chem. A* **2025**, 129 (10), 2655–2666.

Investigating Anti-Kasha dynamics with quantum-mechanically derived force-fields and non-adiabatic molecular dynamics.

J. T. Casanova,¹ S. Giannini,² G. Prampolini,² A. Monari,³ A. Cannizzo¹

¹ Institute of Applied Physics, University of Bern, Bern, Switzerland. ² Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Area della Ricerca del CNR, Via Moruzzi 1, I-56124 Pisa, Italy ³ Université Paris Cité and CNRS, ITODYS, Paris, France; jakob.casanova@unibe.ch

It was recently reported that Pt quinoxdt dithiolene complexes show a photochemical response, which markedly depends on the excitation wavelength revealing an anti-Kasha (AK) behavior. AK response originates from a competition between the functional process in upper photo-excited states and internal conversion towards the lowest excited state of a given multiplicity. Experimental evidence shows that internal conversion, which is typically a few femtoseconds, is in these systems astonishingly slowed down to 1-2 ps.^[1]

In addition, the excitation to higher excited states allows the molecular system to access long-lived conformational configurations not accessible from the lowest excited state. Such systems have raised considerable interest because of the possibility to conceive multi-response molecular devices or to explore novel photochemical routes. This rich body of experimental evidence motivated us to start a computational study based on time-dependent density functional theory aimed at clarifying several unanswered questions: the cause of such low efficient internal conversion, illustrating the complete photocycle including possible intermediated states, revealing is the structure of the long-lived configuration.

In this contribution, we will explore the excited state dynamics using two complementary approaches: Surface Hopping including Arbitrary Couplings (SHARC)^[2] and quantum-derived force field Joyce^[3]. The former allows for tracking down non-adiabatic molecular dynamics of the earliest moments after excitation (for instance Figure 9 shows the total singlet and triplet state population from different excited states). The latter will allow us to explore longer time scales and adopt a statistical approach.

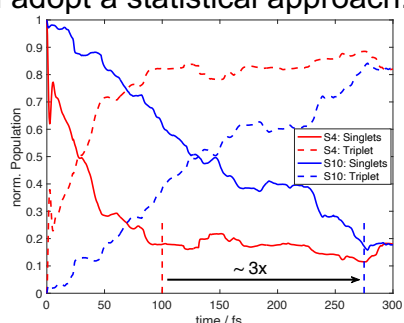


Figure 9: Non adiabatic molecular dynamics from states S4 and S10, grouped by total Singlet and Triplet populations, calculated by SHARC. According to experimental and computational evidence, the excitation of S4 and S10 induce Kasha and anti-Kasha responses from the system, respectively. The latter is evident from the remarkable extension of the single states population.

- [1] M. Gazzetta, F. Artizzu, S. S. Attar, L. Marchio, L. Pilia, E. J. Rohwer, T. Feurer, P. Deplano, A. Cannizzo, *The journal of physical chemistry. A* **2020**, 124, 10687-10693;
- [2] Mai, S.; D. Avagliano, M. Heindl, P. Marquetand, M.F.S.J. Menger, M. Oppel, F. Plasser, S. Polonius, M. Ruckebauer, Y. Shu, D.G. Truhlar, L. Zhang, P. Zobel, L. González. *SHARC3.0: Surface Hopping Including Arbitrary Couplings: Program Package for Non-Adiabatic Dynamics*, 2023; <https://sharc-md.org/>.
- [3] Cerezo, J., Prampolini, G. and Cacelli, I. *Theoretical Chemistry Accounts*, 137, 80 (2018).

Exploring substituents effects on the anti-Kasha reactivity of binuclear Ru(II) photosensitizers

N. Chantry,^a A. Cotic,^{b,c} S. De Kreijger,^a B. Elias,^a L. Troian-Gautier,^{a,d} * A. Cadranel^{b,c,e,f} *

^a Université catholique de Louvain (UCLouvain), Institut de la Matière Condensée et des Nanosciences (IMCN), Molecular Chemistry, Materials and Catalysis (MOST), Place Louis Pasteur 1, bte L4.01.02, 1348 Louvain-la-Neuve, Belgium, noemie.chantry@uclouvain.be

^b Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Química Inorgánica, Analítica y Química Física, Pabellón 2, Ciudad Universitaria, C1428EHA, Buenos Aires, Argentina.

^c CONICET – Universidad de Buenos Aires, Instituto de Química-Física de Materiales, Medio Ambiente y Energía (INQUIMAE), Pabellón 2, Ciudad Universitaria, C1428EHA, Buenos Aires, Argentina.

^d Wel Research Institute, Avenue Pasteur 6, 1300 Wavre, Belgium

^e Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Physical Chemistry I, Egerlandstr. 3, 91058, Erlangen, Germany.

^f Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Interdisciplinary Center for Molecular Materials, Egerlandstr. 3, 91058, Erlangen, Germany.

Solar energy conversion is at the basis of life on Earth through natural photosynthesis. Therefore, chemists tried over the last decades to reproduce it. However, a caveat in natural or artificial photosynthesis is that excited-state population by photon absorption is often accompanied by 20-30% energy loss through vibrational relaxation (VR) and internal conversion (IC).^[1] Thus, the reactive excited state is lower in energy than the one initially formed by photon absorption. Anti-dissipative strategies were postulated to prevent these energy losses or slow down the timescale at which they take place, allowing to trap high-energy excited states useful for photoredox catalysis.

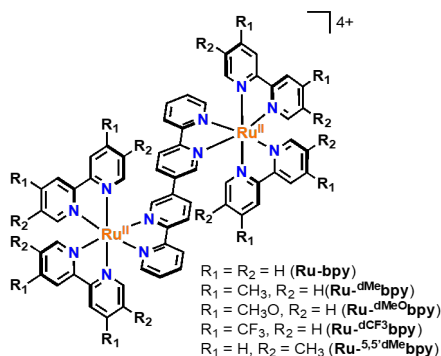


Figure 10: Structure of the complexes

To mediate those VR and IC processes, Kasha's rule needs to be circumvented by decreasing the electronic coupling between excited states. Previous work from our groups focusing on binuclear and trinuclear Ru(II) photosensitizers has highlighted that an anti-dissipative behavior could be achieved by carefully controlling the topology of the ligand bridging the different Ru(II) centers (**Figure 1**). All-*meta* (5,5') connections led to photosensitizers that exhibited an Anti-Kasha behavior while photosensitizers with *para* (4,4') connections behaved like conventional [Ru(bpy)₃]²⁺ photosensitizers.^[2]

In this study, we investigated other factors that could impact the anti-dissipative behavior while keeping the weak electronic coupling scenario provided by the bridging 2,2':5',3'':6'';2'''-quaterpyridine scaffold. Substituents were added on the ancillary 2,2'-bipyridine ligands to influence the energy level of the later *vis-à-vis* the bridging ligand. These changes were investigated using classical spectroscopy methods, (spectro)electrochemistry as well as more advanced nanosecond and femtosecond transient absorption spectroscopy (nsTAS and fsTAS, respectively). This study allowed us to unambiguously identify the precise nature of high-energy excited states, and derive design guidelines for the achievement of anti-dissipative behavior in oligomeric Ru(II) polypyridines relevant for photoredox catalysis.

References

- [1] D. Gust, D. Kramer, A. Moore, T. A. Moore and W. Vermaas, *MRS Bull.*, **2008**, 33, 383-387
- [2] A. Cotic, S. Cerfontaine, L.D. Slep, B. Elias, L. Troian-Gautier and A. Cadranel, *J. Am. Chem. Soc.*, **2023**, 145, 5163-5173.

Dual Photoreactive Ternary Ruthenium(II) Terpyridyl Complexes: A Comparative Study on Visible Light-induced Single-step Dissociation of Bidentate Ligands and Generation of Singlet Oxygen

P. Chatterjee, and A. K. Patra*

^a Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, Uttar Pradesh 208016, India, E-mail: prithac20@iitk.ac.in, akpatra@iitk.ac.in

In this work, we have introduced a phenyl-terpyridine (ptpy) ligand in octahedral Ru(II) core of [Ru(ptpy)(L-L)Cl]⁺ to induce structural distortion for possible photorelease of electronically distinct bidentate ligands (L-L).^{1,2,3} For a systematic study, we designed four Ru(II) polypyridyl complexes: [Ru(ptpy)(L-L)Cl](PF₆), ([1]-[4]), where L-L = 1,2-Bis(phenylthio)ethane (SPH) [1], *N,N,N',N'*-Tetramethylethylenediamine (TMEN) [2], *N1,N2*-Diphenylethane-1,2-diimine (BPEDI) [3] and Bis[2-(diphenylphosphino)phenyl]Ether (DPE-Phos) [4]. The detailed photochemical studies suggest single-step dissociation of L-L from bis-thioether (SPH) complex [1] and diamine (TMEN) complex [2], while no photosubstitution was observed for [3] and [4]. Complex [1] and [2] demonstrated a dual role, involving both photosubstitution and ¹O₂ generation, while [3] and [4] solely exhibited poor to moderate ¹O₂ production. The interplay of excited states leading to these behaviors was rationalized from the lifetimes of the ³MLCT excited states using transient absorption spectroscopy, suggesting intricate relaxation dynamics and ¹O₂ generation upon excitation. Therefore, the photolabile complexes [1] and [2] potentially could act as dual photoreactive agents via photo-triggered release of L-L (PACT) and/or ¹O₂-mediated PDT mechanisms, while [4] primarily can be utilized as PDT agent.

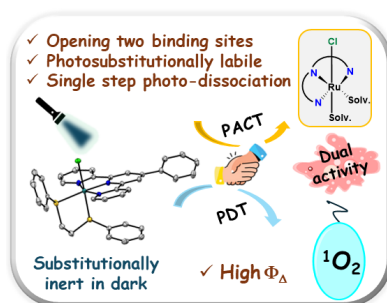


Figure 1. Schematic representation depicting the dual functional activity of the complex upon light exposure.

References

- [1] S. Bonnet, *J. Am. Chem. Soc.* **2023**, 145, 23397-23415.
- [2] B. S. Howerton, D. K. Heidary, E. C. Glazer, *J. Am. Chem. Soc.* **2012**, 134, 8324-8327.
- [3] P. Chatterjee, R. Mishra, S. Chawla, A. K. Sonkar, A. K. De, A. K. Patra, *Inorg. Chem.* **2024**, 63 (32), 14998-15015.

Characteristics of Relaxations for Low-Energy Triplet Excited States of $[\text{Ru}(\text{tpm})(\text{prbim})(\text{L})]^{2+}$ Ions ($\text{L} = \text{NH}_3$ and CH_3CN): Density Functional Modeling and Efficient Metal Center State Quenching Mechanisms

Jie-Ying Chen,^a Li-Chin Yin,^a Ming-Kang Tsai^b and Yuan Jang Chen^a

^aDepartment of Chemistry, Fu Jen Catholic University, Taipei, Taiwan E-mail: 411048041@mail.fju.edu.tw

^bDepartment of Chemistry, National Taiwan Normal University, Taipei, 11677, Taiwan

We synthesized the photoinduced quenching complexes, $[\text{Ru}(\text{tpm})(\text{prbim})(\text{L})]^{2+}$ ($\text{L} = \text{NH}_3$ and CH_3CN), to explore the excited-state relaxations between triplet metal-to-ligand charge-transfer ($^3\text{MLCT}$) and metal-center (^3MC) states, where prbim and tpm are N,N'-propylene-protected 1H, 1'H-2,2'-biimidazole and tris-(1-pyrazolyl)methane, respectively. The observed parameters of the complexes include electrochemical properties, room temperature absorption spectra and the absence of 77K phosphorescence signal. Additionally, we built a computational model as an aid. The $[\text{Ru}(\text{tpm})(\text{prbim})(\text{L})]^{2+}$ complexes did not present a reduction wave of the coordinated prbim moiety in the low cathodic wave region, this phenomenon should be attributed to the fact that the π^* -orbitals of prbim and tpm ligands have too high reduction energy. In this study, the 77K emission spectra of the target complexes were too weak to be detected, and we sought to determine the reasons for this phenomenon. The time-dependent light exposure of the RT absorption spectra for $[\text{Ru}(\text{tpm})(\text{prbim})(\text{NH}_3)]^{2+}$ show a transformation into those of $[\text{Ru}(\text{tpm})(\text{prbim})(\text{AN})]^{2+}$, and the ^3MC states (triplet d-d excited state characters) of DFT modeling of the complex supports the observed quenching mechanism. Furthermore, the DFT modeling of $[\text{Ru}(\text{tpm})(\text{prbim})(\text{NH}_3)]^{2+}$ suggests a possible mechanism of $^3\text{MLCT} \rightarrow ^3\text{MC}$ by adjustments in metal-ligand bond lengths.

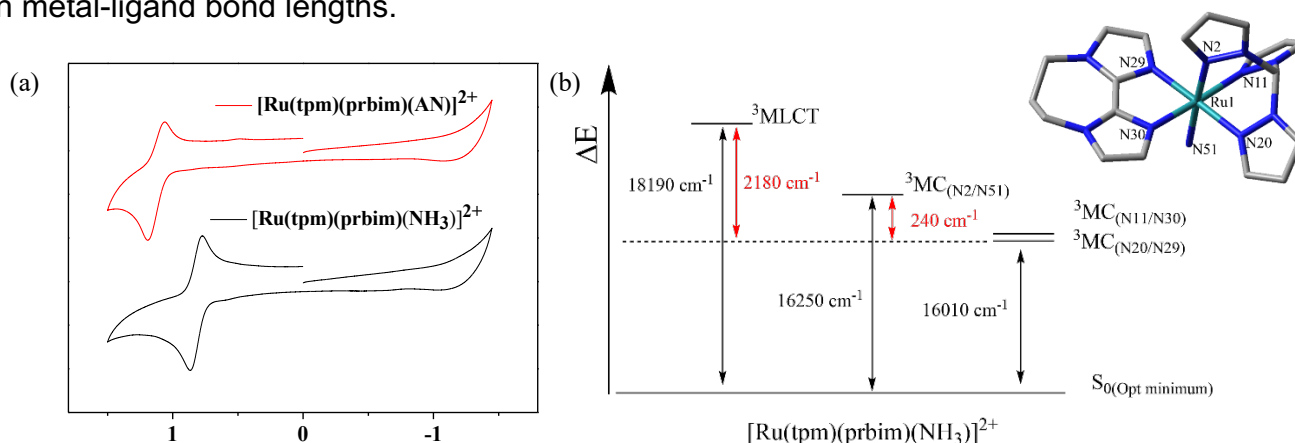


Figure 11. Left panel: Cyclic voltammograms (CV) of the target complexes do not exhibit reduction wave and show the oxidation wave for $\text{Ru}^{2+/3+}$; right panel: The Jablonski diagram illustrates the excited-state relaxation processes and energy gap between the $^3\text{MLCT}$ and ^3MC states for $[\text{Ru}(\text{tpm})(\text{prbim})(\text{NH}_3)]^{2+}$, and suggests a possible mechanism of $^3\text{MLCT} \rightarrow ^3\text{MC}$.

Aknowlegments

This work was funded by the National Science and Technology Council (Taiwan, ROC) through Grants 112-2113-M-030-004 and 113-2113-M-030-006.

The Extremely Slow Radiative-Rate Constant of Phosphorescent Ru- (Monodentate Aromatic-Ligand) Chromophore: ADF Modeling and Spin- Orbit Coupling Mediated Intensity Stealing Mechanics

Yuan Jang Chen,^a John F. Endicott^b and Ming-Kang Tsai^c

^a Department of Chemistry, Fu-Jen Catholic University, Taiwan R.O.C. 054971@mail.fju.edu.tw

^b Department of Chemistry, Wayne State University, Detroit, MI, USA

^c Department of Chemistry, National Taiwan Normal University, Taiwan R.O.C.

The 77 K observations and computational modeling of Ru-bpy and Ru-pz phosphorescent chromophores in $[\text{Ru}(\text{NH}_3)_4(\text{bpy})]^{2+}$ ¹⁻³ and $[\text{Ru}(\text{NH}_3)_5(\text{pz})]^{2+}$ ³⁻⁴ ions were characterized in our earlier work, where bpy and pz refer to 2,2'-bipyridine and pyrazine, respectively. Their 77 K phosphorescence quantum yields (radiative rate constants) [emission energy maxima], $\phi_{\text{em(p)}} (k_{\text{RAD(p)}}) [h\nu_{\text{em(max)}}]$, are 5.5×10^{-4} (12 ms^{-1}) [12400 cm^{-1}] and 0.5×10^{-4} (0.8 ms^{-1}) [11720 cm^{-1}] for $[\text{Ru}(\text{NH}_3)_4(\text{bpy})]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5(\text{pz})]^{2+}$, respectively. The fifteen-fold difference in the $k_{\text{RAD(p)}}$ ratio between $[\text{Ru}(\text{NH}_3)_4(\text{bpy})]^{2+}$ and $[\text{Ru}(\text{NH}_3)_5(\text{pz})]^{2+}$ ions in the Near-IR region must fundamentally be attributed to the striking difference in SOCM-IS contributions, where SOCM-IS refers to spin-orbit coupling mediated intensity stealing from low-energy certain singlet states.⁵⁻⁶ The results of ADF modeling with and without SOC perturbations for two target complexes indicate that the very low SOC amplitude between the intense singlet state ($S_{3(\text{T})}$) and triplet emitting state (T_e) at triplet geometry for $[\text{Ru}(\text{NH}_3)_5(\text{pz})]^{2+}$ has very low SOCM-IS contributions, which contrasts with those for $[\text{Ru}(\text{NH}_3)_4(\text{bpy})]^{2+}$ (see Figure 1), where ADF refers to the Amsterdam Density Functional system.

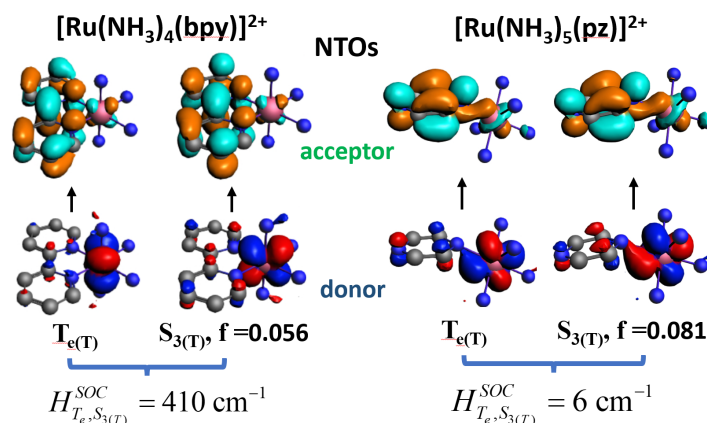


Figure 1. Comparisons of calculated SOC amplitudes between triplet emitting- (T_e) and most intense $S_{3(\text{T})}$ states for $[\text{Ru}(\text{NH}_3)_4(\text{bpy})]^{2+}$ (left) and $[\text{Ru}(\text{NH}_3)_5(\text{pz})]^{2+}$ (right) ions. The natural transition orbitals (NTOs) of T_e and $S_{3(\text{T})}$ at the triplet geometry, obtained from ADF modeling for both ions, display the characteristics of metal-to-ligand charge-transfer, and indicate that the SOC configurations of T_e and $S_{3(\text{T})}$ represent the different donor-Ru($d\pi$) orbital for $[\text{Ru}(\text{NH}_3)_4(\text{bpy})]^{2+}$ and the nearly identical composition of donor-Ru($d\pi$) orbital for $[\text{Ru}(\text{NH}_3)_5(\text{pz})]^{2+}$.

References

- [1] R. A. Thomas et al., *J. Phys. Chem. B* **2015**, 119, 7393.
- [2] R. L. Lord et al., *Inorg. Chem.* **2013**, 52, 1185.
- [3] C. N. Tsai et al., *Inorg. Chem.* **2016**, 55, 7341
- [4] C. N. Tsai et al. *Inorg. Chem.* **2015**, 54, 8495
- [5] B. J. Powell, *Coord. Chem. Rev.* **2015**, 295, 46
- [6] C. M. Marian, *Comput. Mol. Sci.* **2012**, 2, 187



Structure – Properties Relationships in Coordination Complexes of *N,N'*-Disubstituted Amidine Oxide (AMOX) Ligands

M. Lepage,^{1,2} V. A. Montañez Valderrama,^{1,2} E. Lamothe,³ J. Castro,³
G. S. Hanan,³ M. Cibian^{1,2,3}

¹*Department of Biochemistry, Chemistry, Physics and Forensic Science, Université du Québec à Trois-Rivières, Trois-Rivières, QC, G9A 5H7, Canada.*

²*Hydrogen Research Institute, Université du Québec à Trois-Rivières, Trois-Rivières, QC, G9A 5H7, Canada.*

³*Department of Chemistry, Université de Montréal, Montréal, QC, H2V 0B3, Canada.
E-mail: mihaela.cibian@uqtr.ca*

The coordination compounds of amidine oxide (AMOX) ligands present interesting photophysical,[1] redox, and magnetic properties,[2] granting further developments toward functional materials and their potential application in optoelectronic devices and catalysis.

Structure-properties relationships were determined in series of complexes of the same metal but with different AMOX ligand substitution pattern, reflecting the important role of ring substituents and their electronic and steric effects. The type of substituents determines the degree of electron-density delocalization within the chelate ring and onto the ligand, allowing the modulation of the σ -donation, π -donation, and π -acceptance capacity, with direct effect on the metal-ligand interaction, and hence on the properties of the complex.

The examples of AMOX family of cobalt(II) and zinc(II) complexes are given.[1-2] The Co(AMOX)₂ series is relevant with respect to the prediction and control of stereochemistry and spin-states in tetra-coordinated transition metal complexes. The isomerization from square-planar (low-spin) to tetrahedral (high-spin) coordination geometry is observed for this class of compounds, and it was shown that in solution of non-coordinating solvents (e.g. dichloromethane) the equilibrium of the isomerization process is controlled by the nature of the substituents. Additionally, within the Zn(AMOX)₂ family, the type of functional groups on the ligands determines the presence/absence of aggregation induced emission (AIE) properties of the compounds.

Acknowledgments

We are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC), Mitacs, the Québec Center for Advanced Materials (QCAM), the Hydrogen Recherche Institute, the Université du Québec à Trois-Rivières (UQTR), and the Université de Montréal for financial support. We also thank the Department of Biochemistry, Chemistry, Physics, and Forensic Science at UQTR and the the Department of Chemistry at Université de Montréal.

References

- [1] M. Cibian *et al.*, *Eur. J. Inorg. Chem.*, **2018**, 4322
- [2] M. Cibian *et al.*, *Chem. Eur. J.*, **2015**, 21, 9474

Efficient Ferredoxin Reduction by Red-Light Generated Silicon Phthalocyanine Radicals

Author list: Y. Seymen¹, G. Knör², B. S. Sesalan³, S. T. Clausing⁴

Affiliations:

¹Department of Environmental Health, Research Unit Environmental Simulation, Helmholtz Munich, Neuherberg, Germany

²Department of Environmental Technology, Magistrate Linz, A-4041 Linz, Austria

³Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry, Maslak, Istanbul, Turkey

⁴Johannes Gutenberg University, Duesbergweg 10-14, 55128 Mainz, Germany, simon.clausing@uni-mainz.de

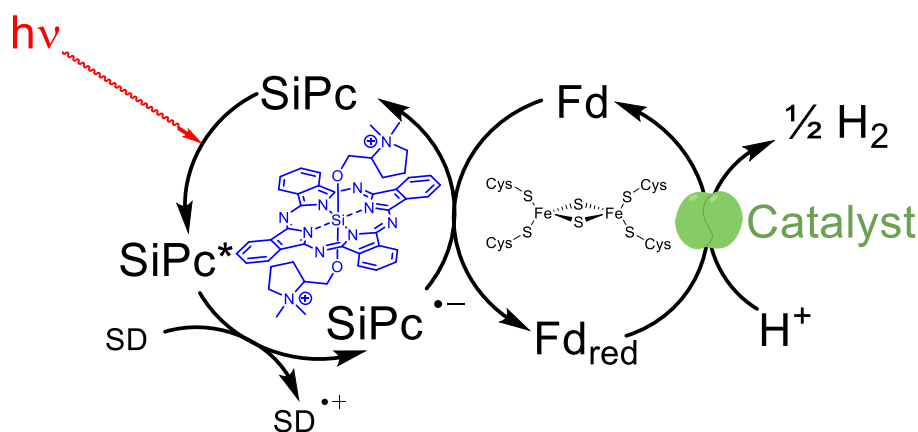


Figure 12. Envisioned photocatalytic cycle

The Silicon Phthalocyanine derivative SiPc (**Figure 1**) absorbs low-energy red light and, in the presence of a sacrificial electron donor (SD), generates the radical anion SiPC^{•-}. This species has been extensively characterized in a previous study.^[1] In this work, further properties of the radical were elucidated, like its significant stability with a half-life of 30 min in aqueous solution. Following this, a system was developed and optimized to efficiently reduce ferredoxin (Fd). Reduced Fd can be reoxidized and reduced again in the same vessel, showing the potential of the system to accumulate high-energy reductants under mild conditions (red light, neutral pH) in analogy to natural photosynthesis.

The thus obtained Fd_{red} could then be used with various catalysts (hydrogenase or cobaloxime^[2]) to generate e.g. hydrogen at any point, as it is remarkably stable in the chosen conditions.

Acknowledgments

The authors would like to thank Vincent Artero for providing cobaloxime samples.

References

- [1] C. Uslan et al., *Chem. Commun.*, 2013, **49**, 8108–8110
- [2] S. R. Soltan et al., *Chem. Commun.*, 2015, **51**, 10628–10631

Multiple Photoinduced Charge Separation in Covalent Molecular Triads: Insights from DFT

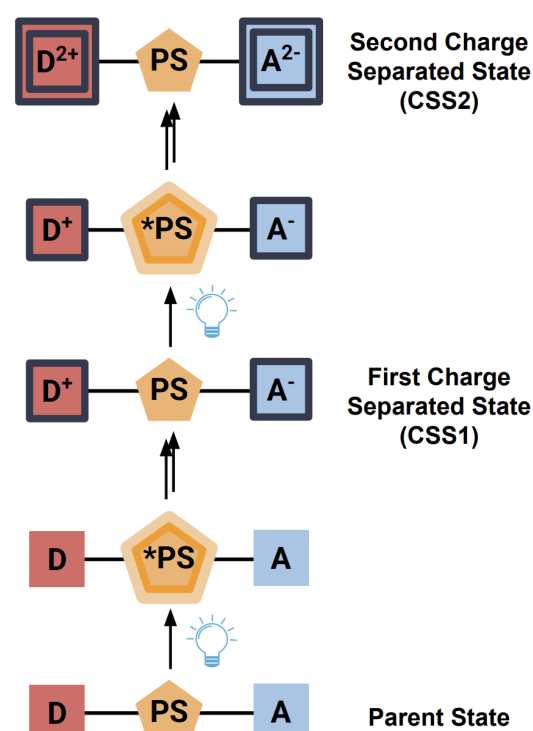
N. ISSOT, I. M. Dixon

Laboratoire de Chimie et Physique Quantiques, CNRS/Université de Toulouse
nicolas.issot@univ-tlse3.fr

Efficient solar energy conversion is a major challenge in relation with climate change, which requires to stop using fossil fuels as primary energy sources. One solution to this problem is the development of solar fuels, among which, dihydrogen can be obtained through water photolysis[1].

A key concept in this reaction, which requires the formal exchange of four electrons, is photoinduced electron transfer (PET). While this process is well understood for a single charge separation in donor-photosensitizer-acceptor (**D-PS-A**) triads, systems allowing the separation of two charges are uncommon[2], and no covalent non biological **D-PS-A** triad able to undergo double PET has been yet reported in the literature. The current challenge and the purpose of our work is to better understand multi-electron processes in these systems.

The initial design of covalent molecular triads **D-PS-A** takes advantage of potential inversion[3], a phenomenon that is observed only with certain types of two-electron donors and acceptors, for which the second redox process is less demanding than the first one, mostly due to structural variations. The photosensitizers used are earth-abundant high-potential molybdenum complexes[4]. The desired double photoinduced charge separation process is shown on Scheme 1.



Scheme 1: molecular **D-PS-A** triad and its Charge Separated States (CSS1 and CSS2) populated through sequential PETs

Our theoretical analysis of these systems is based on thermodynamic data, such as standard potentials or Gibbs energies obtained through DFT-based methods, as well as on the determination of reaction pathways for charge separation and recombination, both thermal and photochemical, using Nudged Elastic Band (NEB), time-dependent DFT (TD-DFT), and spin-flip TD-DFT calculations. This poster discuss about initial triad designs and future guidelines established during my first year of PhD.

References

- [1] J. H. Alstrum-Acevedo, M. K. Brennaman, T. J. Meyer, *Inorg Chem.*, **2005**, 44, 6802-6827
- [2] J. Nomrowski and O. S. Wenger; *J. Am. Chem. Soc.*, **2018**, 140, 5343-5346
- [3] D. H. Evans; *Chem. Rev.* **2008**, 108, 2113-2144
- [4] W. R. Kitzmann et al; *J. Am. Chem. Soc.*, **2023**, 145, 16597-16609

Photochemical Behavior Of Ruthenium(II) Complexes In Choline Geranate (CAGE) Ionic Liquids

M. Costa Verdugo^{1,2}, V. Martínez-Martínez³, L. Salassa^{1,2,4}

¹ Donostia International Physics Center, Paseo Manuel de Lardizabal 4, Donostia, 20018, Spain

² Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia, Kimika Fakultatea, Euskal Herriko Unibertsitatea UPV/EHU, Paseo Manuel de Lardizabal 3, Donostia, 20018, Spain

³ Departamento de Química Física, Universidad del País Vasco UPV/EHU, Apartado 644, Bilbao, 48080, Spain

⁴ Ikerbasque, Basque Foundation for Science, Bilbao, 48011, Spain marta.costa@dipc.org

In this study, we investigate the photophysical and photochemical behavior of three model ruthenium(II) polypyridyl compounds: [Ru(bpy)₃]²⁺ (**1**), [Ru(bpy)₂(py)₂]²⁺ (**2**), and [Ru(tpy)₂]²⁺ (**3**) in water¹ and in unconventional solvents, such as the ionic liquid choline geranate (CAGE IL).

CAGE ILs, composed of choline and geranic acid, have been widely studied for their ability to enhance transdermal, subcutaneous, and oral drug delivery, effectively facilitating the release of antiviral, anticancer, and antifungal drugs without exhibiting in vivo toxicity.²

Herein, UV-Vis spectroscopy was employed to analyze the absorbance of **1–3** before and after irradiation with blue and green light at varying time intervals. In water, only **2** exhibited significant photoactivity, whereas in CAGE IL, both **1** and **2** underwent photoinduced ligand dissociation.³ Compound **3** remained photochemically inactive in both solvents. The influence of CAGE IL concentration in aqueous mixtures was also evaluated, revealing its critical role in the photoreactivity of **1**. Computational studies (DFT) indicated that photoactivity of **1** in CAGE IL originated from the stabilization of the ³MC (metal-centered) state. Additional experiments, including NMR analysis, emission spectroscopy, lifetime measurements, and quantum yield determinations completed the photophysical characterization of **1** in CAGE IL compared to water.

These findings provide insights into the impact of CAGE IL on the photoactivity and stability of ruthenium-based compounds, with potential implications for photochemotherapy and photocatalysis.

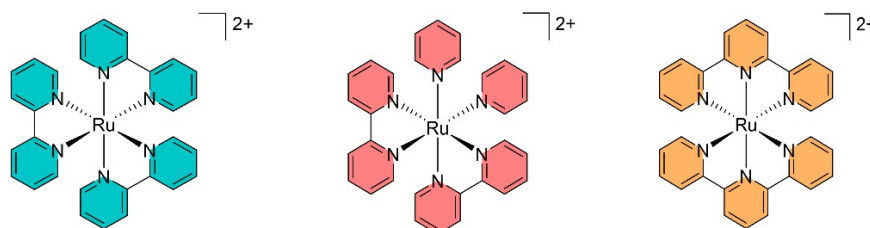


Figure 1. Structure of the ruthenium compounds used in this study

Aknowlegments

The authors thank the Spanish State Research Agency (Grant PID2022-139267OB-I00). DIPC was supported by the “Severo Ochoa” Programme for Centres of Excellence in R&D (MINECO, CEX2018-000867-S).

References

- [1] C. Garino, A. Terenzi, G. Barone, L. Salassa, *J. Chem. Educ.*, **2016**, 93, 292.
- [2] A. Banerjee, K. Ibsen, Y. Iwao, M. Zakrewsky, S. Mitragotri, *Adv. Healthc. Mater.* **2017**, 6, 1601411.
- [3] E. Borfecchia, C. Garino, L. Salassa, T. Rui, D. Gianolio, X. Zhang, K. Attenkofer, L. X. Chen, R. Gobetto, P. J. Sadler, C. Lamberti, *Dalton Trans.*, **2013**, 42, 6564.



Cr^{III} Complex–DNA Interaction as a Source of Induced Circularly Polarized Luminescence and Photodamage

Laura Cuevas^[a], Piedad Herrera^[b], Ana Belén Caballero^[b] and Juan-Ramón Jiménez^[a]

^[a] *Departamento de Química Inorgánica. Universidad de Granada, Avda. Fuente Nueva s/n, 18071, Granada, Spain.*

^[b] *Departamento de Química Inorgánica y Orgánica. Universidad de Barcelona, Carrer de Martí i Franquès, 1-11, 08028, Barcelona, Spain.*

lauracc@ugr.es

Circularly Polarized Luminescence (CPL) is gaining importance as a field of study due to the structural insights it provides into excited states of chiral chromophores, as well as its applications in biomedicine and materials science. Ideal chiral emitters should have (i) high chemical stability, (ii) a large dissymmetry factor (g_{lum}), and (iii) strong light absorption and emission properties. While organic and 4d/5d metal-based luminophores are relatively easy to prepare, they often show low g_{lum} due to dominant electric dipole transitions.¹ In contrast, 4f metal complexes can achieve high g_{lum} values, but they are costly and often labile in solution.² As an alternative, inert and cost-effective Cr^{III} based complexes displaying spin-forbidden photoluminescence (spin-flip) have demonstrated to be promising candidates in this field.³

Typically, generating CPL signals requires resolution of racemic mixtures into enantiopure compounds via techniques such as chiral chromatography or selective crystallization using chiral auxiliary ions. However, it has recently been observed that supramolecular association of racemic helices with DNA (intrinsically chiral) can induce important CPL signal.⁴ In this work, we present: (i) the induction of a strong and positive circularly polarized luminescence (CPL) signal in the 700–800 nm range upon association of the racemic [Cr(dqp)₂]Cl₃ complex (dqp = dqp = 2,6-di(quinolin-8-yl)pyridine) with calf thymus DNA (ct-DNA) in aqueous solution; and (ii) an investigation into the photoreactivity of both enantiomers and the racemic mixture of the complex with ct-DNA, motivated by the high photooxidation potential of the [Cr(dqp)₂]³⁺ excited state ($E[{}^*Cr(dqp)_2]^{3+}/[Cr(dqp)_2]^{2+} = 1.26$ V vs SCE).⁵

These results highlight the potential of such systems as probes for DNA binding, selective photoreactivity and/or as a strategy for developing new CPL-active materials without the need for laborious chiral resolution.

Acknowledgments

Thanks to the financial support from Projects C-EXP-140-UGR23 and PID2022-138090NB-C21.

References

- [1] K. Dhbaibi et al., *Chem. Rev.* **2019**, 119, 8846.
- [2] F. Zinna et al., *Chirality*, **2015**, 27(1), 1-13.
- [3] M. Poncet et al., *ChemPhotoChem*, **2021**, 5 (10), 880–892.
- [4] F. Gan et al., *Chirality*, **2023**, 35(9), 569-576.
- [5] TH. Bürgin et al., *J. Am. Chem. Soc.*, **2022**, 144, 14181–14194.

Femtosecond-spectroscopy of novel Fe(III)-complexes demonstrating a reservoir effect

S. Dabelstein¹, L. Schmitz², M. A. Argüello Cordero¹, F. Fennel¹, J. Steube², L. Fritsch², M. Bauer², and S. Lochbrunner¹

¹) University of Rostock, Institute for Physics, Rostock, Germany

²) Paderborn University, Chemistry Department, Paderborn, Germany

samira.dabelstein@uni-rostock.de

Conventional photosensitizers for photocatalysis are typically derived from rare and valuable precious metals, prompting the search for alternatives based on first-row transition metals [1, 2, 3]. Among these, iron-based photosensitizers emerge as potential candidates but are limited by their short-lived charge transfer states. To overcome this limitation, targeted ligand design is employed as a strategy [2, 3]. This study presents a series of emitting iron(III) complexes modified with chromophores, featuring either phenyl or anthracene groups. The chromophores are attached to the ligand via a methyl spacer (see Figure 1, left).

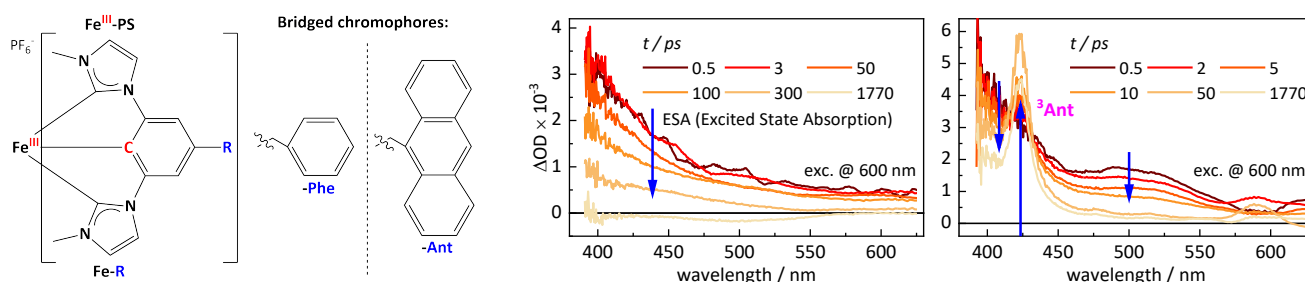


Figure 1 **Left:** Molecular structure of the investigated photosensitizers. **Right:** Ultrafast transient-absorption-spectra at the given delay-times of phenyl-derivative (Fe-Phe) and of the anthracenyl-derivative (Fe-Ant). The complexes are dissolved in acetonitrile and optically excited at 600 nm. The polarizations of the pump and probe pulses are set to magic angle.

While the phenyl-extended complexes exhibit behavior similar to the original complex, the anthracene-extended complexes reveal a reservoir effect, characterized by a population transfer from the ligand-to-metal charge transfer state to the triplet state of anthracene (see Figure 1, right). Additionally, a correlation is observed between the number of attached anthracene units and the rate of population transfer. Our findings, obtained through time-resolved methods, specifically femtosecond transient absorption UV-Vis spectroscopy and streak camera measurements, are discussed in detail.

Aknowlegments

Thanks to SPP 2102 and LiMatI SFB/CRC 1477.

References

- [1] A. Pöpcke, A. Friedrich, S. Lochbrunner, *J. Phys.: Condens. Matter* **2020**, 32, 153001.
- [2] J. Steube et al., *Nat. Chem.* **2023**, 15, 468-474.
- [3] P. Dierks, Y. Vukadinovic, M. Bauer, *Inorg. Chem. Front.* **2022**, 9, 206-220.

Unveiling the Potential of Iridium Complexes in Tissue Imaging

E. Dallerba,¹ M. J. Hackett,¹ M. Massi¹

¹*School of Molecular and Life Sciences, Curtin University, Perth, WA, Australia
elena.dallerba@curtin.edu.au*

The photophysical properties of transition metal complexes can be finely tuned through chemical modifications of their ligands. [1], [2] For this reason, iridium complexes have been extensively studied for cell staining applications. Nevertheless, the application of such complexes as probes for tissue staining remains a relatively unexplored field. This poster presentation will showcase whether ligand modifications can further enhance the photophysical properties of these complexes, enabling the synthesis of probes suitable for biological imaging. Specifically, we assessed a series of luminescent transition metal complexes for their potential as imaging probes in brain tissue samples. Currently, the availability of fluorescent probes for *ex vivo* tissue section imaging is significantly limited compared to those designed for *in vitro* live or fixed cell imaging. This gap poses a challenge for advancing neurobiological research, which relies on fluorescence microscopy to elucidate neurological function and disease mechanisms. In this study, we utilized novel fluorescent probes to stain brain tissue and demonstrated their imaging capabilities using confocal microscopy.

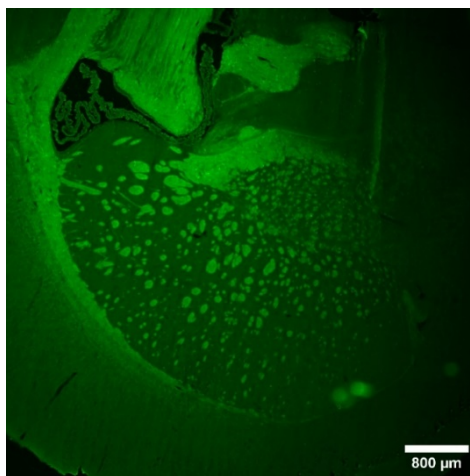


Figure 14. Microscopy image showing the staining of mouse brain tissue using an Ir(III) luminescent probe.

Aknowlegments

Confocal microscopy analysis was performed using the Curtin Health Innovation Research Institute Microscopy and Histology Shared Resources Laboratory with the assistance of Mr Michael Nesbit.

References

- [1] Li G., Nobusyasu S., Zhang B., Geng Y., Yao B., Xie Z., Zhu D., Shan G., Che W., Yan L., Su Z., Dias F., Bryce M. R., *Chemistry – A European Journal*, **2017**, 23, 11761-11766.
- [2] Fiorini V., Zanoni I., Zacchini S., Costa A. L., Hochkoeppler A., Zanotti V., Ranieri A. M., Massi M., Stefan A., Stagni S., *Dalton Transactions.*, **2017**, 46, 12328-12338.

J-dimers of phthalocyanine analogues and how to use them

J. Demuth,^a R. Machan,^a I. Mocak,^a T. Malinsky,^a M. A. El Dahabova,^a J. Holcak,^a S. Bednarik,^a M. Miletin,^a J. Labuta,^{b,c} V. Novakova,^a P. Zimcik^a

^aFaculty of Pharmacy in Hradec Králové, Charles University, Akademika Heyrovského 1203/8, 500 05 Hradec Kralove, Czech Republic;

^bResearch Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

e-mail: jiri.demuth@faf.cuni.cz

Azaphthalocyanines (AzaPcs) are planar macrocyclic compounds with interesting photophysical properties due to their large aromatic system. AzaPcs bearing dialkylamino substitution on the periphery can form supramolecular assemblies called J-dimers in non-coordinating solvents, due to the interaction of the peripheral amine of compound one with the central metal cation of the second compound (Fig. 1).[1] Formation of J-dimer influences photophysical properties of AzaPcs (spectra, production of singlet oxygen and fluorescence) (Fig. 2). For the dissolution of aggregates, ligands with higher binding ability to the central metal cation than the coordination moiety are necessary[2]

In the first part of this study, symmetrical AzaPcs with the different bulkiness of peripheral dialkylamine substitution were synthesized. These compounds were studied from an aggregation point of view. Results led us to the synthesis of unsymmetrical AzaPc derivatives composed of 3 bulky precursors and 1 small one. The final step was switching from non-fluorescent oktaakis(dialkylamino) AzaPcs to alkylsulfanyl to compare the influence of electron effects of peripheral substitution on the stability of J-dimers.

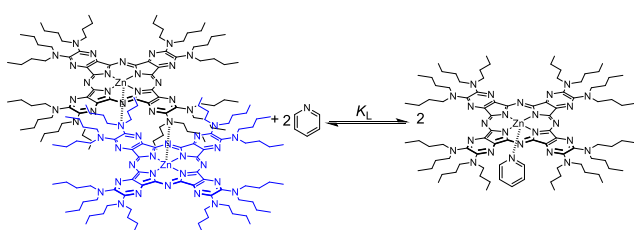


Fig. 1 Dissolution of J-dimer by pyridine.

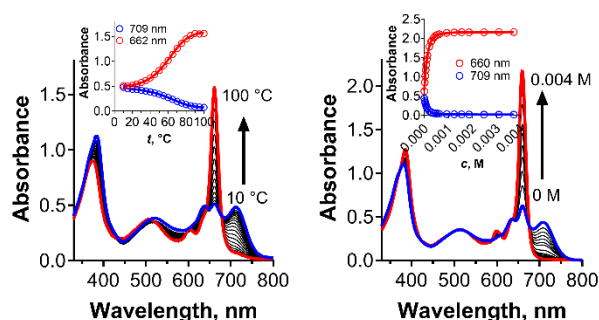


Fig. 2 Changes in absorption spectra during temperature experiments or titration of AzaPc by pyridine (blue – dimer, red – monomer).

Acknowledgments

Thanks to Czech Science Foundation (23-06177S).

References

- [1] V. Novakova et al., *Eur. J. Org. Chem.*, **2008**, (19), 3260-3263.)
- [2] J. Demuth et al., *Inorg. Chem. Front.*, **2025**,12, 1590-160

Photodegradation of Herbicides Using Boron Dipyrromethane (BODIPY) Polymers

E. Derham, S. O'Sullivan, and M. T. Pryce.

School of Chemical Sciences, Dublin City University, Dublin, Ireland

emily.derham5@mail.dcu.ie

While 71% of the Earth is covered in water, only 0.06% is readily available as drinking water.¹ Only 73% of the population has access to clean drinking water, with over 2 billion people living in water-stressed situations.² Contaminants from industrial and agricultural processes readily leech into our environment, causing detrimental effects to our planet and to our health as many of these pollutants have adverse biological and environmental effects. 2-methyl-4-chlorophenoxyacetic acid (MCPA) is the one of the most commonly found herbicides in drinking water, with 2,4-dichlorophenoxyacetic acid (2,4-D) being another. While these herbicides are often found in low concentrations below the WHO limit of 0.7mg/L for MCPA and 0.03mg/L for 2,4-D, they are still linked to some adverse effects such as kidney and liver toxicity and at higher concentrations are linked to some cancers.⁴ They are also suspected endocrine disruptors, and can be found in much higher concentrations in other countries.^{4,5,6} Novel remediation approaches to treat water contaminated with such pollutants are needed. A sustainable approach is to design materials (photosensitisers) that harvest solar energy, and produce reactive oxygen species (ROS), which degrade these pollutants.⁷ We have designed and assessed BODIPY polymers (such as shown in Figure 1) to generate ROS species, and degrade herbicides using visible irradiation. The results of these studies together with the photophysical properties of the polymer will be presented.

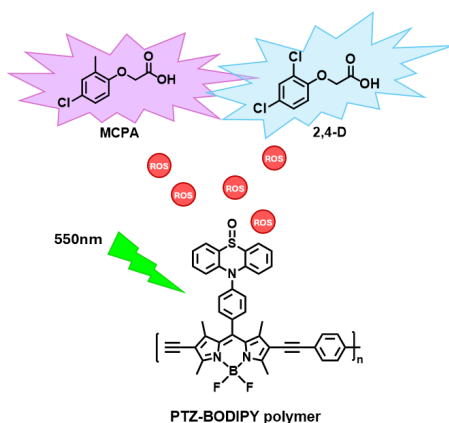


Figure 15. Schematic of herbicide degradation using a PTZ-BODIPY polymer.

- [1] Musie et al, *Heliyon* **2023**, 9 (8), e18685.
- [2] Martin, *Water and Sanitation*, United Nations Sustainable Development.
- [3] EPA-HSE Joint Position Paper, *Pesticides in Drinking Water*, **2019**
- [4] *Guidelines for drinking-water quality: fourth edition*, World Health Organization.
- [5] *Drinking Water and Health*, Health Service Executive **2025**.
- [6] Jayasiri et al, *Environ. Toxicol. Chem.* **2022**, 41 (2), 343–355.
- [7] Wu, B et al, *Environ. Sci. Technol.* **2024**, 58 (45), 20181–20189.

Pyrazole-based Ir^{III} complexes as effective antennas to sensitize Eu^{III}-based emission in ultrasmall NaGdF₄:Eu nanoparticles

Jesús Díaz-Burruedo^a, Juan Ramón Jiménez^a and Juan Manuel Herrera^a

^aDepartamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Av. Fuente Nueva s/n, 18071, Granada, España.

jesdb@ugr.es

Keywords: Lanthanide nanoparticles, Ir^{III} complexes, d→f Energy Transfer.

Fluoride-based lanthanide nanoparticles (LnNPs) are at the forefront of lanthanide luminescence and related applications such as lighting, telecommunications, security inks or bioimaging.¹ LnNPs are chemically and photophysically very stable, with sharp, long-lived emission that can be tuned from the UV to the IR by adjusting lanthanide dopants and concentrations. However, their brightness is about 100 times lower than that of equivalent bulk materials, mainly due to their high surface-to-volume ratio, which promotes non-radiative deactivation of excited states by surface defects. In addition, the forbidden nature of the f-f transitions hinders direct excitation of lanthanide ions, leading to weak emissions.²

To overcome these issues, we propose the use of luminescent d-block chromophores as effective light-harvesting units to sensitize lanthanide emission via d → f energy transfer processes (antenna effect).³ In this presentation we will present our latest results in the search for ultrabright and color-tunable composites based on Eu-doped NaGdF₄ nanoparticles functionalized with pyrazole-based photoluminescence Ir^{III} complexes.

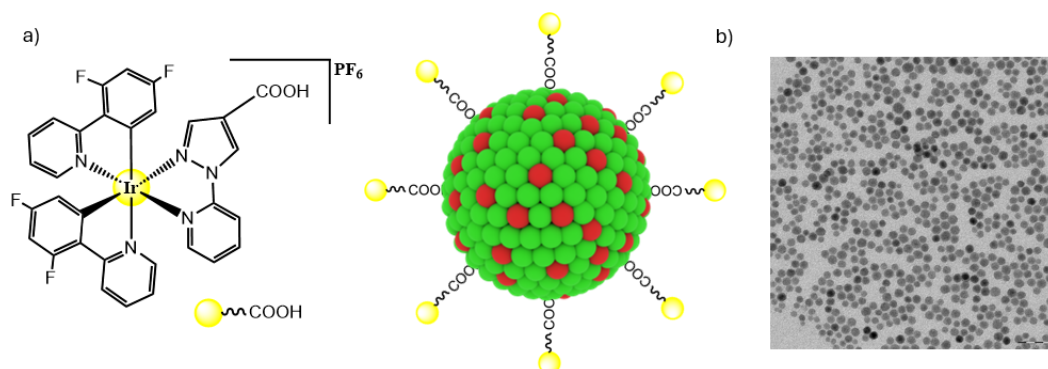


Figure 16. a) Schematic representation of emissive Ir^{III} complex and NaGdF₄:Eu@Ir composite. b) TEM image of NaGdF₄:Eu nanoparticles.

Aknowlegments

Thanks to the project PID2022-138090NB-C21, MICIN/AEI/10.13039/501100011033/FEDER.

References

- [1] L. Wang, S. Han, C. Li, D. Tu, X. Chem., *Acc. Chem. Res.* **2023**, 4, 193.
- [2] C. Cheignon, A. Kassir, L. K. Soro, L. J. Charbonnière, *Nanoscale* **2022**, 14, 13915.
- [3] Y. Ye, J.-R. Jiménez, M. M. Quesada-Moreno, A. Navarro, E. M. Ortega-Naranjo, A. Orte, J. M. Herrera, *Adv. Opt. Mater.* **2024**, 2302954 (<https://doi.org/10.1002/adom.202302954>).

Investigation on One-Electron Reduced Species of Re-1-naphthalimide photosensitizers

Luis G. A. do Nascimento,¹ Sofia Nikolaou¹ and André S. Polo²

¹Department of Chemistry, FFCLRP-USP, Ribeirão Preto, Brazil; ²Center for Natural and Human Sciences, UFABC, Santo André, Brazil.

E-mail: luis_nascimento@usp.br

Rhenium(I) complexes are promising candidates for artificial photosynthesis studies, mainly focused on CO₂ photoreduction.^[1] As this photoreduction requires that the complex act as catalyst and photosensitizer, it is very common that modifications in the organic ligands coordinated to the rhenium center occur to improve one of those characteristics.^[1] In this sense, 1,8-naphthalimide dyes reveal themselves as good ligands for this system, once the ability to suffer one or two consecutive reversible reductions makes their structure a powerful electron reservoir.^[2] Based on this, this work aims to investigate the use of two new rhenium compounds with general formula *fac*-[Re(CO)₃(phen)(NI)]PF₆, where phen = 1,10-phenanthroline and NI = (N)-piridil-1,8-naphthalimide (**1**) or 4-amino-(N)-piridil-1,8-naphthalimide (**2**) through its interaction with the triethanolamine (TEOA). Once the reduction of the complex by this sacrificial reagent, to form the one-electron reduced species (OERS), is a determinant step in the CO₂ photoreduction mechanism,^[1] a fluorescence titration of a deaerated solution of complexes **1** and **2** in N,N-dimethylformamide (DMF) (10⁻⁵ mol/L) with TEOA was carried out, and the data were treated using the Stern-Volmer equation, obtaining the linear fits represented in Figures 1A and 1B. The complex **1** was more sensitive to TEOA than the complex **2**, with a K_{SV} value of 142 (**1**) and 2.77 (**2**), being higher than the precursor *fac*-[Re(CO)₃(phen)(Cl)] (K_{SV} = 3.5).^[1] The reason for this high oxidizing potential of complex **1** is that on the excitation wavelength (λ_{exc} = 350 nm) we promote, simultaneously, a metal-to-ligand charge transfer (MLCT) transition from the Re(dπ) to the π* phen orbitals and a intraligand transition centered in the NI, while in complex **2**, with a λ_{exc} = 430 nm, the main transition observed is the intraligand charge transfer (ILCT) of the amino-naphthalimide. Previous cyclic voltametric studies reveal that the reduction potentials of these naphthalimides are too negative (~ -1.1 V vs NHE) to produce a driving force for the TEOA electron transfer, which explains the low quenching constant of complex **2**. However, in complex **1**, an intramolecular electron transfer from the NI^{•+} excited chromophore to the rhenium center (with the Re⁺⁰ reduction potential nearly to 2.0 V vs NHE) can also occur, as illustrated for the scheme in Figure 1C, explaining why low concentrations of TEOA are necessary to quench the observed photoluminescence, again, when compared with the precursor *fac*-[Re(CO)₃(phen)(Cl)].^[1] This indicates a possible production of a two-electron reduced specie (TERS) in one single stage, revealing a powerful photosensitizer candidate.

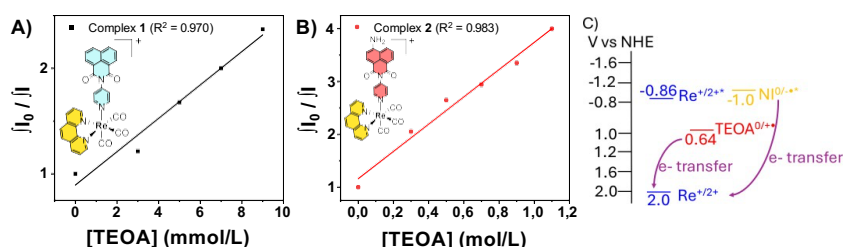


Figure 1. Stern-Volmer plots of the reductive quenching of the excited state of complexes **1** (A) and **2** (B) by TEOA in deaerated DMF at different concentrations (the complexes structures are in the figure) (B); Schematic energy diagram of the reductive quenching of the complex **1** excited state (C)

Aknowlegments: Thanks to Fundação de Amparo à Pesquisa do Estado de São Paulo (Grant number: 2022/16402-0; 2022/03478-8) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (Grant number: 305761/2021-8)

References: [1] A.V. Müller, W.M. Wierzbza, L.G.A. do Nascimento, J.J. Concepcion, S. Nikolaou, D.E. Polyansky, A.S. Polo, *Artificial Photosynthesis* **2025**, XX, XXX; [2] D.R. Case, A. Spear, A.F. Henwood, M. Nanao, S. Dampf, T.M. Korter, T. Gunnlaugsson, J. Zubieta, R.P. Doyle, *Dalton Transactions* **2021**, 50, 3479.

Efficiency and Distance Dependency of Doublet-Triplet Energy Transfer Processes

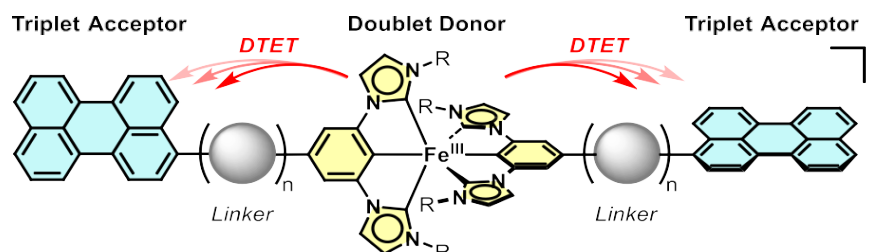
F. Doettinger¹ and O. S. Wenger¹

¹) *Departement Chemie, Universität Basel, St. Johannis-Ring 19, 4056 Basel, Switzerland.*
f.doettinger@unibas.ch

In Nature photoinduced electron and energy transfer processes are prevalent. Under the premise of elaborating a deep understanding of photosynthesis and to enable its artificial imitation, such processes are investigated for example using transition metal complexes. In this context, recent breakthroughs with photoactive coordination compounds based on abundant first row transition metals, e.g. Cr(III)[1], Mn(IV)[2], and Fe(III)[3], brought sustainable photocatalytic systems one step closer towards their application.

Common in these compounds are photoactive doublet states which show activity in the generation of triplet states in organic chromophores. However, the underlying mechanism of doublet-triplet energy transfer (DTET) is barely explored. The related triplet-triplet energy transfer (TTET) on the other hand is well-known. First studies suggest a comparable energy transfer efficiency in DTET similar to the short-ranged Dexter mechanism of TTET[4,5].

Therefore, by studying novel perylene-substituted transition metal complexes of iron(III) (see below) we seek to elaborate the efficiency and distance dependency of the photoinduced DTET using time-resolved spectroscopic techniques.



Inside the above-shown structure, the central iron(III) core (yellow) acts as doublet donor while the organic chromophore perylene (blue) acts as triplet acceptor. Through variation of the linking units (grey) a distance between the two fragments is defined which enables studying the distance dependency of the underexplored DTET.

Acknowledgments

The generous support provided by the German Research Foundation through the Walter-Benjamin Fellowship (F.D.) as well as the Swiss National Science Foundation (O.S.W.) is greatly acknowledged.

References

- [1] S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, *Angew. Chem. Int. Ed.* **2015**, 54 (39), 11572–11576. [2] N. Kaul, E. Asempa, J. A. Valdez-Moreira, J. M. Smith, E. Jakubikova, L. Hammarström, *J. Am. Chem. Soc.* **2024**, 146 (35), 24619–24629. [3] K. Kjær, N. Kaul, O. Prakash, P. Chábera, N. W. Rosemann, A. Honarfar, O. Gordivska, L. A. Fredin, K.-E. Bergquist, L. Häggström, T. Ericsson, L. Lindh, A. Yartsev, S. Styring, P. Huang, J. Uhlig, J. Bendix, D. Strand, V. Sundström, P. Persson, R. Lomoth, K. Wärnmark, *Science* **2018**, 363 (6424), 249–253. [4] C. Wang, F. Reichenauer, W. R. Kitzmann, C. Kerzig, K. Heinze, U. Resch-Genger, *Angew. Chem. Int. Ed.* **2022**, 61 (27), e202202238.

[5] J. Wellauer, F. Ziereisen, N. Sinha, A. Prescimone, A. Velić, F. Meyer, O. S. Wenger, *J. Am. Chem. Soc.* **2024**, 146 (16), 11299–11318.

Mn(I) isocyanide complexes with benzothiadiazole motifs: unravelling the excited-state manifold using RIXS

C. J. Doran¹, C. B. Larsen¹

¹School of Chemical Sciences, University of Auckland, Auckland 1010, New Zealand
cdor231@aucklanduni.ac.nz

Earth-abundant photosensitisers offer the potential to reduce or even remove our dependence on traditional precious-metal photocatalysts, but challenges remain in circumventing the inherently less favourable excited-state ordering of first-row transition-metal complexes.¹ To this end, significant advances in ligand design have been made in recent years,² with one approach combining the use of low valent metal centres such as Mn(I) with strong-field bidentate or tridentate isocyanide ligands, resulting in complexes with >1 ns MLCT lifetimes.³

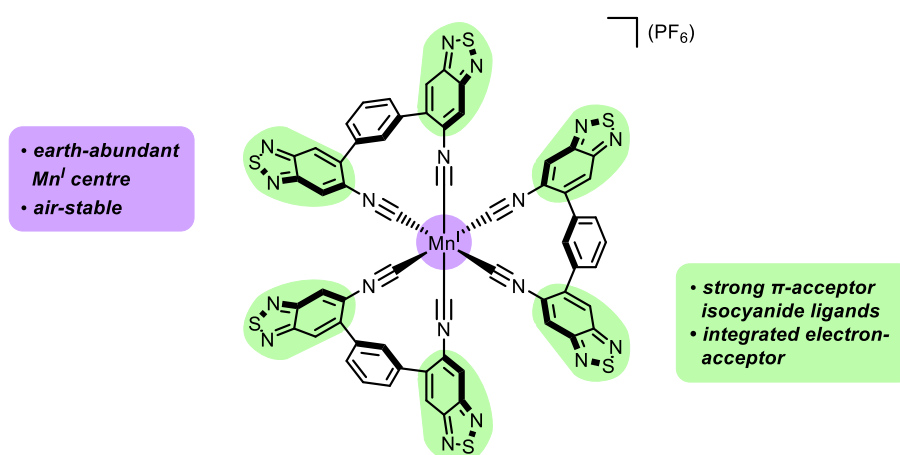


Figure 1. Structure of Mn(I) isocyanide complex incorporating benzothiadiazole moieties.

Owing in part to the strong ligand-field of isocyanide donors, these Mn(I) complexes have suffered from high MLCT state energies and correspondingly poor absorption profiles in the visible spectrum.^{3,4} This work has explored the incorporation of electron-accepting benzothiadiazole moieties into the ligand scaffold (Figure 1) to improve the optical properties of Mn(I) complexes and studied their effect on photophysical properties. Synchrotron studies employing resonant inelastic X-ray scattering (RIXS) techniques were carried out, enabling direct observation of ligand-field state energies and allowing for a full exploration of the excited-state manifold.

References

- [1] J. K. McCusker, *Science* **2019**, 363 (6426), 484-488
- [2] C. J. Doran, S. E. Dillon, C. B. Larsen. Replacing ruthenium and iridium with earth-abundant metals for sustainable photochemistry. *Chemistry in New Zealand* [online periodical] **2024**
- [3] P. Herr, C. Kerzig, C. B. Larsen, D. Häussinger, O. S. Wenger, *Nature Chemistry* **2021**, 13, 956-962
- [4] C. Wegeburg, D. Häussinger, S. Kupfer, O. S. Wenger, *Journal of the American Chemical Society* **2024**, 146 (7), 4605-4619



Light-Driven CO₂ Reduction with a Heptacoordinated Iron(II) Polypyridine Complex

^aF. Droghetti, ^bA. Ruggi, ^cF. Lemken, ^cL. Rulíšek, ^aM. Natali

^aUniversity of Ferrara, Via Luigi Borsari 46, Italy

^bUniversity of Fribourg, Chemin du Musée 9, Switzerland

^cInstitute of Organic Chemistry and Biochemistry of the CAS, Flemingovo náměstí 542/2
Praha 6, Czech Republic

drgfrc@unife.it

The growing necessity to mitigate human-induced CO₂ emissions has driven research toward innovative approaches for converting them into value-added products. Recent findings in designing molecular catalysts for the CO₂ reduction reaction (CO₂RR) have focused on metal complexes with ligands that exhibit a significant degree of electronic delocalization, a feature crucial for reducing overpotential and enhancing selectivity over the competitive hydrogen evolution reaction (HER)^[1,2].

In this communication, we report the catalytic activity of a Fe(II)-based molecular catalyst for CO₂ reduction, featuring a hexadentate, redox-active DBPy-PyA ligand (1-([2,2'-bipyridin]-6-yl)-N-([2,2'-bipyridin]-6-ylmethyl)-N-(pyridin-2-ylmethyl)-methanamine), under electrochemical and photochemical conditions. We optimize the catalytic performance of the Fe(II) complex through a fine-tuning of the proton donor, photon flux, and different photosensitizers, achieving over 99% selectivity and one of the highest reported quantum efficiencies^[3]. Furthermore, time-resolved spectroscopy and DFT calculations provide a mechanistic understanding of electrochemical and photochemical behavior^[4,5].

References

- [1] H. Takeda, C. Cometto, O. Ishitani, M. Robert, *ACS Catal* **2017**, 7, 70–88.
- [2] F. Droghetti, A. Amati, A. Ruggi, M. Natali, *ChemComm* **2023**, 60, 658–673.
- [3] F. Droghetti, L. Villa, A. Sartorel, L. Dell'Amico, A. Ruggi, M. Natali, *ChemSusChem* **2025**, DOI 10.1002/cssc.202402627.
- [4] F. Droghetti, F. Lemken, L. Rulíšek, A. Ruggi, M. Natali, *ACS Catal* **2024**, 16920–16935.
- [5] F. Droghetti, A. Amati, F. Pascale, A. Crochet, M. Pastore, A. Ruggi, M. Natali, *ChemSusChem* **2024**, 17, DOI 10.1002/cssc.202300737.

The Development of Sulfur-Containing, APTRA-Derived Fluorescent Probes with Specific Zn²⁺ Binding

L.L. Duncan¹, C. Hogg and J.A.G. Williams

¹Department of Chemistry, Durham University, South Road, Durham, DH1 3LE.

laura.l.duncan@durham.ac.uk

The divalent cations Mg²⁺, Ca²⁺ and Zn²⁺ are all essential for human life. Consequently, there is great interest in monitoring their concentrations in cells and tissues, in real time, using fluorescent probes in conjunction with fluorescence microscopy.¹ The binding unit of a given probe must be tuned to target different biologically relevant metal ions selectively. With respect to Mg²⁺ detection, *o*-aminophenol-N,N,O-triacetate (APTRA) is a commonly used binding unit, despite the fact it also binds to Ca²⁺ and Zn²⁺ (Figure 1).²

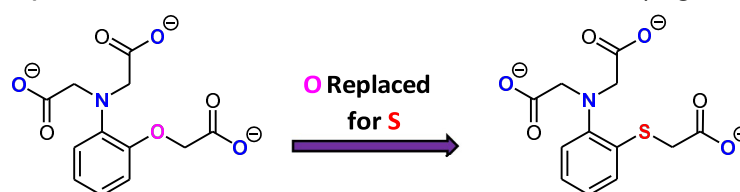


Figure 1 - Structures of APTRA (left) and S-APTRA (right).

Work within the group has focused on new ligands related to APTRA, but which have been modified in such a way that the selectivity for different metal ions changes profoundly. We have discovered that the replacement of the phenolic oxygen atom of APTRA with sulfur gives a new ligand, *o*-aminothiophenol-N,N,S-triacetate (S-APTRA), that binds to Zn²⁺ very strongly, and with high selectivity over Mg²⁺ and Ca²⁺ (Figure 1). We have devised and implemented a synthetic route to fluorescent derivatives of S-APTRA, including a particularly exciting example in which the ligand is connected to a rosamine fluorophore. This new molecule possesses many of the desirable features of a bio-compatible fluorescent probe, including the ability to excite at long wavelengths in the visible region.

We have now shown that this probe gives a significant turn-on emission response upon Zn²⁺ binding, with no interference from either Mg²⁺ or Ca²⁺ (Figure 2). It also has the advantage of improved water solubility compared to many of the other reported Zn²⁺ probes, whilst the high (pentadentate) denticity prevents the formation of ternary complexes with endogenous biological molecules, allowing the sole detection of free Zn²⁺ *in vivo*. This renders S-APTRA-Rosamine a reliable and selective Zn²⁺ probe, with potential application in cellular imaging.

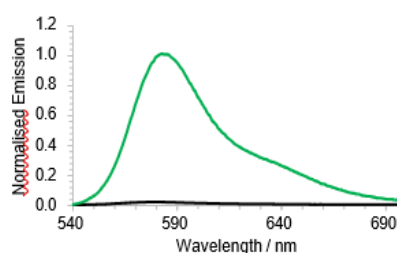


Figure 2 - Emission spectrum of S-APTRA-rosamine (black) and in its Zn²⁺-bound form (green) in aqueous buffer solution (50 mM HEPES, 100 mM KCl, pH 7.21).

References

- [1] K.P. Carter, *Chem. Rev.*, **2014**, 114, 4565-4601, DOI: [10.1021/cr400546e](https://doi.org/10.1021/cr400546e). E.R.H. Walter, C. Hogg, D. Parker, J.A.G. Williams, *Coord. Chem. Rev.*, **2021**, 428, 213622, DOI: [10.1016/j.ccr.2020.213622](https://doi.org/10.1016/j.ccr.2020.213622) [3] L.A. Levy, E. Murphy, B. Raju and R.E. London, *Biochemistry*, **1988**, 27, 4041-4048, DOI: [10.1021/bi00411a021](https://doi.org/10.1021/bi00411a021). M. Brady, S.D. Piombo, C. Hu and D. Buccella, *Dalton Trans.*, **2016**, 45, 12458-12464, DOI: [10.1039/C6DT01557C](https://doi.org/10.1039/C6DT01557C)

Accessing the reservoir effect in Iron^{III}-complexes *via* electron withdrawing linker-groups

N. Düsterhues¹, J. Steube¹ and M. Bauer¹

¹University Paderborn, Warburger Str. 100, 33098 Paderborn, Germany nils.duesterhues@uni-paderborn.de

Photoredox catalysis has proven to be a vital tool in enabling previously unrealized reaction pathways and is therefore a detrimental aspect of moving towards a sustainable future. Commonly employed transition metal complexes are based on platinum group metals, where especially Ru^{II}- and Ir^{III}- complexes have been extensively employed. However, their scarcity and environmental impact contradicts the greater goal of sustainable practices, thus driving the development of more sustainable alternatives.^[1] Recently, Fe^{III}-complexes with strong donor ligands have shown to exhibit interesting photophysical properties, pushing them towards being viable alternatives.^{[1][2]} However, their ²LMCT lifetime has to still be increased.^{[1][2]} Recent work on [Fe(ImP)₂]⁺ (HImP = 1,1'-(1,3-phenylene)bis(3-methyl-1-imidazol-2-ylidene)) based complexes shows a significant increase of the ²LMCT-lifetime when introducing electron withdrawing groups (Fig. 1 (left)) in the ligand backbone.^[3]

In this work, electron withdrawing groups are employed as a linker, connecting the ligand to chromophores, which act as triplet reservoirs. Decoupling the main ligand from the chromophore *via* such a linker, promises to induce both longer-lived ²LMCT states and provide accessible ³Chrom-states to enable a reservoir effect (Fig. 1, right).^[2] Therefore, this approach promises to significantly prolong the observable ²LMCT-lifetimes and increase the catalytic activity compared to [Fe(ImP)₂]⁺.

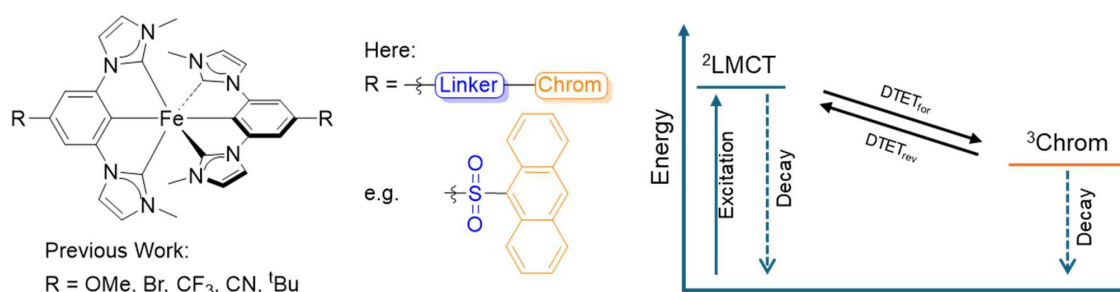


Figure 1. Structure of [Fe(ImP)₂]⁺ based complexes with varied substituents and a possible sulfone- anthracene linker system(left).^{[1][3]} Schematic representation of a possible triplet-reservoir in equilibrium with a ²LMCT-state via DTET (right).^[2]

Aknowlegments

Thanks to the Fonds der Chemischen Industrie and the BMBF for financing this work.

References

- [1] J. Steube, M. Bauer *et al*, *Nat. Chem.* **2023**, 15, 468–474
- [2] J. Wellauer, O. Wenger *et al*, *J. Am. Chem. Soc.* **2025**, 147 (10), 8760–8768
- [3] J. Steube, N. Düsterhues, M. Bauer *et al*, *submitted*.



Understanding multi-timescale effects in a light-driven overall water splitting system

Alexander Eith,^[1,3] Karnamohit Ranka,^[4] Mohini Semwal,^[2,5] Elias Brohmer,^[2] Linda Zedler,^[2,5] Stephan Kupfer,^[2] Benjamin Dietzek-Ivanšić,^[2,5,7] Frances Houle,^[4] Jacob Schneidewind^[1,3,6]

^[1] *Institute of Organic and Macromolecular Chemistry (IOMC), Friedrich Schiller University Jena, Humboldtstraße 10, 07743 Jena, Germany*

^[2] *Institute for Physical Chemistry (IPC), Friedrich Schiller University Jena, Lessingstraße 4, 07743 Jena, Germany*

^[3] *Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich Schiller University Jena, Philosophenweg 7, 07743 Jena, Germany*

^[4] *Lawrence Berkeley National Laboratory (LBNL), 1 Cyclotron Road, Berkeley, CA 94720, United States of America*

^[5] *Leibniz-Institute of Photonic Technology (IPHT), Albert-Einstein-Str. 9, 07745 Jena, Germany*

^[6] *Helmholtz Institute for Polymers in Energy Applications Jena (HIPOLE Jena), Lessingstrasse 12-14, 07743 Jena, Germany*

^[7] *Leibniz Institute of Surface Engineering (IOM), Permoserstraße 15, 04318 Leipzig, Germany
E-Mail: alexander.eith@uni-jena.de*

Photocatalytic water splitting intrinsically combines processes which occur on vastly different timescales, ranging from femtosecond-scale photophysical processes to chemical reactions which can take hours. This complexity is further compounded by the fact that multiple photons must be absorbed to complete the water splitting reaction. Individual photon absorption events may be seconds apart due to the relatively dilute nature of sunlight. It is crucial to understand how these multi-timescale effects work together to enable water splitting, which also reveals mismatches that lead to energy loss or unproductive excitations, ultimately lowering solar energy conversion efficiency.

This contribution will present a multi-time scale study of an overall water splitting system consisting of only a single ruthenium complex. Our previous work has shown that water splitting occurs in this system through a novel mechanism in which two photons with different wavelengths are subsequently absorbed by two different intermediates of the reaction cycle.^[1] Photochemical experiments, combined with transient absorption spectroscopy and computational models have been used to provide insights into different parts of the reaction network that occur on the femto- to nanosecond scale as well as on the scale of seconds to days. A complete kinetic description, based on a stochastic modelling approach, has then been developed to unify these insights into a holistic model spanning all time scales involved in the reaction. This approach provides detailed insights into different sources of inefficiency, which we expect to be generally useful to improve the solar energy conversion efficiency of photocatalytic systems.

Acknowledgments

Financial support by Fonds der Chemischen Industrie (Liebig scholarship for J.S.), Federal Ministry of Education and Research (BMBF independent research group "SINATRA: SolSTEP", grant number 03SF0729) and DFG via the CRC TRR 234 CATALIGHT (project no. 36454990, projects A1, A4, A7) is gratefully acknowledged.

References

- [1] J. Schneidewind, M. A. A. Cordero, H. Junge, S. Lochbrunner, M. Beller, *Energy Environ. Sci.* **2021**, 14, 4427–4436.



Photoluminescence lifetime stability studies of β -diketonate europium complexes based phenanthroline derivatives in Luminescence Solar Concentrators LSCs films

O. Essahili ^[a], M. Ilsouk ^[a], C. Duhayon ^[b], and O. Moudam ^[a]

^[a] *Mr. Othmane Essahili, Ass. Prof. Mohamed Ilsouk, Ass. Prof. Omar Moudam Applied Chemistry and Engineering Research Centre of Excellence (ACER CoE)*

Mohammed VI Polytechnic University (UM6P)

Lot 660, Hay Moulay Rachid, 43150 Benguerir, Morocco E-mail: othmane.essahili@um6p.ma

^[b] *Dr. Carine Duhayon*

Laboratoire de Chimie de Coordination du CNRS Institution

205, route de Narbonne, BP 44099, F-31077 Toulouse Cedex 4, France

Abstract: In this work, five phenanthroline derivatives substituted with different methyl groups have been selected to synthesize β -diketonate-based europium complexes to check the influence of the substitutions on the degradation effect of those complexes in poly(methyl methacrylate) (PMMA) films. The photophysical properties of Eu(III) complexes, including absorbance, excitation, and emission have been carefully investigated in solution, solid-state, and doped in PMMA film. In all these states, the complexes exhibit an impressive red emission at 614 nm with a high photoluminescence quantum yield of up to 85%. The films have been exposed under outdoor, indoor, and dark storage stability lifetime conditions for 1200 hours. The photoluminescence measurements recorded every 400, 800, and 1200 hours demonstrated that the film containing europium complex with phenanthroline ligand substituted by a high number of methyl groups (Eu(TTA)3L5) showed good photoluminescent stability in indoor and dark conditions, and exhibited better resistance to degradation in outdoor conditions compared to other complexes. This study has proved that phenanthroline ligands could be tuned chemically leading to better stability of those types of complexes in films which can be end-used for future stable optoelectronic devices such as luminescent solar concentrators.

Aknowlegments

Thanks to UM6P for funding the project * **Elaboration of sustainable luminescent materials based on rare earth complexes for solar energy conversion***.

References

- [1] O. Essahili, M. Ouafi, M. Ilsouk, O. Lakbita, C. Duhayon, L. Mahi, O. Moudam, ChemistryOpen 13, (May 2024): e202300192. <https://doi.org/10.1002/open.202300192>

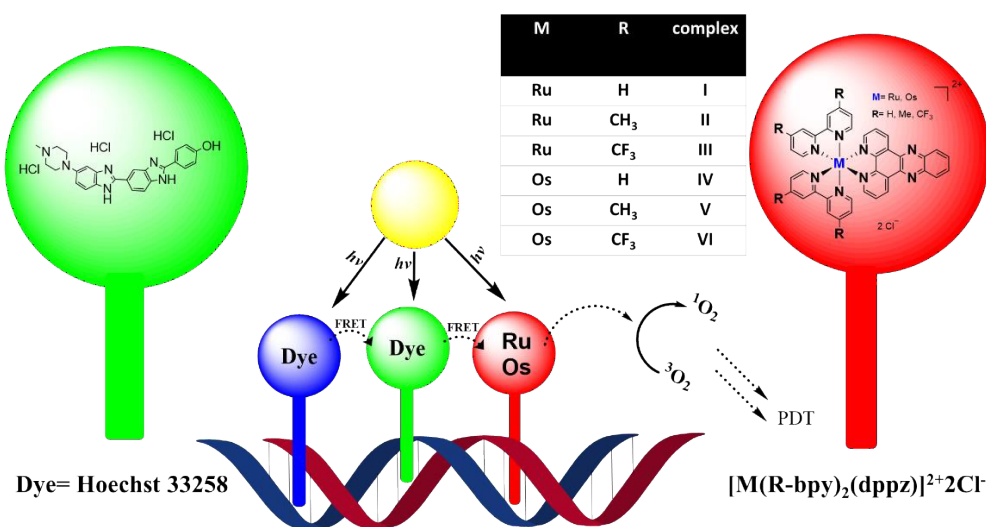
Photophysical Characterization of Ru and Os Phenazine-Based Polypyridine Complexes as Potential Photosensitizers for Photodynamic Therapy

M. Farhadi Rodbari^a, S. Rau^{a*}

^a: Institute of Inorganic Chemistry I, Ulm University, Ulm, Germany, mona.farhadi-

rodbari@uni-ulm.de

Ruthenium (Ru) and Osmium (Os) polypyridyl complexes are promising agents for site-specific photodynamic therapy (PDT) due to their tunable photophysical properties, strong DNA intercalation, and ability to generate ROS upon light activation^{1,2}. Here, we introduce a DNA-templated light-harvesting system combining Ru/Os dipyrrophenazine (dppz) complexes with organic dyes to broaden spectral absorbance utilizing energy transfer via multi-step FRET. The supramolecular assembly improves light harvesting and enables directional energy transfer along the DNA scaffold. Emission studies of [Ru(bpy-R)₂(dppz)]²⁺ confirm intercalation³, thereby inducing altered dye emission, and thus supporting energy transfer within the system. These results underscore the synergy of photophysics and coordination chemistry in developing light-responsive supramolecular systems for biomedical applications.



Scheme 1: Graphical abstract of research project

Acknowledgments

The authors acknowledge funding by the DFG, the GDCh, and the DAAD (PhD scholarship).

References

- [1] Y.Sun, L. E.Joyce, N. M. Dickson, & C.Turro., *Chemical Communications* **2010**, 46, 2426–2428.
- [2] B. C. Poulsen, *Dalton Transactions* **2016**, 45, 18208–18220.
- [3] B. M. Zeglis, V. C. Pierre & J. K. Barton., *Chemical Communications* **2007**, 44, 4565–4579.

Enhancement of Intersystem Crossing in Asymmetrically Substituted BODIPY Dyes

M.A. Filatov

School of Chemical and Biopharmaceutical Sciences, Technological University Dublin,
Grangegorman, Dublin, D07ADY7, Ireland. Email: mikhail.filatov@tudublin.ie

The development of organic photosensitizers with efficient intersystem crossing (ISC) without relying on heavy atoms is a rapidly expanding field. Among various approaches, spin-orbit charge-transfer intersystem crossing (SOCT-ISC) has emerged as a powerful strategy, particularly for donor-acceptor dyads with orthogonal aromatic fragments, such as meso-aryl BODIPYs (Figure 1a).[1] In these systems, triplet excited states are generated from a charge-transfer (¹CT) state formed by electron transfer between the subunits. A promising alternative for achieving high triplet yields is reducing the singlet-triplet energy gap (ΔE_{S-T}), which facilitates ISC without the need for heavy atoms via spin-orbit coupling between S_1 and a higher triplet state (T_n), followed by internal conversion to T_1 . [2]

In this work, we demonstrate that asymmetrical substitution of the BODIPY chromophore effectively reduces ΔE_{S-T} , enabling efficient ISC via the $S_1 \rightarrow T_2$ pathway. A comprehensive study of asymmetrical BODIPYs (**aBDPs**) revealed that this approach is applicable across a diverse range of substitution patterns. We investigated BODIPYs with an electron-rich alkyl-substituted pyrrolic unit and an electron-deficient pyrrolic unit incorporating carbonyl and/or aryl groups or remaining unsubstituted. The resulting compounds exhibited efficient ISC and singlet oxygen generation with quantum yields (Φ_Δ) of up to 0.76, demonstrating their strong potential as photosensitizers. **aBDPs** were further explored as photoinitiators in a photopolymer for holographic recording of diffractive structures. The lead compound, **aBDP8**, exhibited remarkable photopolymerization efficiency, achieving a diffraction efficiency of up to 71% in holographic transmission gratings.[3]

Our findings suggest that tuning molecular asymmetry represents an effective approach for controlling ISC in BODIPY-based photosensitizers. Moreover, this strategy can be synergistically combined with other methods to create hybrid systems with multiple ISC pathways contributing to triplet excited states formation.

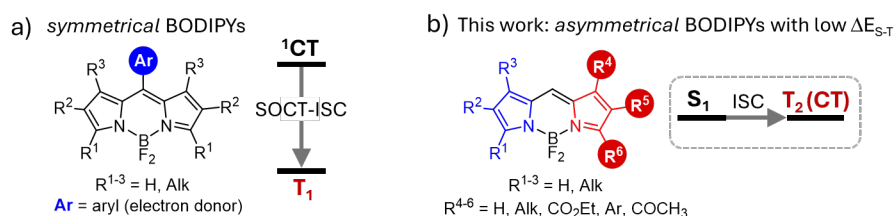


Figure 1. General structures of a) symmetrical BODIPY donor-acceptor dyads undergoing the SOCT-ISC process and b) asymmetrical BODIPY dyes forming triplet excited states via the $S_1 \rightarrow T_2$ pathway.

Aknowlegments

Research Ireland award 21/FFP-A/9214 (DyeSICPhoto) is acknowledged for support of this work.

References

- [1] M.A. Filatov, *Org. Biomol. Chem.* **2020**, 18, 10-27.
- [2] C. M. Marian, *Annu. Rev. Phys. Chem.*, **2021**, 72, 617.
- [3] M.A. Filatov, T. Mikulchyk, M. Hodée, M. Dvoracek, V.N.K. Mamillapalli, A. Sheehan, C. Newman, S.M. Borisov, D. Escudero, I. Naydenova, *J. Mater. Chem. C*, **2025**, doi: 10.1039/D4TC04850D

Sn^{IV}-porphyrins conjugates as bio-inspired models for artificial photosynthesis

G. Fogar,^{a,c} F. Droghetti,^b M. Natali,^b F. Berti,^a D.V. Filippov,^c S. Bonnet,^c E. Iengo^a

^aDepartment of Chemical and Pharmaceutical Sciences, University of Trieste (Italy), ^bDepartment of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara (Italy), ^cLeiden Institute of Chemistry, Leiden University (The Netherlands).

greta.fogar@phd.units.it; g.fogar@lic.leidenuniv.nl

Photosynthesis, a fundamental biological process, involves water oxidation reaction catalyzed by three key components: initial light absorption by the chromophore, followed by oxidation of a tyrosine donor and reduction of a quinone acceptor, coupled with a proton transfer through a *Proton Coupled Electron Transfer* mechanism (PCET). The water oxidation, which occurs in Photosystem II (PSII), is a far more difficult process than proton reduction.¹ By taking advantage of the peculiar opto-electronic and redox properties of Sn^{IV}-porphyrins,² we will here show how conjugation of these chromophores to either a simple amino acid, or a peptide sequence may provide useful models to gain insights in artificial PCET or *unidirectional electron transfer* (ET). The synthesis, characterization, and photophysical behavior of two Sn^{IV}-porphyrin/tyrosine conjugates, which differ in the relative position between the amino acid and the chromophore, will be illustrated (Figure, left).^{3,4} Additionally, some preliminary results on the design and preparation of a Sn^{IV}-porphyrin/YALP conjugate (YALP = hydrophobic α -helical peptide with tyrosine residues, Figure, right) will also be shown. The latter system is designed in order to achieve the more ambitious goal of photo-induced unidirectional ET across a lipid membrane, and thus may serve as a model of PSII.⁵

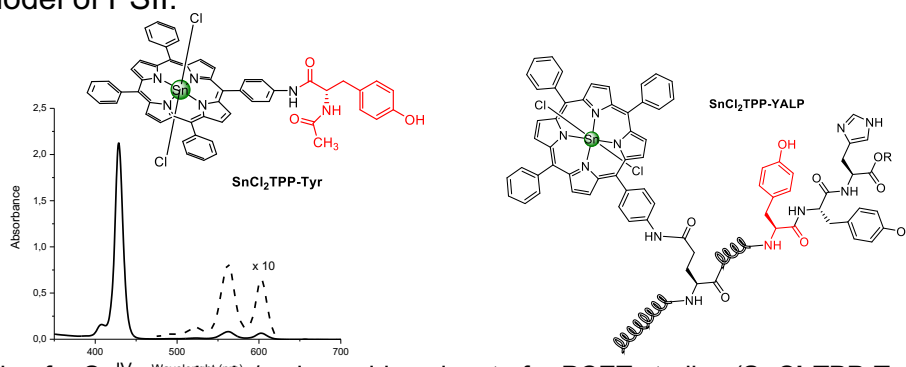


Figure. Example of a Sn^{IV}-porphyrin/amino acid conjugate for PCET studies (**SnCl₂TPP-Tyr**) and schematic representation of a Sn^{IV}-porphyrin/YALP conjugate for transmembrane unidirectional ET studies (**SnCl₂TPP-YALP**).

Acknowledgments

This work was supported by the European Union - Next Generation.

References

- (1) Nelson, N.; Yocum, C. F. *Annu. Rev. Plant Biol.* **2006**, 57 (1), 521–565.
- (2) Arnold, D. P.; Blok, J. *Coord. Chem. Rev.* **2004**, 248 (3–4), 299–319.
- (3) a) Natali, M.; Amati, A.; Demitri, N.; Iengo, E. *Chem. Commun.* **2018**, 54 (48), 6148–6152; b) Natali, M.; Amati, A.; Merchiori, S.; Ventura, B.; Iengo, E. *J. Phys. Chem. C* **2020**, 124 (16), 8514–8525.
- (4) Fogar, G.; Droghetti, F.; Berti, F.; Natali, M.; Iengo, E. *manuscript in preparation*.
- (5) Klein, D. M.; Li, X.; Boyle, A. L.; van der Pol, R.; Sevink, A. J. A.; Brouwer, A. M.; Bonnet, S. *manuscript in preparation*.



A Computational Approach to Emergent Photoactivated Anticancer Therapies Based on Transition Metal Complexes

A. Francés-Monerris

Institut de Ciència Molecular, Universitat de València, P.O.Box 22085, 46071 València, Spain

e-mail: antonio.frances@uv.es

Light exploitation as a source of selectivity in anticancer therapies is gaining interest in the last years.[1] The use of biocompatible wavelengths requires the administration of photoactive chromophores that must be distributed into cancerous cells in sufficient concentration to trigger clinically relevant photodamage upon irradiation of the ill area. Therefore, efficient photophysical and photochemical processes are a prerequisite for new photosensitizers to be candidates for clinical development. Traditionally, light-induced biological damage is exerted through the classical O₂ mediated type I and/or type II photodynamic therapy (PDT) photoreactions. However, the physiological conditions of solid tumors often imply low levels of molecular dioxygen, limiting the outcome of the already clinically approved drugs.[1]

The present contribution will describe recent approaches to circumvent the hypoxia problem from a multidisciplinary perspective, emphasizing however the contributions of computational chemistry in the elucidation of the molecular and electronic mechanisms behind the photodamage. The photoprocesses that will be considered are mediated by molecules based on heavy transition metals.[2-8] The contribution will show recent results on how these non-canonical photosensitizers respond upon light absorption, and how this information reveals the photochemical mechanisms responsible for the biological damage.

Aknowlegments

Research supported by the Grant CNS2024-154908 funded by the Spanish Ministerio de Ciencia, Innovación e Universidades - Agencia Estatal de Investigación (MICIU/AEI/10.13039/501100011033) and by “ERDF A way of making Europe.”

References

- [1] S. Monro *et al*, *Chem. Rev.* **2019**, 119, 797-828.
- [2] M. E. Alberto, A Francés-Monerris, *Phys. Chem. Chem. Phys.* **2022**, 24, 19584-19594.
- [3] J. A. Roque III *et al*, *J. Am. Chem. Soc.* **2022**, 144, 8317-8336.
- [4] H. D. Cole *et al*, *Inorg. Chem.* **2023**, 62, 21181-21200.
- [5] H. D. Cole *et al*, *Inorg. Chem.* **2024**, 63, 9735-9752.
- [6] D. Abad-Montero *et al*, *J. Am. Chem. Soc.* **2025**, 147, 7360-7376.
- [7] E. Ortega-Forte *et al*, *Inorg. Chem. Front.* **2025**, 12, 3367-3383.
- [8] A. M. A. Abdelgawwad, A Francés-Monerris, *J. Chem. Theory Comput.* **2025**, 21, 1817-1830.

Electrochemiluminescence of Earth Abundant Transition Metal Complexes

P.S. Francis,¹ M.L. Pattuwage,¹ T.U. Connell,¹ E.H. Doeven,¹ O.S. Wenger²

¹School of Life and Environmental Sciences, Deakin University, Geelong, Victoria 3220, Australia.
E-mail: paul.francis@deakin.edu.au ²Department of Chemistry, University of Basel,
St. Johannis-Ring 19, 4056 Basel, Switzerland.

Essentially the reverse process to photoredox catalysis (Fig. 1a), electrochemiluminescence (ECL) involves exergonic electron transfers that generate electronically excited states, resulting in the emission of light (Fig. 1b).^[1] ECL enables exceedingly sensitive chemical detection, which has been widely utilized for clinical diagnostics.^[2]

The early development of both photoredox catalysis and ECL focused heavily on [Ru(bpy)₃]²⁺ but increasingly turned to Ir(III) complexes with (photo)chemical and photophysical properties that could be more readily manipulated through ligand structure. Whilst [Ru(bpy)₃]²⁺ remains the benchmark luminophore for ECL, Ir(III) complexes underpin emerging strategies including redox-mediated and multi-color ECL detection.^[3]

Due to the limited availability and increasing cost of precious metals such as ruthenium and iridium, considerable attention has been directed towards more sustainable earth-abundant alternatives for photocatalysis and related applications,^[4,5] but to date, relatively few advances have been reported for ECL detection. This presentation describes the development of new precious (Ru(II), Ir(III)) and earth-abundant first-row (Cr(0), Cr(III), Fe(III)) transition metal luminophores, and the manipulation of their light-producing reaction pathways to create a new generation of ECL systems.

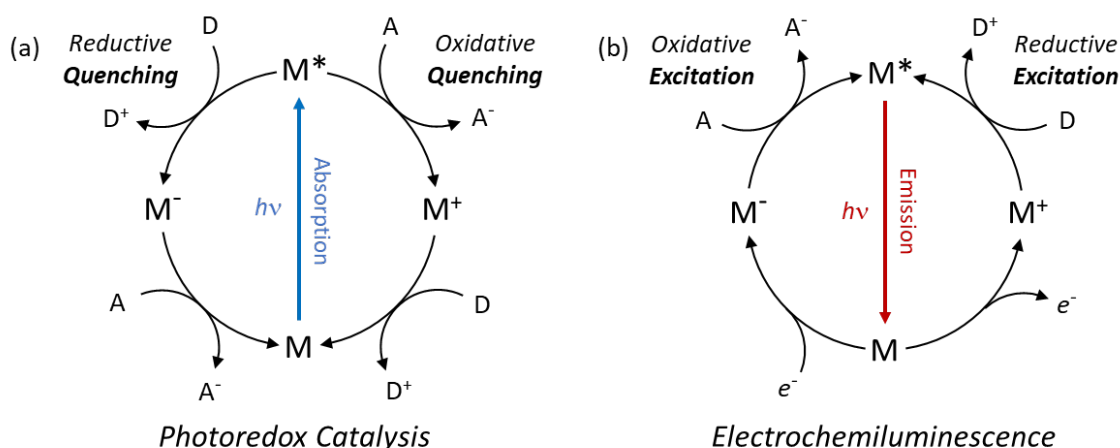


Figure 2. Generalized electron-transfer reaction pathways for (a) photoredox catalysis and (b) ECL, where M is the photocatalyst or luminophore, D is an electron donor (reductant), A is an electron acceptor (oxidant).

References

- [1] E. H. Doeven, *et al.*, *Angew. Chem. Int. Ed.* **2024**, 63, e202319047.
- [2] E. Faatz, *et al.*, in *Analytical Electrogenerated Chemiluminescence* (Ed.: N. Sojic), RSC, **2020**, 443-470.
- [3] N. S. Adamson, *et al.*, *Angew. Chem. Int. Ed.* **2024**, 63, e202412097.
- [4] J. K. McCusker, *Science* **2019**, 363, 484-488.
- [5] N. Sinha, *et al.*, *Nat. Chem.* **2023**, 15, 1730-1736.

New antennae for photoswitchable luminescent lanthanide(III) complexes

Y. Fréroux,^a S. Kiraev,^b A. Banyasz,^b O. Galangau,^a O. Maury,^b L. Norel^{*a} and S. Rigaut^{*a}

^a Univ Rennes, CNRS, ISCR, Université de Rennes, UMR 6226, F-35000 Rennes, France

^b Univ Lyon, CNRS, ENS de Lyon, UMR 5182, F-69007 Lyon, France yoann.freroux@univ-rennes.fr

Lanthanide(III)-based complexes are widely used due to their original emission features such as long-lived and narrow bandwidth luminescence from the visible up to the near infrared spectral range.^[1] Photomodulation of this emission is a fundamental challenge, which has been mostly achieved with visible light emitting Eu(III) complexes, whereas our research group more recently achieved photoswitchable NIR luminescent lanthanide(III) complexes.^[2]

To this end, we have previously designed a new ligand bearing a dithienylethene (DTE) moiety, efficient for quenching the luminescence of lanthanide(III) complexes by energy transfer in only one of its two states, even in the NIR region, paving the way for applications ranging from anti-counterfeiting systems to super-resolution microscopy. However, at this stage, these systems suffer from low brightness and present only destructive readout.^[3] Here, we present a new strategy based on new boranil-based lanthanide(III) complexes displaying (i) an improved brightness with a high on/off intensity quenching ratio, (ii) an antenna effect leading to lanthanide ion NIR emission (Ln = Yb, Er) with a non-destructive readout through selective visible light excitation in the boranil centered absorption band.

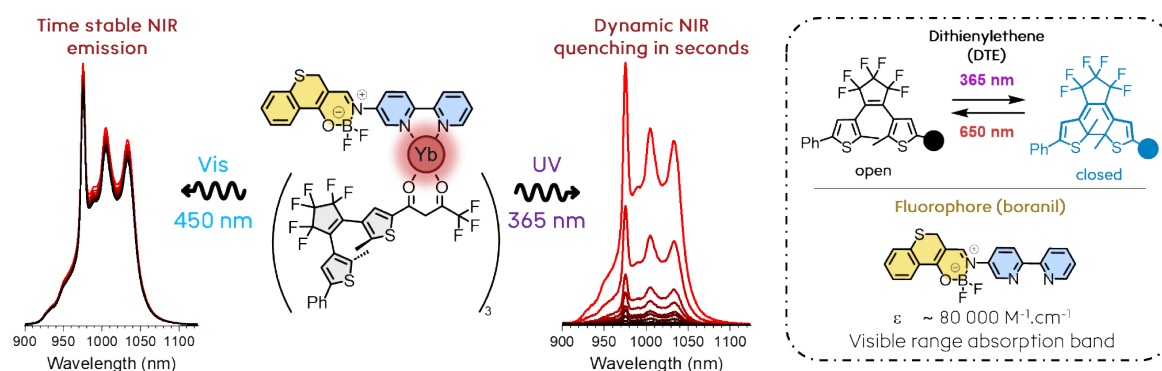


Figure 1. An Ytterbium(III) complex combining a photochromic dithienylethene ligand and a fluorophore as an antenna provides efficient luminescence switching with non-destructive readout behaviour.

Aknowlegments

We thank the Université de Rennes, the ENS de Lyon, the CNRS, the Agence Nationale de la Recherche (2LCDOR - ANR-21-CE07-0063) and LUMOMAT for support.

References

- [1] J.-C. G. Bünzli, *Coord. Chem. Rev.*, **2015**, 293-294, 19-47.
- [2] Y. Fréroux, L. Caussin, N. El Beyrouiti, S. Rigaut, L. Norel, *Handbook on the Physics and Chemistry of Rare Earths*, **2024**, 65, 35-91.
- [3] H. Al Sabea, L. Norel, O. Galangau, H. Hijazi, R. Métivier, T. Roisnel, O. Maury, C. Bucher, F. Riobé, S. Rigaut, *J. Am. Chem. Soc.* **2019**, 141, 20026-20030.

Harnessing an Oxide Relay Pathway in a Molecular Cleft for Light-Driven Water Oxidation

D. Friedewald^{a,c}, O. Anhalt^b and F. Würthner^{a,b}

^a*Institut für Organische Chemie, Universität Würzburg, Am Hubland, 97074 Würzburg (Germany); E-Mail: daniel.friedewald@uni-wuerzburg.de*

^b*Center for Nanosystems Chemistry (CNC), Universität Würzburg, Theodor-Boveri-Weg, 97074 Würzburg (Germany)*

^c*E-Mail: daniel.friedewald@uni-wuerzburg.de*

Harnessing functional groups in the outer coordination sphere to direct catalytic pathways is a powerful yet underexplored strategy. Here, following our earlier work on Ru(bda) water oxidation catalysts (bda = 2,2'-bipyridine-6,6'-dicarboxylate) within enzyme-like catalytic clefts,^[1,2] we demonstrate how a carboxyl-functionalized Ru(bda)-based molecular cleft enables an oxide relay mechanism in light-driven water oxidation. Photocatalytic studies reveal that the methyl ester derivative **Ru(bda)(Carb-COOMe)** follows an intermolecular I2M mechanism involving two Ru centers while the carboxylic acid derivative (**Ru(bda)(Carb-COOH)**) undergoes intramolecular O–O bond formation via an oxide relay pathway taking place at a single Ru center. Single-crystal X-ray analysis of **Ru(bda)(Carb-COOH)** reveals a stabilizing intramolecular hydrogen bond between the carboxyl proton and an oxygen atom of the Ru(bda) unit, which presumably maintains the catalytic center within the cleft during turnover. This is the first time that the oxide relay pathway has been observed under photocatalytic water oxidation conditions. The findings underscore the role of second coordination sphere engineering in modulating reaction pathways and advancing molecular catalyst design.

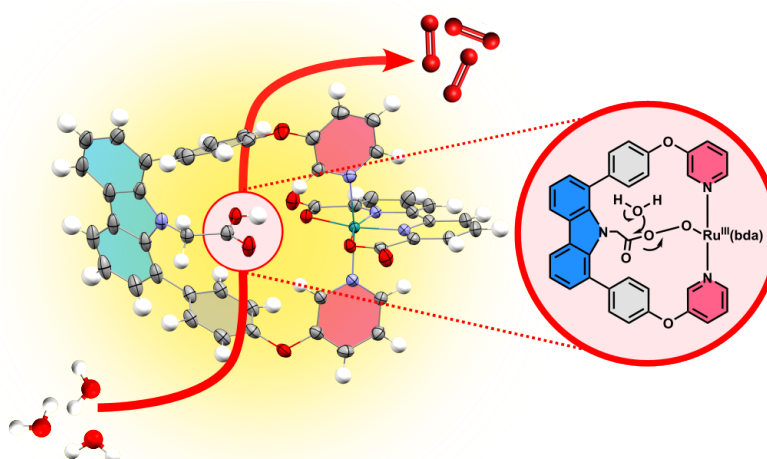


Figure 3. Photocatalytic water oxidation proceeding via the oxide relay pathway.

References

- [1] N. Noll, A.-M. Krause, F. Beuerle, F. Würthner, *Nat. Cat.* **2022**, 5, 867–877. Enzyme-like water preorganization in a synthetic molecular cleft for homogeneous water oxidation catalysis
- [2] N. Noll, F. Würthner, *Acc. Chem. Res.* **2024**, 57, 1538–1549: Bioinspired Water Preorganization in Confined Space for Efficient Water Oxidation Catalysis in Metallosupramolecular Ruthenium Architectures

Antenna effects on the photophysics of luminescent dinuclear chromium(III) complexes

D. Fritzler,^{1,2} H. Reuter,² S. Demeshko,³ F. Meyer,³ C. Wang^{1,2*}

1: Universität Konstanz, Department of Chemistry, Universitätsstr. 10, D-78464 Konstanz

2: Universität Osnabrück, Department of Biology/Chemistry, Barbarastr. 7, D-49076 Osnabrück

3: Georg-August-Universität Göttingen, Institute of Inorganic Chemistry, Tammannstr. 4, D-37077 Göttingen

E-mail: dennis.fritzler@uni-konstanz.de

Dinuclear chromium(III) complexes have been an active research topic in coordination chemistry for many decades due to their unique magnetic and optical properties.^[1] These complexes are usually bridged by one or two oxo- or hydroxo-units, exhibit antiferromagnetic coupling, and are mostly non-luminescent at room temperature. Ferromagnetically coupled dinuclear Cr(III) complexes with room-temperature luminescence remain severely scarce, but they could be fundamentally interesting compounds to allow for the crosstalk of photophysics, photochemistry, and magnetic exchange interactions.^[2]

Recent developments have shown an approach to prepare luminescent dinuclear Cr(III) complexes with ferromagnetic coupling through the combination of chosen bridging ligands and tridentate chelating ligands.^[2] Following these molecular design principles, we present two novel dinuclear Cr(III) complexes in this work, **Cr₂-ref** and **Cr₂-An** (Figure 1). The Cr(III) centers in both complexes are bridged by two hydroxo- and one acetate group, which are seen as crucial bridging elements for ferromagnetic coupling.^[3] Facial coordination of the chosen tridentate chelating ligands to the Cr(III) ions gives **Cr₂-ref** and **Cr₂-An**, while the latter contains two more anthracene-based antennas on the backbone of the chelating ligands. These antennas drastically enhance the absorption in the visible region (Figure 1), which remains a challenge for photoactive Cr(III) complexes. **Cr₂-An** shows broader near-infrared luminescence bands with slightly lower energy than **Cr₂-ref**. With the luminescence lifetime of above 100 ns in solution at room temperature, **Cr₂-An** acts as a suitable photosensitizer for green-to-blue photon upconversion with anthracene-based annihilators.

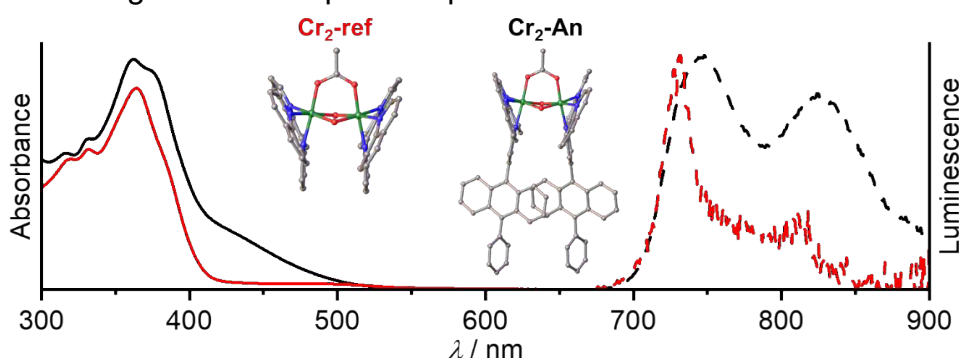


Figure 1. Absorption (solid traces) and luminescence (dashed traces) spectra for **Cr₂-ref** (red) and **Cr₂-An** (black) with the corresponding crystal structures.

References

- [1] A. Døssing, *Coord. Chem. Rev.* **2014**, 280, 38-53.
- [2] a) D. Fritzler, C. Wang, *ChemPhotoChem* **2025**, accepted, e202500094. b) S. Trippmacher, S. Demeshko, A. Prescimone, F. Meyer, O. S. Wenger, C. Wang, *Chem. Eur. J.* **2024**, 30, e202400856.
- [3] H. W. L. Fraser, L. Smythe, S. Dey, G. S. Nichol, S. Piligkos, G. Rajaraman, E. K. Brechin, *Dalton Trans.* **2018**, 47, 8100-8109.

Molecular deactivation dynamics of two photoactive iron (III) complexes

S. Genovese^{1,2}, A. M. Cancelliere¹, F. Nastasi¹, M. P. Laserna³, I. Ciofini³, F. Puntoriero¹,
S. Campagna¹

¹ChiBioFarAm, University of Messina, 31, Viale Ferdinando Stagno d'Alcontres, 98166, Messina, Italia.

²DCBB, University of Perugia, 8, Via dell'Elce di sotto, 06123, Perugia, Italia

³PSL University, Chimie ParisTech, CNRS, Institute of Chemistry for Life and Health Sciences, F-75005 Paris, France

salvatore.genovese1@studenti.unime.it

Transition metal complexes have found a crescent number of applications ranging from solar energy conversion to phototherapy [2]. However, these complexes are mostly made of precious and rare metals with ruthenium playing the predominant role [3]. In the last decade, a lot of effort has been put into the development of systems based on more abundant and less expensive metal complexes, to reach the performances of the precious ones [4]. Here, we report the excited state deactivation dynamics of two luminescent iron (III) complexes using steady-state, time-resolved techniques and computational studies (**Figure 1**).

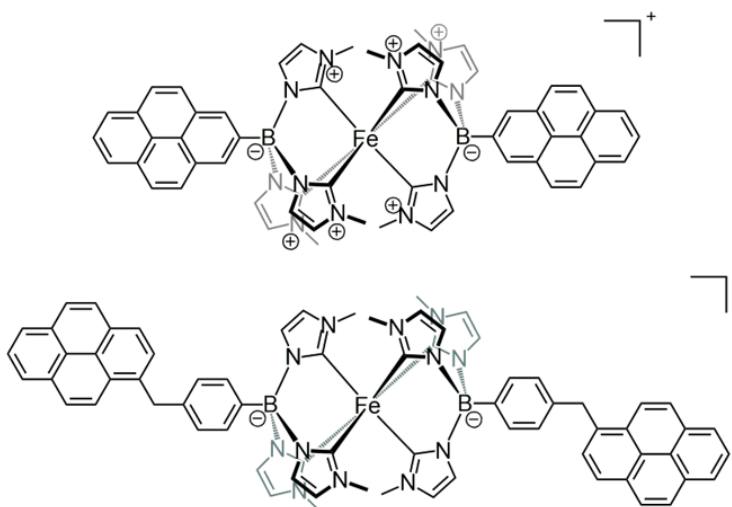


Figure 1. Structure of the two iron (III) complexes.

References:

- [1] S. Campagna, S. Genovese et al., Fe(III) complexes with prolonged luminescence lifetimes and symmetry-breaking charge separation. *Res. Square*, 2024 DOI: 10.21203/rs.3.rs-4002627/v1
- [2] (a) V. Balzani, A. Credi et al., *ChemSusChem*, (2008), 1 (1-2), 26-58 (b) L. C-C Lee, K. K-W Lo, *J. Am. Chem. Soc.* (2022), 144 (32), 14420-14440 (c) M. Idris, S. C. Kapper et al., *Adv. Opt. Mater.* (2021), 9 (8), 2001994
- [3] S. Campagna F. Puntoriero et al., Photochemistry and photophysics of coordination compounds: Ruthenium., *Top. Curr. Chem.*, (2007), 280, 117–214
- [4] O. S. Wenger, *Chem. Eur. J.* (2019), 25 (24), 6043 – 6052

Towards biohybrid systems for water photo-oxidation: design and synthesis of photo- and redox-active molecular components

F. Giorgianni^{a,b}; M.L. Di Pietro^a; S.Campagna^a; S.Serroni^a; F.Nastasi^a; F. Puntoriero^a

^a ChiBioFarAm, University of Messina, 31, V.le F. Stagno d'Alcontres, 98166, Messina, Italy

^b DCBB, University of Perugia, 8, Via dell'Elce di sotto, 06123, Perugia, Italy

federica.giorgianni@dottorandi.unipg.it

Photoinduced water splitting, which involves the conversion of water into hydrogen and oxygen through the absorption of light energy, is a promising approach for renewable energy production. However, realizing efficient and robust systems is still a key challenge.

In photocatalytic cycles, the water photo-oxidation typically involves a bimolecular process between components, making diffusion rate a limiting factor. For this reason, organizing molecules in a covalent or supramolecular system could be a possible solution. ^[1-2] DNA, with its well-defined helical structure and programmable sequence, offers a unique scaffold to bind intercalating molecules with a precise spatial arrangement ^[3] (**Figure 1**).

Our aim is to design hybrid systems for water photo-oxidation, incorporating photosensitizers and catalysts into the DNA structure, which would act both as a scaffold for efficient light absorption and as a redox-active center, exploiting the oxidation potential of nucleobases, such as guanine, which may play a redox-active role.

We report the design and synthesis of photo- and redox-active molecular components—a photosensitizer and a catalyst for water photo-oxidation—based on ruthenium complexes featuring dppz-derived planar ligands capable of DNA intercalation. The structural features of these complexes were elucidated by NMR spectroscopy, while their properties were thoroughly investigated through electrochemical analysis, UV-Vis absorption and luminescence spectroscopy. Electrochemical and kinetic experiments were specifically carried out to assess their ability to function as catalysts for water oxidation.

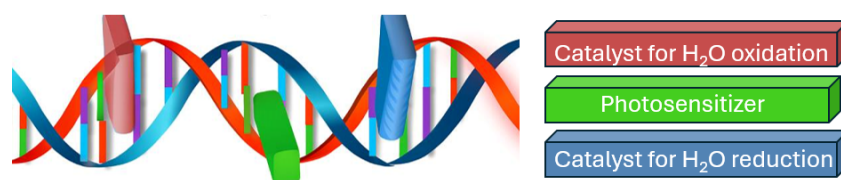


Figure 4. Schematization of the supramolecular assembly goal of the project ^[3]

References

- [1] S. Campagna, F. Nastasi, G. La Ganga, S. Serroni, A. Santoro, A. Arrigo, F. Puntoriero, Phys. Chem. Chem. Phys., **2023**, 25, 1504
- [2] N. Noll, F. Wurthner, Acc. Chem. Res., **2024**, 57, 1538–1549.
- [3] M.L. Di Pietro, G. La Ganga, F. Nastasi, F. Puntoriero, Appl. Sci., **2021**, 11(7), 3038.



Welcome to the Dark Side:

Photoactive Iron Complexes with Microsecond Excited-State Lifetimes

F. Glaser,¹ S. De Kreijger,¹ G. M. Beneventi,² A. Cadranet,^{2,3} L. Troian-Gautier^{1,5}

¹ UCLouvain, Place Louis Pasteur 1/L4.01.02, B-1348 Louvain-la-Neuve, Belgium. E-Mail: felix.glaser@uclouvain.be

² Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstr. 3, 91058, Erlangen, Germany.

³ Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, and CONICET INQUIMAE, Buenos Aires, Argentina.

⁵ Wel Research Institute, Avenue Pasteur 6, 1300 Wavre, Belgium

In recent years, photosensitizer development based on earth-abundant metals or organic dyes as a replacement for precious metal complexes in photoredox catalysis has obtained significant attention.^[1] Iron-based complexes are very attractive for this due to its high abundance in the Earth crust, low toxicity and environmental impact.^[2,3] Up to now, the limited excited-state lifetimes up to a few nanoseconds represent a limiting factor to their widespread use.

One possibility to tackle this issue is the design of molecular dyads composed of a photosensitizer and an energy acceptor. Up to now, the development of dyads mostly focused on excited-state equilibrium to repopulate the iron-based emissive state exploiting a so-called reservoir effect.^[4,5] In contrast, we designed a molecular dyad composed of an energy acceptor attached to an iron-based photosensitizer that exhibited a microsecond-living non-luminescent excited state without repopulation of the iron-centered emissive state.^[6] Photophysical characterization and comparison to the unmodified iron photosensitizer highlighted the benefit of the energy acceptor present in the dyad. In addition to an improved excited-state lifetime, the energy acceptor also changed the excited-state character to triplet. This enables singlet oxygen photosensitization and led to a tenfold increase in cage escape yield for bimolecular electron transfer, in comparison to the unmodified complex. More detailed photophysical analyses uncovered that the mechanism to populate the triplet excited state is more complex than a direct doublet-triplet energy transfer. Our results clearly highlight the advantages of molecular dyads based on iron-based complexes with previously short excited-state lifetimes.

References

- [1] C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, 49, 1057–1070.
- [2] O. S. Wenger, *Chem. Eur. J.* **2019**, 25, 6043–6052.
- [3] F. Glaser, A. Aydogan, B. Elias, L. Troian-Gautier, *Coord. Chem. Rev.* **2024**, 500, 215522.
- [4] S. Campagna, S. Genovese, A. Cancelliere, A. Arrigo, F. Puntoriero *Res. Square* **2024**, DOI: 10.21203/rs.3.rs-4002627/v1.
- [5] J. Wellauer, J., B. Pfund, I. Becker, F. Meyer, A. Prescimone, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, 147 (10), 8760–8768.
- [6] F. Glaser, S. De Kreijger, L. Troian-Gautier, *J. Am. Chem. Soc.* **2025**, 147 (10), 8559–8567.



Resolving Mechanistic Pathways in Bioinorganic Catalysis via Ultrafast X-ray Spectroscopy

R. Gomez Castillo^{1,2}, J. A. Birrel², Oliviero Canelli¹, F. A. Lima³, B. E. Van Kuiken³, M. V. Appelby⁴, N. Ghodrati³, L. Leroy⁵, E. V. Beale⁵, C. Cirelli⁵, P. J. M. Johnson, A. Kahraman⁵, V. Kabanova⁵, J. Gan⁶, H. Shafaat⁶, C. Bacellar⁵, S. DeBeer², M. Chergui¹

¹Laboratory of Ultrafast Spectroscopy (LSU) and Lausanne Centre for Ultrafast Science, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland. ²Max Planck Institute for Chemical Energy Conversion, Stiftr. 34, Mülheim a.d. Ruhr, Germany. ³European XFEL, Holzkoppel 4, Schenefeld, Germany.

⁴Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK. ⁵SwissFEL, Paul Scherrer Institut (PSI), 5232 Villigen, Switzerland.

⁶Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA

The most efficient and sustainable means of storing energy from raw sources involves harnessing chemical bonds utilizing cost-effective catalysts. Many of these catalysts are inspired by bioinorganic systems where transition metal centers mediate complex redox transformations. Heterometallic systems, such as the FeMn cofactor in the ribonucleotide reductase-like enzyme R2lox, have garnered interest due to their unique chemical reactivity compared to their homo analogues. R2lox, in particular, exhibits an unusually efficient light-induced decarboxylation—a rare photoactivity for natural enzymes outside of photosynthesis. This raises fundamental questions about the role of each metal site in the enzyme's reactivity, specifically the identity of the metal involved in the metal-ligand charge transfer (MLCT) that initiates the photochemical process. These questions have been addressed through element-specific femtosecond X-ray absorption spectroscopy (fs-XAS) targeting both Fe and Mn centers in R2lox enzyme and relevant synthetic model complexes. We will present our fs XAS results on Fe-Mn and Fe-Fe enzymes and analogues model complexes and discuss the photoinduced process in the light of their comparison.

"Heteroleptic Copper(I) and Silver(I) Complexes with Me-dpa/Xantphos Ligands as Promising Materials for Light-Emitting Devices"

I.A. González^a, M.P. Herrera^{a,b}, S.A Muñoz^{a,b}, A. Cabrera^b

A Departamento de Química, Facultad de Ciencias Naturales, Matemática y del Medio Ambiente de la Universidad Tecnológica Metropolitana. E-mail: igopnzalezp@utem.cl

b Departamento de Química Inorgánica, Facultad de Química y Farmacia de la Pontificia Universidad Católica de Chile

The transition toward sustainable lighting technologies has driven the development of solid-state light-emitting devices (SSL) based on earth-abundant metals.^{1,2} In this study, two series of heteroleptic complexes were investigated: [Cu(Me-dpa)(Xantphos)]BF₄ (Cu1-2) and [Ag(Me-dpa)(Xantphos)]BF₄ (Ag1-2), where Me-dpa denotes substituted dipyridylamine ligands and Xantphos acts as the auxiliary phosphine ligand.

The Cu(I) and Ag(I) complexes were synthesized and characterized via NMR spectroscopy (¹H, ¹⁹F, ³¹P, ¹¹B), UV-Vis absorption, and cyclic voltammetry. The Me-dpa/Xantphos ligand framework enables fine-tuning of the electronic and photophysical properties of both metal centers, which exhibited an intense emission near 350 nm for both complexes series and green-yellow photoluminescence (483–550 nm) in the solid state, highlighting their potential as active materials for illumination devices. The complexes showed suitable photophysical characteristics with blue and Blue-green color for Ag (I) and Cu(I,) respectively, with stable coordination environments. Positioning these systems as promising candidates for cost-effective, efficient, and environmentally responsible emissive materials, for example, a light electrochemical emitting cell. We are currently conducting different photophysical experiments to understand each system.

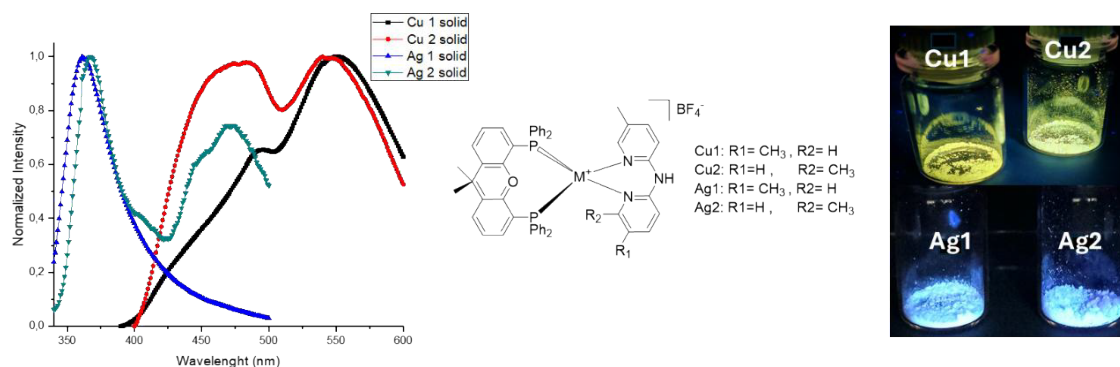


Figure 1. Photoluminescence in the solid state (left) of the complexes series Cu1-2 and Ag 1-2 (middle) and respective picture of the powder (right)

Aknowlegments: Thanks to project FONDECYT N° 1230199

References

- [1] Meiser, S., et al., *Materials Today*, **2014**, 17, 217-223
- [2] Moudam, O., et al., *RCS Advances*, **2015**, 5, 95047-95053

Synthesis, DNA Binding Interactions & Time Resolved Spectroscopy of Ru(II) – Pteridinyll Complexes

D. Graczyk¹, P. Malakar², S. J. Quinn¹

¹ School of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

² Central Laser Facility, STFC Rutherford Appleton Laboratory, Harwell, UK

Email: daniel.graczyk@ucdconnect.ie

Octahedral transition metal polypyridyl complexes with π -extended intercalating ligands such as dipyrldophenazine (dppz) are effective DNA-binding probes due to their high binding affinities, tunable photophysical properties and differential interactions of Λ and Δ enantiomers with chiral DNA systems.^[1,2] There is considerable interest in DNA as a diagnostic and therapeutic target, especially non-canonical forms such as G-quadruplexes, which are implicated in cancers and are involved in gene transcription.^[3] Due to the diverse structure & function of G-quadruplexes, they are a key target for the development of novel probes.

In this work, a family of Ru(II) polypyridyl complexes with hydrogen bonding groups on the terminus of a dppz-type ligand have been synthesised, chirally resolved and their interactions with DNA profiled.^[4] The ancillary ligands determine the photophysical functionality of the complexes as “light-switch” complexes showing luminescence enhancement upon binding, or photo-oxidising capability when in the presence of guanine. Time-resolved infrared spectroscopy has been applied to study excited state dynamics in the absence and presence of DNA, with the complex $[\text{Ru}(\text{phen})_2(\text{L-diamino})]^{2+}$ showing perturbation of C and T DNA base vibrations visible due to the site effect. The compounds have been prepared with a view to study their G-quadruplex binding and potential incorporation into abasic site quadruplexes.

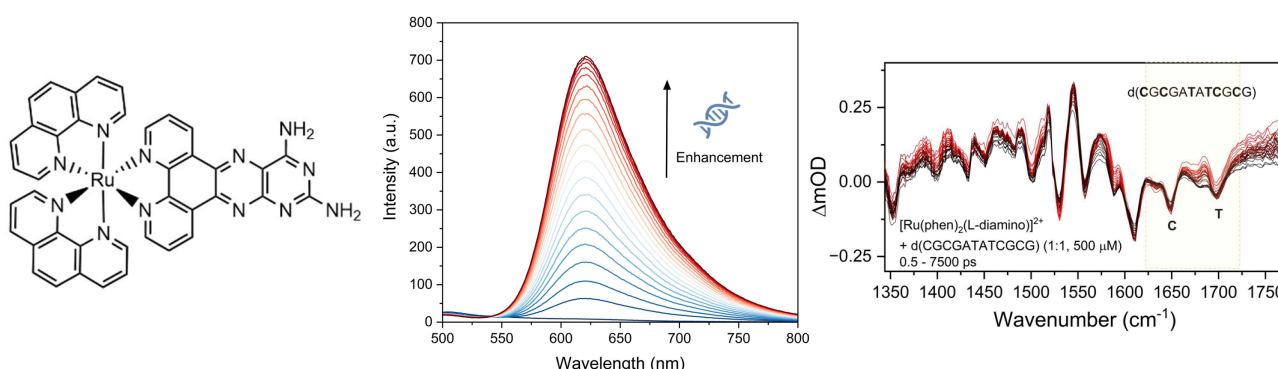


Figure 1. Example of a Ru(II)-pteridinyll complex, luminescence enhancement of $[\text{Ru}(\text{phen})_2(\text{L-diamino})]^{2+}$ vs. st-DNA, and TRIR spectra of the complex in the presence of a DNA dodecamer.

Acknowledgements

D.G. acknowledges funding from Research Ireland (GOIPG/2022/922) and thanks the staff at the RAL CLF for support with time-resolved measurements.

References

- [1] P. M. Keane, S. J. Quinn, J. M. Kelly *et al.*, *Chem. Sci.*, **2020**, *11*, 8600-8609
- [2] M. R. Gill, J. A. Thomas, *Chem. Soc. Rev.*, **2012**, *41*, 3179-3192
- [3] S. Balasubramanian, S. Neidle, *Curr. Opin. Chem. Biol.*, **2009**, *13*, 345-353
- [4] S. R. Dalton, S. J. Nieter-Burgmayer *et al.*, *J. Biol. Inorg. Chem.*, **2008**, *13*, 1133-1148

Highly luminescent 1,3-bis(4-phenylpyridin-2-yl)-4,6-difluorobenzene platinum(II) complexes: Exploring the effect of substituents on the 4-phenylpyridine unit

Giulia De Soricellis,^{1,2} Veronique Guerchais,³ J. A. Gareth Williams,⁴ Daniele Marinotto,⁵ Alessia Colombo,¹ Claudia Dragonetti,¹ Francesco Fagnani,¹ and Dominique Roberto¹

¹ Dipartimento di Chimica, Università degli Studi di Milano, UdR INSTM di Milano, via C. Golgi 19, I-20133 Milan, Italy

² Dipartimento di Chimica, Università di Pavia, Via Taramelli 12, I-27100 Pavia, Italy Dipartimento di Chimica, Università di Pavia, Via Taramelli 12, I-27100 Pavia, Italy

³ Univ Rennes, CNRS, ISCR-UMR 6226, F-35000 Rennes, France, veronique.guerchais@univ-rennes1.fr

⁴ Department of Chemistry, Durham University, Durham, DH1 3LE, UK

⁵ Istituto di Scienze e Tecnologie Chimiche (SCITEC) "Giulio Natta", Consiglio Nazionale delle Ricerche (CNR), via C. Golgi 19, I-20133 Milan, Italy

Luminescent platinum(II) complexes are extensively researched owing to their potential for application in nonlinear optics, bioimaging, sensing, photocatalysis, and electro-luminescent devices. Unlike complexes of d⁸ metal ions such as Ir(III), the square planar geometry favours the formation of bimolecular states – either in the ground state (dimers or higher aggregates) or in the excited state (excimers) – thanks to Pt⋯Pt or ligand⋯ligand intermolecular interactions. These species may emit at lower energies than the isolated molecules, offering an intriguing route to deep-red / NIR-emitting materials, colour modulation according to the local concentration, and even white light emission.

Platinum(II) complexes of the NCN-coordinating ligand 1,3-bis(pyridin-2-yl)benzene (dpyb) are among the brightest and most efficient Pt-based emitters, apparently owing to the combination of a particularly short Pt–C bond and high rigidity, minimising non-radiative decay.^[2]

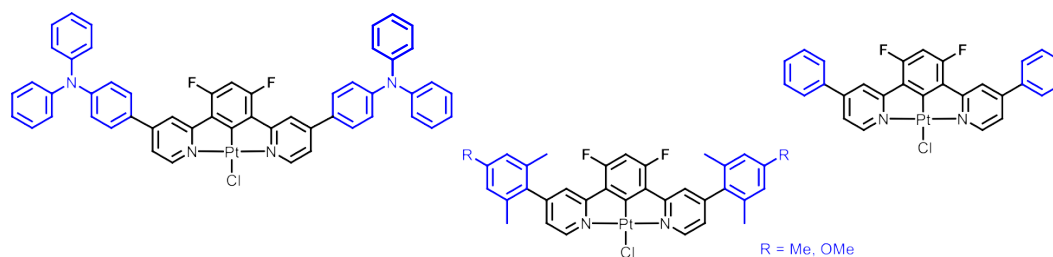


Figure 1. Selected examples of functionalized Pt(II) complexes

In this context, we found that introducing bulky π -delocalized groups at the 4-position of the pyridine rings in Pt(F₂dpyb)Cl {F₂dpybH = 1,3-bis(pyridin-2-yl)-4,6-difluorobenzene} (see Figure 1) is an effective strategy to achieve high luminescence quantum yields, both in solution and in thin films. This approach also enabled the efficient fabrication of OLEDs spanning from blue to red.^[2]

[1] C. Dragonetti, F. Fagnani, D. Marinotto, A. Di Biase, D. Roberto, M. Cocchi, S. Fantacci, A. Colombo, *J. Mater. Chem. C*, **2020**, *8*, 7873 – 7881.

[2] A. Colombo, G. De Soricellis, F. Fagnani, C. Dragonetti, M. Cocchi, B. Carboni, V. Guerchais, D. Marinotto, *Dalton Trans.* **2022**, 51, 12161 – 12169. A. Colombo, G. De Soricellis, C. Dragonetti, F. Fagnani, D. Roberto, B. Carboni, V. Guerchais, T. Roisnel, M. Cocchi, S. Fantacci, E. Radicchi, D. Marinotto, *J. Mater. Chem. C* **2024**, *12*, 9702 – 9715.

X-ray Scattering From Molecular Dynamics Simulations of Photoactivated Molecules in Aqueous Solution

O. Ohlson^{1*}, V. Markmann¹, A. O. Dohn¹, M.M. Nielsen¹, K.B. Møller², K. Haldrup¹, *et al.*

¹ Physics Department, Technical University of Denmark, ² Chemistry Department, Technical University of Denmark

*Olioh@dtu.dk

Ultrafast photoinduced reactions studied at XFELs and synchrotrons yields scattering data with high temporal and spatial resolution. Such data is convoluted, requiring a theoretical model to be deciphered. Using computational simulations, the scattering signal contributions can be theoretically predicted. The cage scattering term, stemming from the solute-solvent interactions, is often studied to gain further insight into the solvation dynamics.

Iron(II)hexacyanide may undergo photoinduced ligand dissociation and aquation (figure 1). However, the intricate reaction mechanism has not yet been pinned down [1-6]. The focus of our work is to model the difference scattering terms for the states along the photoaquation pathway and decipher experimentally obtained data. Using molecular dynamics (MD) simulations to model specific scattering term contributions [7], our preliminary findings indicate a solvent reorientation being required to form a photoaquated species, as well as the photoaquated species being the main product present at $\Delta t=200$ ps with elongated Fe-CN bonds relative the ground state. In addition, the work has also enabled further improvements on modelling accurate scattering signals from computational simulations.

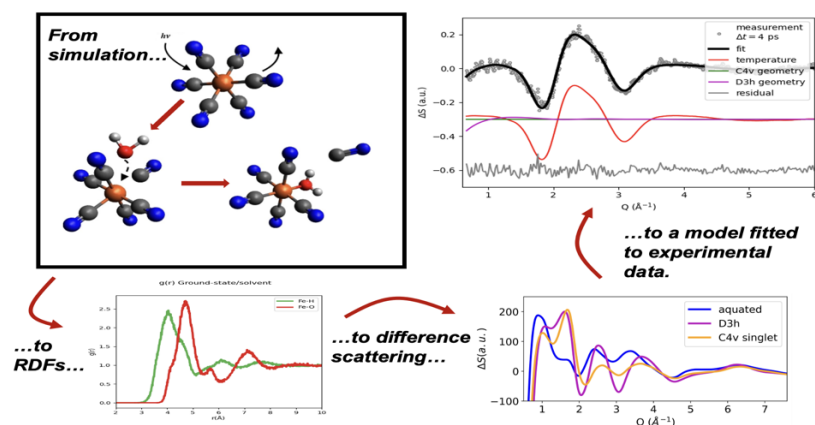


Figure 1: Overview of the Iron(II)hexacyanide photoaquation,

Aknowlegments

Thanks to DANSCATT for supporting the beamtime activities, as well as to Novo Nordisk Foundation for project funding (grant number NFF20OC0061740).

References

- [1] M. Reinhard et al., *Nat. Commun.*, **2023**, 14 (1), 2443. [2] M. Reinhard et al., *JACS*, **2017**, 139 (21), 7335-7347. [3] A. M. March et al., *J. Chem. Phys.*, **2019**, 151 (14), 144306. [4] Shirom, M. and Stein, G., *J. Chem. Phys.*, **1971**, 55 (7), (3372-3378), 3379-3382. [5] V. Vaz da Cruz, et al., *PCCP*, **2022**, 24 (45), 27819-27826. [6] M. Ross, et al., *J. Chem. Phys. B*, **2018**, 122 (19), 5075-5086. [7] A. Dohn et al., *J. Phys. B: At. Mol. Opt. Phys.*, **2015**, 48 (24), 244010.

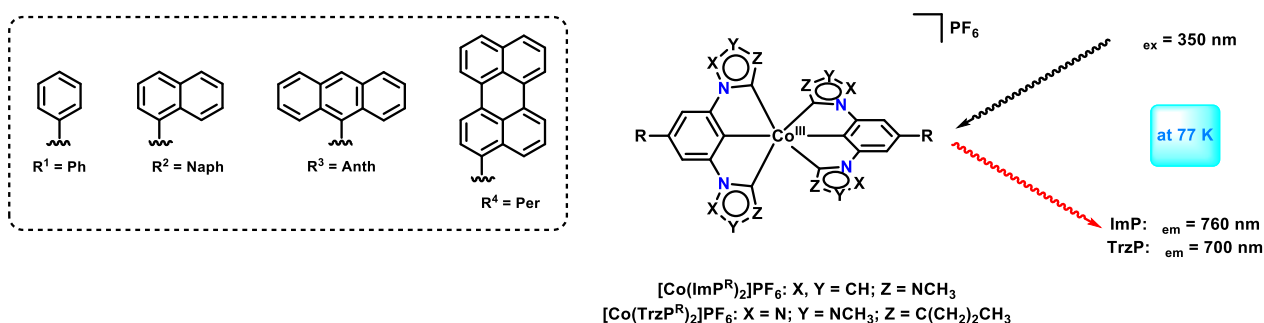
Low-Temperature Emission of Cyclometalated Cobalt(III) Complexes Linked to Organic Chromophores

M. Henning, A. Krishna, L. Fritsch, M. Bauer

Department of Chemistry, Paderborn University, Warburger Str. 100, 33098 Paderborn, Germany

maximilian.henning@upb.de

With the aim of developing new sustainable strategies that reduce the use of fossil fuels, one approach uses photosensitisers which are excited by light absorption and subsequently trigger chemical reactions.¹ These photosensitisers are predominantly based on ruthenium, osmium and iridium. However, owing to their rarity in earth's crust, high costs are associated with them. Thus, this work focuses on synthesising photoactive complexes based on cobalt, which is more common and hence less expensive.² Due to the weak ligand field splitting of 3d metal-based complexes, the excited-state lifetimes are intrinsically short because metal-centred (MC) states allow for rapid deactivation. This is why i) the bichromophoric approach is introduced to prolong lifetimes of excited states by establishing an equilibrium between the triplet state of the chromophore and an emissive triplet metal-to-ligand charge transfer (MLCT) state, and ii) strong σ donor ligands coordinate the metal centre to increase the ligand field splitting which destabilises MC states.^{3,4} Accordingly, two series of cyclometalated cobalt complexes with imidazole- and triazole-based carbenes were synthesised (Fig. 1). These complexes exhibit low-temperature emission originating from a ³MC state. Depending on the type of carbene, the emission is observed in a range of 700 – 760 nm. While these results are already promising, further spectroscopic characterisation is required to fully understand the excited state dynamics.



References

- [1] A. Juris, V. Balzani, F. Barigelli, S. Campagna, P. Belser, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, 84, 85–277.
- [2] P. Dierks, Y. Vukadinovic, M. Bauer, *Inorg. Chem. Front.* **2022**, 9, 206–220.
- [3] Y. Liu, P. Perrson, V. Sundström, K. Wärnmark, *Acc. Chem. Res.* **2016**, 49 (8), 1477–1485.
- [4] P. Dierks, A. Pöpcke, O. S. Bokareva, B. Altenburger, T. Reuter, K. Heinze, O. Kühn, S. Lochbrunner, M. Bauer, *Inorg. Chem.* **2020**, 59 (20), 14746–14761.

Light- and Redox-Controlled ON/OFF Switching in PCET

Masanari Hirahara Yuya Matsuzaki, Kanon Taniguchi, Yuto Yane

Department of Applied Chemistry, Faculty of Engineering, Osaka Institute of Technology, 5-16-1 Omiya, Asahi Ward, Osaka, 535-8585. E-mail masanari.hirahara@oit.ac.jp

Stimuli-responsive functional materials have received significant attention due to their fundamental importance and wide-ranging applications in catalysis^[1] and soft materials.^[2] In this study, stimuli-triggered PCET ON-OFF switching was investigated in a series of ruthenium complexes (PCET = proton coupled electron transfer). The carboxy-ligated complex **1** did not show thermal substitution reaction under various pH conditions. Upon visible light irradiation, **1** underwent photosubstitution, yielding **2** under neutral conditions and **3** in strongly basic conditions (Figure 1, left). The metastable **2** displayed PCET forming Ru^{IV}=O species via Ru^{III}-OH while **1** displayed pH independent one electron oxidation (Figure 1, center). Under neutral to weakly acidic conditions, the oxidation currents for **2** decreased while those for **1** increased with repeated scans, indicating redox-induced conformational changes (Figure 1, right). These light and redox induced conformational changes were observed repeatedly, confirming the reversible PCET ON-OFF switching. Simulations of the cyclic voltammograms aligned well with a model describing a pH independent conformational change from **2**(Ru^{III}-OH) to **1**(Ru^{III}) ($k_{1\text{obs}}$) and a pH dependent electron exchange between **2**(Ru^{III}-OH) and **1**(Ru^{II}) ($k_{2\text{obs}}$). Notably, at pH 8–10, the redox potentials of **1** and **2** differed significantly (>0.25 V), slowing the redox-induced conformational change. Conversely, under weakly acidic condition (pH <6), the potential difference of <0.15 V facilitated rapid conformational change. These findings provide valuable insights for the rational design of stimuli-responsive PCET molecular systems.

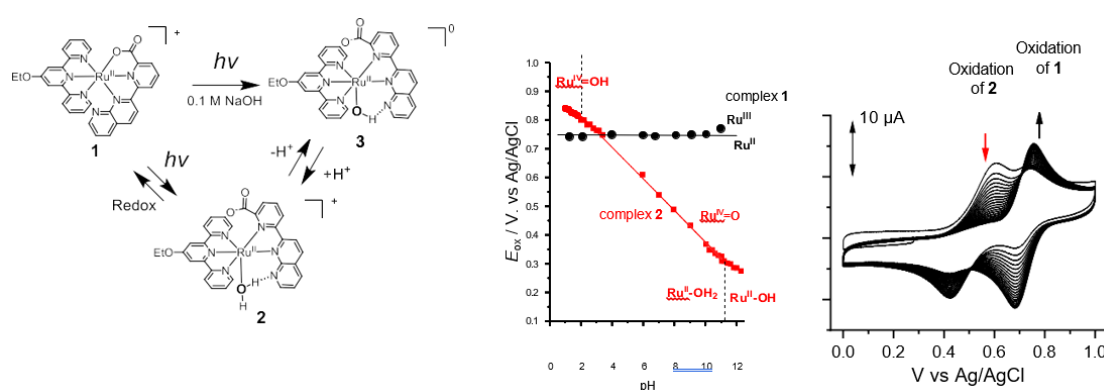


Figure 1. Left: Stimuli responses among **1**, **2**, and **3**. Center: Pourbaix diagram of **1** (black) and **2** (red). Right: Cyclic voltammograms of **2** at pH 7 from 1st to 20th scans. C_{Ru} : 0.5 mM, scan rate: 1 V/s.

Acknowledgments

We thank Prof. S. Masaoka (Osaka Univ.) and M. Kondo (Inst. Sci. Tokyo) for X-ray crystallography.

References

- [1] (a) J. Wang, B. L. Feringa, *Science* **2011**, 331, 1429-1432; (b) M. Kravets, M. Flaibani, M. Szewczyk, P. Posocco, V. Sashuk, *ACS Catalysis* **2023**, 13, 15967-15976.
- [2] Q. Li, *Photoactive Functional Soft Materials: Preparation, Properties, and Applications*, Wiley-VCH, **2018**.

Excited-State Characterization of Novel Iron (II) Isocyanide Complexes Using Ultrafast Spectroscopy

T. Honda, T. Yoshida, T. Ogawa, K. Miyata, K. Onda

Department of Chemistry, Kyushu University, Motooka, Nishi-ku, Fukuoka, Japan.

E-mail: honda.teruyuki.699@s.kyushu-u.ac.jp

Iron (II) complexes are attractive earth-abundant alternatives to Ru(II) or Ir(III) systems, in which long-lived $^3\text{MLCT}$ states are often utilized for photocatalysts or luminescent materials. The weak ligand field splitting in general Fe(II) complexes, however, causes rapid deactivation of $^3\text{MLCT}$ states via low-lying ^3MC states, as seen in $[\text{Fe}(\text{bpy})_3]^{2+}$.
[1]

We have developed novel isocyanide ligands to overcome this limitation, featuring strong σ -donor and π -acceptor properties. Relative to reported isocyanide ligands [2], our ligand incorporates extended π -conjugation and heteroatoms, lowering the π^* orbital energy and stabilizing MLCT-type excited states in Fe (II) complexes. The molecular structure of the synthesized bidentate isocyanide ligands and Fe (II) complex (FeCN) are shown in Fig.1 (a and b). The absorption originating from MLCT was observed around 400 nm (Fig.1 (c)).

The UV-vis transient absorption spectra exhibited three distinct decay components: The first component decayed approx. 2 ps, the second one approx. 20 ps, and the third one over 1 ns. The time-resolved infrared (TR-IR) spectra exhibited the same decay components (Fig. 2) and a spectral high-frequency shift as time progressed. Notably, the ground-state bleach over 1 ns indicates the presence of a long-lived excited state with a nanosecond-scale lifetime. Moreover, FeCN exhibited the luminescence with a *nanosecond-scale* lifetime, of which spectrum is distinctly different from that of the free ligand. Detailed analysis is currently underway, and the findings, including the characterization of a complex with a newly synthesized tridentate ligand, will be presented.

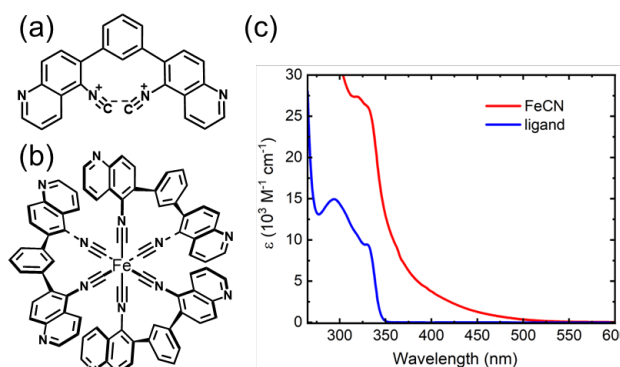


Fig. 1. (a) Novel isocyanide ligand. (b) Molecular structure of the iron isocyanide complex (FeCN). (c) UV-vis absorption spectra.

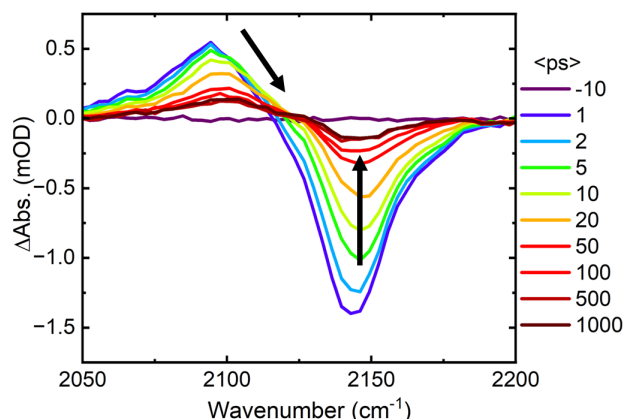


Fig. 2. TR-IR spectra of FeCN in THF (excitation wavelength = 400 nm).

References

- [1] C. Bressler, *et al.*, *Science*, **2009** 323 489-492.
- [2] C. Wegeberg, *et al.*, *J. Am. Chem. Soc.* **2024**, 146, 4605.

Energy Loop-Induced Nonlinear Emission in a Eu(III) Complex via the 7F_1 State Generated through a Radiative Pathway

S. Hosoya¹, M. Wang², T. Nakanishi³, Y. Hasegawa^{2,4}, Y. Kitagawa^{2,4}

¹Graduate School of Chemical Sciences and Engineering, Hokkaido Univ., ²Faculty of Engineering, Hokkaido Univ. ³Research Center for Electronic and Optical Materials, National Institute for Materials Science, ⁴WPI-ICReDD, Hokkaido Univ; Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan. E-mail: shota111018@eis.hokudai.ac.jp

The utilization of higher excited states has attracted considerable attention as a promising strategy for developing advanced photophysical functions, such as up-conversion, nonlinear emission, and reverse saturable absorption^[1,2]. In these processes, intermediate excited states play a crucial role by providing access to higher-energy states via multiphoton or stepwise excitation pathways. These intermediate states are typically generated through endergonic mechanisms, including photon absorption or hot-band formation facilitated by thermal energy. Alternatively, they can also be generated by exergonic processes, such as radiative relaxation or cross-relaxation from higher excited states. This exergonic formation has been effectively exploited in lanthanide-doped inorganic nanoparticles, forming an energy loop that amplifies the overall emission intensity nonlinearly^[3]. However, achieving similar energy loops in organic systems remains challenging, primarily because the intermediate excited states generated by exergonic processes in organic molecules correspond to vibrationally excited levels of the ground state and have very short lifetimes.

In this study, we report the first realization of such an energy loop in a coordination polymer composed of Eu(III) and pyrene-based ligands, $[\text{Eu}(\text{hfa})_3(2,7\text{-POpy})]_n$ (Figure 1a,b). To overcome the transient nature of the intermediate states, we employed the long-lived triplet excited states of the pyrene ligands as energy reservoirs. Under continuous-wave excitation, the radiatively populated Eu(III) 7F_1 state triggered energy transfer from the pyrene ligands, enabling re-excitation to the 5D_0 state before relaxation to the 7F_0 ground state occurred (Figure 1c). This process established an energy loop, leading to pronounced nonlinear emission behavior.

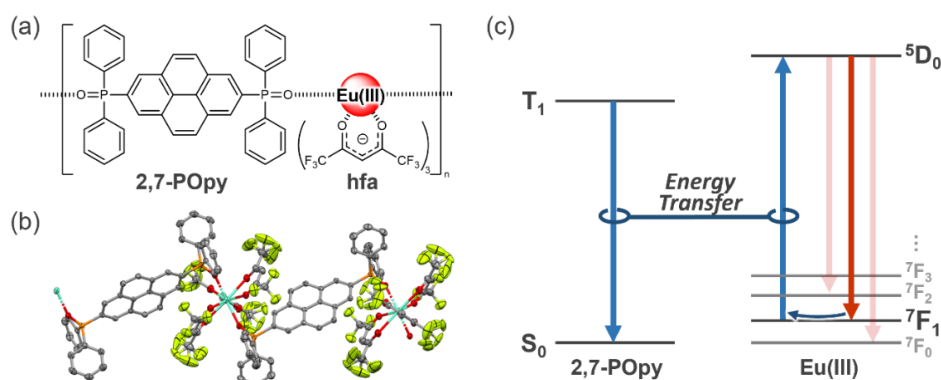


Figure 5. (a) Molecular structure, (b) crystal structure, (c) Schematic photosensitized emission mechanism of the coordination polymer $[\text{Eu}(\text{hfa})_3(2,7\text{-POpy})]_n$.

References

- [1] J. C. Goldschmidt, S. Fischer, *Adv. Opt. Mater.* **2015**, 3, (4), 510. [2] S. Hirata et. al, *Nat. Mater.* **2014**, 13, 938. [3] M. Szalkowski et. al., *Chem. Soc. Rev.* **2025**, 54, 983

Phase-Migrating Z-Scheme Charge Transportation Enables Photocatalytic Molecular Conversions Harnessing Water as an Electron Source

R. Itagaki¹, A. Nakada¹, H. Suzuki¹, O. Tomita¹, R. Abe¹

¹ Graduate School of Engineering, Kyoto University, Kyoto daigaku-katsura, Nishikyo-ku, Kyoto 615-8530, JAPAN. E-mail: itagaki.ren.75h@st.kyoto-u.ac.jp

Photocatalytic molecular conversions giving value added product are of great interest. Ideally, it is desirable to utilize water as an electron source for these molecular conversion reactions. Artificial Z-scheme reaction system composed of two-different photocatalysts is a potential strategy to connect various reductive molecular conversions with water oxidation, as demonstrated in overall water splitting.^[1] However, it is basically difficult to perform organic molecular conversions integrated with water oxidation due to low solubility of organic reactants in water. In this study, we develop a stepwise Z-scheme photocatalytic system utilizing a water/1,2-dichloroethane (DCE) biphasic solution with a ferrocenium/ferrocene (Fc⁺/Fc) phase-migrating electron mediator to connect reductive coupling of benzyl bromide in DCE phase and water oxidation (Figure 1a).

Under visible light, a H₂O/DCE biphasic solution with Fc as an electron donor, a photoredox catalyst, and benzyl bromide (Bn-Br) undergoes reductive coupling to form dibenzyl (Bn₂) in the DCE phase, while Fc⁺ forms in the aqueous phase (Figure 1a, b).^[2] On the other side, Fc⁺ can be utilized as an electron acceptor for photocatalytic water oxidation with a semiconductor photocatalyst in the aqueous phase (Figure 1a, c). More importantly, the ratio of generated Bn₂ and O₂ satisfies the stoichiometry corresponding to the overall reaction (Figure 1b, c). Eventually, the Fc⁺/Fc redox couple transports an electron by the photoredox induced liquid-liquid phase migration to achieve photoreduction of Bn-Br coupled with water oxidation.^[3]

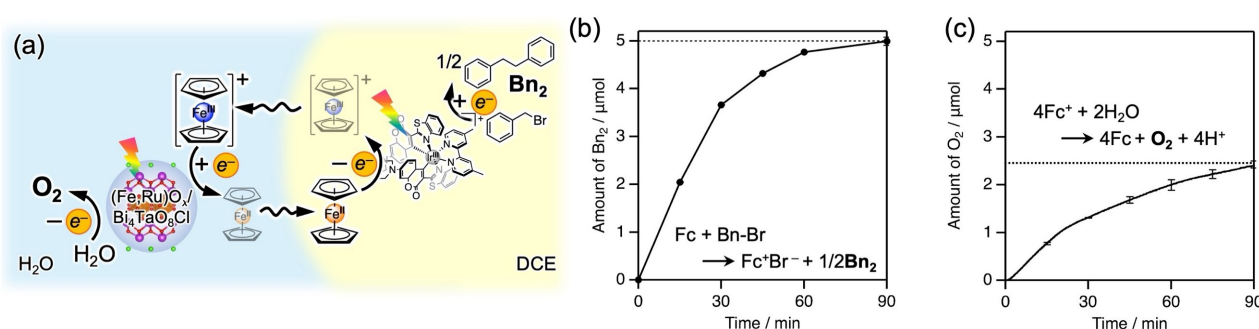


Figure 1. (a) Conceptual scheme of a biphasic Z-scheme photocatalytic system using Fc⁺/Fc as a phase-migrating electron mediator. Time course of half reactions of (b) Bn₂ formation using photoredox catalyst and Fc as an electron donor in a H₂O/DCE (2:1, v/v) biphasic solution under exposure to visible-light (λ = 470 nm), and (b) O₂ evolution using photogenerated Fc⁺ by Bn₂ production as an electron acceptor and a semiconductor photocatalyst under exposure to visible-light (λ = 430 nm) by a stepwise one. The dashed line shows the upper limit of Bn₂ and O₂ evolution expected from the amount of Fc added to these solutions.

References

- [1] R. Abe, J. Tang, et al. *Chem. Rev.* **2018**, *118*, 5201.
- [2] R. Itagaki, S. Takizawa, H.-C. Chang, A. Nakada, *Dalton Trans.* **2022**, *51*, 9467.
- [3] R. Itagaki, A. Nakada, R. Abe, et al. *J. Am. Chem. Soc.* **2025**, *in press*. (DOI: 10.1021/jacs.5c02276)

CPL inducement and energy transfer in Eu(III) complexes by chiral transition metal complexes observed by steady-state and time-resolved CPL spectroscopy

M. Iwamura¹, J. Yamashita¹, T. Takanashi¹, K. Nozaki¹ and T. Tsubomura²

¹University of Toyama, Gofuku 3190, Toyama-shi, Toyama, Japan. ²Seikei University, Kichijoji-Kitamachi 3-3-1, Musashino-shi, Tokyo, Japan. E-mail miwamura@sci.u-toyama.ac.jp

Circularly polarized luminescence (CPL) from achiral or racemic emitting molecules induced by coexisting chiral agents in the media is called induced CPL (iCPL). Such emitting molecules are attracted for the application of highly sensitive chiral sensing. [Eu(pda)₂]⁻ (pda: 1,10-phenanthroline-2,9-di-carboxylic acid, Fig.1) exhibits intense iCPL with chiral molecules such as amino acids.[1][2] In this work, we focused on the iCPL of [Eu(pda)₂]⁻ by Δ(Λ)-[Co(en)₃]³⁺ in aqueous solution. In this system, it is expected that inducement of CPL and energy transfer occurs from the [Eu(pda)₂]⁻ to the Co complex. To investigate both iCPL and energy transfer, CPL spectrum, emission lifetime and time-resolved CPL measurements were conducted. Positive and negative CPL were observed for the ⁵D₀→⁷F₁ transition of [Eu(pda)₂]⁻ in aqueous solution containing Δ- and Λ-[Co(en)₃]³⁺, respectively. The emission decays are well reproduced by three lifetime components: τ₁ (~6 μs), τ₂ (~60-50 μs), and τ₃ (100-700 μs). The shorter lifetime components of τ₁ and τ₂ are attributed to [Eu(pda)₂]⁻ associated with the [Co(en)₃]³⁺, where energy transfer from Eu³⁺ to [Co(en)₃]³⁺ shortens the lifetimes. Time-resolved CPL shows that |g_{lum}| rises in the time region of 0-20 μs and decays in the time region of 0.5~1 ms (Fig. 2). Fitting analysis revealed that the sign of g_{lum} for the τ₁ component is opposite to that of the τ₂ one, and that of the τ₃-component is very close to 0. These results indicate that the solution includes two types of CPL-exhibiting species (τ₁ and τ₂ components). In addition, the CPL signals of the solutions of various concentrations and mole ratios of Δ/Λ-[Co(en)₃]³⁺ showed that CPL is induced by two [Co(en)₃]³⁺ molecules associated to [Eu(pda)₂]⁻ on the homoallosteric effect. These features demonstrate the potential of [Eu(pda)₂]⁻ for a sensing probe molecule using steady-state and time-resolved CPL spectroscopy.

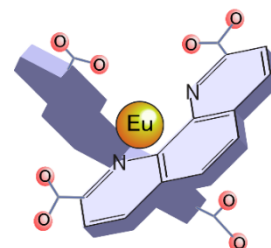


Figure 1. [Eu(pda)₂]⁻

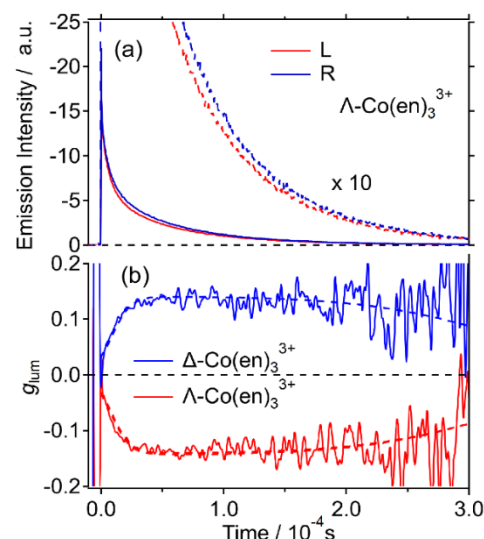


Figure 2. Time-resolved circularly polarized luminescence of [Eu(pda)₂]⁻. (λ_{ex} = 355 nm) Temporal profiles of (a) I_L and I_R and (b) g_{lum} (0 - 0.3 ms, [Eu] = 0.1 mmol/ dm³, [Co] = 0.5 mmol/ dm³)

References

- [1] K Okutani, K Nozaki, M Iwamura, *Inorg. Chem.*, **2014**, (53), 5527
- [2] H. Koike, K. Nozaki., M.Iwamura, *Chem. Asian J.*, **2020**, (15), 85

Organic Functionalization of Thiomolybdates for HER – Enabling the Design of Photocatalytic Dyads

M. Jahn^a, J. Schummer^a, L. Kammerer^a, A. Meyer^a, C. Streb^a

^aDepartment of Chemistry, Johannes Gutenberg University, Duesbergweg 10-14, 55128 Mainz, Germany,
E-Mail: moritz.jahn@uni-mainz.de

Thiomolybdates are a promising class of molecular catalysts for photocatalytic or electrocatalytic hydrogen evolution reaction (HER). [1] The prototype cluster $[\text{Mo}_3\text{S}_{13}]^{2-}$ has been studied for HER catalysis under both homogeneous and heterogeneous conditions, providing a noble metal free alternative to commonly used platinum catalysts. [2,3] Although thiomolybdates have received increasing attention in recent years, their structural diversity remains limited. [4,5] This work focuses on establishing structural modifications of thiomolybdate clusters by functionalization with organic ligands, therefore accessing more structural diversity and investigating in the photocatalytic HER activity of these new compounds. Structural modifications allow to gain further insights into the mechanism of catalytic hydrogen evolution. Furthermore, organic functionalization can be utilized to design dyads containing both, ruthenium-based photosensitizers or organic dyes respectively.

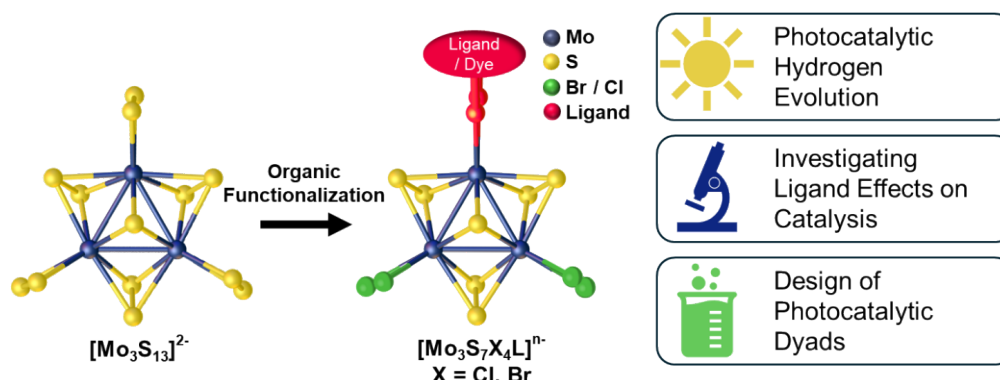


Figure 1. Simplified reaction scheme on the functionalization of $[\text{Mo}_3\text{S}_{13}]^{2-}$ with organic ligands / dye molecules and overview of main objectives.

Acknowledgments

Thanks to Dr. Alexander Mengele and Prof. Dr. Sven Rau (Ulm University) as well as Konrad Hotzel and Prof. Dr. Kalina Peneva (FSU Jena) for providing ligands and dyes. Financial support by the Deutsche Forschungsgemeinschaft DFG (TRR 234 „CataLight“) is gratefully acknowledged.

References

- [1] A. Müller, R. G. Bhattacharyya, B. Pfefferkorn, *Chem. Ber.* **1979**, *112*, 778–780.
- [2] M.-L. Grutzka, A. Rajagopal, C. Streb, P. Kurz, *Sustain. Energy. Fuels*, **2018**, *2*, 1893–1904.
- [3] M. Dave, A. Rajagopal, M. Damm-Ruttensperger, B. Schwarz, F. Nägele, L. Daccache, D. Fantauzzi, T. Jacob, C. Streb, *Sustain Energy. Fuels*, **2018**, *2*, 1020.
- [4] S. Batool, M. Langer, S. N. Myakala, M. Heiland, D. Eder, C. Streb, A. Cherevan, *Advanced Material* **2023**, 2305730.
- [5] V. P. Fedin, M. N. Sokolov, Y. V. Mironov, B. A. Kolesov, S. V. Tkachev, V. Y. Fedorov, *Inorganica Chim Acta* **1990**, *167*, 39–45.

Luminescent Fe (III) Complex Sensitizes Triplet-Triplet Annihilation Upconversion and Catalyzes Photopolymerization

P. Jin,^{1,2} X. Xu,³ Y. Yan,³ H. Hammecke,¹ and C. Wang^{1,2*}

1. Osnabrück University 2. University of Konstanz; 3. Institute of Chemistry, Chinese Academy of Sciences. E-mail: pengyue.jin@uni-konstanz.de

Sensitized triplet-triplet annihilation upconversion (sTTA-UC) often relies on photosensitizers made of precious platinum group metals, such as Pd(II), Pt(II), Ru(II), Ir(III), and Os(II) complexes.[1] A significant segment of contemporary research has steered to first-row transition metals due to their high abundance and low cost.[2] Photoactive complexes based on iron with the greater abundance and economic viability are seen as competitive candidates.[3] Among the Fe(III)-based luminophores, the low-spin 3d⁵ Fe(III) complex [Fe(phtmeimb)₂]PF₆ with tridentate scorpionate ligands (Figure 1) shows multiple nanoseconds luminescence lifetime from the ²LMCT excited state in solution at room temperature,[4] making it a promising photosensitizer for sTTA-UC.

In this work, we use [Fe(phtmeimb)₂]PF₆ for sensitizing green-to-blue upconversion with 9,10-diphenylanthracene (DPA) via underexplored doublet-triplet energy transfer (DTET), which is supported by pre-association between the Fe(III) complex and DPA in their ground states.[5] In the presence of a mediator, the green-to-blue upconversion efficiency Φ_{UC} achieves a 6-fold enhancement to ~0.2% in aerated DMSO at room temperature. The singlet excited state of DPA, accessed via photon upconversion in the Fe(III)/DPA pair, allows efficient photoredox catalytic radical polymerization of acrylate monomers. This study provides a new strategy of using low-cost iron and low-energy visible light for efficient polymer synthesis, which is a significant step for both fundamental research and future applications.

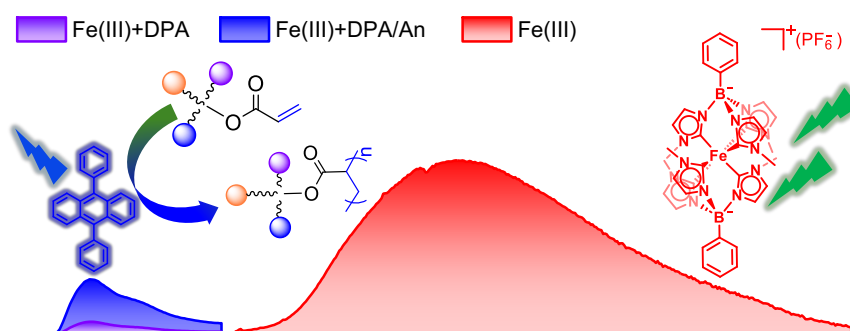


Figure 6. Green-to-blue photon upconversion sensitized by a luminescent Fe(III) complex and the upconversion-driving photocatalytic polymerizations

Aknowlegments

P. Jin and C. Wang thank the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) for the grant with the project number 535142873.

References

- [1] K. Ye, M. Imran, X. Chen and J. Zhao, ACS Appl. Opt. Mater., **2024**, 2, 1803-1824.
- [2] C. Wang, C. Wegeberg and O. S. Wenger, Angew. Chem. Int. Ed., **2023**, 62, e202311470.
- [3] J. Wellauer, B. Pfund, I. Becker, F. Meyer, A. Prescimone and O. S. Wenger, J. Am. Chem. Soc., **2025**, 147, 8760-8768.
- [4] K. S. Kjær, N. Kaul, O. Prakash, P. Chábera, Huang, J. Uhlig, J. Bendix, D. Strand, V. Sundström, P. Persson, R. Lomoth and K. Wärnmark, Science, **2019**, 363, 249-253.
- [5] P. Jin, X. Xu, Y. Yan, H. Hammecke and C. Wang, J. Am. Chem. Soc., **2024**, 146, 35390-35401.

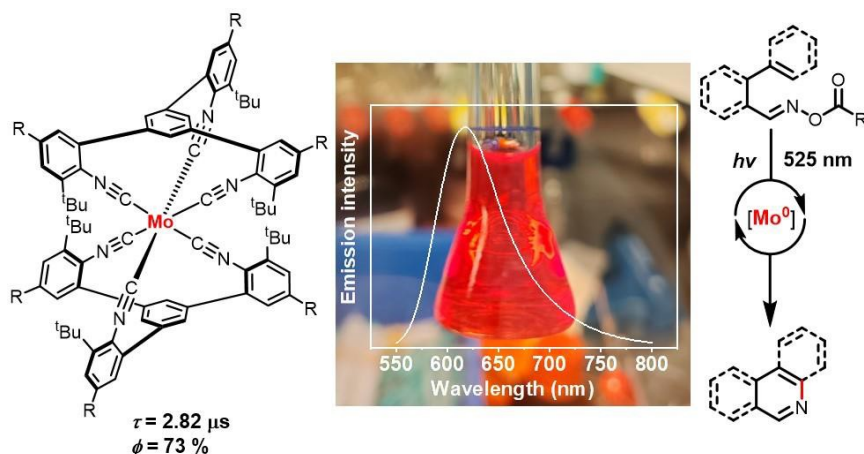
Making Mo(0) a Competitive Alternative to Ir(III) in Phosphors and Photocatalysts

T. Jin, N. Sinha, D. S. Wagner, A. Prescimone, D. Häussinger, O. S. Wenger*

Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056 Basel, Switzerland Email:

tao.jin@unibas.ch

The critical rarity and cost of iridium(III) in phosphorescent lighting and photoredox catalysis drive the pursuit of Earth-abundant alternatives.¹ Here, we present a new class of molybdenum(0) complexes featuring facially coordinating, tripodal arylisocyanide ligands that deliver exceptional photophysical and redox properties². In de-aerated toluene at 20 °C, these bis(tridentate) Mo(0) compounds achieve MLCT lifetimes of 1.8–2.8 μs and photoluminescence quantum yields up to 0.73—eight times higher than [Ru(bpy)₃]²⁺ and rivaling *fac*-[Ir(ppy)₃]. With excited-state oxidation potentials reaching –2.8 V vs. Fc⁺/Fc—approximately 0.7 V more reducing than the –2.1 V benchmark of *fac*-[Ir(ppy)₃]³—these Mo(0) complexes drive visible-light-promoted, net redox-neutral heteroaryl syntheses from acyl oximes bearing a broad range of leaving groups, delivering quantitative to high yields even for substrates unreactive under Ir(III) catalysis.³ Gram-scale cyclizations afford phenanthridines, quinolines, and pyridines in up to 94 % isolated yield. These Mo(0) complexes are synthesized from MoCl₄(THF)₂ in 5–6 straightforward steps—generally in high yields—and remain stable as solids in air for over one year. This work demonstrates that Earth-abundant transition metals can match or exceed noble-metal phosphors in luminescence efficiency and broaden catalytic substrate scope for sustainable photoredox applications.⁴



Acknowledgments

We acknowledge the financial support of the Swiss National Science Foundation (SNSF) under grant number 200020_207329.

References

- [1] Mills, I. N.; Porras, J. A.; Bernhard, S. *Acc. Chem. Res.* **2018**, *51*, 352–364.
- [2] Jin, T.; Sinha, N.; Wagner, D. S.; Prescimone, A.; Häussinger, D.; Wenger, O. S. *J. Am. Chem. Soc.* **2025**, *147*, 4587–4594.
- [3] Jiang, H.; An, X.; Tong, K.; Zhang, Y.; Yu, S. *Angew. Chem. Int. Ed.* **2015**, *54*, 4055–4059.
- [4] Wenger, O. S. *J. Am. Chem. Soc.* **2018**, *140*, 13522–13533.

From Rags to Riches: Enabling Abundant Metals to Exhibit Significant Photophysical and Magnetic Properties Using Efficient Ligand Design

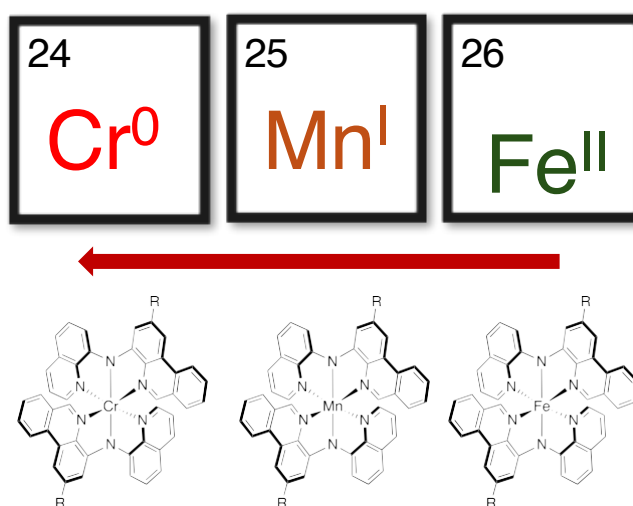
A. Kacperkiewicz,¹ B. K. Sidhu,¹ R. J. Ortiz¹, J. A. G. Williams,² D. E. Herbert¹

¹Department of Chemistry, University of Manitoba, Winnipeg, MB, R3T 2N2, Canada

kacperka@myumanitoba.ca ² Department of Chemistry, Durham University, Durham, DH1 3LE, UK

Coordination chemistry allows one to combine the unique influence of metals on the physical properties of molecules with the ability to further tune these properties using ligand design. Accordingly, coordination complexes can be applied in light emitting diodes, artificial photosynthesis schemes and dye-sensitized solar cells, magnetic materials and sensors, and much more. From a sustainability perspective, the responsiveness of molecular properties to those of the ligand presents the opportunity to rationally engineer the favourable characteristics of heavier, rarer transition metal elements into complexes of more abundant, renewable 3d metals.¹

With this aim in mind, our group has sought to delineate the impact of nitrogen donor motifs and benzannulated C=N moieties on the photophysical, magnetic, and photochemical properties of first- row transition metal coordination complexes.² In this presentation, I will describe ligand motifs with amido (:NR₂) character and their remarkable influence over photophysical properties such as light absorption, excited states, and photochemistry beginning with iron and extending to earlier metals such as manganese and chromium.



Acknowledgements

I would like to thank my group members, my advisor, and our collaborators for their help throughout the years and their contributions to this project.

References

- (1) Wegeberg, C.; Wenger, O. S. Luminescent First-Row Transition Metal Complexes. *JACS Au* **2021**, *1* (11), 1860–1876.
- (2) Herbert, D. E. When Is a Pyridine Not a Pyridine? Benzannulated N-Heterocyclic Ligands in Molecular Materials Chemistry. *Can. J. Chem.* **2023**.

Control of emission wavelength by pH and proton conductivity of cis-Pt(II)-NHC bis(pyridylacetylide) complexes loaded in highly proton-conductive membrane

H. Kamebuchi,¹ C. Shibuya,² N. Takaishi,² B. Zhou²

¹ Graduate School of Science, Department of Physics, Osaka Metropolitan University, Japan

² College of Humanities and Sciences, Department of Chemistry, Nihon University, Japan

E-mail: hkamebuchi@omu.ac.jp

Allowing modulation of emission color by external stimuli in a single transparent material is still challenging and eagerly awaited. To address this issue, we have been developing transparent materials whose emission color can be controlled by proton and DC voltage.^[1-3] Recently, we have focused on blue-emissive platinum(II) complexes with *N*-heterocyclic carbene (NHC) to achieve full-color emission. In this study, [(ⁱPr-NHC)Pt^{II}(C≡C-*n*Py)₂] (**Pt-*n*Py**; ⁱPr-NHCH⁺ = 1-(methylethyl)-3-(2-pyridinyl)-1*H*-imidazolium, HC≡C-*n*Py = *n*-ethynylpyridine (*n* = 2, 3, 4)) with pyridylacetylides has been synthesized and crystallized. Furthermore, the emission behavior of a transparent film incorporating the Pt-NHC complexes in highly proton-conductive membrane (Nafion) has been investigated. The absolute value of the red shift in concentration dependence of the emission spectra of [(ⁱPr-NHC)Pt^{II}(C≡C-*n*Py)₂]@Nafion varies greatly depending on the position of the nitrogen atom in the pyridyl acetylides. Differences in response to pH were also observed, especially in **Pt-2Py@Nafion** (10⁻³ M), where a remarkable color change and emission wavelength shift of >200 nm would be observed. The proton conductivity at 80% RH was estimated as 2.23 × 10⁻³ S cm⁻¹ and 6.87 × 10⁻⁵ S cm⁻¹ for **Pt-3Py@Nafion** and **Pt-2Py@Nafion**, respectively. Additionally, some efforts have been made to control the emission wavelength by applying DC voltage.

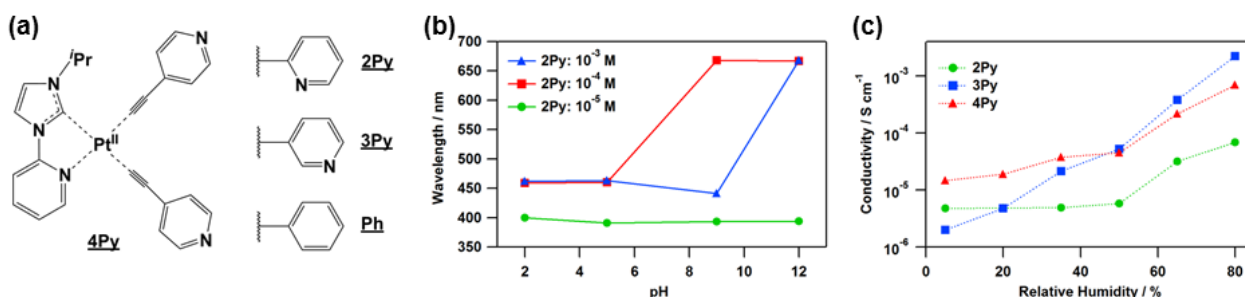


Figure 7. (a) Molecular structure of **Pt-*n*Py**, (b) pH and concentration dependence of emission wavelength in **Pt-2Py@Nafion**, and (c) humidity dependence of proton conductivity of the films (10⁻¹ M).

References

- [1] H. Kamebuchi, T. Yoshioka and M. Tadokoro, *Mater. Adv.* **2020**, *1*, 569.
- [2] H. Kamebuchi, Y. Fujimura, T. Yoshioka, A. Okazawa, M. Tadokoro, N. Kojima, *Crystals* **2020**, *10*, 653.
- [3] H. Kamebuchi, S. Tamaki, A. Okazawa, N. Kojima, *Membranes* **2021**, *11*, 400.

Dye-sensitized solar cells based on Cu(I) complexes containing catechol anchor groups that operate with aqueous electrolytes

L. E. Burmeister¹, F. Doettinger¹, Y. Pellegrin², M. Karnahl^{1,*}

¹ Department of Energy Conversion, Institute of Physical and Theoretical Chemistry, Technische Universität Braunschweig, Rebenring 31, Braunschweig, Germany, michael.karnahl@tu-bs.de

² Nantes Université, CNRS, CEISAM, UMR6230, F-44000 Nantes, France

Dye-sensitized solar cells (DSSCs) are a promising alternative to conventional silicon-based photovoltaics, with the potential for improved cost efficiency and performance.^[1,2] Here, we present an innovative strategy to enhance both the efficiency and stability of DSSCs by introducing catechol-functionalized Cu(I) complexes as sensitizers. A systematic series of three novel dyes was synthesized (Figure 1), consisting of 2,9-dimethyl-1,10-phenanthroline with catechol anchor groups at the 4,7-positions as well as its corresponding homo- and heteroleptic Cu(I) complexes.^[3] Their photophysical and electrochemical properties were investigated by steady-state and time-resolved absorption/emission spectroscopy, cyclic voltammetry and DFT calculations to gain deeper insights into their electronic structures and excited-state properties. Implementation in n-type DSSCs demonstrated that the heteroleptic Cu(I) complex **C2** (Figure 1) achieved a remarkable photoconversion efficiency (PCE) of 1.88%, representing a 35-fold increase compared to previously reported diimine-diphosphine Cu(I)-based DSSCs.^[4] Moreover, the strong binding affinity of the catechol anchors enabled the fabrication of DSSCs with an aqueous electrolyte, which exhibited exceptional stability for at least 10 days. The working principle of these cells is best described as a dual-chromophore system, where the catechol-TiO₂ interaction acts as the primary chromophore, while the Cu(I) complex serves as an antenna chromophore. These findings represent a major step forward in the development of Cu(I)-based DSSCs and highlight the potential of catechol sensitizers for sustainable solar energy conversion.

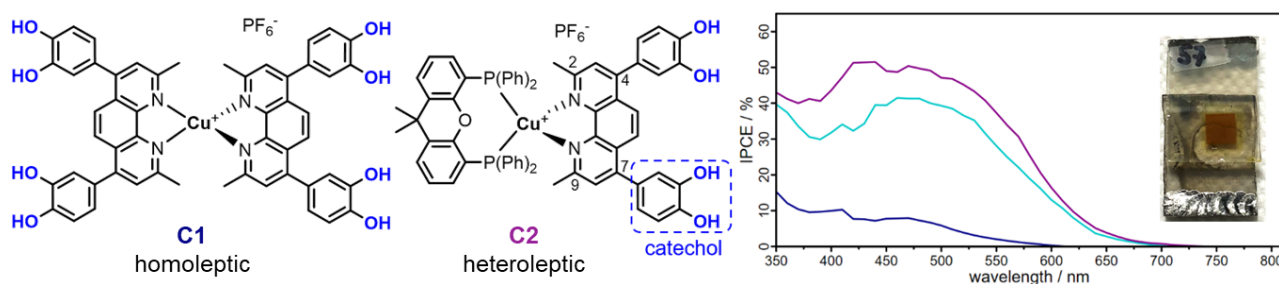


Figure 1. Molecular structures of the homoleptic Cu(I) complex **C1** and its heteroleptic counterpart **C2** (left) and the incident photon-to-current efficiencies (IPCE, right) of the assembled DSSCs based on **C1** (dark blue) and **C2** (magenta).

References

- [1] C. E. Housecroft, E. C. Constable, *Chem. Soc. Rev.* **2015**, 44, 8386-8398.
- [2] M. Sandroni, L. Favereau, A. Planchat, H. Akdas-Kilig, N. Szuwarski, Y. Pellegrin, E. Blart, H. Le Bozec, M. Boujtita, F. Odobel, *J. Mater. Chem. A*, **2014**, 2, 9944-9947.
- [3] F. Doettinger, C. Kleeberg, C. Queffelec, S. Tschierlei, Y. Pellegrin, M. Karnahl, *Catal. Sci. Technol.* **2023**, 13, 4092-4106.
- [4] C. L. Linfoot, P. Richardson, T. E. Hewat, O. Moudam, M. M. Forde, A. Collins, F. White and N. Robertson, *Dalton Trans.* **2010**, 39, 8945-8956.

[FeFe]-H₂ase mimicking complex bearing two organic photosensitisers for photocatalytic H₂ evolution

C. Kasahara^{1,2}, M. K. Farh, K¹. Rediger³, P. Buday¹, S. Gräfe², M. Micheel³, S. Kupfer², M. Wächter^{3,4}, and W. Weigand¹

¹Institute of Inorganic and Analytical Chemistry, University Jena, Humboldtstr. 8, 07743 Jena, Germany

²Institute of Physical Chemistry, University Jena, Lessingstr. 4, 07743 Jena, Germany

³Chemistry Department and State Research Center OPTIMAS, RPTU Kaiserslautern-Landau, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Germany

⁴Institute of Physical Chemistry and Kiel Nano, Surface and Interface Science (KiNSIS), Kiel University, Kiel, Max-Eyth-Straße 1, 24118 Kiel, Germany

chizuru.kasahara@uni-jena.de

Photocatalytic H₂ evolution has attracted interest from the scientific community, and numerous efforts have been made to modify the reaction greener and more sustainable, i.e. substitute precious metals to the earth-abundant elements. One promising compound for the noble-metal-free catalytic centre is [(μ-S)₂Fe₂(CO)₆], the mimic of [FeFe]-H₂ase's catalytic centre (**CAT**), as the enzyme is known to exhibit remarkable H₂ production.^[1] Thereby, applications of [(μ-S)₂Fe₂(CO)₆] derivatives for photocatalytic H₂ production have been investigated by combining with a photosensitiser (**PS**).^[2, 3]

In this contribution, we present a novel molecular catalyst (**PS-CAT**) which builds on our previous joint synthetic-spectroscopic-theoretical studies^[4, 5] and covalently connects two metal-free **PS**s and one **CAT** (Figure 1). The molecular triad structure can avoid diffusion control interaction between **PS** and **CAT**, and (potentially) increase the probability of accessing the excited state of **PS** which triggers photoinduced electron transfer (ET) from **PS** to **CAT**. The new **PS-CAT** was investigated in terms of the electro- and photo-reduction properties, combining experimental and computational approaches to achieve a comprehensive understanding of the (photo)reduction mechanism of the new triad.

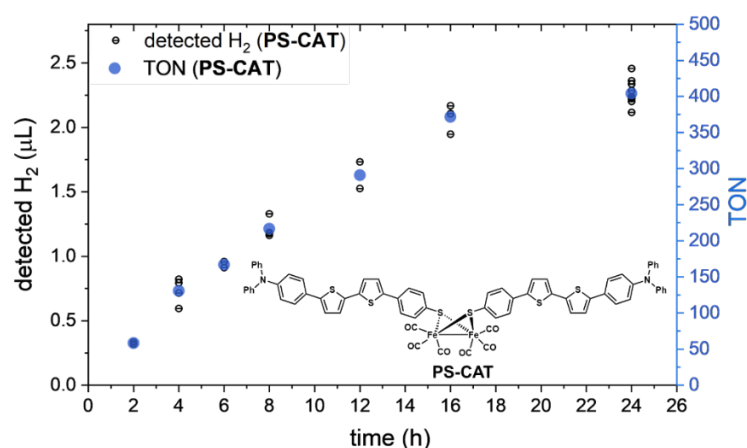


Figure 8. Molecular structure and photocatalytic activity of **PS-CAT**. The reactions were performed under 455 nm irradiation in the presence of 1, 3-dimethyl-2-phenylbenzimidazole in N-Methyl-2-pyrrolidone.

References: [1] J. T. Kleinhaus, F. Wittkamp, S. Yadav, D. Siegmund, U. -P. Apfel, *Chem. Soc. Rev.* **2021**, 50 (3), 1668-1784. [2] J. Amaro-Gahete, M. V. Pavliuk, H. Tian, D. Esquivel, F. J. Romero-Salguero, S. Ott, *Coord. Chem. Rev.* **2021**, 448, 214172. [3] R. Gupta, A. K. Pal, *Sustainable Energy Fuels* **2024**, 8 (20), 4709-4751. [4] P. Buday, C. Kasahara, E. Hofmeister, D Kowalczyk, M. K. Farh, S. Riediger, M. Schulz, M. Wächter, S. Furukawa, M. Saito, et al. *Angew. Chem. Int. Ed.* **2022**, 61 (20), e202202079. [5] C. Kasahara, K. Rediger, M. Micheel, P. Liebing, S. Gräfe, S. Kupfer, M. Wächter, W. Weigand, *ChemCatChem* **2024**, 16, (11) e202400247.

Cell and reactor design for space and time resolved *operando* multi-spectroscopic analysis integration

A. Koba¹, R. Müller², A. Edwards³, J. Popp^{3,4,5}, M. Schmitt³, K. Leopold², D. Ziegenbalg¹

¹Institute of Chemical Engineering, Ulm University; ²Institute of Analytical and Bioanalytical Chemistry, Ulm University; ³Institute of Physical Chemistry, Friedrich Schiller University Jena; ⁴Abbe Center of Photonics Jena, ⁵Leibnitz Institute of Photonic Technologies Jena

Light-driven catalytic systems and their molecular components, specifically the photosensitizer and the catalyst, are known to suffer from degradation due to irradiation or harsh reaction conditions. The underlying mechanisms and kinetics are not yet well understood and investigation attempts often rely on invasive, destructive, and

ex situ analysis techniques. Previous studies have shown that using in situ multi-spectroscopic analytical platforms with IR-ATR and Raman integration^[1] can enable online monitoring of reaction and degradation products with high temporal resolution^[2]. However, reaction engineering concepts are not commonly considered during the design of such platforms, which can lead to uncharacterized and unfavorable reaction conditions and consequently, contribute to accelerated system degradation and challenging data comparability. As part of the CataLight CRC/TRR 234 project C2, this work aims to combine reaction engineering and spectroscopic insights to generate high quality reproducible data in order to generate understanding and ensure comparability of different light-driven systems. The focus lies on the development of characterized homogeneous and membrane measurement cells and reactors, optimized for multi-spectroscopic analyses under both batch and flow conditions. Taking functionalized films into consideration, the high temporal resolution is extended by another dimension through additional spatial information via Raman microscopy and μ XRF mapping. Generated knowledge on degradation can also give an insight into possible repair and self-regulating mechanisms.

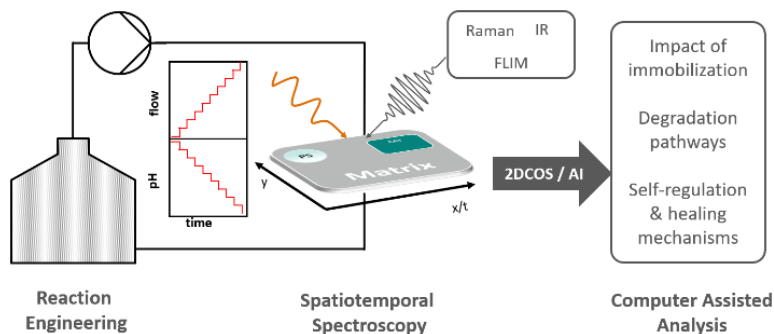


Figure 9. Key objectives overview: combining reaction engineering concepts with spectroscopic insights for generation of high resolution data.

Aknowlegments

The authors acknowledge the support of the German science foundation DFG and its funding to the collaborative research center TRR234 CataLight for funding the research into Light-driven Molecular Catalysts in Hierarchically Structured Materials.

References

- [1] S. Klingler et al., *Angewandte Chemie (International ed.)* 2023, 62 (44), 10.1002/anie.202306287.
- [2] S. Klingler et al., *ACS measurement science au* 2022, 2 (2), 157–166. 10.1021/acsmeasuresciau.1c00048.

How to get 200% H₂ with 25% less energy input using molybdenumsulfide clusters as photocatalysts for HER

Author list: S.H. Kolbinger¹, P.C. Schröder¹, L. Haxha¹, D.Kowalczyk², C. Streb¹

1: Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128 Mainz, henriette.kolbinger@uni-mainz.de

2: Universität Ulm, Helmholtzstraße 18, 89081 Ulm

Molecular metal sulfides, or thiomolybdates, are promising molecular catalysts for the photocatalytic or electrocatalytic hydrogen evolution reaction (HER).^[1] In particular, the prototype cluster $[\text{Mo}_3\text{S}_{13}]^{2-}$ has been used under a variety of homogeneous and heterogenized conditions for HER catalysis. However, this reaction is complex and not yet fully understood. In order to improve the HER performance and stability of the clusters, in-depth understanding of the catalytic mechanisms, as well as processes leading to structural changes and degradation of the clusters is necessary.^[2] In this study the influence of dynamic irradiation on this system was investigated regarding the factors of frequency, LED-intensity and On/Off-ratio. Optimal factor settings were found using Design of Experiments.

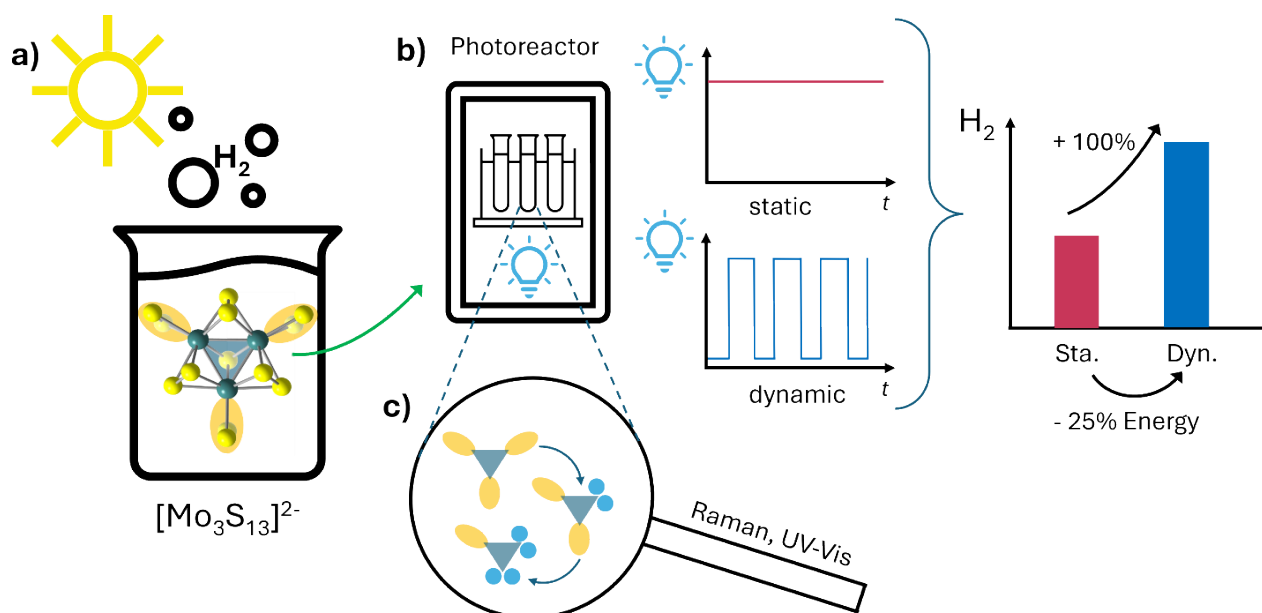


Figure 1. a) Molecular molybdenum sulfide cluster can evolve hydrogen in a suited system using sun light; b) in a photoreactor the different factor settings are simulated and with the optimized setting the double amount of hydrogen can be measured with 25% less energy input; c) Using UV-Vis and Raman spectroscopy to investigate mechanistic steps during the catalysis.

References

- [1] M.-L. Grutzka, A. Rajagopal, C. Streb, P. Kurz, *Sustain. Energy. Fuels*, **2018**, 2, 1893-1904
- [2] M. Heiland, R. De, S. Rau, B. Dietzek-Ivansic, C. Streb, *Chem. Commun.*, **2022**, 58, 4603-4606
- [3] D. Kowalczyk, L. Pengcheng, A. Pannwitz, F. Schacher, W. Weigand, C. Streb, D. Ziegenbalg, *ChemPhotoChem* **2022**, 6

Light Induced Cobalt Stabilized Highly Delocalized Radical for Hydrogen Production

A. Krishna¹, T. Biktagirov¹, F. Hennhofer³, D. Leitner², H. Elgabarty¹, M. Nowakowski¹, L. Fritsch¹, J. Steube¹, A. Schoch¹, R. Schoch¹, H. Egold¹, S. Hohloch², B. Sarkar³, U. Gerstmann¹, W. G. Schmidt¹, M. Bauer^{1*}

¹Paderborn University-33098 Paderborn, Germany. ²University of Innsbruck- 6020 Innsbruck, Austria. ³University of Stuttgart-70174 Stuttgart, Germany.
athul@mail.uni-paderborn.de

The field of photochemistry involving transition metal complexes has gained significant attention in recent years, largely driven by the urgent need to transition from fossil fuels to sustainable energy sources, such as solar power. Organometallic compounds based on precious metals are widely established in photochemical applications, like photocatalytic water splitting, but the extraction of these noble metals and their rareness pose a serious dilemma for their sustainability.

Metalloradicals are also of particular interest as these are capable of exhibiting specific reactivity to certain substrates. Ligand centred electrophilic radicals from transition metals had been previously reported for hydrogen abstraction from Tin based hydrides, thiophenols and organic thiols. [1]

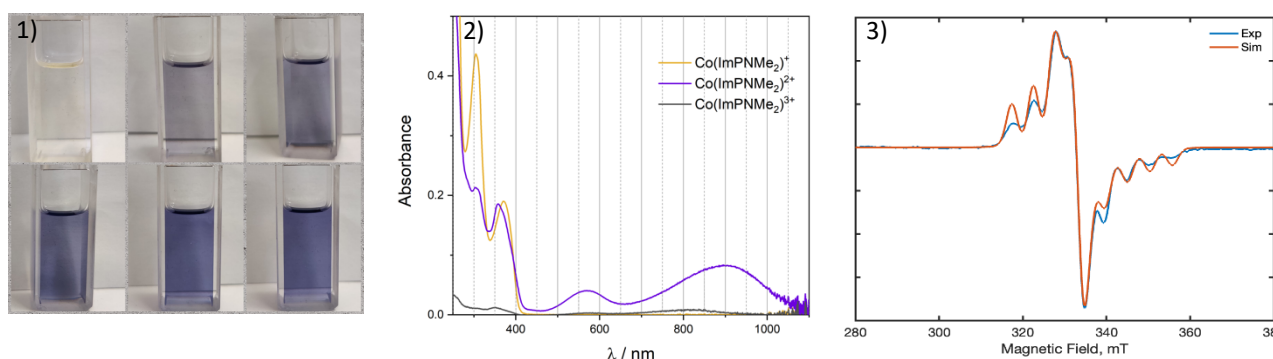


Figure 10). Photo-oxidation of 1 mM solution of $[\text{Co}(\text{ImPNMe}_2)_2]^+$ in $\text{C}_2\text{H}_2\text{Cl}_4$, pictures taken in 2 min intervals. **Figure 2).** SEC-UV-Vis spectra of 1 mM solution of $[\text{Co}(\text{ImPNMe}_2)_2]^+$ in DCM-MeCN. **Figure 3).** Experimental and simulated EPR spectrum measured in a 28 mM frozen solution of $[\text{Co}(\text{ImPNMe}_2)_2]^+$ in $\text{C}_2\text{H}_2\text{Cl}_4$.

Combining these two ideas, we have synthesized a light induced radical system by modifying a very recently reported cyclometalated system based on cobalt ($[\text{Co}(\text{ImP})_2]^+$) [2] and can be exploited for reactions like H abstraction and oxidation of mildly reducing sugars and acids. The radical system is fully characterized by XRD, CV, TD-DFT and MD simulations, UV-Vis, spectro-electro UV-Vis, EPR and NMR spectroscopy.

Aknowlegments

Thanks to German Research Foundation (Deutsche Forschungsgemeinschaft)

References

- [1] T. Buttner, *Science*, **2005**, 307, 235-238
- [2] A. Krishna, *Inorganic Chemistry*, **2025**, 64, (3), 1401–1409

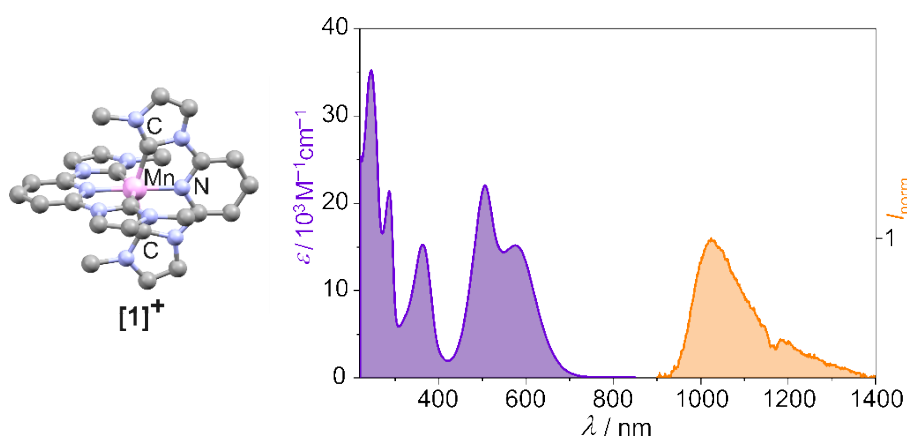
Novel Manganese(I) Complex with a 190 ns Metal-to-Ligand Charge Transfer Lifetime and Luminescence

S. Kronenberger^a, R. Naumann^a, C. Förster^a, N. R. East^a, J. Klett^a, K. Heinze^a

^aJohannes Gutenberg University, Department of Chemistry, 55128, Mainz, Germany.

*skrone@uni-mainz.de

In recent decades high interest for emissive and photoactive transition metal complexes has emerged, due to their attractive properties in lighting^[1] and photocatalysis^[2]. Whereas precious metal complexes, such as [Ru(bpy)₃]²⁺ or Ir(ppy)₃, have dominated this field,^[3] the focus of recent investigations has shifted towards earth-abundant first-row metal centres such as manganese.^[4] Precious metal complexes with the d⁶ valence configuration typically exhibit luminescence from their triplet metal-to-ligand charge transfer (³MLCT) excited states.^[5] However, the intrinsically smaller ligand field of first-row metals causes low-lying metal centred excited states that make luminescence from the MLCT states challenging.^[6] Recently the first two emissive polyisocyanide manganese(I) complexes with luminescence from the MLCT and lifetimes of 0.7 and 1.7 ns have been reported by the WENGER group.^[7]



Here, we present a novel manganese(I) carbene complex **[1]⁺**, which has been characterized via X-ray diffraction, (ns/fs-transient) absorption and emission spectroscopy. The ³MLCT state of **[1]⁺** is very long-lived and luminescent in dry solution. Experimental data has been underlined with density functional theory (DFT) calculations and time-dependent DFT calculations, allowing the assignment of electronic states and the excited state dynamics.^[8]

[1] W. C. H. Choy, W. K. Chan, Y. Yuan, *Adv. Mater.* **2014**, *26*, 5368–5398.

[2] A. Y. Chan, I. B. Perry, N. B. Bissonnette, B. F. Buksh, G. A. Edwards, L. I. Frye, O. L. Garry, M. N. Lavagnino, B. X. Li, Y. Liang, E. Mao, A. Millet, J. V. Oakley, N. L. Reed, H. A. Sakai, C. P. Seath, D. W. C. MacMillan, *Chem. Rev.* **2022**, *122*, 1485–1542.

[3] C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363.

[4] (a) J. P. Harris, C. Reber, H. E. Colmer, T. A. Jackson, A. P. Forshaw, J. M. Smith, R. A. Kinney, J. Telser, *Can. J. Chem.* **2017**, *95*, 547–552. (b) N. R. East, R. Naumann, C. Förster, C. Ramanan, G. Diezemann, K. Heinze, *Nat. Chem.*, **2024**, *16*, 827–834. [5] V. W.-W. Yam, K. M.-C. Wong, *Chem. Commun.* **2011**, *47*, 11579–11592.

[6] C. Förster, K. Heinze, *Chem. Soc. Rev.* **2020**, *49*, 1057–1070.

[7] P. Herr, C. Kerzig, C. B. Larsen, D. Häussinger, O. S. Wenger, *Nat. Chem.* **2021**, *13*, 956–962.

[8] S. Kronenberger, R. Naumann, C. Förster, N. R. East, J. Klett, K. Heinze, submitted.



Photoproduction of carbon monoxide and singlet oxygen by visible-light-driven Re(I)-based PhotoCORMs

Prashant Kumar^{1,2}, Martial Boggio-Pasqua² and Isabelle Dixon²

Affiliations: ¹Department of Chemistry, Christopher Ingold Building, University College London, London WC1H 0AJ, United Kingdom; ²Laboratoire LCPQ, Université de Toulouse III, 118 route de Narbonne, Toulouse, 31400, France. E-mail: prashant.kumar@ucl.ac.uk

Antibiotic-resistant bacteria represent a significant threat to human and animal health, necessitating the exploration of innovative strategies to combat them. Among these approaches, singlet oxygen ($^1\text{O}_2$) and carbon monoxide (CO) have emerged as promising antimicrobial agents, achievable through the utilization of photoactive CO-releasing molecules (PhotoCORMs). Notably, Rhenium(I) complexes exhibit the capability to generate both CO and $^1\text{O}_2$ upon light irradiation. However, a primary challenge in the realm of PhotoCORMs lies in enhancing their absorption properties within the visible spectrum, particularly towards the red end, while preserving their exceptional CO-releasing capacity. [1] The primary objective of this theoretical contribution is to aid in the design of potentially efficient complexes with improved light absorption properties and the ability to sensitize singlet oxygen, thereby minimizing synthetic efforts. We have proposed several novel Re(I) complexes designed to exhibit enhanced absorption towards the red spectrum. To rationalize their photoreactivity, we employ density functional theory (DFT)-based methods. [2] Our focus is on optimizing the structure of Re(I) complexes to efficiently generate both $^1\text{O}_2$ and CO from a single molecule activated by visible light. Additionally, we utilize implicit solvent time-dependent DFT (TD-DFT) to simulate absorption and emission properties, while orbital analysis aids in rationalizing the design choices. The photoreactivity and photosensitization of $^1\text{O}_2$ are further investigated by optimizing the involved triplet excited states ($^3\text{MLCT}$ and ^3MC) in selected complexes. [3] This exploration aims to assess their energy transfer ability to $^3\text{O}_2$ compared to the population of dissociative ^3MC states, if thermally accessible. Energy barriers along the potential energy surface of the lowest triplet excited state are quantified using methods such as Nudged Elastic Band and transition state optimization. Lastly, we optimize key crossover points for inter-system non-radiative crossover deactivation processes. By addressing these aspects, we aim to advance the understanding of Re(I) complexes behavior under light irradiation, particularly concerning their role in generating antimicrobial agents. Through rational design and thorough theoretical investigation, we strive to contribute to the development of efficient PhotoCORMs with enhanced antibacterial properties, thereby addressing the urgent need to combat antibiotic-resistant bacteria.

References

- [1] Zobi, F. (2017). Visible Light-Activated PhotoCORMs. *Inorganics*. 5(2), 24.
- [2] Soupart, A. et al. (2020). Recent progress in ligand photorelease reaction mechanisms: Theoretical insights focusing on Ru (II) 3MC states. *Coordination Chemistry Reviews*, 408, 213184.
- [3] Kumar P, Boggio-Pasqua M, Dixon I. Unravelling the Photodissociative Mechanism of CO-Release in Re(I) Tricarbonyl Complex Using Density Functional Theory. *ChemRxiv*. 2024; doi:10.26434/chemrxiv-2024-p132r.



Towards photoactive 3d transition metal complexes – A computational perspective

S. Kupfer

Institute for Physical Chemistry, Friedrich Schiller University Jena, Helmholtzweg 4, 07743 Jena, Germany

stephan.kupfer@uni-jena.de

Solar energy conversion is among the most promising approaches to transform our energy sector towards sustainability. In this context, photocatalysis allows the conversion of sunlight into chemical energy such as molecular hydrogen. Typically, both the light-harvesting unit as well as the catalytic centres in (supra)molecular photocatalysts heavily rely on precious 4d and 5d transition metals due to their favourable photophysical and electrochemical properties, alongside thermal, light and pH stability. Thus, the broadscale application of such systems is limited by the scarce availability of these metals. Unfortunately, utilizing earth-abundant 3d metal-based photosensitizers, e.g. Fe(II) complexes, suffers from excited-state lifetimes in the ps regime limiting the photocatalytic ability.[1,2]

Here, we investigate the photophysical and photochemical properties of a series of 3d⁶ transition metal complexes and derive detailed insight regarding structure-property relationships.[3] Thereby, we focus on the redox-active charge transfer states which are of particular interest in the frame of photocatalysis as well as on the accessibility of prominent – yet undesirable – excited-state deactivation channels via the so-called metal-centred states. Based on the computational modelling using state-of-the-art multiconfigurational methods and cost-efficient (scalar-relativistic) time-dependent density functional theory in association with time-resolved spectroscopy, we present selected aspects of our theory-driven design concepts to drive the desired electron and energy transfer processes,[3] 2nd coordination sphere effects[4], self-healing strategies[5] to enhance the photostability of earth-abundant transition metal complexes. Finally, we focus on simulating the kinetics of competitive intermolecular electron transfer processes in such photoactive transition metal complexes using semi-classical Marcus theory as well as dissipative quantum dynamics.[6,7]

References

- [1] O. S. Wenger, *Chem. – Eur. J.* **2019**, 25, 6043–6052.
- [2] J. E. Monat, J. K. McCusker, *J. Am. Chem. Soc.* **2000**, 122, 4092–4097.
- [3] C. Wegeberg, D. Häussinger, S. Kupfer, O. S. Wenger, *J. Am. Chem. Soc.* **2024**, 146, 4605–4619.
- [4] K. Witas, S. S. Nair, T. Maisuradze, L. Zedler, H. Schmidt, P. Garcia-Porta, A. S. J. Rein, T. Bolter, S. Rau, S. Kupfer, B. Dietzek-Ivanšić, D. U. Sorsche, *J. Am. Chem. Soc.* **2024**, 146, 19710–19719.
- [5] N. Sinha, J. Wellauer, T. Maisuradze, A. Prescimone, S. Kupfer, O. S. Wenger, *J. Am. Chem. Soc.* **2024**, 146, 10418–10431.
- [6] G. Yang, G. E. Shillito, C. Zens, B. Dietzek-Ivanšić, S. Kupfer, *J. Chem. Phys.* **2023**, 159, 024109.
- [7] G. Yang, L. Blechschmidt, L. Zedler, C. Zens, K. Witas, S. Rau, G. E. Shillito, B. Dietzek-Ivanšić, S. Kupfer, *ChemRxiv* **2024**, DOI: 10.26434/chemrxiv-2024-9fds6.

DESIGN AND STUDY OF NEW PHOTO-ELECTROCHEMICAL CELLS FOR H₂ PRODUCTION

Claudio La Falce,^a Maurilio Galletta^b, Antonio A. Leonardi^{a,b}, Fausto Puntoriero,^{a,b}
Francesco Nastasi^{a,b} and Sebastiano Campagna^a

^a *Dip. di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università di Messina.*

^b *CNR IMM-MESSINA*

claudio.lafalce@unime.it

Solar energy, although abundant, suffers from intrinsic intermittency. A promising approach to overcome this limitation involves its conversion into hydrogen (H₂), a versatile energy carrier that can be stored and utilized on demand.^[1] In this work, we present a novel photocathode based on two-dimensional fractal arrays of ultrathin silicon nanowires (Si NWs), employed as the photoactive material. The Si NWs were fabricated via metal-assisted chemical etching (MACE) using a thin-film metal catalyst, resulting in nanostructures with a high surface-to-volume ratio and enhanced light absorption both key features for efficient photogenerated charge separation.^[2] Platinum nanoparticles were deposited onto the photocathode surface to serve as a catalyst for the hydrogen evolution reaction (HER). This electrode functions as the generator in a collector-generator^[3] photoelectrochemical (PEC) system, where the second working electrode (collector) consists of a fluorine-doped tin oxide (FTO) substrate coated with a thin layer of platinum. The system operates in an acetate buffer solution at pH 4, using a dual-working-electrode configuration that enables real-time monitoring of photogenerated charges and hydrogen production. Preliminary results show stable photocurrent generation and efficient hydrogen evolution, highlighting the potential of fractal Si NW arrays as key components in integrated PEC devices for solar-to-chemical energy conversion.

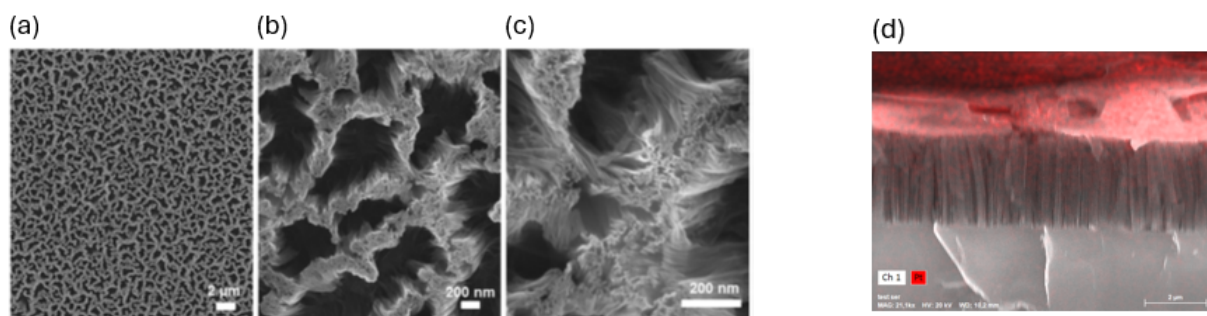


Figure 11. The top panel reports the SEM image of the Si NW array acquired under different magnifications of a) 10, b) 100, and c) 300 kX, respectively. ^[2] d) Cross section of the Si NW after deposition of nano Pt.

This work has been supported by the project "SUN-SPOT: copper indium Sulfide qUaNtUm dotS as Photocatalysts for sun-driven biomass OxidatiOn " funded by the MIUR Progetti di Ricerca di Rilevante Interesse Nazionale (PRIN) Bando 2022 - grant 2022JA3PSC.

"Finanziato dall'Unione europea- Next Generation EU, Missione 4 Componente 1 CUP :J53D23007550 006".

References

- [1] Joel W. Ager, Matthew R. Shaner, Karl A. Walczak, Ian D. Sharpae and Shane Ardof, *Energy Environ. Sci.*, **2015**, 8, 2811-2824.
- [2] A. Leonardi, A. Arrigo, M. J. Lo Faro, F. Nastasi, A. Irrera, *Adv. Energy Sustain. Res.*, **2024**, 5 (9), 2400080.
- [3] Benjamin D. Sherman, Matthew V. Sheridan, Christopher J. Dares, and Thomas J. Meyer, *Analytical Chemistry*, **2024**, issue 42.

Improved Photoinduced Electron Transfer in Azaphthalocyanine-Ferrocene System upon Formation of a Charge-Transfer Complex

J. Lapesova, P. Zimcik

Department of Pharmaceutical Chemistry and Pharmaceutical Analysis, Faculty of Pharmacy in Hradec Králové, Charles University, Akademika Heyrovského 1203, Hradec Králové, 500 03, Czech Republic; lapesovja@faf.cuni.cz

Phthalocyanines (Pcs) and their aza-analogues (AzaPcs) are synthetic dyes that can be used as photosensitizers in photodynamic therapy, fluorescence sensors or fluorescence quenchers depending on the substituents and coordinated cation. For development in the field, it is desirable to study conventional and unconventional mechanisms of quenching to design new and improved analyte-activatable fluorescence sensors and “smart” photosensitizers. It was reported that photoinduced electron transfer (PET) between a strong electron donor, such as ferrocene, and a Pc acceptor leads to fluorescence quenching.¹ The additional nitrogen atoms in the structure of AzaPcs increase the electron-deficient character of the macrocycle compared to Pcs. This difference in the electronic properties makes them more susceptible to PET with electron donors. In this study, we tested quenching of fluorescence of an AzaPc derivative with ferrocene-based quenchers in acetonitrile. The structure of both the AzaPc, and the quencher is designed to favor their interaction by additional supramolecular forces (Figure 1). For this purpose, we chose formation of a charge-transfer complex (CT-complex) based on π - π interactions of an electron-rich and an electron-poor aromatic compounds (derivatives of naphthalene-2,6-diol and viologen, respectively). The quenching in our system was compared to the control systems lacking the key structural motives by Stern-Volmer plot (Figure 1) and proved to be much more efficient. The system was also characterised by means of static and dynamic quenching constant values using steady-state and time-resolved fluorescence measurements.

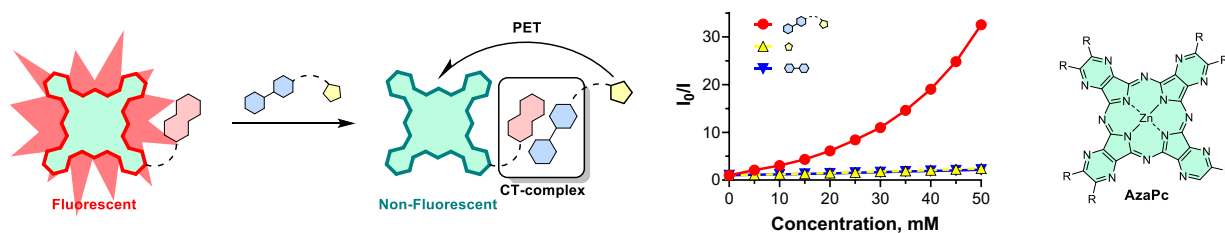


Figure 12. Schematic representation (left) of the principle of the fluorescence quenching by PET (AzaPc – green, ferrocene quencher – yellow) enhanced by formation of a CT-complex (red – electron-rich, blue – electron-poor); Stern-Volmer plot for the designed quencher and its components individually (middle); general structure of a low symmetrical AzaPc derivative (right).

Aknowlegments

This work was supported by Charles University Grant Agency (reg. No. 170223).

References

- [1] J. T. F. Lau, P.-C. Lo, X.-J. Jiang, Q. Wang, D. K. P. Ng, *J. Med. Chem.*, **2014**, 57, 4088-4097.

Fluorescent metal-organic frameworks as an effective alternative for heavy metal detection in aqueous environment

N. Pliatsios,^a N. Anastasiadis^b, P. Oikonomopoulos^c, M. J. Manos,^b G. S. Papaefstathiou,^c T. Lazarides^a

^aLaboratory of Inorganic Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, 54124, Greece, email: npliatsios@chem.auth.gr, tlazarides@chem.auth.gr

^bLaboratory of Inorganic Chemistry, Department of Chemistry, University of Ioannina, Ioannina, 45110, Greece

^cLaboratory of Inorganic Chemistry, Department of Chemistry, National and Kapodistrian University of Athens, Athens, 15784, Greece

Fluorescent MOFs show great promise for applications ranging from phosphor materials to photocatalysis and sensing.[1] In this contribution, we present the synthesis and characterization of two fluorescent MOFs, featuring a functionalized bridging ligand, aiming to examine their efficiency in detecting and/or removing heavy metal ions from wastewater. The crystallinity and phase purity of the materials were determined through PXRD measurements, which revealed the structural resemblance to UiO-66 and MIL-53, respectively. The presented MOFs also exhibit stability in aqueous media. Fluorescence titration experiments in water samples with increasing concentrations of Cu²⁺ ions and in samples with potentially competitive metal ions show strong quenching, with LOD and LOQ values being several orders of magnitude below the proposed limits of the World Health Organization. In summary, the results reveal a correlation between the metal-ligand combination and the detection capabilities of the resulting material.

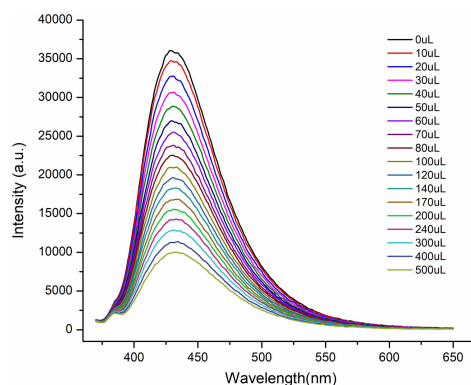


Figure 1. Fluorescence titration of an aqueous suspension of Zr-MOF (0.1 mg mL⁻¹) upon gradual addition of a 10⁻⁴ M aqueous solution of CuCl₂ (λ_{exc} = 340 nm).



Funded by the
European Union
NextGenerationEU
Greece 2.0
NATIONAL RECOVERY AND RESILIENCE PLAN

The research project was supported by the Greece 2.0, Recovery and Resilience Fund financed by the European Union -Next Generation EU and is part of the Action "Research - Create - Innovate" (ID 16971)

References

[1] C. Lai, Z. Wang, L. Qin, Y. Fu, B. Li, M. Zhang, S. Liu, L. Li, H. Yi, X. Liu et al., *Coord. Chem. Rev.*, **2021**, 427, 213565.



Shaping light-driven reactivity: from heteroleptic to homoleptic Ru(II) bisamide complexes for H₂ evolution

G. Lazzaro,^a O. Schott,^b S. Ronzière,^b I. Bahtit,^b X. Liu,^b G. Weng,^b F. Puntoriero,^a
G. S. Hanan,^b G. La Ganga^a

^aDepartment of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, 31 Ave. F. Stagno d'Alcontres, Messina, Italy 98166

^bDepartment of Chemistry, University of Montréal, 1375 Ave. Thérèse-Lavoie-Roux, Montréal, QC H2V0B3
giuliana.lazzaro@unime.it

The development of efficient molecular systems for light-driven hydrogen evolution remains a key objective in artificial photosynthesis.^[1] Here, we report a series of Ru(II) bisamide complexes to evaluate their light-induced performance as photosensitizers in the Hydrogen Evolution Reaction (HER). By transitioning from heteroleptic to homoleptic complexes, we enable fine-tuning of electronic and steric parameters, with the homoleptic species displaying enhanced activity.^[2] This improvement is attributed to the electron-withdrawing nature of the amide substituents on the bipyridine ligands, which lower the LUMO energy level and facilitate charge transfer processes. In addition, pendant pyridine moieties may assist interactions with the cobaloxime catalyst, contributing not only to complex stability but also to more effective substrate binding and redox activity.^[3] These findings highlight the potential of strategically functionalized homoleptic Ru(II) bisamide complexes as efficient photosensitizers in photocatalytic HER systems. Ongoing investigations aim to further clarify the structure-property relationships that govern their performance, guiding the development of robust molecular photocatalysts for sustainable energy conversion technologies.^[4]

Acknowledgements

This work was funded by European Union (NextGeneration EU), Mission 4, component 2 (CUP J53D23007470006). This work has been supported by the project "PHOTOGEN" funded by the MIUR Progetti di Ricerca di Rilevante Interesse Nazionale (PRIN) Bando 2022 - grant _2022AWXS83.

References

- [1] A. Juris, V. Balzani, F. Barigelli, S. Campagna, P. Belser, A. Von Zelewsky, *Coordination Chemistry Reviews* **1988**, 84, 85-277.
- [2] D. Sorsche, M. A.L. Lima, N. Meitinger, K. Prasad, S. Mandal, K. D. Glusac, S. Rau, A. Pannwitz, *Coordination Chemistry Reviews* **2025**, 530, 216454.
- [3] a) E. Rousset, I. Ciofini, V. Marvaud, G. S. Hanan, *Inorganic Chemistry* **2017**, 56, 9515-9524. b) O. Schott, A. K. Pal, D. Chartrand, G. S. Hanan, *ChemSusChem* **2017**, 10, 4436-4441.
- [4] E. Deponi, M. Natali, *Dalton Transactions* **2016**, 45, 9136-9147.

Reaction-Diffusion Simulations of Photoredox Processes in Solution

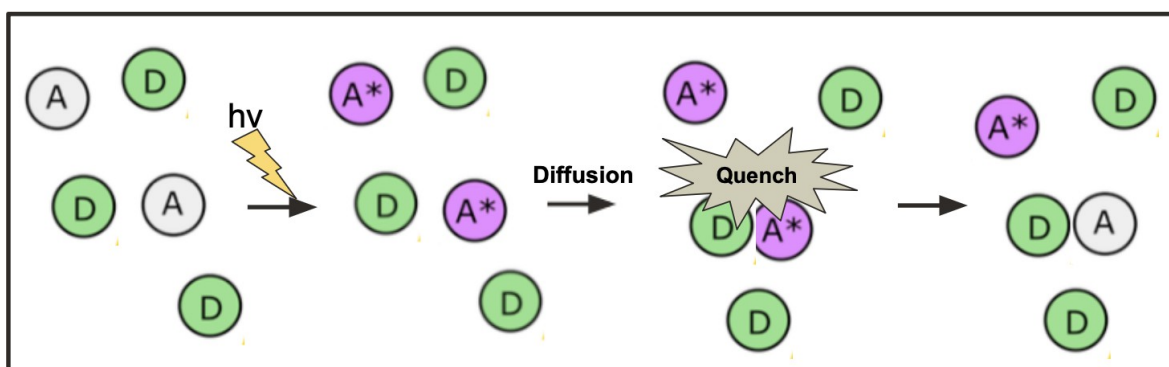
Simon A. Liedtke¹, Martin Trulsson¹, and Petter Persson¹

¹ Computational Chemistry Division, Chemistry Department, Lund University, Box 124, SE-22100 Lund, Sweden

* simon.liedtke@compchem.lu.se

A computational method to simulate bimolecular quenching reactions in solution using coarse-grained reaction-diffusion dynamics is presented and applied to quenching of molecular photosensitizers in solutions.^{1,2,3,4} The simulations are implemented to describe photoinduced reactions involving explicit excited states of light-harvesting species, that can be populated by a pulsed excitation, together with intrinsic deactivation as well as collision quenching from separate quencher species (Scheme 1). The presented simulation methodology is applied to quenching of light-harvesting Fe(III) complexes in electron donating solvents over a wide range of quencher concentrations as a prototype system of experimental interest for the reaction-diffusion dynamics over a wide range of concentrations.³ The results show clear signatures for the transition from classical diffusion-limited Stern-Volmer dynamics to close-contact quencher-photosensitizer interactions at high quencher concentrations, and the simulations are used to assess physically realistic photosensitizer-quenching collision interaction parameters for photoinduced dynamics beyond the classical Stern-Volmer model.

Scheme 1: Collision quenching of donor and excited acceptor



Acknowledgements:

The Swedish Research Council (VR, 2021-05313), the Knut and Alice Wallenberg (KAW, 2016.0059) foundation, the Swedish e-Science initiative eSCIENCE, and NanoLund are acknowledged for support. Computing resources were generously provided by the LUNARC and NSC high performance computing centers via SNIC/NAISS allocations. We thank Prof. Arkady Yartsev for valuable discussions.

References:

1. I. R. Gould and S. Farid, *Accounts of Chemical Research*, 1996, **29**, 522–528.
2. M. H. Gehlen, *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 2020, **42**, 100338.
3. N. W. Rosemann, P. Chábera, O. Prakash, S. Kaufhold, K. Wärnmark, A. Yartsev and P. Persson, *Journal of the American Chemical Society*, 2020, **142**, 8565–8569.
4. S. A. Rice, C. H. Bamford, C. F. H. Tipper and R. G. Compton, *Diffusion-limited reactions*, Elsevier, Amsterdam, 1985.

Characteristics of 77 K Emission for Phosphorescent Os-bpy Chromophore: ADF Modeling and Spin-Orbit Coupling Mediated Intensity Stealing

Yu-Hui Lin ^a, Yuan Jang Chen ^a, Ming-Kang Tsai ^b

^a Department of Chemistry, Fu-Jen Catholic University, Taiwan R.O.C. annlove60504@gmail.com

^b Department of Chemistry, National Taiwan Normal University, Taiwan R.O.C.

In this study, we investigate the role of SOCM-PIS modeling in the spin-forbidden transition phenomenon of highly symmetric complexes, $[M(bpy)_3]^{2+}$ and $[M(bpy)_2(en)]^{2+}$ ($M = Ru(II)$ and $Os(II)$, $bpy = 2,2'$ -bipyridine, $en = ethylenediamine$), where SOCM-PIS refers to the spin-orbit coupling (SOC)-mediated phosphorescence intensity stealing from efficient singlet states.¹⁻² Computational modeling was performed using the Amsterdam Density Functional (ADF) system, focusing on the differences in calculations with and without SOC perturbations. The results indicate that in $Ru(II)$ complexes, spin-orbit coupling induces only slight corrections to the absorption spectra. However, an intense singlet-to-triplet absorption band appears in the lowest absorption-energy region for $Os(II)$ complexes only when SOC perturbations are included in the calculations, consistent with spectral observations.³ Additionally, the observed 77 K emission spectra of the complexes were characterized as metal-to-ligand charge-transfer phosphorescence. Furthermore, the observed absorption and emission parameters, along with results from ADF modeling of M -bpy chromophores in this study, enhance our understanding of how the nuclear charge of heavy atoms influences the SOC formalism.

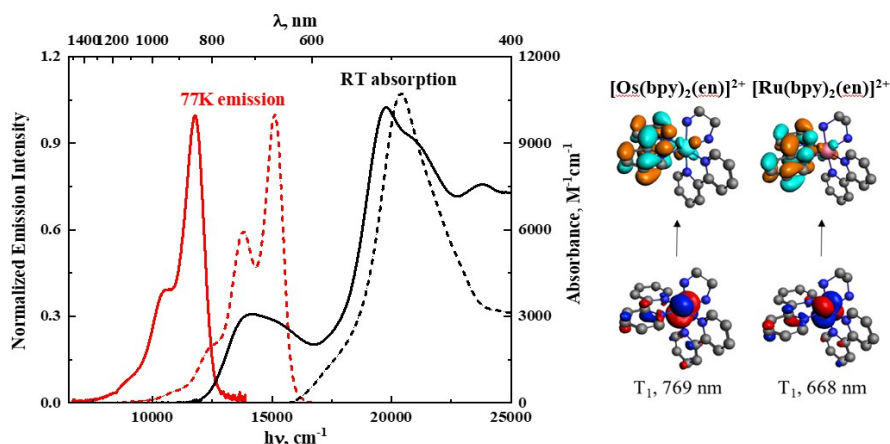


Figure 1. Comparison of the 298 K absorption spectra (black curve, in CH_3CN) and the 77 K emission spectra (red curve, in butyronitrile) of $[Ru(bpy)_2(en)]^{2+}$ (dashed lines) and $[Os(bpy)_2(en)]^{2+}$ (solid lines) in the left panel, along with the T_1 natural transition orbitals (NTOs) shown in the right panel.

Aknowlegments

This work was funded by the National Science and Technology Council (Taiwan, ROC) through Grants NSTC 113-2113-M-030-006.

References

- [1] B. J. Powell, *Coord. Chem. Rev.* **2015**, 295, 46
- [2] C. M. Marian, *Comput. Mol. Sci.* **2012**, 2, 187
- [3] Ronca, E. et al., *J. Phys. Chem. C* **2014**, 118 (30), 17067-17078.

Structure-Property Relationships for Heteroleptic Ag(I) Complexes for Light-Emitting Electrochemical Cells

S. Lipinski,^a Y. Atoini,^a P. B. Coto,^b R. D. Costa^a

^aTechnical University of Munich, Campus Straubing for Biotechnology and Sustainability, Schulgasse 22, 94315 Straubing, Germany. *sophia.lipinski@tum.de*. ^bNanomaterials and Nanotechnology Research Center (CINN), Spanish National Research Council (CSIC), Avda. de la Vega 4-6, 33940 El Entrego, Spain.

Light-emitting electrochemical cells (LECs) are the simplest and cheapest lighting devices as they combine a single-layered device architecture, air-stable electrodes as well as low-cost and up-scalable solution-based fabrication techniques.^[1] Among others, d¹⁰ ionic transition metal complexes (iTMCs) play a key role as electroluminescent emitters toward fully sustainable LECs. In this regard, four-coordinated Cu(I)-iTMCs have been widely studied that enabled to draw design rules for their photophysical properties (e.g. high PLQYs *via* substituents in the ortho position of the N[^]N ligands, how to achieve efficient TADF emitters).^[2] However, much less attention has been devoted to Ag(I)-iTMCs for LECs that is mainly related to their poor electrochemical stability in solution and in devices (LECs) resulting in a current knowledge gap in terms of their photo- and electroluminescent properties.^[3]

Thus, we have started to establish structure-property relationships for cationic heteroleptic Ag(I)-iTMCs ([Ag(N[^]N)(P[^]P)]⁺).^[4] For instance, in powder state, the nature of the excited states (e.g. changes from ¹/₃MLCT/¹/₃LLCT to ¹/₃LC) and PLQYs turned out to be extremely sensitive toward minor changes in the substitution pattern and choice of substituents (positive/negative *Hammett* constants) of the employed N[^]N ligands – corroborated by DFT/TDDFT studies. More striking, unexpected trends for their PLQYs (3–30 %) in powder were found that deviate completely from those established for Cu(I)-iTMCs. In addition, these relationships do not hold upon formation of thin-films resulting in unforeseen electroluminescence in LECs.

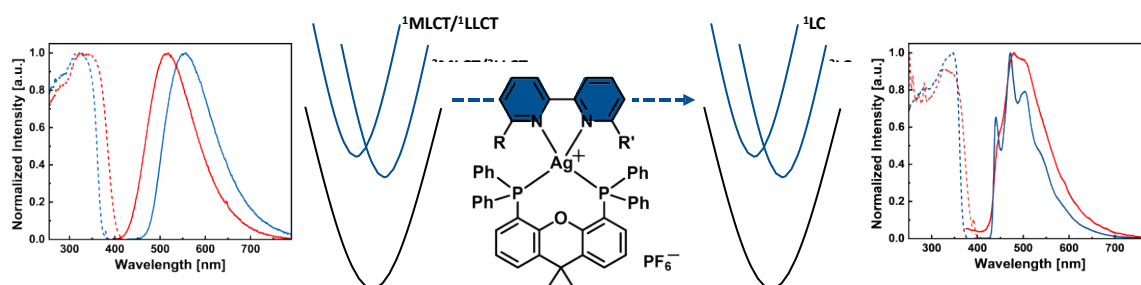


Figure 1. Impact of minor molecular changes on the nature of the excited states.

References

- [1] E. Fresta, R. D. Costa, *J. Mater. Chem. C* **2017**, 5 (23), 5643.
- [2] a) C. E. Housecroft, E. C. Constable *J. Mater. Chem. C* **2022**, 10 (12), 4456. b) A. Farokhi, S. Lipinski, L. M. Cavinato, H. Shahroosvand, B. Pashaei, S. Bellani, F. Bonaccorso, S. Karimi, R. D. Costa, *Chem. Soc. Rev.* **2025**, 54 (1), 266.
- [3] a) E. Fresta, J. M. Carbonell-Vilar, J. Yu, D. Armentano, J. Cano, M. Viciano-Chumillas, R. D. Costa, *Adv. Funct. Mater.* **2019**, 29 (31), 1901797. b) S. Lipinski, L. M. Cavinato, T. Pickl, G. Biffi, A. Pöthig, P. B. Coto, J. Fernandez-Cestau, R. D. Costa, *Adv. Opt. Mater.* **2023**, 11 (15), 2203145.
- [4] S. Lipinski, Y. Atoini, P. Thuéry, J.-L. Schmitt, P. B. Coto, R. D. Costa, *manuscript in preparation*.

Fluorescent J-dimers of Phthalocyanines

K. Lmcharrag, P. Zimčík*, V. Nováková*

Department of Pharmaceutical Chemistry and Pharmaceutical Analysis, Faculty of Pharmacy in
Hradec Králové, Charles University, Akademika Heyrovského 1203, Hradec Králové 50003
email: lamchark@faf.cuni.cz

Phthalocyanines (Pcs) and their a-analogue (AzaPcs) are synthetic macrocyclic dyes composed of four isoindoline units connected by azomethine bridges^{1,2}. Upon the discovery of Pcs, significant interest was generated to them due to their applications³ as dyes and pigments, in optoelectronics, as catalysts, gas sensors, for liquid crystals or as photosensitizers in photodynamic therapy, where light absorption in far-red or near-infrared region above 680 nm triggers the release of reactive oxygen species. The properties mentioned above are typically related to the monomolecular state of the molecules. The planar Pc core tends to form H-type aggregates in vast majority of cases that are characterized by the eliminated fluorescence emission and the increase in absorption at blue shifted wavelengths. However, in specific situations upon proper design, atypical and extremely rare, slipped J-dimers are observed being formed, unlike H-dimers, they exhibit red shifted absorption band and retained fluorescence (unless it is quenched by other photophysical processes). This project focuses on the synthesis of fluorescent J-dimers which will include synthesis of precursors, followed by cyclotetramerization, photophysical and spectral evaluation of prepared macrocycles. This study will unlock a potential way for J-dimers to be used in a wider range of sensing applications where strong fluorescence and water solubility are essential.

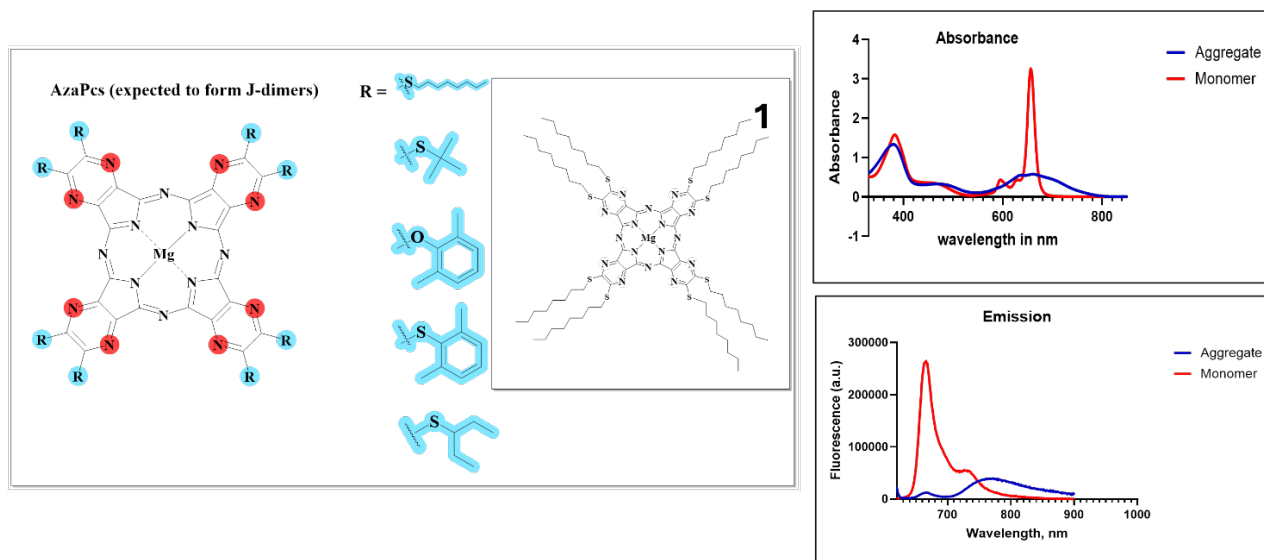


Figure 13. Schematic representation of the target AzaPcs that are expected to form J-dimers, and absorbance and emission spectras of 1.

Thanks to Charles University Grant Agency (No.414725).

References

- [1] G.de la Torre, C.Claessens,Torres, Chem. Commun, 2007, 2000-2015.
- [2] V.Novakova, , M. P. Donzello,C.Ercolani,P. Zimcik.P.A Stuzhin, Coord. Chem. Rev,2018, 361, 173
- [3] D.Wohrle.G.Schnurpfeil, S.G. Makarov, A.Kazarin, O.N. Suvorova, ,Macroheterocycles 2012, 5,191-202

Investigating the Photophysical Properties and Activity of a Zinc Porphyrin Appended Polyethylenimine Polymer Towards Solar Driven Water Splitting

P. Loftus, L. Tabrizi, and M. T. Pryce

Email: patrick.loftus7@mail.dcu.ie

*School of Chemical Sciences, Dublin City University, Glasnevin, Dublin, D09 V289, Ireland*⁴

The adverse effects of climate change have become an increasingly prominent issue globally. Hence, there has been growing research interest in developing solutions to alleviate the harmful impacts of climate change. One such solution is to replace fossil fuels with H₂ gas as a clean source of energy, releasing only H₂O as a by-product of combustion.¹ Herein, the activity of a branched polyethylenimine polymer towards the photocatalytic reduction of H₂O to H₂ gas will be presented. The polymer has been appended with zinc tetraphenyl porphyrin units via amide linkages (Figure 1). Incorporation of the porphyrin units within the polymer framework, results in intense electronic absorptions in the visible region of the electromagnetic spectrum thus, making the polymer suitable for application in solar driven photocatalytic hydrogen evolution.² The rate of H₂ evolution of the polymer using a range of catalytic conditions (polymer concentration, catalyst type, sacrificial agent), together with both steady-state and, time-resolved photophysical studies will be presented.

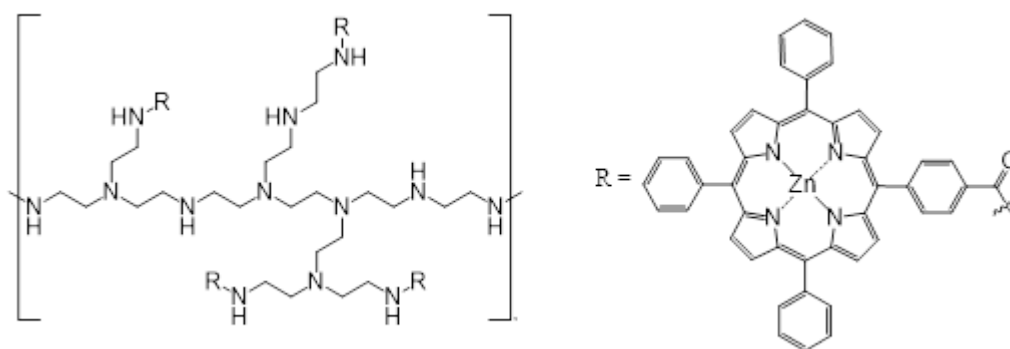


Figure 1. Structure of PEI-ZnTPP.

Aknowlegments

Thanks to The Sustainable Energy Authority of Ireland for funding this research under grant 22/RDD/890.

References

- [1] Prakash, K.; Mishra, B.; Díaz, D. D.; Nagaraja, C. M.; Pachfule, P. Strategic Design of Covalent Organic Frameworks (COFs) for Photocatalytic Hydrogen Generation. *J. Mater. Chem. A* **2023**, *11* (27), 14489–14538.
- [2] O'Neill, J. S.; Kearney, L.; Brandon, M. P.; Pryce, M. T. Design Components of Porphyrin-Based Photocatalytic Hydrogen Evolution Systems: A Review. *Coordination Chemistry Reviews* **2022**, *467*, 214599.

Effect of electronic parameters and distortion on the inverted Marcus behavior of bidentate Co^{III} photocatalysts

J. Löseke, L. Fritsch, H. Elgabarty, M. Bauer

Department of Chemistry, Paderborn University, Warburger Str. 100, 33098 Paderborn, Germany

jannik.loeseke@uni-paderborn.de

The Marcus inverted behavior of tris-bidentate Co^{III} complexes gives rise to the possibility of controlling the activation barrier for excited state relaxation, and therefore the excited state lifetime, via tuning the electronic parameters of the utilized ligands.^[1–3] The presented theoretical investigation focuses on the tunability of the energy difference between the ground and the excited state, through the electronic parameters of the ligands. Strong dependence of increasing σ -donor strengths, and in non meridional complexes a lesser dependence on reduced π -donor strengths, was found. Furthermore, significant overestimation of the relaxation activation barrier by Marcus theory was detected and attributed to changed distortion modes in the crossing point structure. So while a general trend of the singlet triplet energy gap using the electronic parameters can be identified, a complete account incorporating the activation barrier requires an understanding of the underlying cause for the trigonal-bipyramidal distortion mode.

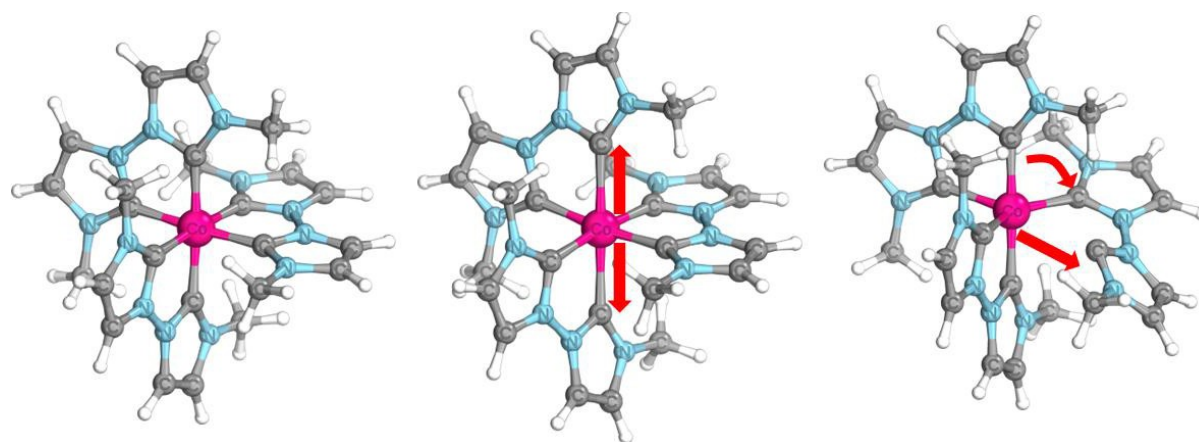


Figure 1. Visualization of the singlet (left), triplet (middle) and crossing point (right) structures. The observed distortions are highlighted using arrows. The triplet structure exhibits an elongation along one axis consistent with expectations for a partially occupied d_{z^2} orbital, while the crossing point structure exhibits an distortion towards a trigonal-bipyramidal structure.

References

- [1] A. Y. Chan, A. Ghosh, J. T. Yarranton, J. Twilton, J. Jin, D. M. Arias-Rotondo, H. A. Sakai, J. K. McCusker, D. W. C. MacMillan, *Science (New York, N.Y.)* **2023**, 382, 191.
- [2] O. S. Wenger, *Chemistry (Weinheim an der Bergstrasse, Germany)* **2019**, 25, 6043.
- [3] J. K. McCusker, *Science (New York, N.Y.)* **2019**, 363, 484.

Photocatalytical Reactions using Co^{III}(ImP)- and Fe^{II}(ImP)-complexes

F.Lux^{1*}, J.Steube¹, A. Krishna¹ and M.Bauer¹

¹University Paderborn, Warburger Straße 100, 33098 Paderborn, Germany

*franziska.lux@upb.de

The use of photoredox catalysis is critical as it can enable previously elusive transformations to access value-added products for pharmaceuticals.^[1,2] The use of second- and third-row transition metal complexes such as Ru^{II}- or Ir^{III}-polypyridyl species as photoredox catalysts is already established for various reactions.^[1] However, for continued and sustainable application, first-row metals like iron or cobalt are preferred. The challenge with these metals lies in their lower ligand-field splitting, leading to shorter excited-state lifetimes due to decay processes. To lengthen the lifetimes, the MC-states can be destabilized by using strong σ - donor ligands and supporting octahedral geometry while MLCT-states can be stabilized with π - acceptor ligands or by electronic delocalization. Additionally, the Marcus theory, specifically the Marcus-inverted region can be leveraged for longer lifetimes of the cobalt complexes as an increase in the excited-state energy correlates with a rise of the activation energy barrier for the decay.^[1]

Here, we report testing the EvoluChem PhotoRedOx Box TCTM photoreactor and the first experiments on boronic acid hydroxylation with Co^{III}(ImP)- and Fe^{II}(ImP)-complexes (Fig. 1). Future work will explore the effect of different metal centers and ligands on the photoredox properties.

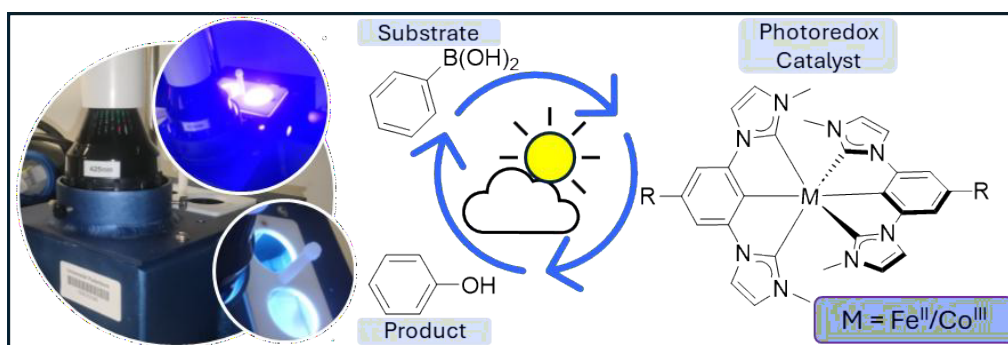


Figure 1. Schematic representation of the investigated photoredox catalytic reaction utilizing Fe(II) and Co(III) complexes as catalysts

Aknowlegments

Thanks to my workgroup for their support for this project.

References

- [1] A.Chan, *Science*. **2023**, 382 (6667), 191–197.
- [2] M.Bryden,, *Chem. Sci.* **2024**, 15, 3741–3757.

Microscopic studies of vapochromic behaviors in molecular crystals of [Re(CO)₃Br(ppt)]

X. Ma,¹ K. Enomoto,¹ K. Ishii,¹ Y. Matsuda,² M. Abe²

¹Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba Meguro-ku, 153-8505 Tokyo, Japan. ²Department of Material Science, Graduate School of Science, University of Hyogo, 3-2-1, Kouto, Kamigori, Ako, Hyogo, 678-1297 Japan. maxiao22@iis.u-tokyo.ac.jp

Gentle stimuli-induced molecular crystalline phase transition and/or structural transformation have been sometimes called as “Soft Crystals”.^{1,2} Super-resolution microscopes, which have been mainly developed for biological cells, would be appropriate for investigating such molecular crystalline single-crystal-to-single-crystal (SC-SC) phase transitions if they accompany luminescent changes, because time-dependent, three-dimensional behaviors can be traced with meso/micro spatial resolutions.³

In this study, *fac*-[Re(CO)₃Br(ppt)] (Figure 1a) crystals, which exhibit a vapor-induced SC-SC phase transition accompanying phosphorescence change (Figure 1b) were meso/microscopically investigated using super-resolution confocal laser microscopy, with an attachment for vapochromism measurements. Briefly, the crystals were initially placed on a cover glass with a frame. After CHCl₃ was injected into reservoirs in the frame, followed by sealing the system with a top cover. Immediately after closing the top, three-dimensional phosphorescence images and their spectra, as well as corresponding transmitted light microscopy images, were observed.

The dynamic, microscopic, SC-SC phase transition processes were successfully traced under CHCl₃ vapor exposure in a ~100 μm-sized non-solvated crystal. Figure 1c show typical confocal laser phosphorescence microscopy images overlapped with transmitted light microscopy images of the crystal before and after exposure to CHCl₃ vapor. CHCl₃-solvated crystalline form initially occurred at the crystalline peripheral area, and then expanded toward the center. They propagated with keeping μm-order rectangular shapes, which should reflect the cooperative phenomenon of this SC-SC phase transition.

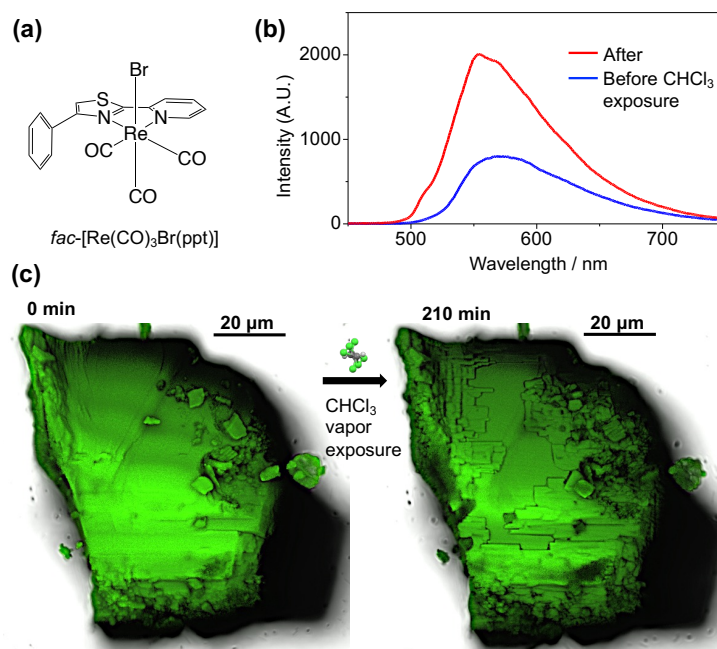


Figure 1. (a) Molecular structure of *fac*-[Re(CO)₃Br(ppt)], (b) emission spectra of *fac*-[Re(CO)₃Br(ppt)] before and after exposure to CHCl₃ vapor, and (c) top view of three-dimensional confocal laser phosphorescence microscopy images overlapped with transmitted light microscopy images of a ~100 μm-sized crystal, 0 min and 210 min after CHCl₃ vapor exposure.

References

- [1] M. Kato, *et al. Chem. Eur. J.*, **2019** 25, 5105.
- [2] M. Kato in *Soft Crystals: Flexible Response Systems with High Structural Order*, Eds.: M. Kato, K. Ishii, Springer, Singapore, **2023**, pp.13-21.
- [3] K. Ishii, *et al., J. Phys. Chem. C.*, **2021**, 125, 21055–21061.

FERROCENE-BASED MOLECULAR LOGIC GATES BASED ON PHOTOINDUCED ELECTRON TRANSFER

David C. Magri

Department of Chemistry, Faculty of Science, University of Malta, Msida, MSD 2080, Malta.

david.magri@um.edu.mt

Molecular logic-based computation continues to attract considerable attention as the field contemplates societal applications.^{1,2} Since the inception of the first AND logic gate for two cations, photoinduced electron transfer (PET) remains a steadfast design concept. Ferrocene is an icon organometallic compound owing to its stability, ease of functionalization and reversible redox character, which makes it a versatile building block in functional systems.³ Our interest has been in developing ferrocene-based molecular logic gates based on PET.^{4,5} These logic gates are typically designed in a modular format with an electron-donor (ferrocene), a fluorophore (i.e. 4-amino-1,8-naphthalimide) and a proton receptor (tertiary amine) with a fluorescence readout.^{6,7} We are pursuing various applications of these inventions such as smart coatings for the early detection of corrosion⁸ and lab-on-a-molecule systems for detecting a congregation of biologically relevant analytes.⁹

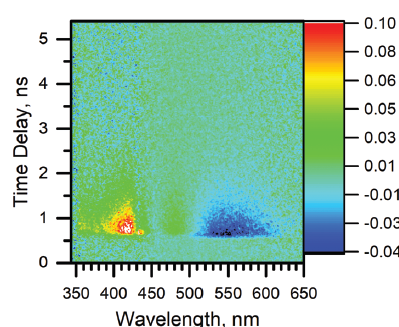
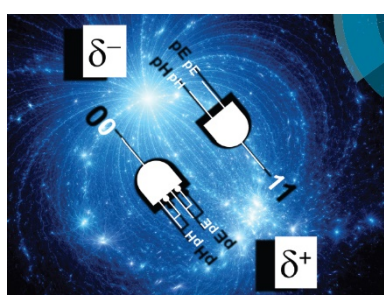


Figure 14. Front cover image of two logic gates in an electrical field and a transient absorption map of a fluorescent molecular logic gate for acid and oxidant.

Acknowledgements

Xjenza Malta, RIDT, The Embassy of France to Malta, the CNRS and the University of Malta are gratefully acknowledged for financial support.

References

- [1] A. P. de Silva, *Molecular Logic-based Computation*, RSC, Cambridge, UK, **2013**.
- [2] K. Szaciłowski, *Infochemistry: Information Processing at the Nanoscale*, Wiley, Chichester, UK, **2012**.
- [3] L. Fabbrizzi, The ferrocenium/ferrocene couple: a versatile redox switch, *ChemTexts*, **2020**, 6, 22.
- [4] D. C. Magri, Redox-Fluorescent Molecular Logic Gates based on Photoinduced Electron Transfer, in *Fluorescent Chemosensing and Bioimaging* ed. S. K. Sahoo, CRC Press, **2025**, Ch. 13, 276-299.
- [5] D. C. Magri, *Coord. Chem. Rev.*, **2021**, 426, 213598, 1-13.
- [6] J. C. Spiteri, S. A. Denisov, G. Jonusauskas, S. Klejna, K. Szaciłowski, N. D. McClenaghan, D. C. Magri, *Org. & Biomol. Chem.* **2018**, 16, 6195-6201.
- [7] J. Grech, J. C. Spiteri, G. J. Scerri, D. C. Magri, *Inorg. Chim. Acta.* **2023**, 544, 121176.
- [8] G. J. Scerri, J. C. Spiteri, D. C. Magri, *Mater. Adv.* **2021**, 2, 434-439.
- [9] G. J. Scerri, J. C. Spiteri, C. J. Mallia, D. C. Magri, *Chem. Commun.* **2019**, 55, 4961-4964.

Theoretical Insights and Struggles on The Series of 3d⁶ Metal Complexes

T. Maisuradze¹, E. Brohmer¹, P. Yaltseva², A. Prescimone², O.S. Wenger², S. Kupfer¹

¹Friedrich Schiller University Jena, Department of Physical Chemistry, Helmholtzweg 6, 07743 Jena, Germany. ²Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056 Basel, Switzerland
tamar.maisuradze@uni-jena.de

Photoactive transition metal complexes have attracted considerable interest for applications in a range of areas including photocatalysis, phototherapy and (photo-)electronics. Due to their abundance, special effort has been put in to develop 1st row TMCs with long lived excited states. New ligand design strategies for 1st row TMCs have shown a favourable increase of the excited state lifetimes to the nanosecond range. [1,2] Time-dependent density functional theory (TD-DFT) is one of the most frequently applied methods for excited state simulations due to its simplicity and reasonable accuracy. However, single determinant and highly functional-dependent TD-DFT sometimes struggles to correctly predict the excited state properties of charge transfer states or to account for double or triple excitations. Therefore, in the following study we have applied state of the art restricted active space second-order perturbation theory (RASPT2) method and scalar-relativistic TD-DFT simulations to 3d⁶ Co(III) carbene complex (**Figure 1**) to investigate the initial excitation process in the Frank-Condon region. RASPT2 calculations have showed excellent agreement with experimental data. The RASPT2 and TD-DFT results were similar, therefore, the cost-effective TD-DFT method was utilized to further the understanding of excited state processes such as intersystem crossing pathways and competitive relaxation processes. We applied TD-DFT to isoelectronic and isostructural 3d complexes featuring Cr(0), Mn(I), Fe(II), and Ni(IV) to investigate the correlation between effective nuclear charge and excitation and relaxation processes (**Figure 1**). Subsequently, the influence of the electronic properties were studied for Co(III) polypyridine complexes.

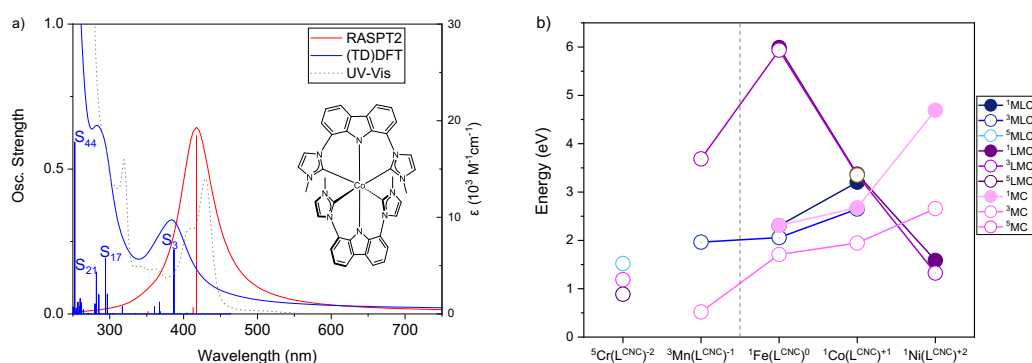


Figure 15. a) Simulated absorption spectra at RASPT2 and TD-DFT levels of theory, b) energy trends of the ^{1/3}MC, ^{1/3}MLCT/ILCT, ^{1/3}LMCT states for the series of isoelectronic 3d metal complexes.

References

- [1] G. Morselli, C. Reber, O.S. Wenger, *JACS* **2025**, 147 (14), 11585-12360
- [2] N. Sinha, B. Pfund, C. Wegeberg, A. Prescimone, O. S. Wenger, *JACS* **2022**, 144 (22), 9523-10096

Supramolecular interaction in Ru-Co and Ru-Fe complexes for efficient solar-driven hydrogen evolution and CO₂ reduction

F. Mancini^a, A. Bianco^a, A. Ruggi^b, G. Bergamini^a

^aDepartment of Chemistry "Giacomo Ciamician", University of Bologna, Italy

^bDepartment of Chemistry, University of Fribourg, Switzerland

E-mail: francesca.mancini27@unibo.it

Cyano (CN)-bridged ruthenium complexes, such as [Ru(bpy)_xCN_y], are known to form photoactive supramolecular assemblies via cyanide group coordination to metal ions. These complexes exhibit remarkable redox and photophysical properties, and their ability to form polynuclear structures has been well-documented [1-2].

In this study, we explore the potential of [Ru(bpy)₂CN₂] within the field of solar energy conversion, focusing on its application to molecular hydrogen evolution and CO₂ reduction.

The primary objective is to enhance the electron transfer from the photosensitizer to the catalyst through supramolecular interaction, thereby improving the efficiency of the photoreactions.

We investigate the formation of the supramolecular adduct between [Ru(bpy)₂CN₂] and hexadentate polypyridyl cobalt and iron complexes [3-4].

Spectroscopic titrations were employed to monitor changes in absorbance, luminescence intensity, and lifetimes of the [Ru(bpy)₂CN₂] complex upon addition of the catalyst. Our results demonstrate the successful formation of 1:1 supramolecular adducts, exhibiting a high association constant ($K_{\text{ass}} \sim 10^5 \text{ M}^{-1}$), which results in efficient static quenching of the ruthenium complex emission.

The photocatalytic system comprises the [Ru(bpy)₂CN₂] photosensitizer, the catalyst and 1,3-dimethyl-2-phenylbenzimidazoline (BIH) as sacrificial electron donor, operating in an acetonitrile medium. Depending on the catalyst employed, the photocatalytic cycle promotes one of the two photoreactions with highly promising performances: hydrogen evolution in the presence of the cobalt complex and CO₂ reduction in the presence of the iron complex.

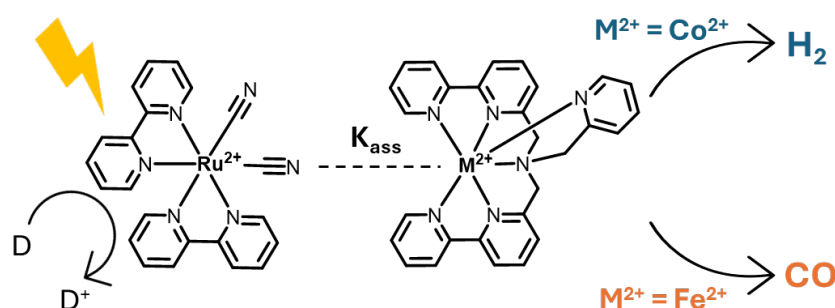


Figure 16. Schematic representation of the photo-driven hydrogen evolution and CO₂ reduction mechanisms through Ru-Co and Ru-Fe supramolecular interactions.

References

- [1] T. Lazarides et al., *Journal of the American Chemical Society*, 2007, 129 (13), 4014-4027.
- [2] M. G. Kinnaird et al., *Chemical Physics Letters*, 1982, 88 (3), 275-280.
- [3] F. Lucarini et al., *Chemistry—A European Journal*, 2017, 23 (28), 6768-6771
- [4] F. Droghetti et al. *ChemSusChem*, 2024, 17 (4), e202300737.



Comparison of Iridium Sensitizers Employed in the Photoelectrochemical Generation of Added-Value Organics

Andrea Mantovani,^a Edoardo Marchini,^a Annagioia Mastrolorenzo,^b Paola Manini,^b Mirco Natali ^a

^a *Department of Chemical, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, 44121 Ferrara, Italy. Email: andrea.mantovani@unife.it*

^b *Department of Chemical Sciences, University of Naples Federico II, Via Cintia 4, 80126 Napoli, Italy.*

The pressing issues of climate change need the development of sustainable technologies.^[1] Dye-sensitized photoelectrochemical cells (DSPECs) represent a promising approach to this challenge. In this regard, great attention has been paid in the last years towards the development of photoanodes for the water oxidation to dioxygen. However, this reaction still constitutes a major challenge due to its strict kinetic requirements and strategies have been recently envisioned to replace water oxidation with more favorable reactions.^[2] Within this framework, the present study targets the investigation of two different cyclometallated iridium complexes featuring highly positive oxidation potentials as sensitizers onto TiO₂ electrodes for the light-driven oxidation of organics into added-value products. In particular, two different processes have been considered, namely the oxidation of benzyl alcohol to benzaldehyde^[3] and a Diels-Alder reaction.^[4] The critical role of the sensitizer in the formation of the target products will be examined in details by combining photoelectrochemical measurements and optical spectroscopy.

References

- [1] C. Wang, M. Amiri, R. T. Endean, O. Martinez Perez, S. Varley, B. Rennie, L. Rasu, S. H. Bergens, *ACS Appl. Mater. Interfaces* **2018**, 10, 24533–24542.
- [2] M. Natali, A. Sartorel, A. Ruggi, *Front. Chem.* **2022**, 10, 1-8.
- [3] G. Di Carlo, C. Albanese, A. Molinari, S. Carli, R. Argazzi, A. Minguzzi, F. Tessore, E. Marchini, S. Caramori, *ACS Appl. Mater. Interfaces* **2024**, 16, 14864–14882.
- [4] M. D. Turlington, S. Ahmed, K. S. Schanze, *ACS Catal.* **2024**, 14, 12512–12517.

A deep insight into the role of basic additives in the charge injection of Fe(II)-based complexes

E. Marchini,¹ F. Ruani,² B. Ventura,² N. Armaroli,² M. Pastore,³ P. C. Gros,³ S. Caramori¹

¹University of Ferrara, 44121 Ferrara, Italy, edoardo.marchini@unife.it; ²Istituto per la Sintesi Organica e la Fotoreattività (ISOF), CNR, 40129 Bologna, Italy; ³Université de Lorraine, CNRS, 54000 Nancy, France

Since the pioneering contribution of Ferrere and Gregg, iron complexes have demonstrated the ability to undergo charge injection into a semiconductor substrate, despite the low Power Conversion Efficiency (PCE) of the resulting Iron-Sensitized Solar Cells (Fe(II)-SSCs) [1]. Recently, we reported a panchromatic co-sensitization strategy based on Fe(II)-NHC complexes, achieving an exceptionally high photocurrent density of 9 mAcm⁻² [2]. Nevertheless, the PCE remains limited by the low open-circuit photovoltage (V_{OC}), which generally is typically improved by tuning the TiO₂ Fermi Level position through the addition of an electron-rich base, such as tert-butyl pyridine (TBPY), to the electrolyte. However, despite the injection driving force on the order of 1 eV, which suggests no thermodynamic limitations, the presence of these alkaline additives proves detrimental in the system's efficiency. To date, the reasons behind the photocurrent loss remains cryptic. Herein, we reported a deep investigation on the role of tert-butyl pyridine in Fe(II)-SSCs and its impact on photocurrent suppression, combining photoelectrochemical analysis with ultra-fast spectroscopy. Thermodynamics effects contribute to the performance degradation, as depicted by the Marcus parabola trend. Nevertheless, compared to well-established ruthenium complexes, it is not sufficient to outline the observed losses.

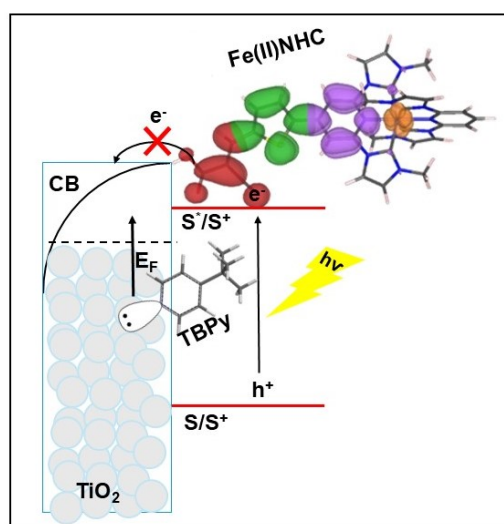


Figure 17. Schematic representation of an Fe(II)-SSC, with the absorption of TBPY onto TiO₂ also depicted.

References

- [1] Ferrere, Gregg, *JACS* **1998**, 120 (4), 843-844
- [2] Reddy-Marri, Marchini, Diez Cabanes, Argazzi, Pastore, Caramori, Philippe C. Gros, *Chem. Sci.* **2023**, 14, 4288-4301

A novel water-dispersible microemulsion of a supramolecular copolymer for drug delivery systems

M. Mazzaferro,^{1,2*} D. Crisafulli,¹ M. Milone,¹ G. T. Patanè,¹ F. Puntoriero,¹ I. Pisagatti,¹
A. Notti,¹ M. F. Parisi,¹ G. Gattuso¹

¹ Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche ed Ambientali, Università degli Studi di Messina, Viale F. Stagno d'Alcontres, 31, 98166 Messina, Italy; ² Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, via Elce di Sotto, 8, 06123 Perugia, Italy.

*martina.mazzaferro@studenti.unime.it

Supramolecular polymers¹ are macromolecular assemblies composed of monomeric units held together by non-covalent and reversible interactions that can be successfully used in the design of stimuli-responsive systems. We reported recently the formation of a photo-active supramolecular copolymer from a dicarboxylic acid bis-pillar[5]arene (**H**) and a mixture of two complementary bis-guest molecules: alkylidene-bis-imidazole (**G1**) and perylene-bisimide-bis-imidazole (**G2**).² The supramolecular copolymer **H/G1/G2** preserves the key properties of its two-component precursors -the solubility of **H/G1** and the light-responsive behavior of **H/G2**- resulting in a system that can switch the luminescence signal depending on the binding or release of **G2** within the pillararene cavities.

In order to transfer the properties of this water-insoluble system to an aqueous environment, in this study we describe the formation and characterization of water-dispersable microemulsified nanoparticles³ created by incorporating **H/G1** and **H/G1/G2** polymers into water-dispersible CTAB, highlighting their potential for biomedical applications.

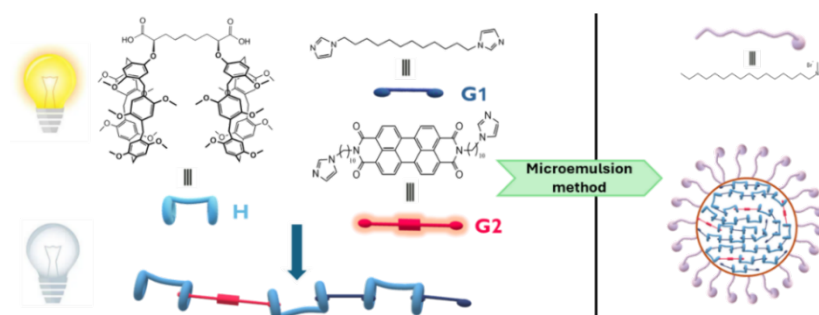


Figure 18. Mechanism of supramolecular polymer formation and its dispersion in water medium.

Aknowlegments

This work was partially funded by the project PRIN 2022 PNRR "P2022YJZ5F".

References

- [1] A. Notti, I. Pisagatti, F. Nastasi, S. Patanè, M. F. Parisi, G. Gattuso, *J. Org. Chem.*, **2021**, 86, 1676–1684.
- [2] M. Mazzaferro, D. Crisafulli, F. Mancuso, M. Milone, F. Puntoriero, A. Irto, S. Patanè, V. Greco, A. Giuffrida, I. Pisagatti, A. Notti, M. F. Parisi, G. Gattuso, *Org. Chem. Front.*, **2024**, 11, 6293–6303.
- [3] M. Bominathan, M. Arunachalam, *ACS Appl. Polym. Mater.*, **2020**, 2, 4368–4372.

Dynamic processes in photoactive metal-containing rotaxanes

N. Pairault,^a A. Silswal,^a I. Shepeleva,^b N. Descarli-Oliveira,^a G. Jonusauskas,^b N. D. McClenaghan^a

^aUniversity of Bordeaux & CNRS, Institut des Sciences Moléculaires, France.

^bUniversity of Bordeaux & CNRS, LOMA, France.

E-mail : nathan.mcclenaghan@u-bordeaux.fr

Rotaxanes are ring-on-thread mechanically-interlocked molecules (MIMs) which represent versatile platforms to study a range of fundamental processes, including light-matter interactions and fast intercomponent electronic energy transfer processes, for example.[1,2] Amongst several systems studied in Bordeaux, we turn our attention to triplet-triplet annihilation photon up-conversion (TTA-UC), where absorption of light of long wavelength leads to the emission of photons of higher energy.[3] The inherent structure of MIMs offers opportunities to profit from the relative dynamic between MIMs components and from the mechanical bond which inhibits diffusion-based issues that can affect the TTA-UC process. In this context, we are investigating the control of the TTA-UC process within a MIM incorporating sensitizers and annihilators, in an autonomous manner. Herein we present the synthesis and preliminary spectroscopic analyses of prototype [3]rotaxane integrating two anthracene-containing annihilators coupled with two ruthenium complex-based photosensitizers, to intramolecularly induce the TTA-UC process.

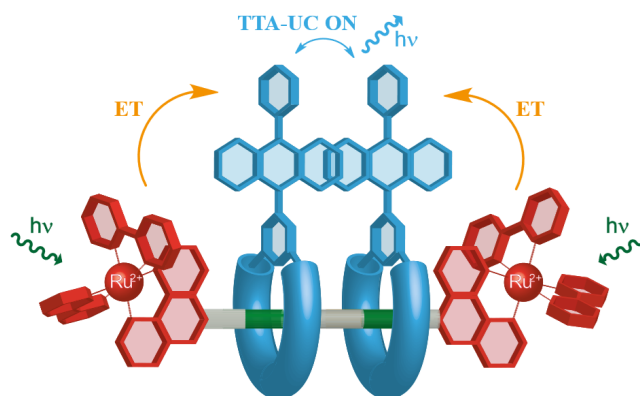


Figure 19. Cartoon representing intra-rotaxane triplet fusion leading to upconverted (TTA-UC) light output.

Acknowledgements

Funded by the European Union (AURORA project, grant agreement n° 101109260). Views and opinions expressed are those of the authors only and do not necessarily reflect those of the European Union or Marie-Curie actions. Neither the European Union nor the granting authority can be held responsible for them.

References

- [1] S. Yu, A. Kupryakov, J. E. M. Lewis, V. Martí-Centelles, S. M. Goldup, J.-L. Pozzo, G. Jonusauskas, N. D. McClenaghan, *Chem. Sci.* **2021**, 12, 9196-9200.
- [2] S. A. Denisov, Q. Gan, X. Wang, L. Scarpantonio, Y. Ferrand, B. Kauffmann, G. Jonusauskas, I. Huc, N. D. McClenaghan, *Angew. Chem. Int. Ed.*, **2016**, 55, 1328-1333.
- [3] T.N. Singh-Rachford, F. N. Castellano, *Coord. Chem. Rev.* **2010**, 254, 2560

Photochemistry, electron transfer and catalysis mapped by a combination of ultrafast laser and X-ray spectroscopies

I Meikle*, M V Appleby, I I Ivalo, E L Race, G Williams, D Chekulaev and J A Weinstein

*University of Sheffield, imeikle1@sheffield.ac.uk

Copper(I) diimine complexes have been studied since the late 1970s due to their interesting electron dynamics and structural distortions. Heteroleptic $[\text{Cu(I)}(\text{diimine})(\text{diphosphine})]^+$ complexes are currently subject to extensive interest, due to the characteristics they can exhibit. Most interestingly, a metal-to-ligand charge transfer (MLCT) within the visible range, ideal for dye-sensitised solar cell (DSSC) and water purification applications.¹ They also display temperature activated delayed fluorescence (TADF) and the potential for long lived excited states.² Copper(I) complexes are thoroughly attractive molecules, with their low cost, high abundance and simple synthesis.

The key issue of these tetrahedral, four coordinate structures is the structural reorganization which occurs upon photo irradiance, promoting a fast relaxation pathway to the ground state. Through structural adaptations the excited state lifetimes can be prolonged. We report the synthesis and structure and of new heteroleptic Copper(I) complexes, containing varying diimine ligands. Followed using ultrafast laser and X-ray spectroscopies to map the photochemistry, electron transfer and catalysis of Copper(I) complexes.

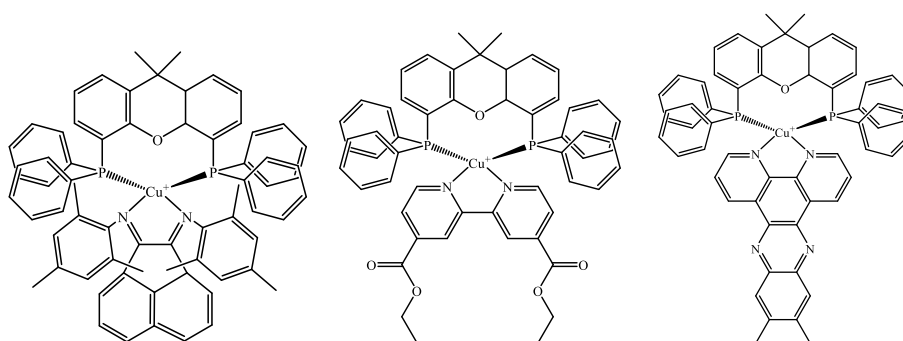


Figure 20. Structures of photosensitising heteroleptic Copper(I) complexes.

Aknowlegments

Co-funded by the UK XFEL Physical Sciences Hub. Thanks to EU XFEL, Swiss Light Source and Stanford Synchrotron Radiation Laboratory.

References

- [1] M. V. Appleby, P. G. Walker, D. Pritchard, S. Van Meurs, C. M. Booth, C. Robertson, M. D. Ward, D. J. Kelly and J. A. Weinstein, *Mater. Adv.*, **2020**, 1, 3417–3427
- [2] C. Sandoval-Pauker, M. Santander-Nelli and P. Dreyse, *RSC Adv.*, **2022**, 17, 10653–10674

Charge transfer dynamics in molecular-based photoanodes for solar fuels production

M. Milani,^a E. Marchini,^a A. M. Cancelliere,^b A. Amadeo,^b G. La Ganga,^b S. Caramori,^a S. Berardi^a

^a Department of Chemistry, Pharmaceutical and Agricultural Sciences, University of Ferrara, Via L. Borsari 46, Ferrara, Italy.

^b Department of Chemical, Biological, Pharmaceutical and Environmental Science, University of Messina, via F. Stagno d'Alcontres 31, Messina, Italy
martina.milani@unife.it

A Dye-Sensitized Photoelectrosynthetic Cell (DSPEC) is a photoelectrochemical device capable of storing solar energy in chemical bonds, mimicking natural photosynthesis. It combines a molecular chromophore and a catalyst on the surface of wide-bandgap, n-type semiconductors like Titanium Dioxide (TiO₂).¹ The chromophore absorbs light and injects electrons into the TiO₂ conduction band, which are then transferred to an external circuit to drive reactions like proton reduction. At the same time, hole transfer from the oxidized dye to the immobilized catalyst (typically a metal complex) occurs, with the latter mediating water oxidation (WO), enabling efficient renewable energy conversion.²

In this work, we present new sensitizers based on Ru(II) polypyridine (RuP1 and RuP2, **Figure 1**), in which a pyridine functionality is used for anchoring the S to the FTO/TiO₂ surface, and a molecular WO catalyst of the Ru(bda)-family (with bda = 2,2'-bipyridine-6,6'-dicarboxylic acid, **Figure 1**), bearing vinyl groups. These moieties should allow for the stable linkage to the semiconductor surface by exploiting electropolymerization to other vinyl introduced through silane chemistry.³

In order to determine the charge transfer ability of the new sensitizers, the photophysical and photoelectrochemical properties have been firstly probed in various electrolytes containing electron donors, pointing out a non-ideal directionality of the charge transfer state responsible for charge injection. However, reductive quenching² of the excited state allows, in certain cases, for the generation of a sizable photocurrent.

Further studies will be aimed at preparing new molecular-based photoanodes, either coupling these dyes and the WOC species in a type-I configuration (**Figure 1**) or in the form of a supramolecular dyad (type-II configuration).⁴

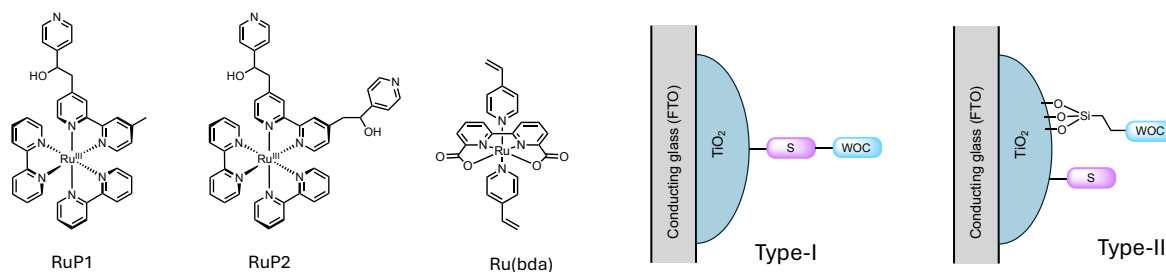


Figure 21. Structures of the sensitizers (S) and catalyst (WOC) and photoanodes possible configurations.
Acknowledgment: This project received funding from PRIN MUR project "Photogen" (Prot. 2022AWXS83).

References

- [1] A. Kobayashi *et al.* *Coord. Chem. Rev.* **2022**, 467, 214624.
- [2] F. Ronconi *et al.* *Dalton Trans.* **2016**, 45, 14109-14123.
- [3] T.T. Li *et al.* *ACS Energy Lett.* **2019**, 4, 629-636.
- [4] A. M. Cancelliere *et al.* *J. Chem. Phys.* **2024**, 160, 084709.



Red and NIR emitting Zn(II)-salen complexes for sensing and biological applications

Pablo Msellem,¹ Nayla N.K. Takeuti,^{1,2} Luigi Menduti,² Giovanni Valenti,³ Luisa De Cola^{1,2}

¹ Mario Negri Institute for Pharmacological Research (IRCCS), Milan, Italy

² Department of Pharmaceutical Sciences (DiSFarm), University of Milan, Milan, Italy

³ Department of Chemistry Giacomo Ciamician, University of Bologna, Bologna, Italy

pamsellem@marionegri.it

The use of organic and organometallic compounds expressing thermally activated delayed fluorescence (TADF) properties has developed tremendously in the last decade.^[1,2] The long emission lifetimes and high quantum yields resulting from the reverse intersystem crossing (RISC) mechanism between the triplet state and the singlet state make this type of luminophores especially interesting to use in sensing, imaging and immunoassays.^[3–5] In order to reduce sensitivity of the luminophores to the quenching of the triplet state by triplet oxygen, recent works focused on the development of nanomaterials encapsulating and isolating the compound from its environment, providing also a solution for water-solubilization.^[3]

This work's objective is to develop new earth-abundant metal complexes expressing red luminescence and to generate the emissive state by photo- or electroexcitation. The compounds designed and synthesized are red and NIR emitting Zn(II)-salen complexes. To have the emission in the red region we have functionalized the macrocyclic ligand with donor and acceptor moieties. Their chemical, photophysical and electrochemical properties have been investigated in toluene, DMSO and acetonitrile.

The mechanism for the red and NIR emission is described and corroborated by the solvent and temperature dependent experiments. In addition the electrochemical data are analyzed to confirm that the emission is generated by a charge transfer process.

We envisage the use of such materials in sensing applications and as imaging probe for in vitro assays.

Acknowledgments

The authors thank the ECLectic Horizon MSCA Doctoral Network (Grant agreement n° 101119951) and the ECLipse EIC Pathfinder (Grant agreement n° 101046787) for the funding.

References

- [1] Dos Santos, J. M. *et al. Chem. Rev.* **2024**, 124, 13736–14110.
- [2] Ferraro, V. *et al. Adv. Sci.* **2024**, 11, 2404866.
- [3] Ni, F. *et al. Adv. Opt. Mater.* **2020**, 8, 1902187.
- [4] Chen, W. *et al. Chin. Chem. Lett.* **2019**, 30, 1717–1730.
- [5] Fracassa, A. *et al. Chem. Sci.* **2024**, 15, 17892–17899.

“If you like it you should put a ring on it” Rotaxanes as supramolecular protective motifs in reductive heterodinuclear photocatalysis

Marius Müßler,^a Mohini Semwal,^c Louis Blechschmidt,^c Linda Zedler,^d Konstantinos Zois,^e Patrick Hoffmann,^b Max von Delius,^b Leticia González,^e Benjamin Dietzek-Ivanšić,^c Alexander Klaus Mengele,^a Sven Rau.^{*a}

a Institute of Inorganic Chemistry I, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany, marius.muessler@uni-ulm.de

b Institute of Organic Chemistry I, Albert-Einstein-Allee 11, 89081 Ulm, Germany

c Friedrich Schiller University Jena, Institute of Physical Chemistry, Helmholtzweg 4, Jena, Germany

d Leibniz Institute of Photonic Technology, Research Department Functional Interfaces, Albert-Einstein-Str. 9, Jena, Germany

e Institute of Theoretical Chemistry, Vienna University, Währinger Str. 17 A-1090, Vienna

Alkyne bonds offer great potential as a potent spacing group in bridging ligands for key functionalities in light-driven catalysis based on ruthenium polypyridyl complexes.^[1]

While providing great co-planarity of the polyaromatic backbone, alkynes tend to undergo hydrogenation when being exposed to reductive conditions (e.g. in presence of sacrificial electron donors), leading to a loss in efficient communication and diminished catalysis.

Herein, we present the utilization of a macrocycle (cucurbit[7]uril; CB[7]) used as a protective motif for the labile alkyne linkage and leading ultimately to the formation of a heterodinuclear rotaxane structure capable for NAD⁺ hydrogenation (Figure 1). The implementation of the macrocycle showed extended durability of the catalyst by shielding the alkyne moiety from being irreversibly reduced.

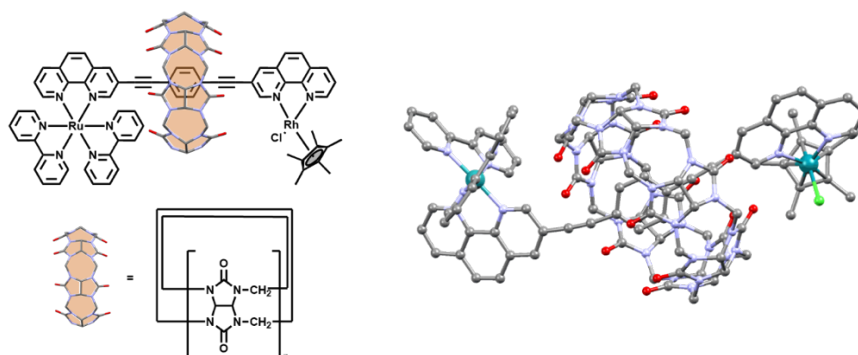


Figure 22: Molecular depiction & DFT structure of Hetero[2]Rotaxane.

Acknowledgments

Funding by the Deutsche Forschungsgemeinschaft (German Research Foundation) via the TRR CATALIGHT, Projektnummer 364549901, TRR 234, A1 & C3.

References

- [1] Zedler, L., Wintergerst, P., Mengele, A.K., Rau, S. *et al.*, Nat Commun **13**, 2538 (2022).

Tuning the photophysical properties of π -extended Cu-bibenzimidazole complexes

S.A. Nair, R. Jocher, D. Sorsche and S. Rau

*Institute of Inorganic Chemistry I, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany,
sandra.anila-nair@uni-ulm.de*

In this study, we focus on the synthesis, structural characterization, and photophysical studies of novel heteroleptic Cu(I) complexes containing bibenzimidazole (bbim) and Xantphos ligands, with the aim of advancing sustainable photocatalytic materials. Copper, as an earth-abundant and cost-effective alternative to precious metals, offers tunable redox and luminescence properties, making it an ideal candidate for photochemical applications. Through strategic ligand modifications, including π -system extension in bbim derivatives, significant bathochromic shifts in absorption spectra were achieved, enhancing visible light utilization. The modified bbim ligands were synthesized via Negishi coupling and the Cu complexes were prepared using conventional one-pot-synthesis, with X-ray crystallography confirming their structural integrity and hydrogen-bonding interactions. Photophysical analysis, including UV-Vis absorption and emission spectroscopy, revealed strong correlations between ligand structure and photophysical properties. Modified bbim ligands exhibited extended emission wavelengths compared to standard bbim also translating in the properties of the Cu complexes.

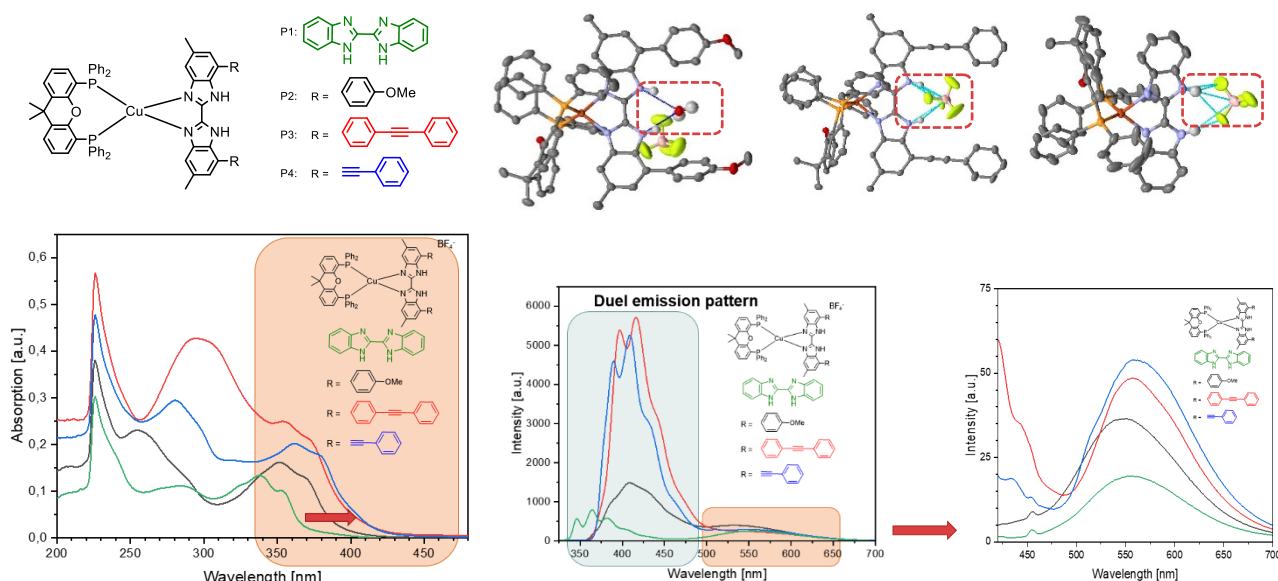


Figure 1: Novel copper-based PS with bibenzimidazole ligands, X-ray structure of different Cu(I) complexes, UV-vis and emission spectroscopic data.

References:

- [1] Huang, T. H., Hu, Q. L., Zhao, F. Z., Zheng, D., Liu, Q., Wu, T. C., & Chen, J. (2020). *Journal of Luminescence*, 227, 117530.
- [2] Zhang, Y., Schulz, M., Wächter, M., Karnahl, M. & Dietzek, B *Coord. Chem. Rev.* 356, 127–146 (2018).
- [3] Giereth, R., Reim, I., Frey, W., Junge, H., Tschierlei, S., & Karnahl, M. (2019). *Sustainable Energy & Fuels*, 3(3), 692-700.
- [4] Kuang, S.M.Cuttell, D. G.McMillin, D. R.Fanwick, P. E. & Walton, R. A. *Inorg.Chem.*41,3313–3322 (2002).
- [5] Tsubomura, T., Kimura, K., Nishikawa, M. & Tsukuda, T. *Dalton Trans.* 44, 7554–7562 (2015).



Conjugated polymer photocatalysts with a built-in metal complex for CO₂ reduction

Akinobu Nakada, Kotaro Ishihara, Shunsuke Asai, Yasunori Satake, Ryu Abe

Department of Energy and Hydrocarbons Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: nakada@scl.kyoto-u.ac.jp

Reductive conversion of CO₂ into energy-added molecules has been an important subject in various fields including materials chemistry, catalysis, electrochemistry, and photochemistry, from viewpoints of both decreasing CO₂ concentration and gaining energy and carbon resources. Among the various methods and schemes proposed, visible-light-driven CO₂ reduction in combination with water oxidation, one of the representative models of artificial photosynthesis, is an attractive solution because it enables abundant water and inexhaustible solar energy to be used to produce value-added chemicals. Molecular metal complexes and semiconductors are promising candidates for photocatalysts that can reduce CO₂ to CO, formate, formaldehyde, or other hydrocarbons. Although both molecular metal complexes and semiconductors have strengths and weaknesses, their weaknesses (low oxidation ability and low selectivity for reduction reactions) can be overcome via the construction of a suitable molecule/semiconductor hybrid material. However, facilitating electron transfer at the molecule/semiconductor junction while suppressing unfavorable back electron transfer events is challenging.

Recently, organic conjugated polymers have emerged as new candidates for photocatalyst materials. The organic polymers not only exhibit semiconducting properties due to the extended p-conjugation but also have the molecular designability. Metal-based catalytic sites are frequently required to selectively reduce CO₂. Hence, the design principle, that maximizes the synergy between the conjugated skeleton and catalyst moiety, is strongly desired for achieving efficient photocatalytic CO₂ reduction. Herein, we show strong impacts of excited charge distribution in conjugated polymer photocatalysts with a site-selectively incorporated Ru(II) complex catalyst, which are elucidated by a combination of ultrafast spectroscopy and theoretical calculation, on their photocatalytic activity for CO₂ reduction.¹⁻³

References

- [1] A. Nakada, R. Miyakawa, R. Itagaki, K. Kato, C. Takashima, A. Saeki, A. Yamakata, R. Abe, H. Nakai, H.-C. Chang, *J. Mater. Chem. A* 10, 19821 (2022).
- [2] K. Ishihara, A. Nakada, H. Suzuki, O. Tomita, S. Nozawa, A. Saeki, R. Abe, *J. Mater. Chem. A* 12, 30279 (2024).
- [3] A. Nakada, S. Asai, C. Zhang, K. Ishihara, H. Suzuki, O. Tomita, A. Saeki, R. Abe., *Sustain. Energy Fuels*, in press [DOI: 10.1039/D5SE00142K].

Benzothiazole-Quinoline based sensor for selective detection of Fe³⁺ ions and its applications

N.Nehra^{a,b}, R.Kaushik^c, Kanika^d, Rahul^d, R.Khan^d

^aDepartment of Chemistry, National Institute of Technology, Kurukshetra, Haryana, India

^bPresent Address: Department of Pharmaceutical Chemistry and Pharmaceutical Analysis, Faculty of Pharmacy in Hradec Kralove, Charles University, Czech Republic ^cChemical Oceanography Division, CSIR- National Institute of Oceanography, Dona Paula, Goa, India

^dChemical Biology Unit, Institute of Nano Science and Technology, Mohali, Punjab, India

Email: nehran@faf.cuni.cz

Although, iron is highly abundant and crucial for several body functions and physiological processes, the excess amount of iron in the body can also be fatal.¹ Iron ion contamination and toxicity is one of the most challenging issues for living beings. Over the last century, rapid industrialization, iron extraction and the mismanagement of industrial waste disposal has led to iron contamination in water bodies.¹ Consequently, there is a growing need to develop iron sensors which can be employed for detection in biological as well as real water samples.² 8-hydroxyquinoline is well-known for its strong affinity towards transition metals including Fe³⁺ ions^{3,4}. Therefore, we have developed a novel fluorescent probe, **4HBTHQTz** based on benzothiazole-quinoline-triazole moieties. In this molecule, the 4-(benzothiazol-2-yl) phenolic (4-HBT) unit acts as a fluorophore. The probe exhibits strong fluorescence, which is selectively quenched in the presence of Fe³⁺ ions at 380 nm (λ_{ex} = 320 nm). The detection limit of **4HBTHQTz** with Fe³⁺ is found to be 0.64 μ M, which is lower than the WHO recommended limit in drinking water. **4HBTHQTz** works efficiently over the pH range of 5-8, and it has shown promising results for quantitative detection of Fe³⁺ in various water samples including tap, river and seawater. Moreover, its applicability to biological system was confirmed through fluorescence cell imaging in L929 mouse fibroblast cells. Overall, **4HBTHQTz** offers several advantages, including high selectivity, quick detection, and low limit of detection for Fe³⁺ ions.

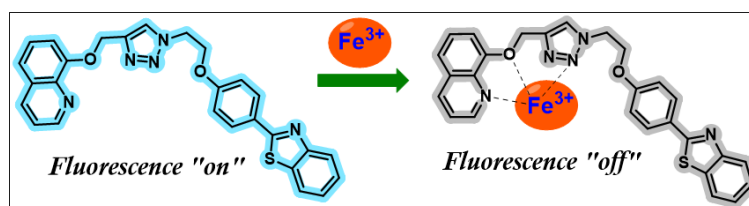


Figure 23. Representation of 4HBTHQTz.

NN thanks the project New Technologies for Translational Research in Pharmaceutical Sciences /NETPHARM, project ID CZ.02.01.01/00/22_008/0004607, co-funded by the European Union for providing the financial support.

References

- [1] Z. Li, J.Hou, S.Wang, L.Zhu J.Shen, *Coord. Chem. Rev.*, **2022**, 469, 214695
- [2] N.Nehra, R.Kaushik, *Anal. Methods*, **2023**, 15(40), 5268-5285
- [3] F.Ahmed, H.Xiong, *Dyes Pigments*, **2021**, 185, 108905
- [4] N.Duan, H.Wang, Y.Li, S.Yang, H.Tian, B.Sun, *Coord. Chem. Rev.*, **2021**, 427, 213557

Tunning Electron-Accepting Properties of Phthalocyanines for Charge Transfer Processes

S. Bednarik, J. Demuth, J. Kernal, M. Miletin, P. Zimcik, V. Novakova

Faculty of Pharmacy in Hradec Kralove, Charles University, Ak. Heyrovskeho 1203, 500 03 Hradec Kralove, Czech Republic, veronika.novakova@faf.cuni.cz

Phthalocyanines (Pcs) are aromatic macrocyclic compounds composed of four isoindole units linked by nitrogen atoms. Thanks to their advantageous photophysical properties, Pcs and their aza-analogues are widely used as dyes, photosensitizers in photodynamic therapy of cancer, in solar cells, as chemical sensors, in non-linear optics or as catalysts.^[1] In many of these applications, Pcs play fundamental role as electron-acceptors; thus, the study of structural features affecting their electron-accepting properties is highly desirable. A series of low-symmetry zinc(II) Pcs, in which one, three, or four benzene rings were replaced for pyrazines, was prepared and decorated with electroneutral (alkylsulfanyl) or strongly electron-withdrawing (alkylsulfonyl) groups to study the role of the macrocyclic core as well as the effect of peripheral substituents.^[2] Electrochemical studies revealed that the first reduction potential (E_{red}^1) is directly proportional to the number of pyrazine units in the macrocycle. Introduction of alkylsulfonyl groups had a very strong effect and resulted in a strongly electron-deficient macrocycle with $E_{red}^1 = -0.48$ V vs SCE (in THF).^[2] The efficiency of intramolecular-charge transfer (ICT) from the peripheral bis(2-methoxyethyl)amine group to the macrocycle was monitored as a decrease in the sum of $\Phi_{\Delta} + \Phi_F$ and correlated well with the determined E_{red}^1 values. The strongest quenching by ICT was observed for the most electron-deficient macrocycle. Importantly, an obvious threshold at -1.0 V vs SCE was observed over which no ICT occurs.^[2] Disclosed results may substantially help to improve the design of electron-donor systems based on Pcs.

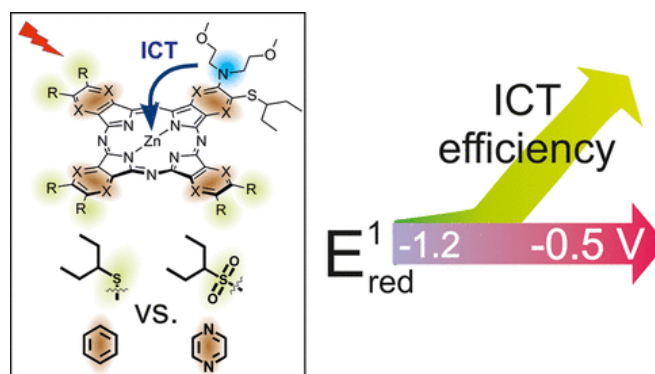


Figure 24. Schematic representation of the project.

Acknowledgments

The project was done thanks to the financial support from the Ministry of Education, Youth and Sports under the ERC CZ programme (LL2318).

References

- [1] V. Novakova, M.P. Donzello, C. Ercolani, P. Zimcik, P.A. Stuzhin, *Coord. Chem. Rev.* **2018**, 361, 1–73.
- [2] S. Bednarik, J. Demuth, J. Kernal, M. Miletin, P. Zimcik, V. Novakova, *Inorg. Chem.* **2024**, 63 (19), 8799–8806.

Exploration of Molecular Design to Achieve Nanosecond Excited States in Fe(II) Complexes Towards Long-Lived Triplet States

T. Ogawa,^a T. Honda,^a T. Wakabayashi,^a T. Yoshida,^a K. Miyata,^a and K. Onda^a

^a Kyushu University. E-mail: ogawa.tomohiro.954@m.kyushu-u.ac.jp

First-row transition metal complexes gain intense attention as alternatives to photofunctional precious metal complexes. While Fe(III) complexes are now luminescent and applicable to many applications due to their nanosecond lifetimes, seeking long-lived triplet excited states of d⁶ Fe(II) complexes remains significantly important toward microsecond lifetimes as analogs of the Ru(II) polypyridyl complexes. Here, we will present two new concepts of Fe(II) complexes to extend insights into their excited states.

To create Fe(II) complexes with strong ligand fields, we aimed to synthesize an air-stable hexacarbene Fe(II) complex. As recent papers reported, strongly σ -donating hexa-N-heterocyclic carbene (NHC) ligands provide Fe(III) states under air. Here, a triazole-based NHC ligand was chosen due to its slightly weaker yet strong ligand field to stabilize Fe(II) hexacarbene complex. We successfully isolated the air-stable Fe(II) hexacarbene complex and its metal-to-ligand charge transfer (MLCT) excited state was analyzed by fs-transient absorption spectroscopy. Although the obtained MLCT lifetime was still short-lived (<1 ps), the ease of handling of air-stable Fe(II) hexa-NHC complexes would accelerate research on exploring longer-lived ³MLCT states.¹

As another approach, we investigated isocyanide ligands suitable for Fe(II) complexes. Aryl isocyanides are excellent ligands for Cr(0) and Mn(I) complexes to form MLCT visible light absorption bands, however, its π^* orbital is too high for Fe(II) complexes.² Here, we pursue an isocyanide ligand suitable for Fe(II) complexes. Our Fe(II) complex with a newly synthesized quinoline-based isocyanide exhibited MLCT absorption around 400 nm, and its photophysical properties were analyzed by various measurements such as UV-vis transient absorption spectroscopy, time-resolved IR spectroscopy, and Kerr-Gate luminescence spectroscopy. Interestingly, bleach of the C-N stretching peak remains more than 1 ns in time-resolved IR spectra (Figure 1). This nanosecond-order excited state is roughly matching with the decay of the luminescence. This implies potentially luminescent Fe(II) isocyanide with nanosecond lifetimes was achieved by our extended isocyanides.³ The detailed analysis and full excited-state picture of these new Fe(II) complexes will be discussed in this contribution.

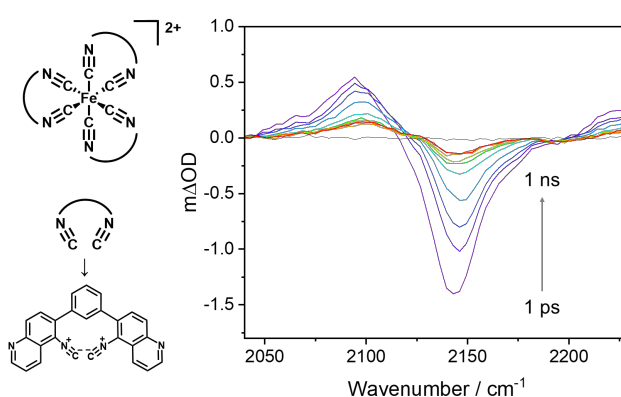


Figure 25. Molecular structure of Fe(II) isocyanide complex and its TR-IR spectra of C-N stretching modes ($\lambda_{\text{ex}} = 400$ nm)

References

- [1] T. Ogawa, T. Wakabayashi, *et al.*, to be submitted.
- [2] C. Wegeberg, *et al.*, *J. Am. Chem. Soc.* **2024**, *146*, 4605.
- [3] T. Ogawa, T. Honda, *et al.*, to be submitted.

Time-Resolved Spectroscopic Studies on Reaction Mechanism in Complex Artificial Photosynthesis Systems

K. Onda,¹ R. Nagao,¹ M. Oura,¹ T. Honda,¹ T. Ogawa,¹ K. Miyata,¹ H. Ozawa,¹ K. Sakai,¹ K. Maeda,² and Y. Kuramochi³

¹Department of Chemistry, Kyushu University, Motoooka, Nishi-ku, Fukuoka, Japan.

²Department of Chemistry, Institute of Science Tokyo, Ookayama, Meguro-ku, Tokyo, Japan.

³Department of Science, Kindai University, Kowakae, Higashiosaka, Osaka, Japan.

konda@chem.kyushu-univ.jp

Practical artificial photosynthesis systems are composed of several components with different functions, such as metal complexes, semiconductor nanoparticles, and electrodes. Because the reaction in the system takes place with multi-electron and multi-step processes, revealing the reaction mechanism is still challenging. To address this issue, we have developed various time-resolved spectroscopic methods applicable to such complex systems, including time-resolved infrared spectroscopy, UV-vis transient absorption spectroscopy, and time-resolved photoluminescence spectroscopy in a wide temporal range from femtoseconds to milliseconds. By combining these state-of-art methods, we have revealed the electron transfer mechanism and intermediate species in dyad photocatalysts for CO₂ reduction (Fig. 1a) [1-5], the role of exciplex states in hybrid photocatalysts composed of a metal complex and a semiconductor nanoparticle for CO₂ reduction (Fig. 1b) [6], the electron transfer processes from a photosensitizer to an electrode in dye-sensitized photoelectrochemical cells (DSPEC) for H₂O oxidation (Fig. 1c), and the photoexcited processes at an electrode under the applying voltage in DSPEC for CO₂ reduction (Fig. 1d).

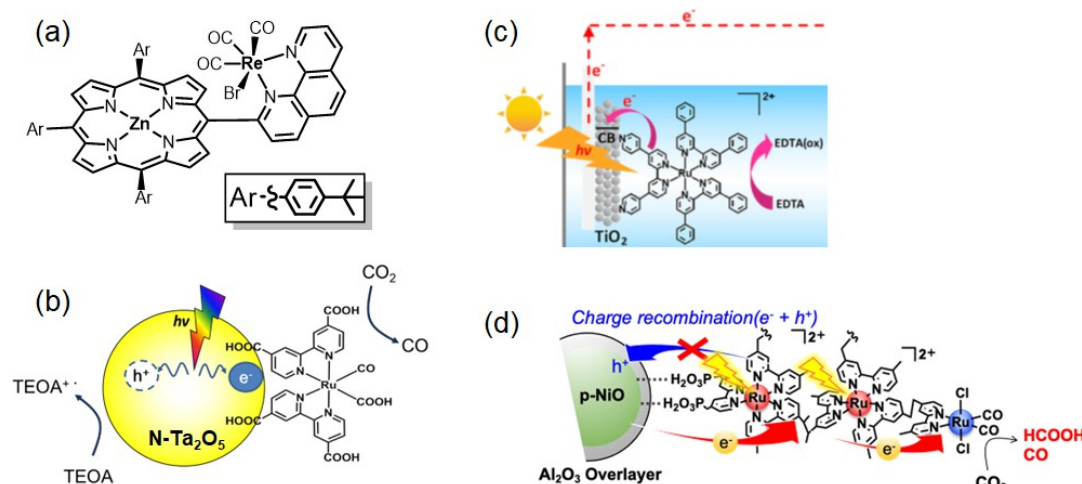


Figure 1. Complex artificial photosynthesis systems we studied using time-resolved spectroscopic methods: (a) dyad photocatalyst for CO₂ reduction, (b) hybrid photocatalyst for CO₂ reduction, (c) hybrid photoanode for H₂O oxidation, and (d) hybrid photocathode for CO₂ reduction.

References

- [1] T. Honda, et al. *Inorg. Chem.* **2024**, 63, 23524-23533.
- [2] K. Kamogawa, et al. *ACS Catalysis* **2023**, 13, 9025-9032.
- [3] K. Kamogawa, et al. *Chem. Sci.* **2021**, 12, 9682-9693.
- [4] Y. Yamazaki, et al. *Inorg. Chem.* **2019**, 58, 11480-11492.
- [5] K. Koike, et al. *Chem. Sci.* **2018**, 9, 2961-2974.
- [6] S. Sato, et al. *Chem. Eur. J.* **2021**, 27, 1127-1137.

Full ThrOTTLE tr-IR:

Time resolved IR Spectroscopy in Combination with Electrochemistry for Photochemical and Photophysical Investigation of Transition Metal Complexes and (Catalytic) Redox Intermediates

K. Oppelt¹, P. Hamm¹

Department of Chemistry, University of Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland;
kerstin.oppelt@chem.uzh.ch

Redox intermediates, crucial for understanding photo- and electrocatalytic processes, are often difficult to isolate and characterize with traditional spectroscopic or spectroelectrochemical methods. Hence, a Full Throughput Optically Transparent Thin-layer Electrochemical cell [1,2] with stopped-flow sample transport has been developed for optical-pump IR-probe transient absorption spectroscopy of pre-electrolyzed samples. Rhenium tricarbonyl complexes in various oxidation states serve as the subject in the first application of this combined electrochemical and spectroscopic tool. Time resolved infrared spectra of different reduction intermediates on ps to μ s timescales were recorded. The quite complex IR-SEC spectra (Fig.1a) can be analyzed using lifetime density analysis [3], enabling differentiation of multiple molecular intermediates by their excited state dynamics and character (Fig.1b). Adding these new analytic coordinates enhances classic FTIR-SEC.

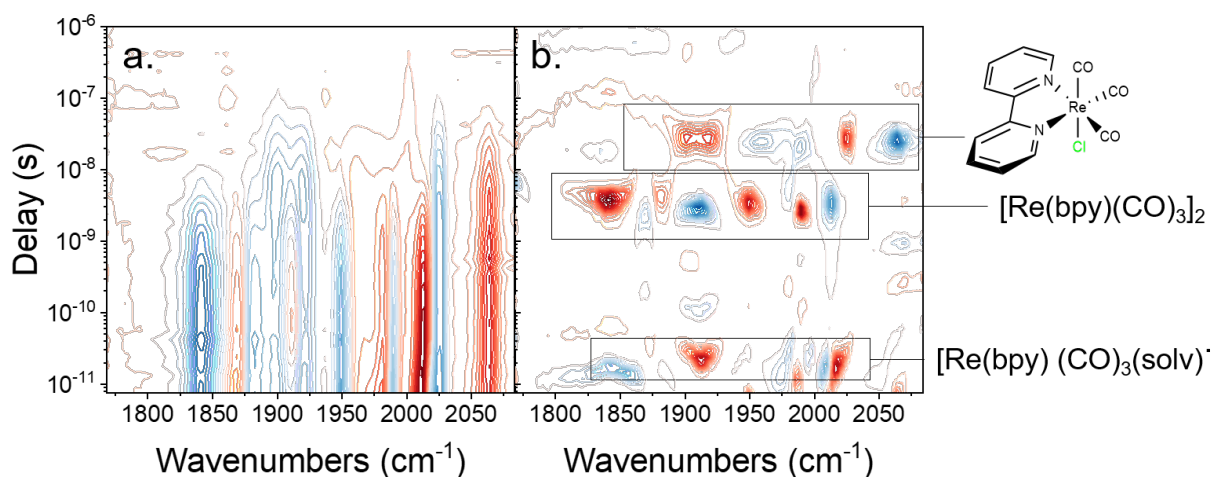


Figure 26. a. tr-IR of pre-reduced $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ b. Lifetime density plot of a. and assignment of different reduction intermediates by their excited state lifetime [1].

As a second example for the FullThrOTTLE tr-IR method we study photo-triggered electron transfer reactions to electrochemically pre-reduced catalysts, focusing on three-component systems with earth-abundant transition metal complexes on timescales up to 1s.

References

- [1] K.Oppelt, P.Hamm, *J. Phys.Chem.C* **2024**, 128 (38), 16040-16049
- [2] M. Krejčík, M. Daněk, F. Hartl, *J. Electroanal. Chem. Interf. Electrochem.* **1991**, 317 (1-2), 179-187
- [3] V. Lórenz-Fonfría, H. Kandori, *Applied Spectroscopy* **2006**, 60 (4), 407-417

Boron Dipyrromethenes (BODIPYs) for Antimicrobial Photodynamic Therapy (aPDT)

S. O'Sullivan¹; L. Tabrizi¹; K. Turzanska²; I. P. Clark³; D. Fitzgerald-Hughes²; M. T. Pryce¹

¹School of Chemistry, Dublin City University, Glasnevin, Dublin, D09 V209, Ireland.

²Clinical Microbiology, Royal College of Surgeons Ireland, Beaumont Hospital, Beaumont, Dublin, D09 V2N0, Ireland.

³Central Laser Facility, Research Complex at Harwell, STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot, Oxfordshire OX11 0QX, United Kingdom.

stephen.osullivan63@mail.dcu.ie

The prevalence of multidrug resistant (MDR) microbes due to the overuse and misuse of antibiotics has put an enormous strain on healthcare systems worldwide and will continue to grow into a much more significant problem if no alternative treatments are found for these pathogens. As 10,000,000 people are expected to die annually from MDR related disease in 2050,¹ it is paramount that alternative treatments are found. One such alternative which has shown promise is antimicrobial photodynamic therapy (aPDT). Originally developed for treatment of cancers, photodynamic therapies involve the use of a photosensitive dye to harvest light energy and use it to produce reactive oxygen species (ROS) to kill microbes. Our studies have focused on boron dipyrromethenes (BODIPYs) as the photosensitiser with modifications to give more desirable properties for aPDT, such as an increased redshift in the absorption spectrum to allow the compounds to absorb more cell-penetrating wavelengths of light, polar and non-polar substituents to tune the dyes to different solvents, whilst retaining a high ROS yield. These modified BODIPYs bear anthracene moieties in the *meso*-position, which is known to push the BODIPY onto the triplet hypersurface, which results in ROS generation.^{2,3} Further substitution of the β -positions of the BODIPY core gave rise to different degrees of redshifting, depending on the level of conjugation of the substituent. Both the polar and non-polar synthesised BODIPYs retained their high ROS yields, with a singlet oxygen quantum yield measured for BDP-2 of 0.76, in DCM, exc. at 528 nm, compared to the unsubstituted parent BODIPY, with a quantum yield of 0.82 in DCM, exc. At 500 nm. The photophysical pathways taken by the BODIPYs to the triplet surface were modelled using DFT-calculations. These compounds were then screened against various Gram (-) and Gram (+) bacteria to determine their suitability for further investigation as potential aPDT analogues. Upon irradiation with green light (550 nm), BDP-2 showed strong antibacterial effects against gram (+) species, even in the case of MRSA, with low dark toxicity to the bacteria, and low cytotoxicity to mammalian cells.

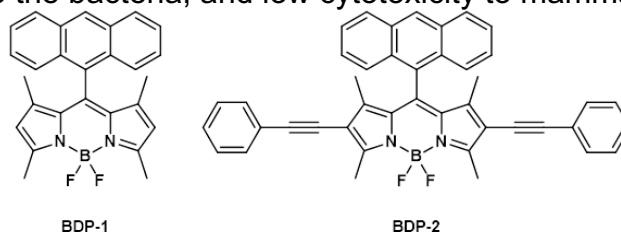


Figure 27. Structures of BODIPYs discussed throughout the abstract.

Acknowledgements

Financial support from SFI (19/FFP/6882 award) is gratefully acknowledged.

References

- [1] T. Thompson, The Staggering Death Toll of Drug-Resistant Bacteria. *Nature* **2022**.
- [2] Z. Wang, B. Dick, Insights into the Efficient Intersystem Crossing of Bodipy-Anthracene Compact Dyads with Steady-State and Time-Resolved Optical/Magnetic Spectroscopies and Observation of the Delayed Fluorescence. *J. Phys. Chem. C* **2019**, 123 (1), 265–274.
- [3] M. A. Filatov, Heavy-Atom-Free BODIPY Photosensitizers with Intersystem Crossing Mediated by Intramolecular Photoinduced Electron Transfer. *Org. Biomol. Chem.* **2019**, 18 (1), 10–27.

Conformational Switching of a Nano-Size Urea-bridged Zn(II)Porphyrin Dimer by External Stimuli

Chandrani Pal¹, Bapan Saha², Sankar Prasad Rath^{*1}

¹Department of Chemistry, Indian Institute of Technology Kanpur, India ²Department of Chemistry, Southern Illinois University Carbondale, United States E-mail: cpchem20@iitk.ac.in

For the first time, explicit stabilization of all the three conformers, viz. (*cis, cis*), (*cis, trans*) and (*trans, trans*), of a 'nano-sized' highly-flexible urea-bridged Zn(II)porphyrin dimer have been achieved via careful manipulations of external stimuli such as solvent dielectrics, temperature, anionic interactions, axial ligation and surface-induced stabilization.¹ The conformers differ widely in their structures, photophysical properties, chemical reactivity with chiral substrates and thus have vast potential applicability.²⁻⁴ Low temperature promotes the stabilization of (*cis,trans*)-conformer while rise in temperature facilitates flipping to the (*cis, cis*) one. Significantly, exclusive stabilization of the (*trans, trans*)-isomer has been illustrated using acetate anion which facilitates H-bonding with the two amide linkages of the urea spacer. Remarkably, HOPG surface facilitates stabilization of the energetically challenging (*trans, trans*)-conformer via CH $\cdots\pi$ and $\pi\cdots\pi$ interactions with the solid surface to the porphyrinic cores. DFT calculations demonstrate that the relative stability of the conformers can be modulated upon slight external perturbations as also observed in the experiment. Several factors contributing towards the conformational landscape for the highly flexible urea-bridged porphyrin dimers have been mapped here.

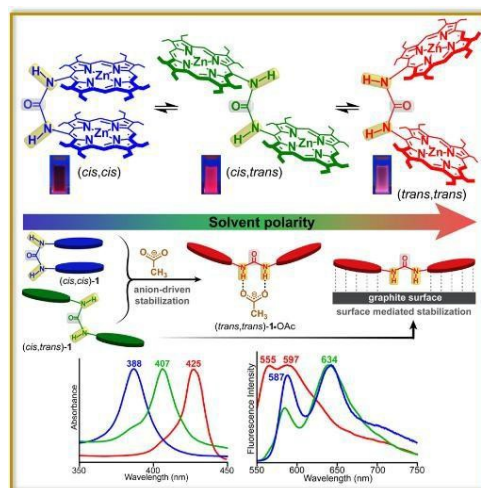


Figure 1. Three possible conformers of a urea-bridged Zn(II)porphyrin dimer and their selective stabilization investigated through advanced spectroscopic methods.

Aknowlegments

We thank IIT Kanpur for providing all the facilities and support and Prof. Thiruvancheril G. Gopakumar for his help in performing the AFM studies.

References

- [1] B. Saha, C. Pal, H. Malik, T. G. Gopakumar, S. P. Rath, *Chem. Eur. J.* **2024**, *30*, e202402536.
- [2] A. Dhamija, D. Chandel, S. P. Rath, *Chem. Sci.* **2023**, *14*, 6032.
- [3] B. Saha, D. Chandel, S. P. Rath, *Inorg. Chem.* **2022**, *61*, 2154.
- [4] A. Dhamija, B. Saha, D. Chandel, H. Malik, S. P. Rath, *Inorg. Chem.* **2020**, *59*, 801.

Near-Infrared Electrochemiluminescence from Chromium(III) Complexes in Mixed Annihilation Systems

M.L. Pattuwage,¹ P.S. Francis,¹ T.U. Connell,¹ E.H. Doeven,¹ O.S. Wenger²

¹School of Life and Environmental Sciences, Deakin University, Geelong, Victoria 3220, Australia.
E-mail: mpattuwage@deakin.edu.au ²Department of Chemistry, University of Basel,
St. Johannis-Ring 19, 4056 Basel, Switzerland.

Electrochemiluminescence (ECL) describes a phenomenon in which electrochemically generated species react to form excited state species that emit a photon of light to return to their ground state.¹ By understanding the Gibbs free energy required to populate the luminophore's excited state (ΔG_{es}), suitable intermediates can be generated from two different precursors.²

[Ru(bpy)₃]²⁺ remains the ECL luminophore used for commercial clinical diagnostic systems, and Ir(III) complexes are of great interest due to their favourable photophysical and redox properties that are readily tuneable through ligand modification. Luminescent complexes of Earth-abundant metals, however, are highly desirable as alternatives to the abovementioned precious metal complexes, for more sustainable ECL practices.

This presentation describes the use of the mixed annihilation strategy to generate intense NIR ECL from Cr(III) complexes, aimed at informing the future development of Earth-abundant-metal-centred ECL luminophores. In the few prior ECL studies of Cr(III) complexes, it was noted that greater ECL intensities were observed when applying potentials to reduce the complex beyond the Cr^{3+/2+} couple.^{3,4} In our study, we characterise this effect using the 'spooling' ECL technique at different reactant concentrations, using a Cr(III)/Ir(III) mixed annihilation system (See Fig. 1).

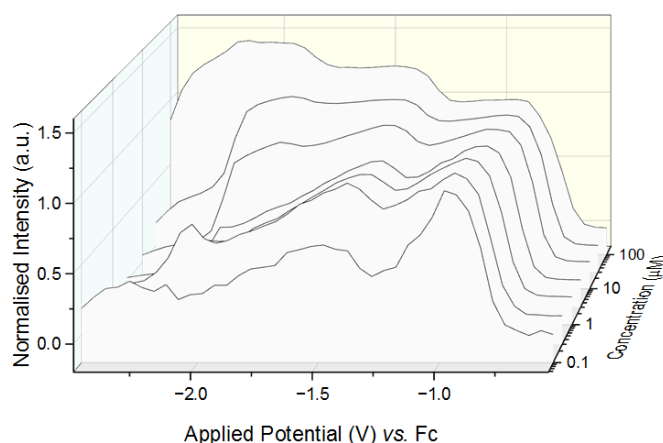


Figure 28. Normalised ECL intensity versus applied reduction potential and Cr(III) concentration, generated by 'spooling' ECL, for a Cr(III)/Ir(III) mixed annihilation ECL system.

References

- [1] S. Parveen, *et al.*, Springer Berlin, **2007**, 1, XIII, 152
- [2] E. Kerr, *et al.*, *Chem Sci*, **2016**, 7, 5271-5279.
- [3] N. A. P. Kane-Maguire, *et al.*, *Inorg. Chem.*, **1987**, 26, 2340-2342.
- [4] F. Bolleta, *et al.*, *Inorg. Chim. Acta*, **1982**, 62, 207-213.

Disaggregation Kinetics of TPPS J-Aggregates under Mild Acidic to Neutral pH: The Synergistic Role of Albumin and Gold Nanoclusters

T. Paviglianiti^{1*}, A. Romeo¹, L. M. Scolaro¹ and M.A. Castriciano¹

¹Department of Chemical, Biological, Pharmaceutical and Environmental Sciences,
University of Messina, Viale F. Stagno D'Alcontres 31, 98166 Messina, Italy

* teresa.paviglianiti@studenti.unime.it

Water-soluble meso-tetrakis(4-sulfonatophenyl)porphyrin (TPPS) J-aggregates exhibit remarkable optical and electronic properties, including sharp absorption bands, resonance light scattering, and enhanced nonlinear optical response,^{1,2} making them promising candidates for biomedical photonics and nanotechnology applications. While numerous reports address the growth of these assemblies under acidic pH, comparatively few have examined their disassembly under mild acidic to neutral environment, where proton dissociation drives rapid disaggregation of these nanostructures.^{3,4}

To fill this gap, we investigate the disaggregation kinetics of preformed TPPS J-aggregates in aqueous solutions across a pH range of 4 to 7. We explore stabilization strategies employing protein-based systems. Human serum albumin (HSA) was utilized to stabilize the aggregates, effectively slowing deprotonation and extending their lifetime from few seconds to several hours, depending on pH and protein concentration. To further enhance stability, we synthesized fluorescent, water-soluble gold nanoclusters encapsulated within bovine serum albumin (BSA–Au NCs)⁵ and combined them with TPPS J-aggregates. Under optimal conditions, this hybrid system increased the aggregate half-lifetime up to several days, highlighting a synergistic stabilization effect. Disassembly kinetics, monitored via UV/Vis spectroscopy, followed a stretched exponential decay. The rate constants exhibited a second order dependence on the proton concentration and increased with higher stabilizer concentrations, confirming the molecular role of albumin in modulating proton dissociation. The combination of kinetic insights and stabilization strategies by hybrid organic/inorganic species deepen our understanding of porphyrins aggregates behavior under unconventional conditions and opens new opportunities for controlled disassembly and light-driven biomedical applications.

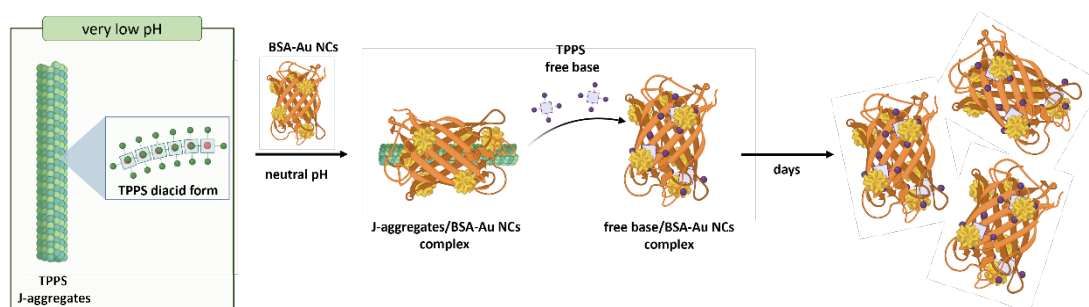


Figure 29. Visual summary of the stepwise disassembly of TPPS J-aggregates stabilized by a protein–gold nanocluster hybrid system. Created in <https://BioRender.com>

References

- [1] E. Collini et al., *J Mater Chem* **2006**, vol. 16, no. 16, p. 1573.
- [2] P. J. Collings et al., *J Phys Chem B* **1999**, vol. 103, no. 40, pp. 8474–8481.
- [3] I. G. Occhiuto et al., *Molecules* **2020**, vol. 25, no. 23, p. 5742.
- [4] A. Romeo et al., *J Am Chem Soc* **2014**, vol. 136, no. 1, pp. 40–43.
- [5] J. Xie et al., *J Am Chem Soc* **2009**, vol. 131, no. 3, pp. 888–889.

Single Active Ligand in Iridium Complexes for Near Infrared Phosphorescent OLEDs

A. Antonello,^a U. Giovannella,^a A. Bossi,^a M. Penconi^a

^a Istituto di Scienze e Tecnologie Chimiche “Giulio Natta”, Consiglio Nazionale delle Ricerche, via G. Fantoli 16/15, via A. Corti 12, Milan, Italy.

marta.penconi@cnr.it

Near-infrared (NIR) phosphorescent organic light-emitting diodes (PhOLEDs) emitting above 700 nm are rising attention for applications in bio-imaging, night-vision, telecommunication and security surveillance.^[1] Emissive cyclometalated Ir(III) complexes are key candidates, already used in commercial screens and displays, but the need to maintain high quantum efficiencies and good thermal stabilities suitable for thermal evaporation processing, while pushing the emission towards the NIR, remains challenging. We present our patented strategy for the chemical design of the C^N ligand in Ir(III) complexes to lower the emission energy through the expansion of the π -system and the introduction of substituent with different electronic effects.^[2] Moreover, we propose a novel approach for the construction of the complex based on a single NIR-active ligand with important advantages in terms of synthesis and material processing,^[3] while enabling NIR phosphorescence of quantum efficiency comparable to the homoleptic and bis-heteroleptic complexes. The emitters have proven effective in realizing fully evaporated devices with multilayers of organic and organometallic materials.

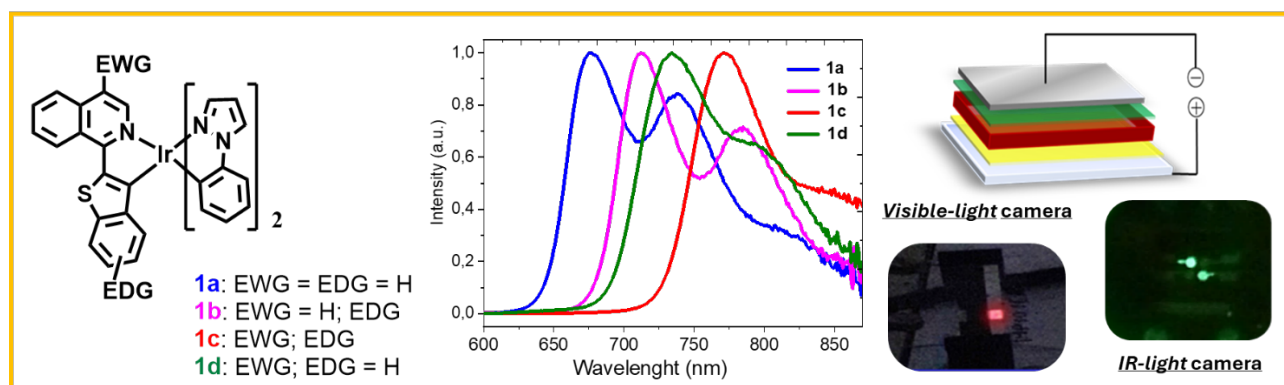


Figure 30. Near-Infrared (NIR) emitters and their PhOLEDs.

Aknowlegments

Thanks to (grant n. 20225P4EJC) MEET: Mechanism Enhanced ECL Technology; Kenosistec srl; Progetto ‘SmartMatLab centre’ Regione Lombardia and Fondazione CARIPLO (12689/13,7959/13).

References

- [1] A. Zampetti, A. Minotto, and F. Cacialli, *Adv. Funct. Mater.* **2019**, 29, 1–22.
- [2] A. Bossi, U. Giovannella, S. Kesarkar, M. Penconi, *Patent IT 102023000012492* 16/06/2023 e *PCT/IB2024/055589* 07/06/2024.
- [3] M. Penconi, A. Babu Kajjam, M.-C. Jung, M. Cazzaniga, C. Baldoli, D. Ceresoli, M. E. Thompson, A. Bossi, *Chem. Mater.* **2022**, 34, 574–583.



3D printed hybrid photocatalytic cement composites

Waldemar Pichór⁽¹⁾, Paulina Szoldra⁽¹⁾, Maksymilian Frąc⁽¹⁾

⁽¹⁾ AGH University of Krakow, Mickiewicza 30, 30-059 Krakow, Poland, pichor@agh.edu.pl

Nitrogen oxides pose a serious environmental threat, negatively affecting both the climate and human health, as they are a major source of pollution. Therefore, placing photocatalytic building materials near NO_x emission sources, such as road pavements and infrastructure, is an effective strategy for reducing pollutant concentrations in the air [1].

Titanium dioxide nanoparticles have been incorporated into cement-based composites to achieve airpurifying functions. The concept of effective hybrid cement composites is based on applying a printed TiO₂-cement path on the surface of the cementitious underlays instead of incorporating TiO₂ into the entire volume of the material. The 3D printing technique allows for the precise formation of 3D structures in the volume and on the surface of the material. The phase composition and porosity of the cement-based material, as well as air humidity and UV intensity, have an influence on photocatalytic effectiveness during the degradation of chemical contaminants. There is an optimal content of TiO₂ in which the decomposition of pollutants by the photocatalytic cementitious composites is the most effective. This content depends on various factors, e.g. phase composition, grain distribution, porosity, and dispersion of TiO₂ nano-powder in the cement matrix. Increasing the amount of TiO₂ above the optimal value results in a decrease in operating efficiency.

The main effect of the research was the design and production of a hybrid composite with a cement composite mesh printed on the surface cement-based material with a photocatalytic additive with high efficiency in the decomposition of nitrogen oxides under UV radiation. The photocatalytic tests were performed in a prototype chamber that ensures laminar airflow over the tested sample, which allows precise setting of flows, air humidity, and UV radiation intensity within wide limits. The results were referred to composites whose surface was made entirely of a composite with a photocatalytic additive.

Aknowlegments

This research was funded by the AGH University of Krakow program titled "Excellence initiative—research university"

References

- [1] M. Hunger, G. Hüsken and H.J.H. Brouwers „Photocatalytic Degradation of Air Pollutants—From Modeling to Large Scale Application. Cement and Concrete Research 2010, 40, 313-320.

Ultrafast time-resolved infrared spectroelectrochemistry

Martin Pižl^{a,b}, Greg Greetham^c, František Hartl^b

^a Department of Inorganic Chemistry, University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, Czech Republic

^b Department of Chemistry, University of Reading, Reading RG6 6DX, United Kingdom

^c Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 0QX, UK

martin.pizl@vscht.cz

Spectroelectrochemical (SEC) studies are often conducted with air-tight optically transparent thin-layer electrochemical (OTTLE)^[1] cells adapted to vibrational spectroscopic techniques – infrared spectroscopy, resonance Raman spectroscopy, or vibrational circular dichroism. Pump-probe ultrafast spectroscopy investigates vibrational properties, identifies ultra-short-lived intermediates, and describes conformational changes.

This contribution will introduce a new time-resolved infrared spectroelectrochemical (TRIR SEC) technique tailored for investigating the excited-state dynamics of in situ generated redox products with a ps–ns time resolution. The purpose-developed OTTLE cell requires programmed rastering in the aperture area of the working electrode (WE) to suppress overheating, avoid light scattering, obtain an appreciable S/N ratio and secure stability during long scanning times. An accurate potential control over the active WE minigrad area is required to diminish potential drifting and facilitate studies of multistep redox series.

The potential of the TRIR OTTLE cell for studying short-lived intermediates is demonstrated on photoexcitation of the radical anions of the complexes $[M(CO)_4(NN)]$ ($M = Mo$ or W ; $NN = 1,4$ -di(*tert*-butyl)-1,4-diazabuta-1,3-diene and 4,4'-dimethyl-2,2'-bipyridine) involved in photo-assisted electrocatalytic reduction of carbon dioxide. The nature of the lowest-energy quadruplet excited states responsible for efficient CO dissociation triggering the catalytic process has been revealed.

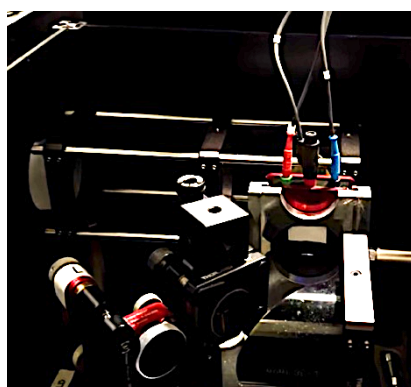


Figure 31. TRIR OTTLE cell.

Acknowledgments

This work was financially supported by the Czech Science Foundation (project 23-05760O), by the project "The Energy Conversion and Storage", funded as project No. CZ.02.01.01/00/22_008/0004617 by Programme Johannes Amos Comenius, call Excellent Research and by spin-out company Spectroelectrochemistry Reading. We would like to thank Ian P. Clark, and Partha Malakar for helping us set up our measurements in Rutherford Appleton Laboratory, Central Laser Facility, Harwell Campus, Didcot, UK, and for support from the Science and Technology Facilities Council (access grants 2022-2024).

Molecular dyad immobilized in soft matter for HER

M.S. Puthanagady^{a,b}, N. Vashishtha^b, L. Zedler^b, Y. Utievskiy^c, F. Schacher^c, S. Rau^d, B.D. Ivanšić^{e*}

^a Institute for Physical Chemistry, FSU, Helmholtzweg 4, 07743 Jena, Germany;

^b Leibniz-IPHT, Albert-Einstein-Straße 9, 07745, Jena, Germany

^c Jena Centre for Soft Matter (JCSM), FSU, Jena, Philosophenweg 7, D-07743, Jena, Germany

^d Institute of Inorganic Chemistry I, Albert-Einstein-Allee 11, 89081 Ulm

^e Leibniz Institute for Surface Modification Permoserstraße 15, 04318 Leipzig, Germany

mariet.puthanagady@uni-jena.de

Increasing global energy demands and limited availability of non-renewable sources have led to novel pathways for Hydrogen Evolution Reaction (HER) with growing interest in photochemical molecular device (PMD) equipped with a photocentre, a bridging ligand and a catalytic centre as HER catalyst. In this study, we investigate a hybrid photocatalytic system composed of the photoactive molecular dyad (tbbpy)₂Ru(tpphz)PtI₂ surrounded with a polymeric system, PDha-g-AMPS-g-mPEG₁₀₀₀. This integrated system has shown enhanced hydrogen evolution reaction (HER) catalysis, reflected by a significantly higher turnover number. The focus of the current work is to understand the underlying mechanism responsible for this increased catalysis' efficiency and to decode the influence of polymer on the excited state dynamics, using spectroscopic techniques and photochemistry. We employed in-situ, ultrafast transient absorption (TA) spectroscopy of the catalytic solution under different irradiation hour to capture the initial stages of the redox process. It was observed that polymer sustains presence of the active form of catalyst, mono hydrogenated bridge, for up to 60 hours of irradiation. Along with this, resonance Raman and UV-Vis measurements were carried out to follow the interaction of polymer with the catalyst and stability of the catalytic solution respectively. These insights will contribute to the development of efficient and durable polymer-supported photocatalytic systems.

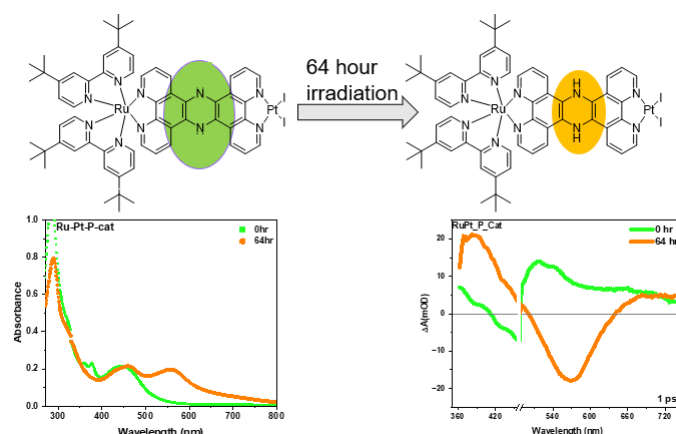


Figure 1. UV-Vis and TA spectra at 0 and 64 hr of irradiation showing formation of doubly hydrogenated bridge (inactive form) via mono hydrogenated bridge (active form) from the initial species.

Acknowledgments

I would sincerely like to thank everyone involved in the project and Deutsche Forschungsgemeinschaft (DFG) for financial support via the TRR 234 CATALIGHT (project number 364549901, project B11).

References

- [1] M.G. Pfeffer, C. Müller, E.T.E. Kastl, *et al.*, Nature Chemistry 2022, volume 14, pages500–506
- [2] C.V. Suneesh, B. Balan, H. Ozawa, Phys. Chem. Chem. Phys., 2014, volume 16, 1607-1616



Plastics detection using Hydrogels Functionalized with Switchable Iridium Complexes

Nicolò Quadrio,¹ Clara Zehe,² Luigi Menduti,¹ Nicholas Rossi,² Luisa De Cola^{1,2}

¹Department of Pharmaceutical Science DISFARM Università degli Studi di Milano

²Department of Molecular Biochemistry and Pharmacology, Istituto di Ricerche Farmacologiche Mario Negri
IRCCS

nicolo.quadrio@unimi.it

Micro- and nanoplastics are increasingly recognized as significant environmental pollutants, with their toxicity influenced by factors such as particle size, polymer type, and exposure conditions. Among the deleterious effects of these pollutants we can count endocrine disruption, inflammation, oxidative stress and metabolic disturbances. [1] Hydrogels, known for their excellent water retention capacity, high adsorption, reversible swelling, and biocompatibility, are promising materials for environmental remediation. [2]

In the detection of nano- and microplastics, the most exploited luminescence-based strategy involves the use of fluorophores able to stain MPs. In this field, detection of the solvatochromic response of organic dyes (e.g. Nile red) to their surrounding polarity is one of the main interesting properties exploited for plastic detection. The use of hydrophobic dyes leads to their aggregation causing low emission problems, used to monitor the interaction with hydrophobic materials. [3] Organometallic complexes, with their color tunability and longer excited state lifetimes, can be a solution to the limitations of organic dyes.

In this contribution we report on neutral Ir(III)-complexes functionalized hydrogels able to switch on their emission upon interaction with hydrophobic plastics due to their de-aggregation, limited oxygen diffusion and increase rigidity due to the intermolecular interactions with the surrounding materials. The triplet state emission allows to monitor the switch-on of the phosphorescence by time resolved measurements. [4]

We show that a simple hydrogel covalently bound to Ir(III) complexes can indeed recognize and interact with PET plastics, and work is in progress to differentiate different microplastics by modulating the nature of the excited states.

References

- [1] K. Pellegrini, T.C.B. Pereira, T.G. Maraschin, *Sci. Total Environ.*, **2023**, 878, 162954
- [2] Yang J. et al., *Int J Biol Macromol*, **2021**, 189, 53-64
- [3] a) C. Capolungo, D. Genovese, M. Montalti, E. Rampazzo, N. Zaccheroni, L. Prodi *Chem. Eur. J.* 2021, 27, 17529–17541; b) M. Cingolani, E. Rampazzo, N. Zaccheroni, D. Genovese, L. Prodi *Environ Sci Nano*, **2022**, 9, 582–588
- [4] F. Fiorini, E. Longhi, A. Lázaro, D. Di Prisco, G. Tamboia, G. Alonci, L. Menduti, L. De Cola *Chem. Eur. J.* **2025**, e202404572

Ultrafast Laser Control of Photochemical Reactions in Light-Harvesting Transition Metal Complexes

Emily L. Race, Michael D. Horbury, Paul Scattergood, Dimitri Chekulaev, Anthony J. M. H. Meijer and Julia A. Weinstein

Department of Chemistry, School of MPS, University of Sheffield

Email: elrace1@sheffield.ac.uk

Artificial photosynthesis (AP) is at the forefront of solar chemistry research. Pt(II) donor-bridge-acceptor complexes hold potential as AP systems due to their extensive electron transfer pathways upon irradiation with light. The nature and lifetime of the excited states formed can be modified synthetically through variation of both the strength of the donor/acceptor moieties and also the extent of electronic coupling to the Pt(II) bridge. It has also been demonstrated that external laser perturbation can be utilised to manipulate and potentially control the population and lifetimes of different excited states. Control is applied via specific infrared laser excitation which, when applied to specific vibrations within the molecule, can selectively increase or decrease the yield of a certain electron transfer pathway. A particular state of interest is the charge separated state (CSS) due to its high potential energy.

The aim of this work is to design and synthesise complexes that could exhibit the CSS, investigate their electron transfer pathways using different ultrafast spectroscopic techniques, and externally control the lifetime of the desirable states.

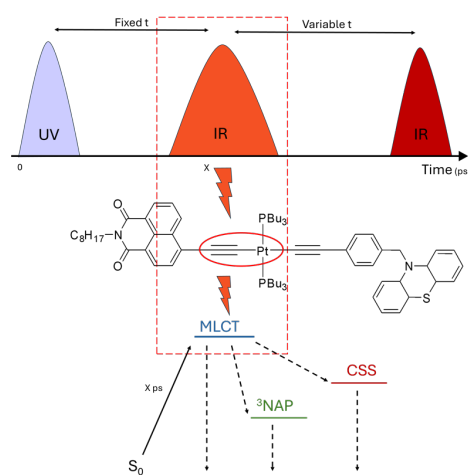


Figure 32. The mechanism of IR perturbation for electron transfer control.

Aknowlegments

We thank the University of Sheffield, the EPSRC and the Lord Porter Laser Laboratory.

References

- [1] M. Delor, T. Keane, P. A. Scattergood, I. V. Sazanovich, G. M. Greetham, M. Towrie, A. J. Meijer and J. A. Weinstein, *Nature chemistry*, **2015**, 7, 689–695.
- [2] M. Delor, P. A. Scattergood, I. V. Sazanovich, A. W. Parker, G. M. Greetham, A. J. Meijer, M. Towrie and J. A. Weinstein, *Science*, **2014**, 346, 1492–1495.



Prolonging Ru(bpy)₃²⁺ Luminescence Lifetime in Silica Nanoparticles via Energy Reservoir Mechanism

Y. Addis Alemu, D. Genovese, M. Montalti, L. Prodi, E. Rampazzo

Department of Chemistry Giacomo Ciamician, via Selmi 2, Bologna, Italy
enrico.rampazzo@unibo.it

Encapsulation within nanostructures is a versatile strategy for tuning the properties and enhancing the stability of molecular dyes. In particular, silica nanoparticles (SNPs) can incorporate photoactive units due to their favorable optical and chemical properties.[1] Dye-doped SNPs can exhibit high brightness, arising from the co-localization of many fluorophores in the nanoparticle volume and, in some cases, from their segregation from the surrounding environment.[2] Additional features can be achieved by exploiting inter-luminophore energy transfer interactions within the nanoparticles to develop fluorescent markers for multiplexed assays.[3]

Inter-luminophore energy transfer interactions can also be exploited in supramolecular systems containing Ru(II) polypyridine complexes coupled to pyrene moieties.[4] These systems in deaerated solutions have longer-lived pyrene triplet state acting as an energy reservoir for the faster deactivating phosphorescent state of the Ru(II) complex, which has very similar energy. This equilibration increases the excited state lifetimes of the Ru(II) complexes up to a few tens of μ s.

Inspired by this energy reservoir mechanism, we report a self-organized SNPs system prepared with a reverse microemulsion strategy containing the Ru(bpy)₃²⁺ complex and a water-soluble, positively charged pyrene derivative. The confinement of these two components in the SNP provides the proximity for the energy equilibration and sufficient shielding from the dynamic quenching mechanisms involving dioxygen. These doped SNPs - in aerated conditions - showed a remarkable increase in the excited state lifetime of Ru(bpy)₃²⁺, reaching values up to 20 times higher than those of the complex in aerated aqueous solutions. These self-organized nanosystems are possible candidates for time-gated luminescence applications or the development of excited-state lifetime-based probes.

References

- [1] J.G. Croissant *et al.* *Nat. Rev. Mater.* **2020**, 5, 886-909; S. Bonacchi *et al.* *Angew. Chem. Int. Ed.* **2011**, 50, 4056-4066.
- [2] Zanuti A. *et al.* *Angew. Chem. Int. Ed.* **2020**, 59, 21858-21863.
- [3] L. Wang *et al.* *Nano Letters* **2006**, 6, 84-88; D. Genovese *et al.* *Angew. Chem. Int. Ed.* **2013**, 52, 5965-5968; E. Rampazzo *et al.* *J. Phys. Chem. C*, **2014**, 118, 9261-9267.
- [4] W. E. Ford *et al.* *J. Phys. Chem.* **1992**, 96, 2917-2920; D.S. Tyson *et al.* *J. Phys. Chem. A* **1999**, 103, 10955-10960; A.F. Morales *et al.* *Inorg. Chem.* **2002**, 41, 6711-6719; Y. Leydet *et al.* *Inorg. Chim. Acta* **2007**, 360, 987-994.

Spectroscopies from perturbation theories

V. Robert^a, L. Delafosse^a, O. Bindech^a, S. Yalouz^a

Laboratoire de Chimie Quantique de Strasbourg, 4 rue Blaise Pascal 67000 Strasbourg-FRANCE, Institut de Chimie de Strasbourg, CNRS, Université de Strasbourg

What is the most appropriate theoretical approach to provide both physical interpretations and accurate energy differences? While density functional theory may meet theoretical limits when spin-coupled systems are examined, wave-function methodologies meet computational limits with intractable calculations. Accurate energies determination calls for demanding wavefunction expansions. An elegant alternative is the use of perturbation theory, with challenges arising from quasi-degenerate states or inter-system crossing.

The proposed method follows a step-by-step construction of the energy levels, combining Rayleigh-Schrödinger (RS) perturbative scheme and a Brillouin-Wigner (BW) expansion. The construction of updated partitionings (see Figure 1) allows one to access energies and wavefunctions from a well-tempered expansion that calls for small numerical efforts and guarantees spectroscopic accuracy. The method can be applied to coordination compounds where a detailed description of ground and excited states is determinant.

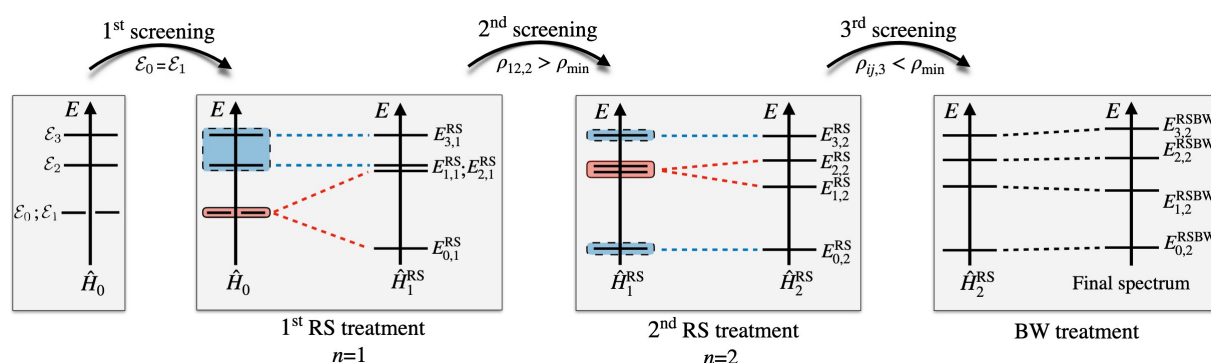


Figure 1. For perturbation scheme expansion to converge, the partitioning is determinant. The method uses a step-by-step partitioning that allows for the accurate description of energy states.

References

- [1] L. Delafosse, A. Hussein, S. Yalouz, V. Robert, *Electron. Struct.* **2024**, 6, 015009.
- [2] O. Bindech, B. Valentin, S. Yalouz, V. Robert, *Electron. Struct.* **2024**, 6, 045009.



Pulse Radiolysis Time-Resolved Infrared Spectroscopic Studies of Mn(I) and Re(I) Tricarbonyl CO₂ Reduction Catalysts

J. Rochford^a, M.Z. Ertem^b, D.C. Grills^b

^a Department of Chemistry, University of Massachusetts Boston, 100 Morrissey Boulevard, Boston, MA 02125, USA.

^b Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973-5000, USA.

E-mail: jonathan.rochford@umb.edu

The catalytic conversion of CO₂ to reduced forms of carbon by homogeneous transition metal catalysts remains a hugely popular, yet highly challenging, area of inorganic chemistry. An increased understanding of proton-coupled electron transfer (PCET) mechanisms in CO₂ reduction is essential for the thermodynamic and kinetic optimization of targeted product selectivities. For example, the use of a photochemical or electrochemical bias to drive the proton-coupled CO₂ reduction can give rise to disparate product distributions, primarily related to competing two-electron reduction pathways for CO, HCO₂⁻ and H₂ formation. Homogeneous Mn(I) and Re(I) tricarbonyl catalysts have received much attention in this regard and have provided great insight relating to the PCET pathways of CO₂ conversion. The technique of pulse radiolysis combined with time-resolved infrared spectroscopy (PR-TRIR) is uniquely positioned to inform on catalyst activation mechanisms for both photo- and electrocatalytic pathways.¹ PR utilizes a short, high-energy electron pulse for the rapid production of radical ions, and when coupled with TRIR it becomes a very powerful technique capable of the rapid production, identification, and kinetic monitoring of short-lived intermediates that are involved in redox catalysis. This presentation will summarize our findings on the mechanistic investigations of homogeneous Mn(I) and Re(I) tricarbonyl CO₂ reduction catalysts, combining PR-TRIR analysis with more conventional photochemical and spectro-electrochemical techniques.²⁻⁵

References

- (1) Grills, D. C.; Polyansky, D. E.; Fujita, E. Application of Pulse Radiolysis to Mechanistic Investigations of Catalysis Relevant to Artificial Photosynthesis. *ChemSusChem* **2017**, *10*, 4359-4373.
- (2) Grills, D. C.; Farrington, J. A.; Layne, B. H.; Lyman, S. V.; Mello, B. A.; Preses, J. M.; Wishart, J. F. Mechanism of the formation of a Mn-based CO₂ reduction catalyst revealed by pulse radiolysis with time-resolved infrared detection. *J. Am. Chem. Soc.* **2014**, *136*, 5563-5566.
- (3) Ngo, K. T.; McKinnon, M.; Mahanti, B.; Narayanan, R.; Grills, D. C.; Ertem, M. Z.; Rochford, J. Turning on the protonation-first pathway for electrocatalytic CO₂ reduction by manganese bipyridyl tricarbonyl complexes. *J. Am. Chem. Soc.* **2017**, *139*, 2604-2618.
- (4) McKinnon, M.; Ngo, K. T.; Sobottka, S.; Sarkar, B.; Ertem, M. Z.; Grills, D. C.; Rochford, J. Synergistic metal-ligand redox cooperativity for electrocatalytic CO₂ reduction promoted by a ligand-based redox couple in Mn and Re tricarbonyl complexes. *Organometallics* **2019**, *38*, 1317-1329.
- (5) Blaszczak, V.; McKinnon, M.; Suntrup, L.; Aminudin, N. A.; Reed, B.; Groysman, S.; Ertem, M. Z.; Grills, D. C.; Rochford, J. Steric and Lewis Basicity Influence of the Second Coordination Sphere on Electrocatalytic CO₂ Reduction by Manganese Bipyridyl Complexes. *Inorg. Chem.* **2022**, *61*, 15784-15800.

Synthesis Of Low-Symmetrical Silica-Phthalocyanines With Axial Modification For Photodynamic Therapy

L. D. RODRIGUES, V. NOVAKOVA

Department of Pharmaceutical Chemistry and Pharmaceutical Analysis, Faculty of Pharmacy in Hradec Králové, Charles University, Akademika Heyrovského 1203, Hradec Králové 50003

Email ID:rodrigule@faf.cuni.cz

Photodynamic therapy (PDT) is an effective form of cancer therapy involving a photochemical reaction with a photosensitizer (PS), light and molecular oxygen¹. Phthalocyanines (Pcs) one of such PSs, are aromatic macrocycles having 18 π -electron comprised of four isoindole units linked together through their 1,3-positions by aza bridges. Pcs have maximal absorption in the phototherapeutic window of tissues (i.e., 650-800 nm), and can produce high singlet oxygen making them optimal PSs for PDT for cancer. The main drawback of clinically approved PSs is their cumulation in the body and subsequent skin photosensitivity. It may be overcome by precise targeting of cancer tissue. Further, lipophilic character of Pcs and their tendency to aggregation hinder their wider use in practice. We developed a method to prepare unique Pcs with three different modifiable sites - one for binding a targeting moiety, another to introduce a switchable group (activated in vivo), and a moiety increasing the hydrophilicity and decreasing aggregation. This could be achieved by low-symmetrical silicon(IV) Pc (SiPc, Fig.1), that can be functionalized on the periphery as well as at axial positions². Unfortunately, a reasonable synthetic pathway for their preparation is still lacking because generally used template formation of macrocycle does not give satisfactory results. We have, therefore, developed a new method based on synthesis of low-symmetrical metal-free Pc followed by coordination of Si(IV) to the centre and introduction of axial ligands. Unexpectedly, we observed an interesting ring contraction as a side reaction. Conditions were studied in detail to describe the key parameters for formation of contracted macrocycle as well as for maximising yields of target SiPcs. Conjugation of prepared SiPc with aptamer as a targeting moiety and its biological evaluation will follow.

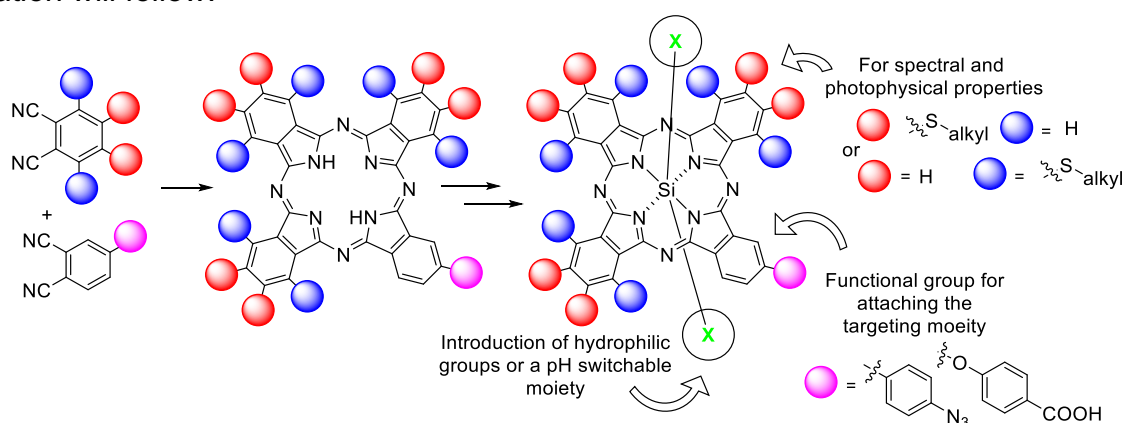


Figure 33. Developed method toward low-symmetrical SiPcs

This work was supported by ERC-CZ (Reg. No. LL2318).

References

- [1] Lo, P. C., Rodríguez-Morgade, M. S., Pandey, R. K., Ng, D. K., Torres, T., Dumoulin, F., Chem. Soc. Rev., **2020**, 49, 1041.
- [2] Mitra, K., Hartman, M.C.T., Org. Biomol. Chem., **2021**, 19, 1168.

From ruthenium to iron: New perspectives on DNA-intercalating metal complexes

Evgenia Ryndin¹, Niklas Klosterhalfen², Dr. Linda Zedler², Prof. Dr. Benjamin Dietzek-Ivanšić^{2,3}, Dr. Alexander K. Mengele¹, Dr. Dieter Sorsche¹, Prof. Dr. Sven Rau¹

1. Ulm University, Institute of Inorganic Chemistry 1, Albert-Einstein-Allee 11, 89081 Ulm

2. Leibniz IPHT, Albert-Einstein-Straße 9, 07745 Jena

3. FSU Jena, IPC, Lessingsstraße 4, 07743 Jena; IOM Leibniz Permoserstraße 15, 04318 Leipzig

E-mail: evgenia.ryndin@uni-ulm.de

Photoactive ruthenium complexes have emerged as promising candidates for applications such as photodynamic therapy (PDT). By employing polyaromatic nitrogen-based ligands like dppz (dipyrido[3,2-a:2',3'-c]phenazine), these complexes have successfully been intercalated into DNA through π - π interactions.^[1] However, the increasing demand for sustainable and cost-effective alternatives has shifted attention toward iron — a more abundant and environmentally friendly metal. In earlier literature reports iron complexes have already been studied for their interaction with DNA,^[2] but recent breakthroughs in ligand design have made it possible to develop longer-lived N-heterocyclic carbene-based iron complexes with improved stability and photoreactivity.^[3] This study introduces related novel iron complexes featuring N-heterocyclic carbenes and dppz-like ligands, which were for the first time examined for their ability to intercalate into DNA.

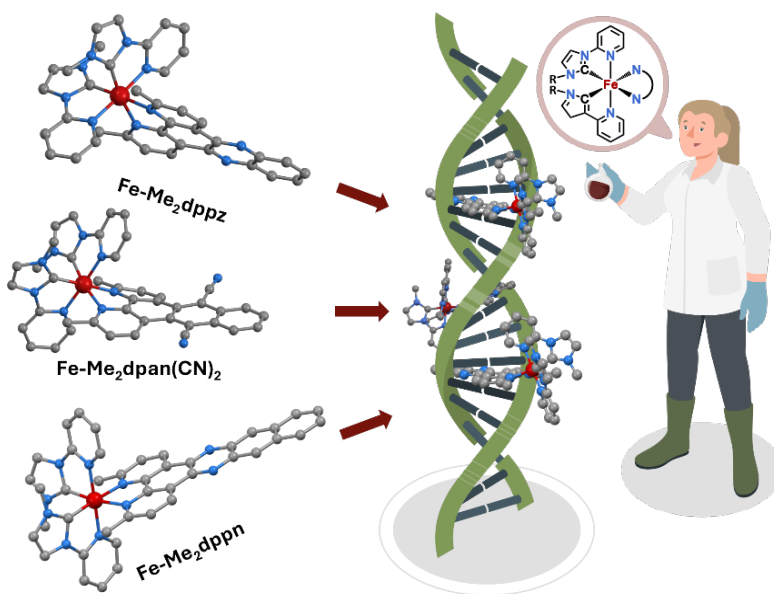


Figure 34: Molecular structures of the investigated DNA-intercalating iron complexes (left) and a conceptual representation of DNA-intercalated iron–dppz complexes.

Aknowlegments

E. R. thanks the support program for female scientists ProTrainU, Gender Equality Office, Ulm University Ulm, and the DFG-funded transregional collaborative research center TRR 234 – CataLight for their financial support.

References

- [1] M. R. Arkin et al., *Science* **1996**, 273, 475-480
- [2] W. Mudasir et al., *Spectrochimica Acta A: Molecular Biomol Spect* **2007**, 66 (1), 163–170
- [3] Witas, K. et al.; *Journal of the American Chemical Society* **2024**, 146, 19710–19719

Fine-tuning the Excited State Dynamics of Ruthenium(II) Polypyridyl Complexes with Benzazole-Substituted 8-Hydroxyquinolines

Abhijit Saha¹, Sucheta Kundu², Anindya Datta², Ashis K. Patra^{*1}

¹ Department of Chemistry, Indian Institute of Technology Kanpur, U.P. 208016, India

² Department of Chemistry, Indian Institute of Technology Bombay, Mumbai 400076, India E-mail: asaha@iitk.ac.in

A series of structurally related bistridentate heteroleptic Ru(II) polypyridyl complexes: [Ru^{II}(tppy)(8-HQL^{S/N/O})]⁺ (**Ru1-Ru3**) were synthesized, where **tppy** = *p*-tolyl terpyridine and **8-HQL^{S/N/O}** are monoanionic N⁺N⁺O-donor tridentate ligands (**8-HQL^X**), derived from 8-hydroxyquinoline (8-HQ), viz. **8-HQL^S** = 2-(2'-benzothiazole)-8-hydroxyquinoline, **8-HQL^N** = 2-(2'-benzimidazole)-8-hydroxyquinoline, **8-HQL^O** = 2-(2'-benzoxazole)-8-hydroxyquinoline. The electronic structure of these rigid ligands was systematically tuned by varying the non-coordinating heteroatom (S, NH, O) in the five-membered heterocyclic ring, impacting the electronic properties, redox potentials, excited state lifetimes deactivation pathways and photophysical behavior of the corresponding Ru(II) complexes.¹⁻⁴ Given their reasonable excited state lifetime and ¹O₂ generation ability, these heteroleptic Ru(II) complexes demonstrated potential as photocatalysts for oxidation of organic substrates.

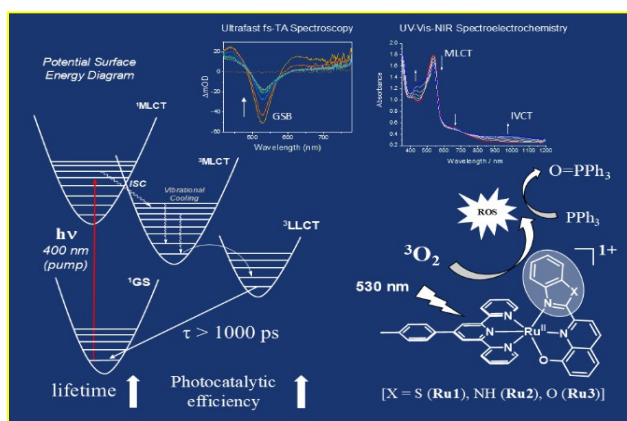


Figure 1. Systematic variation in five membered ring heterocycles of 8-hydroxyquinoline ligand backbone impacting on the overall excited state lifetime and dynamics of the heteroleptic bis(tridentate)Ru(II) polypyridyl complexes.

Acknowledgments

We thank IIT Kanpur for infrastructures and providing High Performance Computing (HPC-2013) facility for the DFT calculations.

References

- [1] D. M. Arias-Rotondo, J. K. McCusker, *Chem. Soc. Rev.* **2016**, 45, 5803-5820.
- [2] D. J. Stufkens, A. Vlček Jr., *Coord. Chem. Rev.* **1998**, 177, 127-179.
- [3] M. El. Ojaimi, R. P. Thummel, *Inorg. Chem.* **2011**, 50, 10966-10973.
- [4] R. Mishra, A. Saha, P. Chatterjee, A. Bhattacharyya, A. K. Patra, *Inorg. Chem.* **2023**, 62, 18839-18855.

Anti- Kasha emission from Co(III)-Amidine-*N*-oxide complexes: photophysics and reactivity

A. Saha,^a G. Turner,^a M. Cibian,^b S. Serroni,^c S. Campagna,^c S. Genovese,^c G. S. Hanan,^a
and F. Nastasi.^c

- a. Dept. de Chimie, Université de Montréal, Montréal, Québec H3C 3J7, Canada
b. Dépt. de biochimie, chimie, physique et science forensique and Institut de recherche sur l'hydrogène, Université du Québec à Trois-Rivières, Canada
c. Dipartimento di Scienze Chimiche, Biologiche, Farmaceutiche e Ambientali and Interuniversity research center SOLAR-CHEM, University of Messina

arindam.saha@umontreal.ca

The photophysical properties of 3d metal complexes remain a fascinating field of study, particularly when transitioning from the rare 2nd and 3rd row metal complexes towards their 1st row congeners.¹⁻³ Here, we present a series of novel photoactive Co(III) metal complexes based on amidine-*N*-oxide ligands. These complexes exhibit unusual anti-Kasha type singlet emissions. Contrary to the widely accepted Kasha emitters¹⁻³ which emit from the lowest-lying excited state, these complexes show room temperature fluorescence from higher-lying states consisting of an admixture of $^1\pi-\pi^*$ and intra-ligand charge-transfer ($^1\text{ILCT}$) character. Detailed steady state and ultrafast spectroscopy alongside extensive theoretical calculations establish the electronic factors governing this behavior. The structural rigidity and higher-lying π orbitals of the ligands render these metal complexes photoactive. Due to the high excited state reduction potential, these complexes can effectively reduce 4-iodotoluene and pyrazine.^[4]

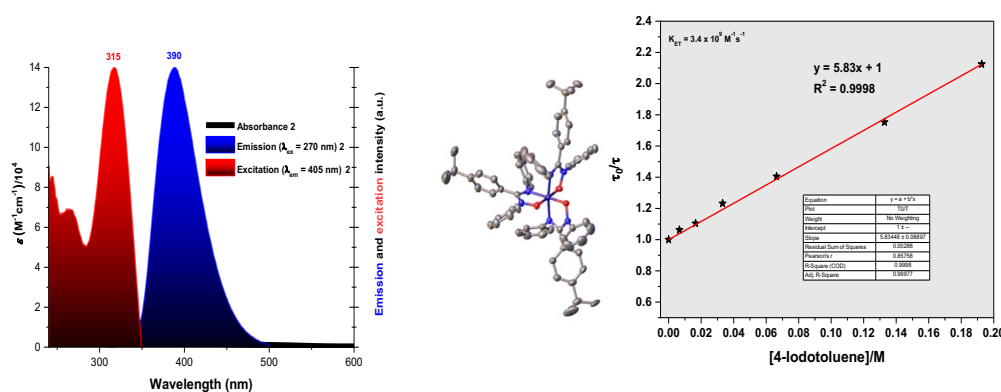


Figure 35. Graph showing the absorbance and emission spectra for one of the Anti-Kasha Co(III) complex (left) and graph for quenching studies (right)

Aknowlegments

AS, GT, GSH thank FRQNT, CCVC, CQMF, NSERC and UdeM for financial support. SC, SS, SG and FN thank NextGeneration EU and European Union-FSE-REACT-EU for funding.

References

- [1] A. K. Pal, C. Li, G. S. Hanan, E. Zysman-Colman, *Angew. Chem. Int. Ed.* **2018**, 57, 8027
- [2] Y. Zhang, T. S. Lee, J. M. Favale, D. C. Leary, J. L. Petersen, G. D. Scholes, F. N. Castellano, C. Milsmann, *Nat. Chem.*, **2020**, 12, 345
- [3] N. Sinha, C. Wegeberg, D. Häussinger, A. Prescimone, O. S. Wenger, *Nat. Chem.*, **2023**, 15, 1730
- [4] A. Saha, G. Turner, M. Cibian, S. Serroni, S. Genovese, S. Campagna, F. Nastai, G.S. Hanan, *manuscript in preparation*

Light-driven Catalytic Activity and Deactivation Processes of Thio(oxo)molybdate Hydrogen Evolution Reaction Catalysis

L.T. Schleicher¹, S.H. Kolbinger¹, C. Streb¹

¹: Johannes Gutenberg-University Mainz, Germany, Duesbergweg 10-14, 55128 Mainz, lschleic@students.uni-mainz.de

Thiomolybdates and thiooxomolybdates function as molecular catalysts for light-driven or electrocatalytic hydrogen evolution reaction (HER).^[1] The well-known prototype cluster $[\text{Mo}_3\text{S}_{13}]^{2-}$ has undergone numerous studies regarding catalytic activity and deactivation processes.^[2] However, for other thiomolybdates such as $[\text{Mo}_2\text{S}_{12}]^{2-}$ and thiooxomolybdates like $[\text{Mo}_2\text{O}_2\text{S}_6]^{2-}$ less is understood of their catalytic activities and the respective mechanism. In order to fully understand the catalytic activity and the application of thio(oxo)molybdates, important parameters for these clusters need to be explored. In this study photocatalytic systems containing $[\text{Mo}_2\text{S}_{12}]^{2-}$ or $[\text{Mo}_2\text{O}_2\text{S}_6]^{2-}$ were explored in regards of optimal solvent composition and the influence of stirring. Furthermore, possible deactivation processes were monitored using Raman-spectroscopy. The interpretation of both the catalytic activity and the deactivation processes was supported by modern DFT calculations.

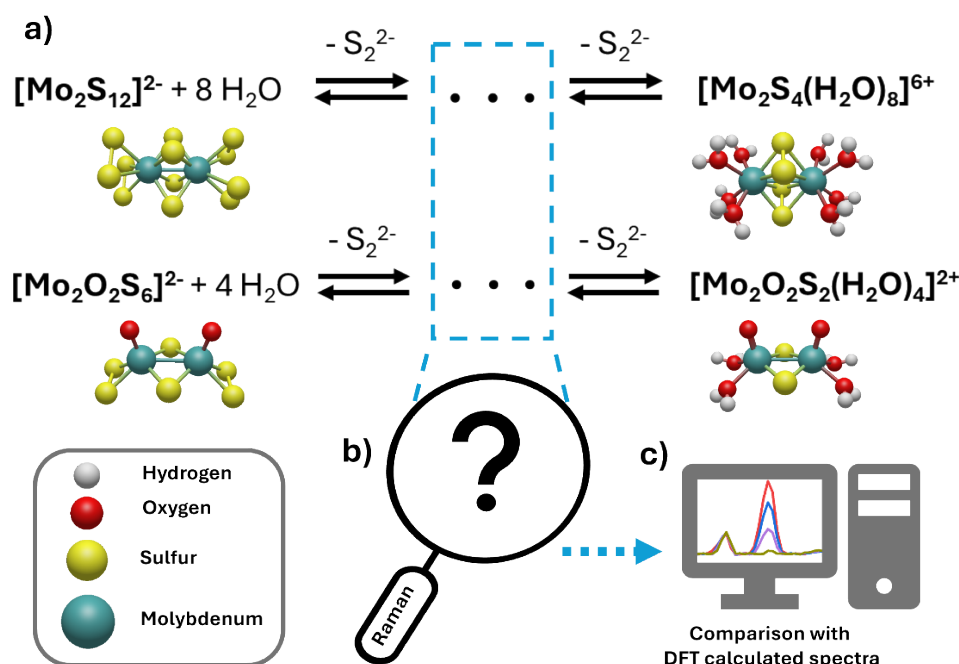


Figure 1. a) $[\text{Mo}_2\text{S}_{12}]^{2-}$ and $[\text{Mo}_2\text{O}_2\text{S}_6]^{2-}$ might undergo ligand exchange with the solvent (water) over a certain period. b) Possible ligand exchange is monitored using Raman spectroscopy. c) The resulting spectra and their kinetics are evaluated and compared to DFT calculated spectra.

References

- [1] M.-L. Grutzka, A. Rajagopal, C. Streb, P. Kurz, *Sustain. Energy. Fuels*, **2018**, 2, 1893-1904
- [2] M. Dave, A. Rajagopal, M. Damm-Ruttensperger, B. Schwarz, F. Nägele, L. Daccache, D. Fantauzzi, T. Jacob, C. Streb, *Sustainable Energy Fuels* **2018**, 2, 1020-1026.

Metallonitrenes As Key Intermediates In C–N bond Formation

T. Schmidt-Räntsch,^a H. Verplancke,^b L. I. Domenianni,^c M. Bauer,^c P. Vöhringer,^c M. C. Holthausen,^b S. Schneider^a

a) Institut für Anorganische Chemie, Georg-August-Universität Göttingen, Tammannstraße 4, 37077 Göttingen, Germany

b) Institut für Anorganische und Analytische Chemie, Goethe-Universität Frankfurt a.M., Max-von-Laue-Str. 7, 60438 Frankfurt a.M., Germany

c) Clausius-Institut für Physikalische und Theoretische Chemie, Rheinische Friedrich-Wilhelms-Universität, Wegelerstr. 12, 53115 Bonn, Germany

E-Mail: till.schmidt-raentsch@uni-goettingen.de

Transition metal catalyzed nitrene transfer has evolved as a powerful synthetic tool for C–N bond formation. Key intermediates are group 9–11 nitrene species ($M\leftarrow NR$), which have been associated with nitrene (3NR) or imidyl ($^2NR^-$) character of the nitrogenous ligand.^[1] In contrast, nitrogen atom transfer from nitrido species ($M\equiv N$) is strongly underdeveloped.^[2]

In this presentation, we report that irradiation of group 10 azide complexes leads to formation of metallonitrenes ($M-N$), a novel class of compounds that feature a nucleophilic, nitrogen-centered biradical.^[3] The photochemical formation of the Pt metallonitrene has been examined in detail by transient fs-UV-pump/IR-probe spectroscopy as well as DFT computations.^[4] Concerning chemical reactivity, the metallonitrene undergoes selective nitrogen insertion into C–H bonds, and a catalytic protocol for selective aldehyde amidation by N-atom transfer was developed with the Pd(II) azide complex.^[3b] Reactivity with olefins (styrene) does not lead to aziridination, but instead, unusual C=C double bond cleavage is observed.^[5] Mechanistic investigations revealed that reactivity of the metallonitrene can vary between radical or nucleophilic for different substrates.

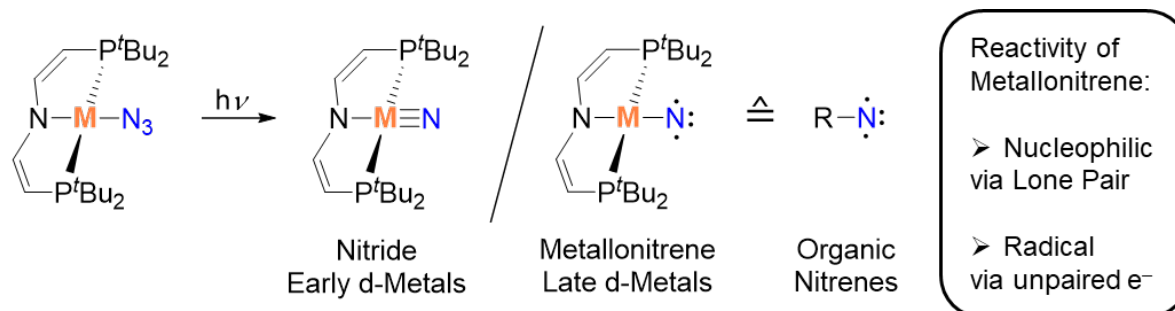


Figure 36. Irradiation of azide complexes can lead to nitrides ($M\equiv N$) or metallonitrenes ($M-N$), depending on the metal. The latter are similar to organic nitrenes with respect to electronic structure and reactivity.

References

- [1] a) H. M. L. Davies, J. R. Manning, *Nature* **2008**, 451, 417–424. b) Y. Park, Y. Kim, S. Chang, *Chem. Rev.* **2017**, 117, 9247–9301. c) M. Goswami, B. de Bruin *et al.*, *J. Am. Chem. Soc.* **2015**, 137, 5468–5479. d) K. Carsch, T. Betley *et al.*, *Science* **2019**, 365, 1138–1143.
- [2] M. N. Cosio, D. C. Powers, *Nat. Rev. Chem.* **2023**, 7, 424–438.
- [3] a) J. Sun, S. Schneider *et al.*, *Nat. Chem.* **2020**, 12, 1054–1059. b) T. Schmidt-Räntsch, S. Schneider *et al.*, *Angew. Chem. Int. Ed.* **2022**, e202115626.
- [4] L. I. Domenianni, M. Bauer, T. Schmidt-Räntsch, S. Schneider, P. Vöhringer *et al.*, *Angew. Chem. Int. Ed.* **2023**, e202309618.
- [5] T. Schmidt-Räntsch, S. Schneider *et al.*, *JACS Au* **2024**, 4, 3421–3426.

Computational Insights into the Photodissociation Mechanism of Terpyridine-Based Ruthenium(II) Complexes

S. Scoditti^{1,2,3}, E. Sicilia², L. Salassa^{1,3,4}

¹ Donostia International Physics Center, Paseo Manuel de Lardizabal 4, Donostia, 20018, Spain

² Department of Chemistry and Chemical Technologies, University of Calabria, Via P. Bucci, Rende, 87036, Italy

³ Polimero eta Material Aurreratuak: Fisika, Kimika eta Teknologia, Kimika Fakultatea, Euskal Herriko Unibertsitatea UPV/EHU, Paseo Manuel de Lardizabal 3, Donostia, 20018, Spain

⁴ Ikerbasque, Basque Foundation for Science, Bilbao 48011, Spain
stefano.scoditti@dipc.org

Ruthenium(II) complexes have emerged as promising candidates for phototherapeutic applications.[1] They are primarily investigated for Photodynamic Therapy (PDT) and Photoactivated Chemotherapy (PACT). In PDT, light-triggered population of long-lived excited states (e.g. ³MLCT or ³LC) enables the efficient generation of reactive oxygen species (ROS), which induce cellular oxidative stress. Conversely, PACT requires ³MLCT-³MC conversion and the subsequent population of ³MC states, as these have dissociative character and can promote the release of (bioactive) ligands and/or the formation of reactive Ru-aqua species. Therefore, the predominance of PDT or PACT activity depends on ³MLCT-³MC energy barriers and excited-state lifetimes. Interestingly, recent studies by Turro and co-workers suggest that in terpyridine-based Ru(II) complexes, acetonitrile dissociation occurs directly from the ³MLCT state, as complexes with higher ³MLCT-³MC energy barriers exhibit increased ligand exchange quantum yields.[2] This unexpected trend suggests an alternative mechanism, prompting further investigation into excited-state reactivity in Ru-based photoactive systems. In this contribution, we present computational studies on the photodissociation mechanisms of selected complexes from the Turro's series, namely **Ru₁** and **Ru₂** (Figure 1), to rationalize how the ³MLCT-³MC conversion, acetonitrile release, and subsequent water coordination at the Ru center influence the photochemical efficiency of these prospective PACT agents.

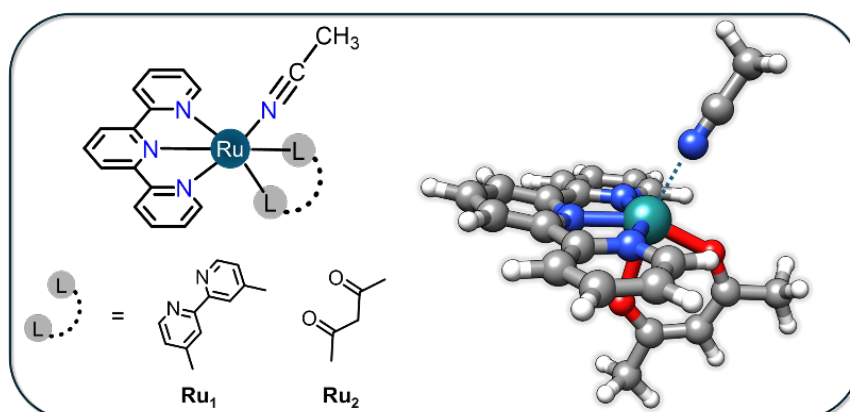


Figure 37. Structure of **Ru₁** and **Ru₂** complexes and transition state structure of the acetonitrile release of **Ru₂**

References

[1] S. Bonnet, *J. Am. Chem. Soc.*, **2023**, 145 (43), 23397-23415

[2] S. J. Steinke, E. J. Piechota, L. M. Loftus, C. Turro, *J. Am. Chem. Soc.*, **2022**, 144 (44), 20177-20182

Control of Emission Efficiency and Color by Mixed Crystals of Platinum(II) and Palladium(II) Complexes in One-dimensional Chain

K. Segawa,^{a,b} M. Yoshida,^{b,c} K. Onda,^a and M. Kato^b

^aKyushu Univ.; ^bKwansei Gakuin Univ.; ^cUniv. Osaka

E-mail: segawa.kaito.148@s.kyushu-u.ac.jp

Square-planar Pt(II) complexes with the 5d⁸ electronic configuration often exhibit ³MMLCT emission in the visible region due to Pt···Pt interactions arising from the one-dimensional stacked structures. In contrast, Pd(II) complexes with the 4d⁸ electron system form very weak Pd···Pd interactions, and there are extensively few examples of ³MMLCT emission.^[1] We recently developed a cyclometalated Pd(II) complex with the Pd···Pd interaction, K[Pd(CN)₂(dFppy)]·H₂O (dFppy = 2-(4,6-difluorophenyl)pyridinate; **Pd-dFppy**) as the Pt(II) complex analogue (**Pt-dFppy**) (Fig. 1).^[2] The different behaviors of the temperature-dependent emission were explained by the difference in the electronic delocalization of the ³MMLCT excited state in the stacked column between **Pd-dFppy** and **Pt-dFppy**. However, the ³MMLCT excited state of the Pd(II) complex is localized in the excited dimer, which easily induces structural distortion, and resulting in weak luminescence. In this study, we prepared mixed crystals of **M-dFppy** (M = Pt, Pd) and investigated the emission behavior of mixed crystals by thermal changes and revealed that the formation of various excited oligomers enables enhanced emission efficiency and color tuning.

Mixed crystals with different ratios (Pt/Pd = 1:0.5–1:13) were confirmed to be isomorphous by single-crystal (SXRD) and powder X-ray diffraction (PXRD) measurements. These mixed crystals showed different emission colors depending on the Pt/Pd ratio (Fig. 2(a)), and homogeneous dispersion of Pt and Pd in the elemental mapping by Energy Dispersive X-ray (EDX) analysis. These findings suggest that the Pt(II) and Pd(II) complex units are randomly mixed in the one-dimensional chains. Interestingly, the emission quantum yields increased from 0~2% for the pure Pt(II) and Pd(II) complexes to 64% by forming mixed crystals at RT. In addition, the broad emission spectra of the mixed crystals at RT split into several bands at 77 K (Fig. 2(b)). The origin of split emission bands is suggested to be the formation of local excited oligomers with different Pt/Pd ratios. The details will be discussed.

References

- [1] W. Lu *et al.*, *Chem. Commun.*, **2018**, 54, 5319-5322.
- [2] T. Saito *et al.*, *Chem. Sci.*, **2024**, 15, 14497-14505.

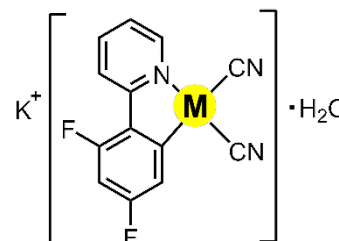


Fig. 1 Structural formula of K[M(CN)₂(dFppy)]·H₂O (M = Pt, Pd)

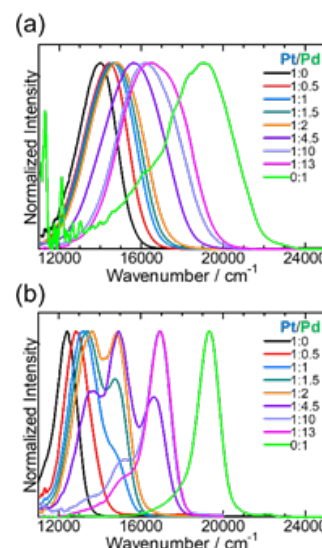


Fig. 2 Emission spectra at (a) RT and (b) 77 K (λ_{ex} = 350 nm).

Unraveling Solvent Polarity Effects in Thermally Activated Delayed Fluorescence Through Time-Resolved Spectroscopy

M. Semwal^{1,2}, A. Tombrink³, T. Maisuradze¹, S. Kupfer¹, B. Esser³, B. Dietzek-Ivanšić^{1,2,4}

¹Institute of Physical Chemistry, Friedrich Schiller University Jena, 07743 Jena, Germany

²Leibniz Institute of Photonic Technology, Research Department Functional Interfaces, Albert-Einstein-Str. 9, Jena, Germany mohini.semwal@uni-jena.de

³Institute of Organic Chemistry II and Advanced Materials, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany

⁴Leibniz-Institut für Oberflächenmodifizierung e.V. (IOM), Permoserstraße 15, 04318 Leipzig, Germany

Thermally activated delayed fluorescence (TADF) has emerged as an effective approach to harvest triplet state for organic light-emitting diodes (OLEDs) due to their ability to achieve fluorescence via reverse intersystem crossing (RISC)^[1,2] This study presents a comprehensive investigation into the photophysics of a TADF-active organic chromophore namely Cbzdpzp (Figure 1). Our fs-transient absorption measurements reveal photoexcitation of Cbzdpzp leads to the formation of a singlet charge-transfer state (¹CT) which then forms a triplet state through intersystem crossing. The singlet state is relatively stabilized in polar solvent (MeCN as compared to toluene), which can reduce the singlet-triplet energy gap (ΔE) leading to a larger rISC rate (k_{RISC}). This stabilization also increases nonradiative decay (k_{nr}) from the ¹CT state. This leads to an overall decrease in delayed fluorescence efficiency (ϕ_d). In contrast, in non-polar solvents (toluene), we note a slower k_{RISC} and improved quantum yield. Upon coordination of Cbzdpzp to Rh, a faster excited-state quenching suggests an electron transfer process. In the next step, the chromophore was embedded in a polymer film matrix where we observed a long-lived ¹CT state and higher emission, demonstrating a promising strategy for OLED applications. Herein, we will discuss these findings in more detail, that will provide critical insights into the interplay between the fluorescence efficiency and the local environment (such as solvent polarity or immobilization from solution to film).

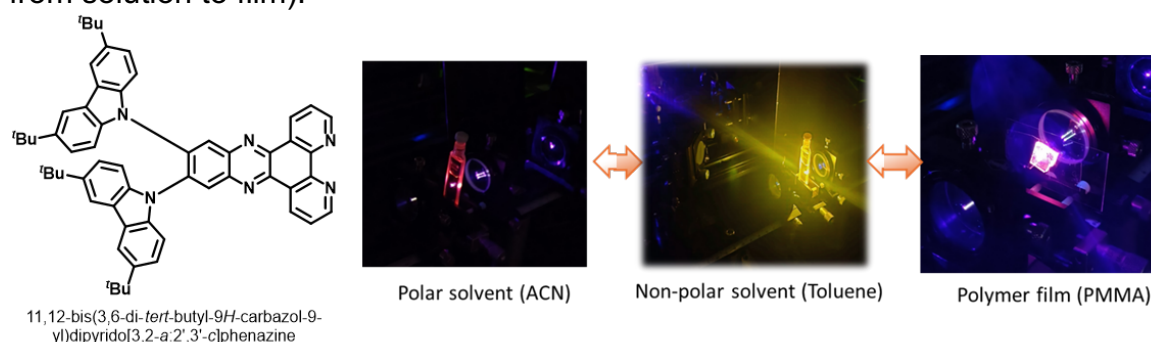


Figure 1: Emission Enhancement of Cbzdpzp: Transition from Polar to Non-Polar Solvents and Immobilization within polymer matrix

Aknowlegments

We thank the German Science Foundation for funding via the TRR 234 CataLight (project number 364549901; projects A1 and A6).

References

- [1] E. Zysman-Colman et al., Nat Commun 15 **2024**, 7439
- [2] T. Goodson III et al., Journal of the American Chemical Society **2020**, 142 (18), 8074

Conformation Dependent Emission and Circularly Polarized TADF in Linear CDP Copper (I) Complexes

I. Sen, O. Mrózek and A. Steffen

indranil.sen@tu-dortmund.de and andreas.steffen@tu-dortmund.de

Inorganic Chemistry, Department of Chemistry and Chemical Biology

TU Dortmund University, D-44227, Dortmund, Germany

Chiral organometallic charge transfer complexes have great potential nowadays and practical applications of circularly polarized organic light emitting diodes (CP-OLEDs).^[1] For this reason, the synthesis of racemic and chiral homoleptic copper (I) complexes supported by racemic and chiral ^{BIN}CDP (Carbodiphosphorane) ligand with binaphthyl ring in the backbone is described.^[2] Depending on the conformation, which determines the MLCT emission energies and thermally activated delayed fluorescence (TADF) efficiencies as well as the energy gap between singlet and triplet (ΔE_{ST}). [^{BIN}CDP₂Cu]X {X – Br and PF₆} showing orange to deep red emission ranges from 605 to 715 nm in solution, in powders, and in rigid polystyrene film. Comparing [^{Me}cAAC₂Cu]PF₆, which was Copper (I) based blue phosphorescent emitter (λ_{em} – 398nm) to this is homoleptic ^{BIN}CDP copper (I) complex with TADF behavior.^[3] The design motif leads to the first homoleptic linear MLCT complex with conformation dependent emission with a radiative rate constant of $0.71 \times 10^5 \text{ s}^{-1}$ in solution state and remarkable dissymmetry factor $\pm 1.5 \times 10^{-2}$ in polystyrene film.

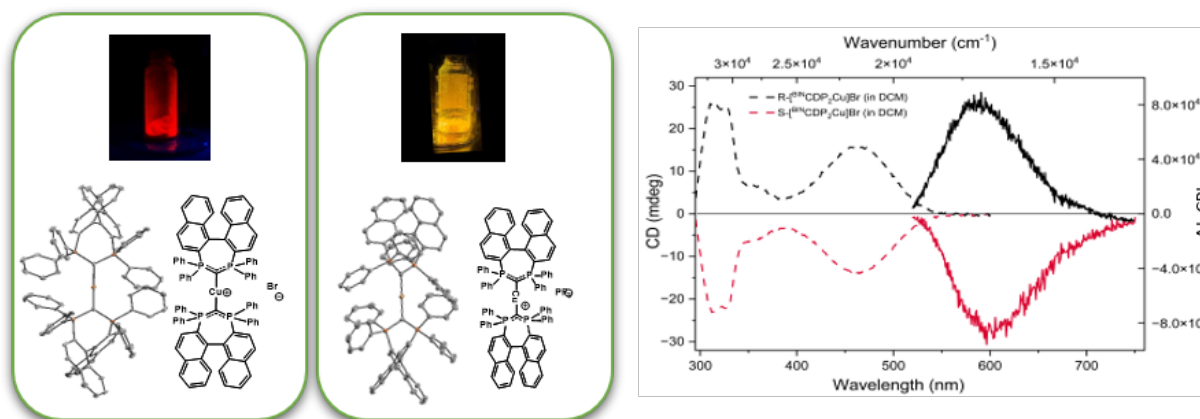


Figure 38. Conformational dependent emission and circularly polarized Luminescence Property

Aknowlegments

Financial support by the Deutsche Forschungsgemeinschaft (DFG STE1834/4-2) is gratefully acknowledged.

References

- [1] A.M.T. Muthig, O. Mrózek, T. Ferschke, M. Rödel, B. Ewald, J. Kuhnt, C. Lenczyk, J. Pflaum, A. Steffen, *J. Am. Chem. Soc.* **2023**, *145*, 4438-4449.
- [2] T. Dunaj, C. Krampe, J. Heinrichs, F. Müller, B. Neumüller, X. Xie, I. Kuzu *Eur. J. Inorg. Chem.* **2024**, *27*, e202400170
- [3] M. Gernert, U. Müller, M. Haehnel, J. Pflaum, A. Steffen, *Chem. – Eur. J.* **2017**, *23*, 2206-2216.

Temperature Dependency of the Light-Driven Hydrogen Evolution Reaction using Thiomolybdate Clusters

L.A. Senz¹, S.H. Kolbinger¹, C. Streb¹

¹: Johannes Gutenberg-Universität Mainz, Duesbergweg 10-14, 55128 Mainz, luis.senz@uni-mainz.de

Thiomolybdates were found as promising catalysts for the light-driven hydrogen evolution reaction (HER) with a benefit of being earth abundant and less expensive compared to noble metals. The model cluster $[\text{Mo}_3\text{S}_{13}]^{2-}$ has already been the center of many investigations. However, its complex reaction mechanism is not fully understood yet. The influence of dynamic irradiation upon the system was topic of earlier research. Now, the influence of temperature within a temperature range of -12 °C to 50 °C is investigated in this work. A photoreactor was modified and 3D printed containing a temperature control unit which was specially designed. Photocatalysis at different temperatures was compared by turnover number (TON) and photon efficiency (PE). The trend found indicates that lower temperatures are beneficial for the catalysis. Possible explanations will be shown in this work.

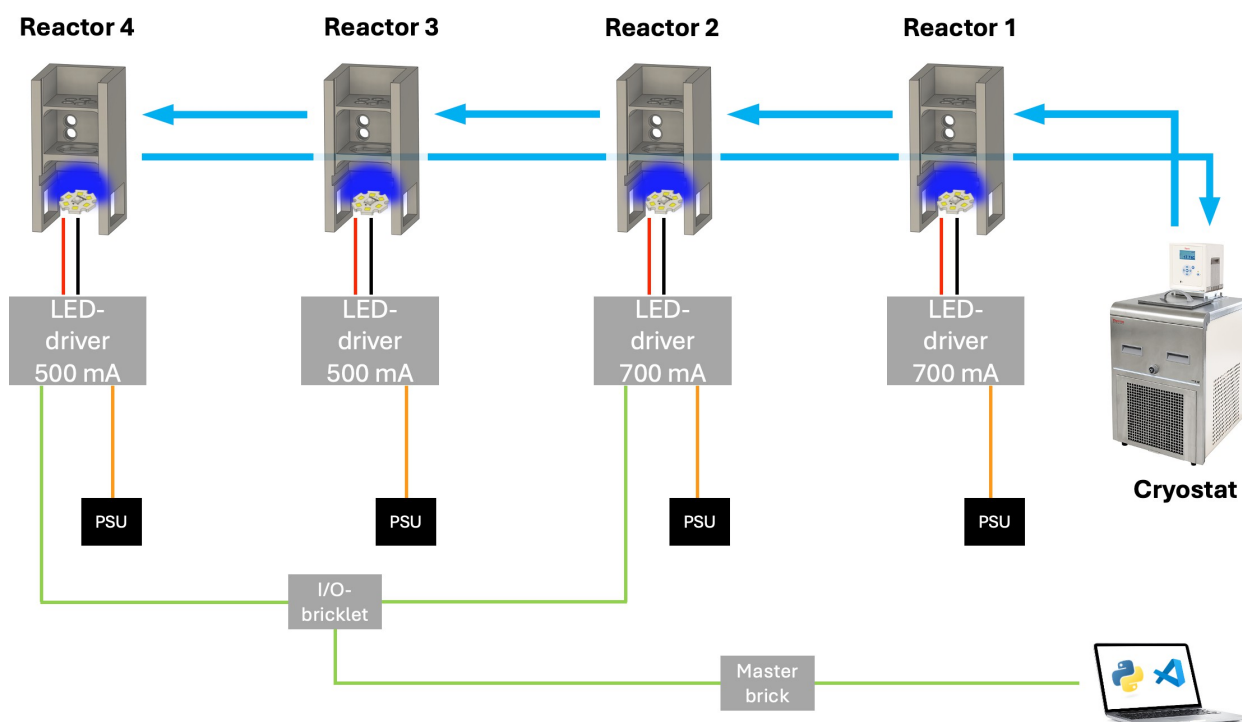


Figure 1. The setup of the four photoreactors. The temperature control unit inside the reactors is tempered by a cryostat. The LEDs are powered through a LED driver. The dynamic irradiation is achieved by using an I/O-bricklet to pulse the LEDs at the desired frequency with the desired ON/OFF-ratio.

References

- [1] M. Sender, F. L. Huber, M. C. G. Moersch, D. Kowalczyk, J. Hniopek, S. Klingler, M. Schmitt, S. Kaufhold, K. Siewerth, J. Popp, B. Mizaikoff, D. Ziegenbalg, S. Rau, *ChemSusChem* **2022**, 15
- [2] D. Kowalczyk, L. Pengcheng, A. Pannwitz, F. Schacher, W. Weigand, C. Streb, D. Ziegenbalg, *ChemPhotoChem* **2022**, 6
- [3] M. Heiland, R. De, S. Rau, B. Dietzek-Ivansic, C. Streb, *Chem. Commun.*, **2022**, 58, 4603-4606

Excited state processes in a supramolecular photocatalyst – a quantum computational investigation

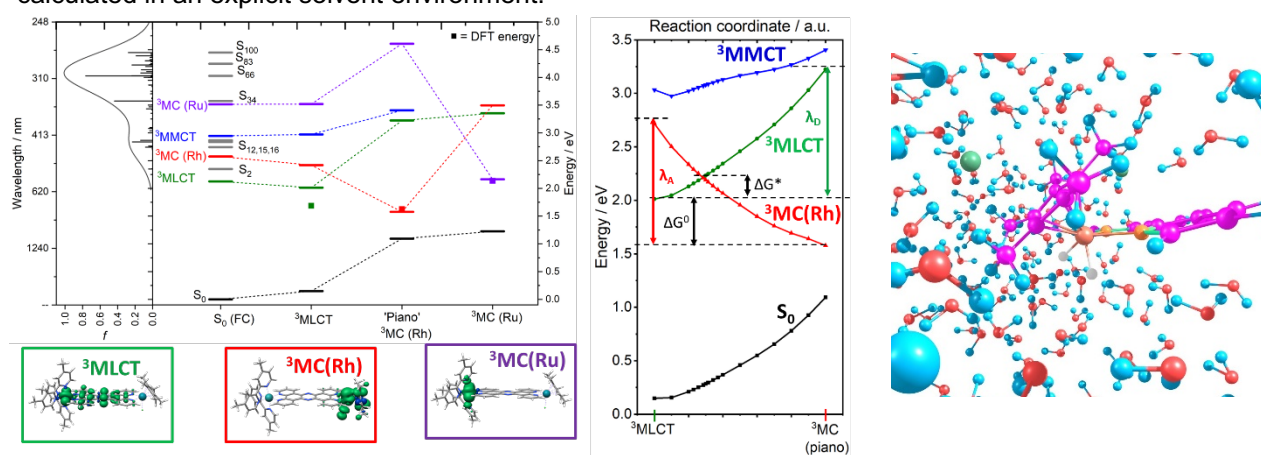
G. E. Shillito¹, S. Kupfer¹

¹Institute for Physical Chemistry, Friedrich Schiller Universität Jena, Jena, 07743, Germany
georgina.shillito@uni-jena.de

The photophysical properties of a model supramolecular photocatalyst are investigated using a suite of quantum computational methodologies. The photocatalyst, denoted **RutpphzRhCp*** is comprised of a Ru(II) photosensitiser, a highly conjugated bridging moiety and a Rh(III) catalytic centre.¹ Previous investigations have demonstrated that thermally driven chloride dissociation is the gating process for reduction of the Rh(III) centre and subsequent formation of a catalytically active intermediate.^{2, 3}

Herein electron and energy transfer processes from the initial photoexcitation of the Ru(II) photocenter, to structural rearrangement and ligand dissociation in the excited state regime are explored using (TD)DFT methods. The dissociation energies of the Cl⁻, as well as other possible ligands (H₂O, MeCN, Br⁻) are also investigated. Electron transfer rates are predicted using semi-classical Marcus theory and a possible mechanism for catalytic hydrogen generation at the Rh centre is explored using molecular and metadynamics simulations.

Figure 39. Left: Excited state energies at optimised ground state, ³MLCT, ³MC_(Rh) and ³MC_(Ru) geometries; Centre: Marcus potential energy curves of the ³MLCT and ³MC_(Rh) states; Right: Snapshot of catalytic centre calculated in an explicit solvent environment.



References

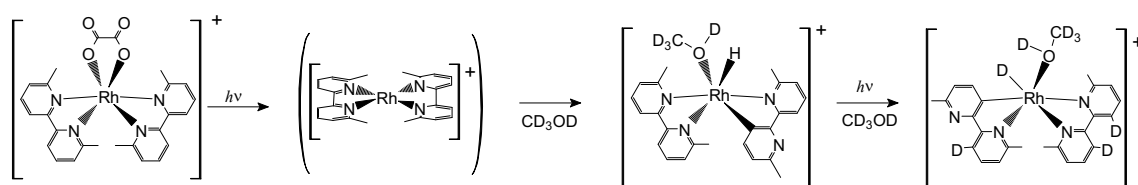
- Shillito, G. E.; Rau, S.; Kupfer, S., *ChemCatChem* **2023**, e202201489.
- Blebschmidt, L.; Zedler, L.; Mengele, A. K.; Rau, S.; Dietzek-Ivanšić, B., *Chemical Communications* **2025**, 61, 2508-2511.
- Zedler, L.; Mengele, A. K.; Ziem, K. M.; Zhang, Y.; Wächter, M.; Gräfe, S.; Pascher, T.; Rau, S.; Kupfer, S.; Dietzek, B., *Angew. Chem. Int. Ed.* **2019**, 58, 13140-13148.

Sequential H/D exchanges and Rh-H/Rh-C σ bond formations resulting from auto cyclometallation during photoirradiation of bis(6,6'-dimethyl-2,2'-bipyridine)(oxalato)rhodium(III) complex in methanol-d₄

S. Tanaka, S. Hattori, K. Shinozaki

Department of Materials Sciences, Graduate School of Nanobioscience, Yokohama City University, Yokohama 236-0027 JAPAN

Photoirradiation to bis(6,6'-dimethyl-2,2'-bipyridine)(oxalato)rhodium(III) ($[\text{Rh}(\text{N}^{\wedge}\text{N})_2(\text{ox})]^+$) caused the dissociation of ox followed by the formation of unprecedented Rh(III) complex $[\text{Rh}^{\text{III}}(\text{N}^{\wedge}\text{N})(\text{C}^{\wedge}\text{N})(\text{H})(\text{CD}_3\text{OD})]^+$ ($\text{C}^{\wedge}\text{N} = [6,6'\text{-dimethyl-2,2'-bipyridine-3-yl-}\kappa\text{C}^3, \kappa\text{N}^1]^+$) with Rh–H and Rh–C σ bonds in CD_3OD . Although $[\text{Rh}^{\text{III}}(\text{N}^{\wedge}\text{N})(\text{C}^{\wedge}\text{N})(\text{H})(\text{CD}_3\text{OD})]^+$ was converted to $[\text{Rh}^{\text{I}}(\text{N}^{\wedge}\text{N})_2]^+$ by further photoirradiation, the auto-cyclometallation due to the steric hindrance between methyl groups of $\text{N}^{\wedge}\text{N}$ ligands reproduced the Rh(III) complex. Surprisingly, the resultant Rh(III) complex was $[\text{Rh}(\text{N}^{\wedge}\text{N})(\text{C}^{\wedge}\text{N}^{\text{D}})(\text{D})(\text{CD}_3\text{OD})]^+$, whose H atoms in Rh–H bond and at 3, 3'-positions of $\text{N}^{\wedge}\text{N}$ ligand had been exchanged with D atoms. The H/D exchange reaction proceeded at other 3,3'-positions of N-N ligands.



Scheme 1. H/D exchange and Rh–H/Rh–C σ bond formation by photoirradiation.

References

- [1] S. Tanaka, S. Hattori, K. Shinozaki, *Chem. Eur. J.* **2024**, *30*, e202402067.

Stabilizing High Spin States in Fe(II)-N_{amido} Complexes to Tune Visible Light Absorption and Excited State Behaviour

B.K. Sidhu,¹ R.J. Ortiz,¹ C. Wegeberg,^{2,3} Petter Persson,⁴ Arkady Yartsev,² D.E. Herbert¹

¹ Department of Chemistry, 144 Dysart Road, University of Manitoba, Winnipeg, MB R3T 2N2, Canada. sidhub34@myumanitoba.ca ² Division of Chemical Physics, Department of Chemistry, Lund University, 22100 Lund, Sweden. ³ Current affiliation: Department of Chemistry, Physics and Pharmacy, University of Southern Denmark, 5230 Odense M, Denmark. ⁴ Division of Computational Chemistry, Department of Chemistry, Lund University, 22100 Lund, Sweden

Iron coordination complexes have long been sought as a sustainable replacement for precious metal sensitizers in applications that exploit photo-generated excited states, from luminescent materials to photoredox catalysis to dye-sensitized solar cells. The main shortcoming of iron-based dyes is their short-lived charge transfer (CT) excited states which result from rapid relaxation to low-lying metal centered states. Photophysics of Fe(II) complexes so far have been dominated by low-spin, singlet ground states, while the photophysics originating from high spin, quintet ground states stay underexplored. This talk will shine light on ligand design strategies to stabilize high spin ground states in pseudo-octahedral Fe(II)-N_{amido} complexes while maintaining strong visible light absorption, and how that influences the excited state behaviour of these complexes compared to their low spin congeners.

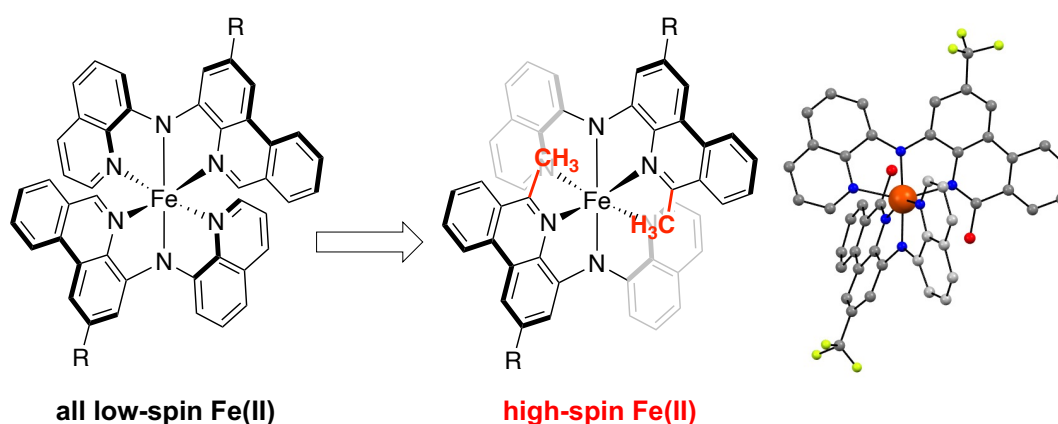


Figure 40. Stabilizing high spin, quintet ground states in pseudo-octahedral Fe(II)-N_{amido} complexes

Acknowledgments

Thanks to my supervisor David Herbert, everyone in the Herbert group, and to our collaborators Christina Wegeberg, Arkady Yartsev, and Petter Persson from Lund University.



Plasmon-Enhanced CO₂ Reduction to Liquid Fuel via Modified UiO-66 Photocatalysts

A. Elsafi ^{1,2}, Z. Theihmed ¹, A. Al-Yafei ³, A. Alkhateeb ¹, A. Abotaleb ¹, M. Anwar ¹, K. Mroue ¹, B. Aissa ¹, and A. Sinopoli ^{1,4}

¹*Qatar Environment and Energy Research Institute (QEERI), Hamad Bin Khalifa University (HBKU), Doha P.O. Box 34110, Qatar;*

²*Materials Science and Technology Graduate Program, Department of Physics and Materials Science, Qatar University, Doha P.O. Box 2713, Qatar;*

³*Department of Chemistry and Earth Sciences, College of Arts and Sciences, Qatar University, Doha P.O. Box 2713, Qatar;*

⁴*Department of Chemical, Biological, Pharmaceutical and Environmental Sciences, University of Messina, V.le F. Stagno d'Alcontres 31, 98166, Messina, Italy.*

E-mail: Alessandro.sinopoli@unime.it

Metal–organic frameworks (MOFs) are emerging as promising materials for photocatalytic applications due to their high surface areas, tunable porosity, and the ability to incorporate functional guests. In this study, the zirconium-based MOF UiO-66 was modified with various metal nanoparticles (NPs) — including Au, Cu, Ag, Pd, Pt, and Ni — to enhance its photocatalytic efficiency for the reduction of CO₂ into liquid fuels under visible light. Structural and morphological analyses confirmed successful metal loading without disrupting the crystallinity of UiO-66, as evidenced by preserved XRD patterns and uniform NP distribution observed in TEM/SEM imaging.

BET surface areas ranged from 985 m²/g for Cu@UiO-66 to 1532 m²/g for Ni@UiO-66, directly impacting CO₂ adsorption capacities, with Ni@UiO-66 achieving the highest uptake at 2.27 mmol/g. Optical characterizations revealed strong plasmonic absorption features, particularly in Au@UiO-66 and Cu@UiO-66, which correlated with enhanced light harvesting. Among the tested catalysts, Au@UiO-66 exhibited a remarkable methanol yield of 656.54 μmol·g⁻¹·h⁻¹, far surpassing the base UiO-66 (0 μmol·g⁻¹·h⁻¹), while Cu@UiO-66 achieved the highest ethanol production at 12.45 μmol·g⁻¹·h⁻¹. [1] Other compositions showed moderate to low activity, with Pt and Pd demonstrating limited selectivity.

These findings highlight the crucial role of plasmonic resonance and metal selection in modulating the catalytic behaviour of MOF-based systems. This work provides a comprehensive evaluation of plasmonic metal@UiO-66 composites and their potential for sustainable solar-driven CO₂ conversion into high-value fuels such as methanol and ethanol.

Aknowlegments

For supporting this study, Qatar Environment and Energy Research Institute (QEERI, at Hamad Bin Khalifa University) is gratefully acknowledged. Additionally, the authors would like to express their appreciation to Hamad Bin Khalifa University's core laboratory staff, namely Akshath Shetty, Anas Abutaha, Mujaheed Pasha, Janarthanan Ponraj, and Yongfeng Tong for their assistance with the materials characterization.

References

- [1] A. Elsafi, Z. Theihmed, A. Al-Yafei, A. Alkhateeb, A. Abotaleb, M. Anwar, K. Mroue, B. Aissa, and A. Sinopoli. *Catalysts* **2025**, 15, 70.

Synthesis and Resolution of *tris*-Heteroleptic Ruthenium Polypyridyl Complexes as Chiral DNA Binding Luminescent Probes

S. N. Smith,¹ S.J. Quinn¹

¹University College, Dublin (UCD), Belfield, Dublin 4
simon.smith@ucd.ie

bis-Heteroleptic ruthenium(II) polypyridyls (RuPPs) containing π -extended aromatic ligands are known to act as 'turn-on' luminescent probes or as photo-damaging agents through enantiomer dependent intercalative binding to B-DNA.^[1] RuPPs have also been reported to bind to G-quadruplex (G4) forming sequences prevalent in telomeres and oncogenes.^[2] *tris*-heteroleptic RuPPs offer an additional way to achieve topologically selective binding to G4 loop regions but are comparatively less studied due to the lack of generality in the method of synthesis and the challenges associated with purification due to ligand scrambling.

This study presents an efficient route to access a small library of *tris*-heteroleptic RuPPs from ruthenium(II) *p*-cymene dimer, accessing the target RuPPs in good yields (12–40% over two steps). These complexes have also been resolved into their constituent stereoisomers by a chiral stationary phase-HPLC (CSP-HPLC) method recently refined by our group ($\Delta T_{R(\Lambda-\Delta)} > 5$ mins).^[3] Incorporating the most frequently encountered bidentate ligands in the literature, the impact of ligand substitution on the excited state behaviour is non-intuitive, and can include substantially red-shifted emission compared to *bis*-heteroleptic analogues ($\lambda_{em} = 690$ nm vs *ca.* 610 nm). The influence of ligand substitution on the binding affinity of the complexes with B-DNA and sensitivity of the luminescent response to different G4 quadruplex structures will also be presented, as well as preliminary results with RuPPs diastereomers containing non-symmetric ligands with distinct photophysical properties.

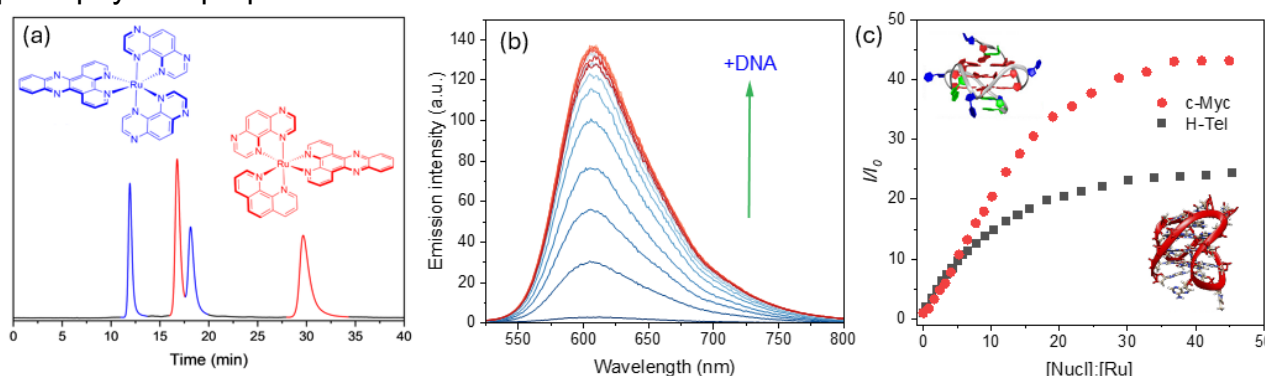


Figure 41: (a) Chromatogram of the resolution of a *tris*-heteroleptic complex containing a *bis*-heteroleptic complex as an impurity by chiral stationary phase-HPLC (CSP-HPLC). (b) luminescence titration of a *tris*-heteroleptic complex with B-DNA (stDNA). (c) luminescence response in the presence of different quadruplex structures.

Acknowledgments

Authors acknowledge Research Ireland for funding (SFI 21/FFP-P/10126 *PhotoGene*).

References

- [1] (a) F. E. Poynton, et al, *Chem. Soc. Rev.* **2017**, 46, 7706-7756; (b) H. K. Saeed, et al, *Chem. Commun.*, **2020**, 56, 1464-1480.
- [2] (a) M. Stitch, D. Avagliano, D. Graczyk, I. P. Clark, L. González, M. Towrie, S. J. Quinn, *J. Am. Chem. Soc.* **2023**, 145, 21344-21360 (b) D. Saadallah, M. Bellakhal, S. Amor, J.-F. Lefebvre, M. Chavarot-Kerlidou, I. Baussanne, C. Moucheron, M. Demeunynck, D. Monchaud, *Chem. Eur. J.* **2017**, 23, 4967
- [3] S. N. Smith, D. Graczyk, M. Stitch, A. Auville, V. Stadler, S. J. Quinn, *Eur. J. Inorg. Chem.* **2025**, e202400836.

Room-Temperature Phosphorescence of Cocrystals of Aromatic Bisimides and Triplet Sensitizer Pt(acac)₂

S. Soldner, F. Brust, M.-J. Sun, V. Stepanenko, O. Anhalt, M. B. Sárosi, M. Stolte,
F. Würthner

Universität Würzburg, Institut für Organische Chemie and Center for Nanosystems Chemistry
(CNC), Am Hubland, 97074 Würzburg, Germany. simon.soldner@uni-wuerzburg.de

Core-unsubstituted naphthalene bisimides (NBIs) are known in literature to be poor emitters with low quantum yields in solution.^[1] We could recently demonstrate that the phosphorescence with quantum yield up to $\Phi_{\text{PL}} = 25\%$ of NBIs can be activated by the triplet sensitizer platinum(II) acetylacetonate (Pt(acac)₂).^[2] Subsequently, four sterically shielded aromatic bisimides are synthesized and their ability to form cocrystals with the Pt(acac)₂ is investigated.^[3] Single crystals of the individual electron-deficient bisimides are studied first, **NBI2** showing bright blue fluorescence Φ_{PL} of up to 28%. After successful cocrystallization of all four aromatic bisimides with the electron-rich Pt(II) complex, two different stoichiometries, either 1:1 or 1:2, are found in the crystalline solid state. While two NBIs show strong and long-lived room-temperature phosphorescence (RTP) with Φ_{PL} exceeding 50%, the other two aromatic bisimides show only minor photoluminescence at 298K, but a bright low-temperature phosphorescence at 80 K. Theoretical calculations reveal the importance of changing the magnetic quantum number m_l of the involved d -orbitals at the platinum center as well as the alignment of the Pt(II) center above an aromatic C—C bond for an efficient intersystem crossing in these hybrid systems. In a proof-of-concept study we could show that doping a layer of NBI with Pt(acac)₂ affords red RTP-emitting cocrystalline LEDs with external quantum efficiencies over 0.2%.^[4]

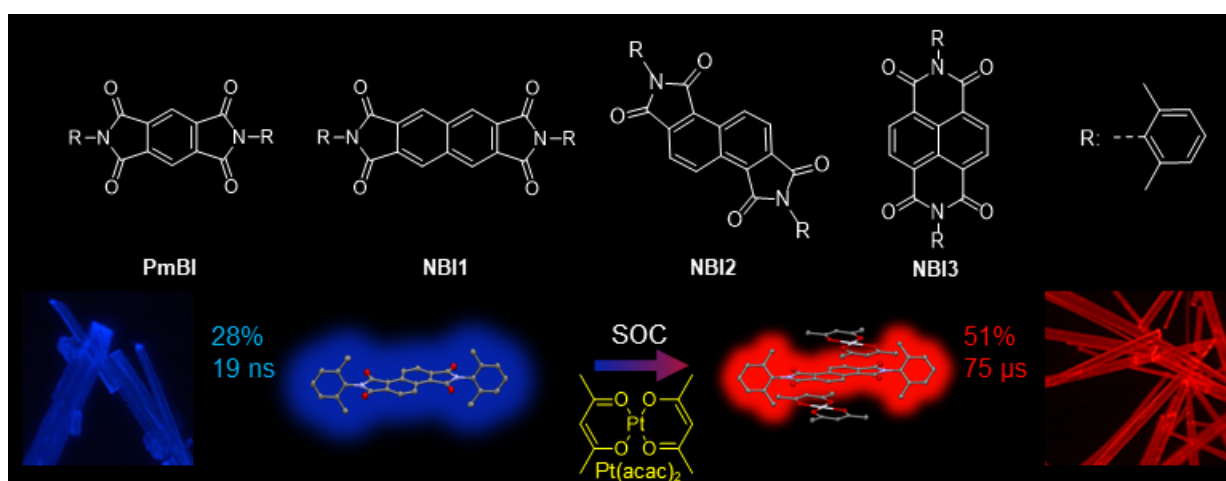


Figure 42. Chemical structures of the four investigated bisimides: **PmBI**, **NBI1**, **NBI2** and **NBI3**. **NBI2** shows by itself a blue fluorescence with $\Phi = 28\%$ in the solid state, which is shifted to a bright red phosphorescence with up to 51% in its 1:1 cocrystal with the triplet sensitizer Pt(acac)₂.

References

- [1] A. Nowak-Król, K. Shoyama, M. Stolte, F. Würthner, *Chem. Commun.* **2018**, 54, 13763.
- [2] M.-J. Sun, O. Anhalt, M. B. Sárosi, M. Stolte, F. Würthner, *Adv. Mater.* **2022**, 34, 2207331.
- [3] S. Soldner, M.-J. Sun, O. Anhalt, M. B. Sárosi, M. Stolte, F. Würthner, *Adv. Funct. Mater.* **2025**, 35, 2412843.
- [4] F. Brust, S. Soldner, V. Stepanenko, M. Stolte, F. Würthner, *Adv. Optical Mater.* **2025**, 13, 2402117.

Photocatalytic CO₂ Reduction and H₂ Evolution in Aqueous Media with Water-soluble Complexes

F. Sueyoshi, X Zhang, K. Yamauchi, K. Sakai

Department of Chemistry, Faculty of Science, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan. sueyoshi.fumika.622@s.kyushu-u.ac.jp

Artificial photosynthesis has attracted much attention in recent years as one of the promising approaches to address the energy crisis and global warming. One of the interests has also concentrated on the development of fully aqueous photocatalytic system. With this aim, our group recently

reported highly efficient and selective photocatalytic CO₂-to-CO conversion by using a sulfonlated heteroleptic copper(I) photosensitizer (**CuPS**³⁻) and a cobalt porphyrin CO₂ reduction catalyst (**CoTMPyP**) (Figure 1a and 1b).¹ Our spectrophotometric titration experiments revealed that **CuPS**³⁻ and hexamethonium (**HM**²⁺) form a 1:2 adduct in water (Figure 1b), which results in substantial enhancement in the luminescence lifetime and quantum yield.² Additionally, the formation of 1:2 adduct effectively leads to more efficient photocatalytic CO₂ reduction based on the enhanced efficiency of reductive quenching (Figure 1c).²

On the other hand, we have also explored Pt-based single-molecular photocatalysts for H₂ evolution reaction in water. The dimerization of the catalyst has been considered to play a key role of stabilizing the hydride intermediate based on the metal-metal bonding.³ We synthesized dinuclear platinum photocatalysts (**Pt2**⁴⁺, Figure 2) to stabilize the hydride intermediate during photocatalysis. The cationic pyridinium moieties are incorporated to enhance water solubility, while the rigid macrocyclic chelating ligand is expected to promote Pt–Pt interactions. The photocatalytic activity of **Pt2**⁴⁺ and its monomeric analogue (**Pt1**²⁺, Figure 2) was investigated by photochemical and electrochemical technique.

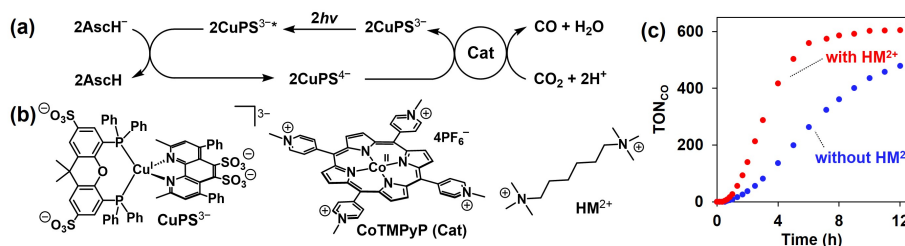


Figure 43. (a) Photocatalytic CO₂ reduction driven by **CuPS**³⁻. (B) The structure of **CuPS**³⁻, **CoTMPyP** and **HM**²⁺. (C) Photocatalytic activities for CO formation in the presence (red) or absence (blue) of **HMCl**₂ (50 mM). Photolysis was carried out in CO₂-saturated NaHCO₃ solution (0.1 M, pH = 6.7) solution (5 mL) containing **CoTMPyP** (5 μM), **CuPS**³⁻ (0.5 mM) and AscHNa (5 mM) at 25 °C under Xe lamp irradiation (λ > 400 nm, 300 mW cm⁻²).

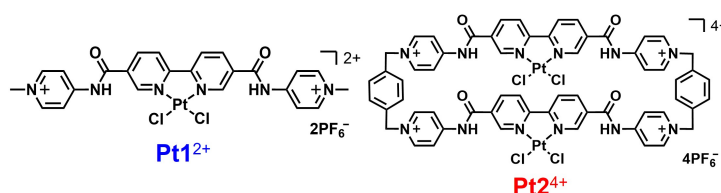


Figure 2. The structures of **Pt1**²⁺ and **Pt2**⁴⁺.

References

- [1] X. Zhang, K. Yamauchi, K. Sakai, *ACS Catal.* **2021**, 11, 10436-10449.
- [2] F. Sueyoshi, X. Zhang, K. Yamauchi, K. Sakai, *Angew. Chem. Int. Ed.* **2023**, 62, e202217807.
- [3] K. Sakai, H. Ozawa, *Coord. Chem. Rev.* **2007**, 251, 2753-2766.



Photocatalytic degradation of nitrogen oxides (NO_x) in photoreactor with granulated regolith with TiO₂

Paulina Szoldra⁽¹⁾, Maksymilian Frąc⁽¹⁾, Waldemar Pichór⁽¹⁾

⁽¹⁾ AGH University of Krakow, Mickiewicza 30, 30-059 Krakow, Poland, szoldra@agh.edu.pl

Air purification in space bases is a key element in ensuring the safety and health of the crew in enclosed environments. In such bases, like the International Space Station (ISS), the air must be continuously monitored and processed to remove contaminants and maintain the proper atmospheric composition. Small amount of harmful substances, such as ammonia, formaldehyde, or nitrogen oxides, can appear in the air, deriving from construction materials, equipment, or human activities.

Due to the advanced air purification systems, space station crews can operate in a closed environment for extended periods, which is essential for long-duration space missions. Regolith granules coated with titanium dioxide (TiO₂) layers are a promising material for air purification in space bases.

The aim of the research was to develop a technology utilizing regolith as a carrier for photocatalytic (TiO₂) coatings for air purification in closed systems, such as space habitats. The work includes preparing regolith granules with a binder to ensure durable deposition of TiO₂ layers and designing an efficient bed for flow-through photoreactors.

A novel continuous flow photoreactor with TiO₂-coated granulated regolith beads was developed and applied for the degradation of nitrogen oxides (NO_x). An effective photocatalyst was obtained in the form of granulated regolith that are the carrier of the functional TiO₂ photocatalytic layer. The decomposition of NO_x in the presence of granulated regolith with TiO₂ thin films was studied under various UV light intensities (10 W/m², 15 W/m², 20 W/m²), humidities (30%, 50%, 70%), and gas flow rate (0.75 dm³/min, 1.0 dm³/min, 1.25 dm³/min).

Aknowlegments

This research was funded by the AGH University of Krakow program titled "Excellence initiative—research university"

Thermochromic circularly polarized luminescence for homochiral tetracopper(I) clusters

K. Takahara,¹ R. Murakami,¹ D. Suzuki,² Y. Imai,² Y. Ozawa,¹ T. Suzuki,³ M. Abe¹

¹Graduate School of Science, University of Hyogo; ²Graduate School of Science and Engineering, KINDAI University; ³Research Institute for Interdisciplinary Science, Okayama University. takahara@sci.u-hyogo.ac.jp

Cubane-like tetranuclear copper(I) iodide clusters are well-known to show a luminescent color variation owing to the dual emission accompanied by the change of external temperature or pressure. No examples of cubane-like tetranuclear copper(I) complexes originated from chiral pyridine-type ligands have been reported. Herein, we report on synthesis, crystallization, and thermochromism of solid-state circularly polarized luminescence for a new enantiomeric pair of complex (*R,R,R,R*)- and (*S,S,S,S*)-[Cu₄I₄(L)₄], where L stands for a chiral pyridine-type ligand (Figure 1).

The complexes were prepared and crystallized in toluene, and single-crystal X-ray diffraction analysis and solid-state emission spectroscopy were performed. In the crystal structure, 2-fold helical networks supported with intermolecular hydrogen bonds were observed. Temperature-dependent color change of emission and circularly polarized luminescence (CPL) was observed. In addition, as lowering the temperature, the compound passed through the point of an emission of complete molecular white-light.

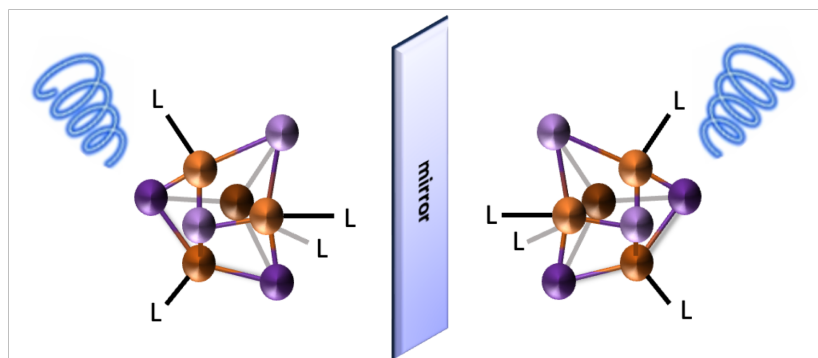


Figure 1. The expected molecular structures of enantiomer (*R,R,R,R*)- and (*S,S,S,S*)-[Cu₄I₄(L)₄] and the exhibition of circularly polarized luminescence (CPL).

Acknowledgements

This work was supported by JSPS KAKENHI, Grant No. JP24K23108, Hyogo Science and Technology Association, and the grant-in-aid for Young Researcher at University of Hyogo. In addition, the progress of this work was accelerated under the auspices of University of Hyogo Science and Technology Foundation.

References

- [1] H. Kitagawa, Y. Ozawa, K. Toriumi, *Chem. Commun.* **2010**, 46, 6302–6304, DOI:10.1039/c0cc01434f



Ultrafast Photophysical and Photochemical Dynamics of Hexahalobismuthates(III)

F. T. Gameda, V. Vorobyev, A. N. Tarnovsky

*Department of Chemistry and the Center for Photochemical Sciences, Bowling Green State
University, USA. E-mail: atarnov@bgsu.edu*

The excited-state relaxation dynamics and the photochemical reaction mechanisms in halide complexes of heavy ns^2 metal ions such as bismuth(III) halides, are of considerable interest to the conversion and storage of solar energy [1]. Many prospective bismuth-based halide perovskites, a low-toxicity and low-cost alternative to lead-based halide perovskites, adopt a MX_6 octahedral structural motif. Population of the low-energy triplet ligand-to-metal charge-transfer (LMCT) excited state of octahedral BiI_6^{3-} , hexaiodobismuthate(III), was proposed to be followed by the rapid electron-transfer-driven intramolecular formation of the metal-ligated diiodide bond between two adjacent former iodide ligands [2,3]. We have examined the very initial excited-state dynamics in this (BiI_6^{3-}) and related ($BiBr_6^{3-}$ and $BiCl_6^{3-}$) complexes by means of ultrafast transient absorption spectroscopy with dispersed, broadband probing. The results suggest that upon direct excitation with the visible light the BiI_6^{3-} system is promoted into the triply degenerate $^3T_{1u}$ Franck-Condon excited state, which corresponds to the Jahn-Teller symmetry-induced conical intersection. The complex decays out of the Franck-Condon region with a 46-fs time constant by distortion, removing the electronic degeneracy. The ultrafast decay of the $^3T_{1u}$ populates the $^3\pi$ LMCT state in a stepwise, time-dependent manner at 190 and 550 fs after the excitation event, indicating that the access of the $^3T_{1u}/^3\pi$ LMCT coupling region is controlled by the reaction mode with a ~ 360 fs vibrational period (frequency, $\sim 92\text{ cm}^{-1}$) in which tetragonal distortion and/or totally symmetric stretching are likely involved. First and second passages in the coupling region result in coherent population transfer of four- and one fifth fractions, respectively, of the total $\sim 80\%$ $^3\pi$ LMCT product state population. The remaining population ends up in the nearly degenerate 'trap' triplet metal-centered excited state. This population dynamics and branching in the coupling region is compared with that in $BiBr_6^{3-}$ and $BiCl_6^{3-}$, where LMCT excited states occur at higher energies with respect to that of the ground electronic state.

References

- [1] L. Troian-Gautier, M. D. Turlington, S. A. M. Wehlin, A. B. Maurer, M. D. Brady, W. B. Swords, G. J. Meyer, *Chem. Rev.* **2019**, 119, 4628–4683.
- [2] A. B. Maurer, K. Hu, G. J. Meyer, *J. Am. Chem. Soc.* **2017**, 139, 8066–8069.
- [3] F. T. Gameda, V. Vorobyev, A. N. Tarnovsky, *J. Phys. Chem. A* **2022**, 126, 1254–1267.

Photodriven charge accumulation on Cu(I) 4*H*-imidazolate complexes

L. Thomisch¹, M. Schulz²

¹Friedrich-Schiller-University Jena, luise.thomisch@uni-jena.de; ²Innovent Technology Development Jena

The photoactive Cu(I)4*H*-imidazolate complexes undergo a light-driven two-electron reduction in the presence of an electron and proton donor, such as DMT, BIH or BNAH. The resulting species is stable under inert conditions but releases the stored charges upon addition of an electron acceptor in a light independent process. The system therefore offers a temporal separation of the light and dark reaction. (Spectro)electrochemical investigations indicated a proton-coupled electron transfer pathway.^[1] However, the photoreduction mechanism as well as the structure of the reduced species have so far remained elusive. Systematic investigations with BIH revealed a stepwise single-electron reduction via a radical intermediate. Single crystal X-ray crystallographic studies as well as NMR studies in solution surprisingly revealed a rearrangement of the coordination environment of the metal centre from the initial tetrahedral to a trigonal geometry. The excess charges are compensated via protonation of both exocyclic nitrogen atoms. The presence of protons potentially renders the reduced Cu(I)4*H*-imidazolate complexes hydride/ hydrogen atom donors.

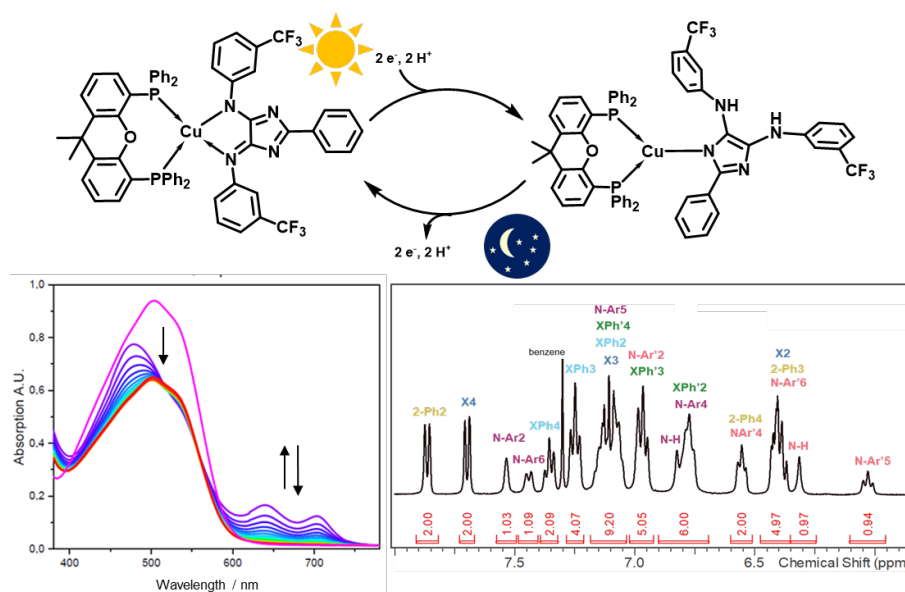


Figure 44. General scheme of the reaction system (top); UV-Vis absorption spectra recorded during the photoreduction of Cu(I)-4H-imidazolate complexes (bottom, left); ¹H-NMR spectrum of the photoreduction product (bottom, right).

Aknowlegments

Thanks to the Transregional Collaborative Research Center TRR234 - CataLight

References

- [1] M. Schulz, N. Hagmeyer, F. Wehmeyer, G. Lowe, M. Rosenkranz, B. Seidler, A. Popov, C. Streb, J. G. Vos, B. Dietzek, *J. Am. Chem. Soc.* **2020**, *142*, 15722–15728

Doublet charge transfer emission of Ce(III) complex with β -diketonate ligand

T. Tomikawa^a, K. Saita^b, Y. Ono^{c,d}, T. Akama^e, M. Wang^f, S. Shoji^g, M. Kobayashi^{c,e}, K. Fushimi^f, T. Nakanishi^h, T. Taketsugu^{c,e}, Y. Hasegawa^{e,f} and Y. Kitagawa^{e,f}

a. Grad. Sch. Chem. Sci. Eng., Hokkaido Univ., Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan.

b. Grad. Sch. Nanobio., Yokohama City Univ., 22-2 Seto, Kanazawa-ku, Yokohama 236-0027, Japan.

c. Fac. Sci., Hokkaido Univ., Kita 10, Nishi 8, Kita-ku, Sapporo 060-0810, Japan.

d. Institute for Quantum Chemical Exploration, Kohnan 1-9-36, Minato-ku, Tokyo 108-0075, Japan.

e. WPI-ICReDD, Hokkaido University, Kita 21, Nishi 10, Kita-ku, Sapporo 001-0021, Japan.

f. Fac. Eng., Hokkaido Univ., Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan.

g. Fac. Eng., Nara Women's Univ., Kitaouya-Nishimachi, Nara 630-8506, Japan.

h. National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

E-mail: lelysblanc871@eis.hokudai.ac.jp

Open-shell luminophores with character doublet-doublet transitions are attractive photofunctional materials for use in organic light-emitting diodes (OLED) and optical sensors¹. Among them, luminescent trivalent cerium (Ce(III)) complexes, which have a single unpaired 4f-electron, become promising candidates as blue and green luminophores². Previously, Ce(III) complex with strong-field ligands provides efficient doublet emission based on stabilized 4f-5d excited state³. The demand of strong ligand field restricts flexibility of design for organic ligands.

In this study, we explore an alternative emission mechanism based on doublet charge-transfer (CT) emission from the ligand π^* - to Ce(III) 4f-orbitals (Figure 1) for broadening the design space for creating luminescent Ce(III) complexes. The CT excited state forms below the 4f-5d excited states using strong electron-acceptor ligand, resulting in observable CT emission. To demonstrate our concept, we synthesized Ce(III) complexes containing hexafluoroacetylacetonates (hfa) as strong electron-acceptor ligands (**Ce(III)-hfa-L**; Fig. 2) and compared their photophysical properties with trivalent gadolinium (Gd(III)) and tetravalent cerium (Ce(IV)) complexes (**Gd(III)-hfa-L** and **Ce(IV)-hfa**; Figure 2). Time-resolved emission analyses revealed that **Ce(III)-hfa-L** exhibited characteristic emission band at around 520 nm. TD-DFT calculation suggested that this emission band is attributed to CT transition. In addition, nonradiative deactivation pathway analyses from CT excited state indicated that rigid organic ligands are critical for enhancing doublet CT emission in Ce(III) complexes.

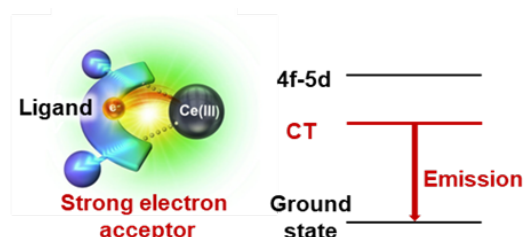


Figure 45. Conceptual illustration of charge transfer emission from π^* - to 4f orbitals.

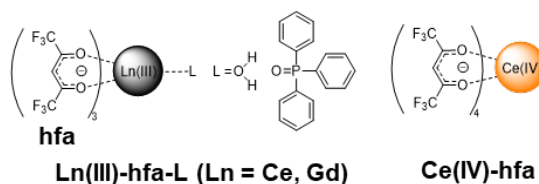


Figure 2. Molecular structures of **Ln(III)-hfa-L** and **Ce(IV)-hfa**.

References

- [1] R. Matsuoka et al., *Coord. Chem. Rev.* **2022**, 467 (15), 214616
- [2] S. Gao et al., *Chem. Soc. Rev.* **2023**, 52 (9), 2875
- [3] L. Wang et al., *Light Sci. Appl.* **2020**, 9, 157

Synthesis, Characterization and Study of a novel Fe(II)-complex as potential photosensitizer

S. Torres Gonzalez^{1*}, M. Bauer¹

¹Faculty of Sciences, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany

simon.torres.gonzalez@uni-paderborn.de

The search for alternatives replacing *Noble Metals* in the field of photochemistry has caught great attention in the last few years. Specifically, a lot of interest relies on Iron, since it is inexpensive and more ecologically benign. Indeed, many strategies have been evaluated to improve the lifetime of emerging Fe-catalysts^[1]. Leis *et al.* synthesized a photoreactive Fe(II)-complex based on a 2-phenylphenanthroline ligand (**Fig. 1A**)^[2], which showed the population of a ³MLCT excited state with a lifetime of $\tau = 2.4$ ns. Additionally, the sensitizing capability of the complex was proven to mimic the photochemistry of Ru- and Ir-based sensitizers, becoming a promising prospect for establishing 3d⁶ metals in photocatalysis.

In this work, we present a novel Fe(II)-complex based on 4,7-Diphenyl-1,10-phenanthroline (**Fig. 1B**). The incorporation of phenyl moieties is expected to either serve as a reservoir for an excited state population^[3] or to produce an antenna effect^[4]. Further incorporation of electron-donor and electron-withdrawing groups in *p*-position of the phenyl rings will allow us to gain depth knowledge on the influence in the electronic properties, coordinative and structural stability of the complexes.

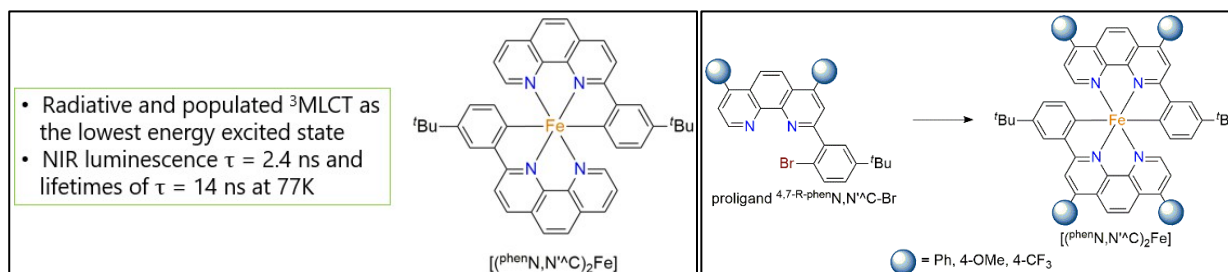


Figure 1. (A) Photoreactive Fe(II)-complex reported by Leis *et. al.* **(B)** Fe(II)-complexes presented in this work.

Acknowledgments

Thanks to German Research Foundation (Deutsche Forschungsgemeinschaft).

References

- [1] P. Dierks, *et. al. Inorg. Chem. Front.* **2022**, 9, 206-220.
- [2] W. Leis, *et. al. J. Am. Chem. Soc.* **2022**, 144, 1169-1173.
- [3] A. Francés-Monerris, *et. al. Theor. Chem. Acc.* **2019**, 138, 13522.
- [4] P. Dierks, *et. al. Inorg. Chem.* **2020**, 59, 14746-14761.

Three-Coordinate Cu(I) Complexes of Anionic N-Heterocyclic Carbenes

S. Tschierlei^{1,*}

¹ Department of Energy Conversion, Institute of Physical and Theoretical Chemistry, Technische Universität Braunschweig, Rebenring 31, Braunschweig, Germany, s.tschierlei@tu-bs.de

² Institute of Inorganic and Analytical Chemistry, Technische Universität Braunschweig, Hagenring 30, 38106 Braunschweig, Germany.

Three-coordinate Cu(I) complexes have garnered significant interest due to their unique photophysical properties, yet their potential as photosensitizers remains underexplored.^[1,2] Here, we present a new class of neutral three-coordinate Cu(I) complexes featuring an anionic N-heterocyclic carbene ligand with a weakly coordinating tris(pentafluorophenyl)-borate moiety (WCA-NHC, see Figure 1).^[3,4] This design enhances solution stability and photophysical performance. A combination of steady-state and time-resolved spectroscopy, electrochemical analysis and quantum chemical calculations reveals that these complexes exhibit strong metal-to-ligand charge transfer (MLCT) absorption, thermally activated delayed fluorescence (TADF) and extended excited-state lifetimes (up to 8.6 μ s). Their high excited-state energies ($\approx$ 2.7 eV) enable efficient triplet energy transfer, as demonstrated in the norbornadiene-to-quadricyclane photoisomerization (see Figure 1). Additionally, temperature-dependent emission studies confirm a pseudo-Jahn-Teller distortion in the excited state, highlighting the role of structural relaxation in tuning emission properties. The long-lived excited states and high quantum yields (up to 11.5%) facilitate efficient energy transfer, making these complexes promising candidates for photoredox catalysis. These findings expand the applicability of three-coordinate Cu(I) photosensitizers and demonstrates that strategic ligand design can overcome previous limitations.

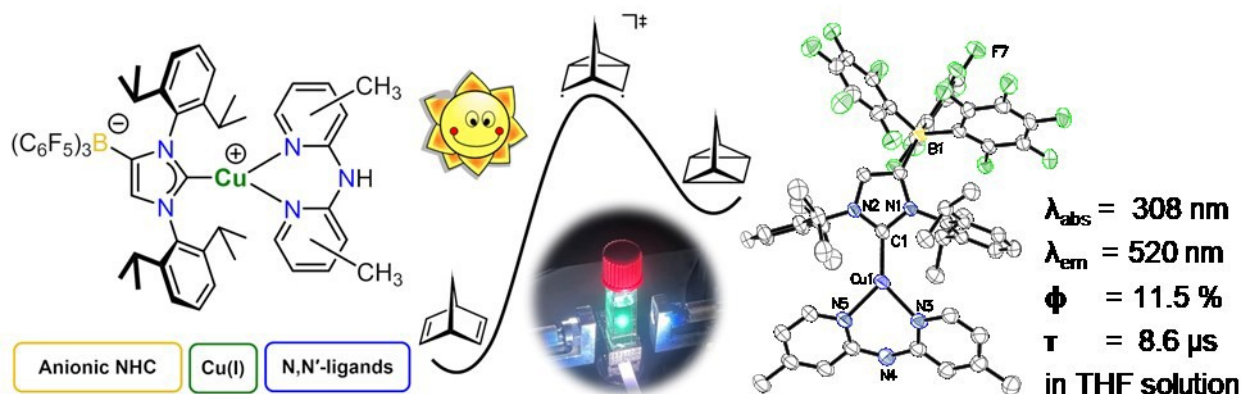


Figure 1. General structure of neutral [(WCA-NHC)Cu(N'N)] complexes (left) and a representative X-ray structure of complex C4 along with its main photophysical properties (right).

References

- [1] R. Marion, F. Sguerra, F. Di Meo, E. Sauvageot, J.-F. Lohier, R. Daniellou, J.-L. Renaud, M. Linares, M. Hamel, S. Gaillard, *Inorg. Chem.* **2014**, 53, 17, 9181-9191.
- [2] P. Schmeinck, D. Sretenović, J. Guhl, R. Kühnemuth, C. A. M. Seidel, C. M. Marian, M. Suta, C. Ganter, *Eur. J. Inorg. Chem.* **2023**, 26, e202300416.
- [3] S. Kronig, C. G. Daniliuc, P. G. Jones, M. Tamm, *Angew. Chem. Int. Ed.* **2012**, 51, 3240-3244.
- [4] L. P. Ho, M. Tamm, *Chem. Eur. J.* **2022**, 28, e202200530.

Synthesis of highly luminescent, isomorphous Ag^I and Cu^I complexes; Effect of halogenido ligands on emission and relaxation

T. Kuwahara, H. Ohtsu, K. Tsuge

Graduate School of Science and Engineering, University of Toyama, Toyama 930-8555, Japan
tsuge@sci.u-toyama.ac.jp

Various Cu^I halogenido complexes with interesting luminescence properties have been reported, whereas luminescent Ag^I halogenido complexes are less than the Cu^I complexes, and the Ag^I complexes showing MLCT emissions are more limited because Ag 4d-orbitals are more stable than Cu 3d-orbitals.¹ We have prepared Ag^I halogenido complexes [Ag₂X₂(PPh₃)₂(R-pyz)]_n using pyrazine and methylpyrazine with low-lying π* orbitals, which lead to the CT-type emission.² Here, we report the related Ag^I complexes [Ag₂X₂(PPh₃)₂(Me₂pyz)]_n (Me₂pyz: 2,5-dimethylpyrazine; X: I, Br, Cl) together with the Cu^I congeners [Cu₂X₂(PPh₃)₂(Me₂pyz)]_n (X = I, Br). Both the Ag^I and Cu^I complexes showed the CT-type emission and formed isomorphous single crystals, which unambiguously offset the structural effect to clarify the effect of metal and halogenido ligands on luminescence properties.

All the complexes showed thermally activated delayed fluorescence from the CT states in the visible region (Figure 1a). In case of the Ag^I complexes, the emission maxima of iodido and bromido complexes were similar (Δ: 14 nm) whereas those were largely different (Δ: 55 nm) in case of the Cu^I complexes. We evaluated the energy of S₁ and T₁ states experimentally using excitation and emission spectra to find that relaxation in ESs were more remarkable in Ag^I complexes than in Cu^I complexes and that the electronic effect of halogenido ligands was comparable to the effect of relaxation in emissive ESs (Figure 1b).

Similar energy emissions among Ag^I or Cu^I congeners with different halogenido ligands are frequently used to judge the effect of the halogenido ligands on the emissive ESs. However, the results of the Me₂pyz complexes with isomorphous structures reveal that relaxation significantly affects the emission energy for Ag^I and Cu^I complexes.

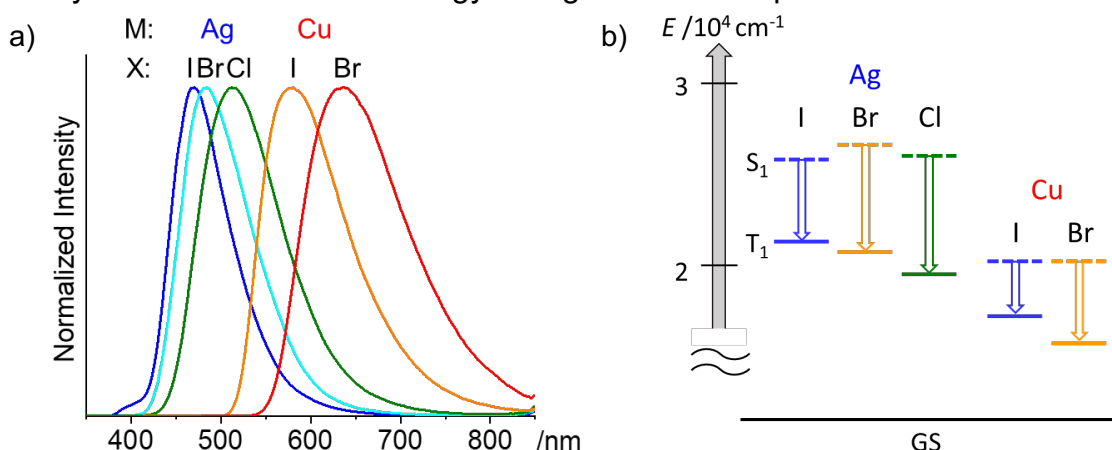


Figure 46. Emission spectra of [Cu₂X₂(PPh₃)₂(Me₂pyz)]_n (a) and the energy diagram (b).

References

- [1] H. Takeda, A. Kobayashi, K. Tsuge, *Coord. Chem.Rev.* **2022**, 470, 214700.
- [2] T. Kuwahara, H. Ohtsu, K. Tsuge, *Inorg. Chem.* **2021**, 60, 1299-1304.
- [3] T. Kuwahara, H. Ohtsu, K. Tsuge, *Inorg. Chem.* **2024**, 63, 8120-8130.

Heteroleptic copper (I) complexes as suitable photosensitizers for new photo-induced organic transformations

F. Urbain^a, A. Janssens^{a,b}, A. Müllender^{a,b}, G. Evano^b, C. Moucheron^a

^a*Organic Chemistry and Photochemistry, Université libre de Bruxelles (U.L.B), CP 160/08, 50 Av. F.D. Roosevelt 1050 Bruxelles, Belgium. Florent.Urbain@ulb.be*

^b*Laboratory of Organic Chemistry, Université libre de Bruxelles (U.L.B), CP 160/08, 50 Av. F.D. Roosevelt 1050 Bruxelles, Belgium.*

Photoactive copper (I) complexes appear to be an attractive alternative to noble metal complexes, which are the most studied to date, especially complexes based on ruthenium (II) and iridium (III).¹ As a result, part of the research in photochemistry has gradually focused on the development of heteroleptic copper (I) complexes. Among the important examples, heteroleptic bis-diimine bis-diphosphine complexes $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ are currently the most efficient. These complexes show interesting photophysical as well as electrochemical properties, such as long excited-state lifetimes, high luminescence quantum yields and flexible redox properties, all of which can be tuned *via* the nature of the ligands.² These numerous characteristics allow to consider the use of such complexes as suitable photosensitizers for the development of various photo-induced organic transformations.³ Concomitantly, the recent and thorough study of a large number of $[\text{Cu}(\text{N}^{\wedge}\text{N})(\text{P}^{\wedge}\text{P})]^+$ complexes has allowed to establish a fine relationship between the structure of the ligands and the properties of the corresponding complex, and thus to choose ligands with appropriate characteristics to obtain a complex with the desired properties. Using this information, new families of heteroleptic copper (I) complexes are emerging,⁴ which may also exhibit suitable properties for photoredox catalysis. We will present some examples of organic transformations relying on copper-based photocatalysts such as the formation of C-C bond or C-H bond⁵ using $[\text{Cu}(\text{bcp})(\text{DPEPhos})]\text{PF}_6$.

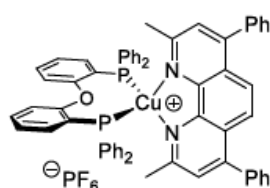


Figure 47. Structure of the $[\text{Cu}(\text{bcp})(\text{DPEPhos})]\text{PF}_6$ complex

References

- ¹Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C., *Chem. Rev.*, **2013**, 113, 5322–5363.
- ²Zhang, Y.; Schulz, M.; Wächter, M.; Karnahl, M.; Dietzek, B., *Coord. Chem. Rev.* **2018**, 356, 127–146.
- ³Jacob, C.; Baguia, H.; Dubart, A.; Oger, S.; Thilmany, P.; Beaudelot, J.; Deldaele, C.; Peruško, S.; Landrain, Y.; Michelet, B.; Neale, S.; Romero, E.; Moucheron, C.; Van Speybroeck, V.; Theunissen, C.; Evano, G., *Nat. Commun.* **2022**, 13, 560.
- ⁴Beaudelot, J.; Oger, S.; Peruško, S.; Phan, T.-A.; Teunens, T.; Moucheron, C.; Evano, G., *Chem. Rev.* **2022**, 122, 16365–16609.
- ⁵Michelet, B.; Deldaele, C.; Kajouj, S.; Moucheron, C.; Evano, G., *Org. Lett.* **2017**, 19, 3576–3579.



***in cellulo* investigation of the excited state dynamics of biologically relevant photoactive compounds**

A. Valavalkar,^{1,2} A. Chettri,^{1,2} T. Yang,^{1,2} H. Cole,³ G. Shi,³ C. Cameron,³ U. Pischel,⁴ S. McFarland,³ B. Dietzek-Ivanšić^{1,2,5}

¹*Institute of Physical Chemistry, Friedrich Schiller University Jena, Lessingstrasse 4, 07743 Jena, Germany*

²*Leibniz Institute of Photonic Technology (Leibniz-IPHT), Albert-Einstein-Strasse 9, 07745 Jena, Germany abha.valavalkar@leibniz-ipht.de*

³*The University of Texas at Arlington, 700 Planetarium Place, Texas 76019-0065, USA*

⁴*University of Huelva, Campus de El Carmen s/n, 21071 Huelva*

⁵*Current Address: Leibniz Institute of Surface Modification, Permoserstraße 15, 04318 Leipzig*

Biologically relevant chromophores are ubiquitously employed in sensing, imaging, and therapy. Certain organic fluorophores as well as metal coordinated compounds find application as photoactive functional colorants. They exhibit photobiological activity due to their tunable excited state and electron or energy transfer processes.^[1] Ruthenium coordinated complexes are used as photosensitisers in photodynamic therapy, with TLD1433 to be the first Ruthenium based photo drug to enter clinical trials.^[2]

While the target site of application for these small molecule functional colorants is the human body, there exists a gap in current state of the art, in elucidating the photophysical processes that they undergo in biologically relevant surrounding. A part of this study involves looking at the influence of rational design on ultrafast processes. The next step is to measure the photophysical properties of these dyes and relevant functional molecules in live human cells and to establish a structure-function relationship. We report *in cellulo* kinetics of borylated arylisoquinolines with different terminal groups.^[3] We also investigate Ruthenium based photosensitisers in live human cancer cells (MCF7)^[4] to further understand the therapeutic action they deliver in an environment that closely resembles the target site of application. In addition to the characterisation of the excited stated dynamics, we believe this study will further aid rational design of functional molecules, which could be tailored with specificity to a cellular microenvironment.

Acknowledgments

AV would like to thank SFB1278 PolyTarget for funding.

References

- [1] J. Li, T. Chen, *Coordination Chemistry Reviews* **2020**, 418, 213355.
- [2] A. Chettri, J. A. Roque, K. R. Schneider, H. D. Cole, C. G. Cameron, S. A. McFarland, B. Dietzek, *ChemPhotoChem* **2021**, 5, 421–425.
- [3] T. Yang, A. Valavalkar, A. Romero-Arenas, A. Dasgupta, P. Then, A. Chettri, C. Eggeling, A. Ros, U. Pischel, B. Dietzek-Ivansic, *Chemistry (Weinheim an der Bergstrasse, Germany)* **2023**, 29, e202203468.
- [4] A. Chettri, T. Yang, H. D. Cole, G. Shi, C. G. Cameron, S. A. McFarland, B. Dietzek-Ivanšić, *Angewandte Chemie International Edition in English* **2023**, 62, e202301452.



Identification of Metal-Centered Excited States Using Ultrafast Soft X-ray Spectroscopy

N. Ghodrati,¹ L. Adriano,¹ S. Berry,² Y.-P. Chang,¹ S. Eckert,³ A. Föhlisch,^{3,4} M. Fondell,³
N. Huse,⁵ L. Le Guyader,¹ J. Penner-Hahn,² A. Scherz,¹ R. Sension,² B. E. Van Kuiken¹

¹European XFEL, 22869 Schenefeld, Germany. ²University of Michigan, Ann Arbor, MI 44109, USA.

³Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany.

⁴Institut für Physik und Astronomie, Universität Potsdam, 14476 Potsdam, Germany. ⁵University of Hamburg, 22761 Hamburg, Germany. benjamin.van.kuiken@xfel.eu

Directly utilizing the metal-centered (MC) excited states of coordination complexes for photochemical applications has recently gained much interest.¹⁻⁴ In this contribution, the state-selectivity of soft X-ray L-edge ($2p \rightarrow 3d$) spectroscopy for MC excited states of 3d transition metal complexes will be presented for probing these states on both the picosecond (synchrotron) and femtosecond (XFEL) timescales.

First, this state-selectivity will be demonstrated in the limiting case of a spin-flip excited state of Cr(III). The lowest-lying doublet excited state of pseudo-octahedral Cr(III) complexes possess the same t_{2g}^3 orbital occupation as the ground state, and these states have nested potential energy surfaces. Synchrotron-based transient Cr L-edge XAS with ~ 70 ps time-resolution is used to show that there is a clear signature of the 2E spin-flip state that forms in $\text{Cr}(\text{acac})_3$ following LMCT excitation.⁵ Ligand field theory and *ab initio* quantum chemistry calculations demonstrate why this state selectivity exists for L-edge spectroscopy despite the similarities between the ground and excited state geometry and electronic structure.

Next, we will report a new high-sensitivity setup for fs time-resolved soft X-ray studies of coordination complexes in solution at European XFEL. Previous soft X-ray absorption experiments at FELs have been limited to high-concentration samples (> 100 mM), but this new setup exhibits ~ 20 μOD sensitivity enabling studies on sub-10 mM samples of coordination complexes. The setup is validated by observing the excited state cascade in a 7 mM sample of cyanocobalamin with ~ 100 fs time-resolution.⁶ Furthermore, the L-edge

XAS is used to show that the S_1 excited state possesses significant MC ($d_{\pi} \rightarrow d_{z^2}$) character contrasting with previous studies that predicted an LMCT excited state.⁷

References

- [1] Förster and K. Heinze, *Chem. Phys. Rev.* **2022**, 3, 041302.
- [2] Bürgin, Glaser and Wenger, *J. Am. Chem. Soc.*, **2022**, 144, 14181–14194.
- [3] Ting, Garakyaraghi, Taliaferro, Shields, Scholes, Castellano and Doyle, *J. Am. Chem. Soc.*, **2020**, 142, 5800–5810.
- [4] Alowakennu, Ghosh and McCusker, *J. Am. Chem. Soc.*, **2023**, 145, 20786–20791.
- [5] Ghodrati, Eckert, Fondell, Scherz, Föhlisch, Van Kuiken, *Chem. Sci.* **2025**, <https://doi.org/10.1039/D4SC07625G>
- [6] Ghodrati, Van Kuiken, *et al. in preparation*.
- [7] Lodowski, Jaworska, Andruniow, Garabato, and Kozłowski. *Phys. Chem. Chem. Phys.*, **2014**, 16, 18675



Key factors influencing cage escape in photoinduced electron transfer.

A. K. Vega Salgado¹ and L. Troian-Gautier^{1,2}

¹UCLouvain, Institut de la Matière Condensée et des Nanosciences (IMCN), Molecular Chemistry, Materials and Catalysis (MOST), Place Louis Pasteur 1/L4.01.02, B-1348 Louvain-la-Neuve, Belgium

^{1,2}Wel Research Institute, Avenue Pasteur 6, 1300 Wavre, Belgium
ana.vegasalgado@uclouvain.be

The interaction between an excited-state photosensitizer and a quencher within an encounter complex can give rise to bimolecular electron transfer, leading to the formation of the corresponding geminate radical pair. The cage escape yield, i.e. the separation of the geminate radical pair is key for many light induced transformations. Many factors have been proposed to affect the cage escape process, such as the spin, the driving force for forward or reverse electron transfer, viscosity, etc [1,2]. One of the parameters that has been proposed to influence the cage escape is the driving force for forward or reverse electron transfer between a photosensitizer and a quencher [2,3,4].

In here, we investigated the effect of spin and driving force for forward and reverse electron transfer using 8 Ruthenium and 4 Osmium photosensitizers and using phenothiazine and tris(4-methoxyphenyl)amine as electron donors. Quenching rate constants, determined by steady-state and time-resolved spectroscopic techniques, ranged from 9×10^7 to $1.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile. The cage escape yields were determined through comparative actinometry method, using changes in molar absorption coefficients that were determined by spectroelectrochemistry. Clear trends with driving force as well a spin state were observed, where cage escape yields were larger for Ru(II) than Os(II) photosensitizers and were also larger when the driving force for geminate charge recombination was located furthest in the Marcus inverted region.

Aknowlegments

This work was supported by the “Action de Recherche Concertée” through the project “UNCAGED” under grant no. 23/28-135.

References

- [1] A. Ripak, A.K. Vega Salgado, D. Valverde, S. Cristofaro, O.Y. de Gary A, B. Elias, and L. Troian-Gautier. Journal of the American Chemical Society, (2024). 146(32), 22818-22828.
- [2] M.J. Goodwin, J.C. Dickenson, A. Ripak, A.M. Deetz, J.S. McCarthy, G.J. Meyer, and L. Troian-Gautier, Chemical Reviews 2024 124 (11), 7379-7464
- [3] S. De Kreijger, F. Glaser and L. Troian-Gautier, Chem Catalysis, 2024, vol.16, 101110.
- [4] A. Ripak, S. De Kreijger, R.N. Sampaio, C.A. Vincent, É. Cauët, I. Jabin, U.K. Tambar, B. Elias, L. Troian-Gautier, Chem Catalysis, 2023, vol.3, 100490.

NHC-GOLD(I)-AMIDO COMPLEXES FOR PHOTOCATALYSIS

V. Voloshkin,^b M. Villa,^a E. Martynova,^b M- Beliš,^b K. Van Hecke,^b P. Ceroni,^a S. Nolan^b

^a Department of Chemistry "Giacomo Ciamician", University of Bologna, Via Selmi, 2, 40126 Bologna, Italy. Email: marco.villa11@unibo.it

^b Department of Chemistry and Centre for Sustainable Chemistry Ghent University, Krijgslaan 281, S-3, 9000 Ghent (Belgium).

Photoactive transition metal complexes are widely used in photocatalysis. In the last years, several reports of highly luminescent, two-coordinate, d10 metal complexes of coinage metals (Cu, Ag, Au) are reported [1]. The development of efficient and operationally simple synthetic routes to carbene-metal-amido complexes (CMA) and binuclear gold(I)-amido complexes bearing aromatic/aliphatic-bridges are reported [2]. This family of complexes was prepared under mild and sustainable conditions, resulting in moderate to excellent yields of the targeted metal complexes.

Photophysical studies on CMA complexes reveal that the presence of gold (Au) plays a crucial role in extending the excited-state lifetime to hundreds of microseconds. As a result, these CMAs exhibit strong potential as photocatalysts, demonstrating high catalytic efficiency as sensitizer for the [2+2]-cycloaddition of coumarins and unactivated alkenes.

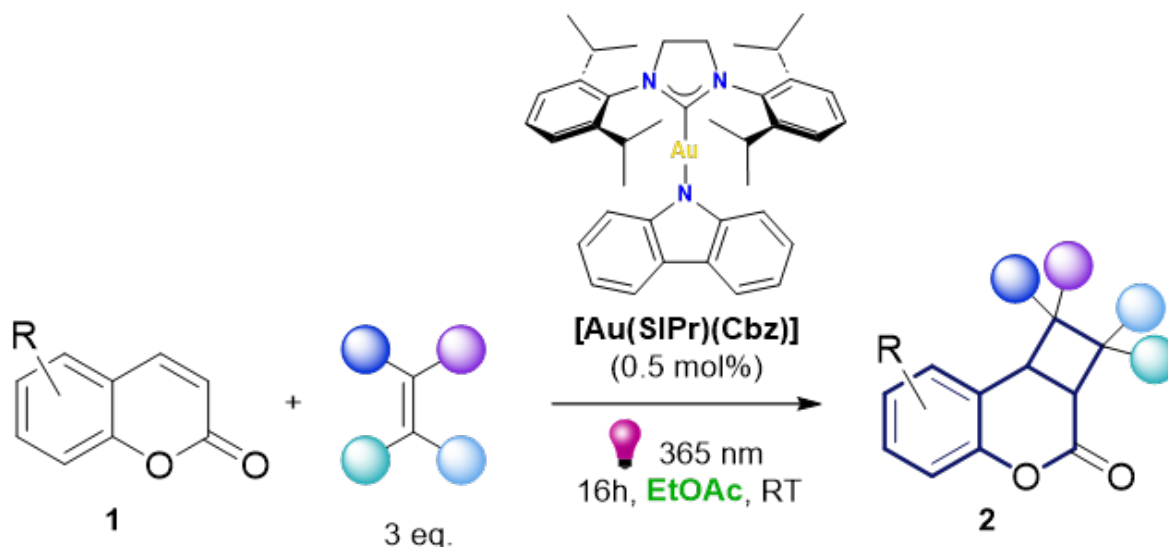


Figure 48. Scheme of the coumarin [2+2] cycloaddition sensitized by the NHC-Gold(I)-Amido complex

Acknowledgments

M.V. acknowledge the project SUN-SPOT funded by the MIUR Progetti di Ricerca di Rilevante Interesse Nazionale (PRIN) Bando 2022 - grant 2022JA3PSC

References

- [1] F.-H. Yu, X.-F. Song, G.-H. Liu, X. Chang, K. Li, Y. Wang, G. Cui, and Y. Chen, *Chem. Eur. J.* **2022**, e20220243
- [2] N. V. Tzouras, E. A. Martynova, X. Ma, T. Scattolin, B. Hupp, H. Busen, M. Saab, Z. Zhang, L. Falivene, G. Pisanò, K. Van Hecke, L. Cavallo, C. S. J. Cazin, A. Steffen, S. P. Nolan, *Chem. Eur. J.* **2021**, 27, 11904

Long-lived terphenyl radical anion super-reductant for photocatalysis formed *via* upconversion

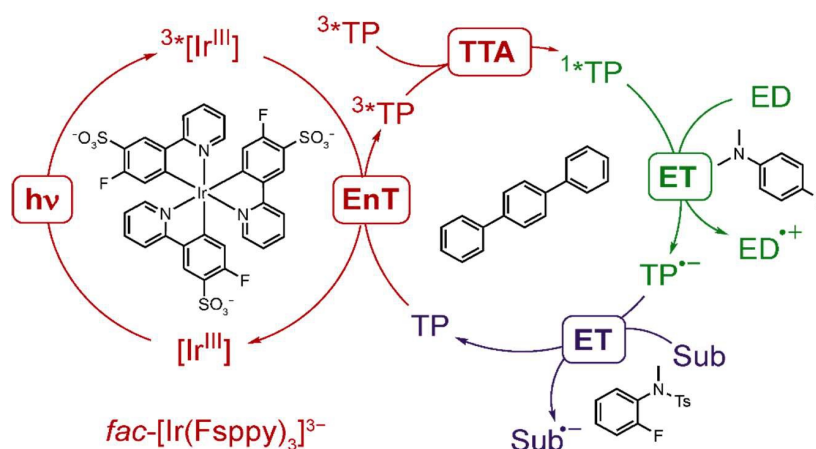
Dorothee S. Wagner¹, Felix Glaser^{1,2}, Daniel Häussinger¹, Oliver S. Wenger¹

¹ Department of Chemistry, University of Basel, St. Johannis-Ring 19, 4056, Basel, Switzerland

² Present address: Institut de la Matière Condensée et des Nanosciences (IMCN), Université catholique de Louvain, Place Louis Pasteur 1, 1348 Louvain-la-Neuve, Belgium

In biphotonic excitation, the energy of two photons with longer wavelengths is combined to yield higher energy intermediates. One approach using this concept is the conPET mechanism, where a photocatalytically generated radical anion is excited to form a highly reducing species. Typically, these excited radical anions are very short lived.^[1] Another method for biphotonic excitation is sensitization-initiated electron transfer via upconversion employed in this work.^[2] Here, this process generates a terphenyl radical anion with a very long lifetime and a reduction potential comparable to many excited radical anions featuring far shorter lifetimes.

The investigated mechanism involves a triplet-triplet energy transfer (TTET) from an iridium(III) photosensitizer excited by blue light (450 nm) to a *p*-terphenyl annihilator. The quenching of the iridium(III) excited-state was studied in a Stern-Volmer analysis, while the excited state absorption of the triplet state of *p*-terphenyl was observed by transient UV-Vis absorption (TA) spectroscopy. Triplet-excited *p*-terphenyl then undergoes triplet-triplet annihilation upconversion (TTA-UC). The lowest excited singlet state of *p*-terphenyl, formed via upconversion, is then reductively quenched by a sacrificial electron donor. The resulting radical anion species was observed by TA spectroscopy. Due to a lifetime in the microsecond range and a reduction potential of -2.5 V vs SCE, this radical anion species is able to reduce CO₂ and other inert substrates for thermodynamically demanding reactions such as dehalogenations or detosylations. The kinetics of the reactions show clear evidence for a fast biphotonic reaction mechanism.



References

- [1] B. Pfund, D. Gejsnæs-Schaad, B. Lazarevski, O. S. Wenger. *Nat. Commun.* **2024**, 15, 4738.
- [2] F. Glaser, C. Kerzig, O. S. Wenger. *Chem. Sci.* **2021**, 12, 9922.

Luminescent Cyclometalated Iridium(III) Polypyridine Complexes Modified with Dendritic Guanidinium Moieties as Molecular Glues for Combined Chemo-photodynamic Therapy

J.-W. Wang,^a K. Okuro,^{*b} and K. K.-W. Lo.^{*a}

^aDepartment of Chemistry, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, P. R. China. Email: jwang884-c@my.cityu.edu.hk.

^bState Key Laboratory of Synthetic Chemistry and Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China.

Over the last decade, transition metal complexes have garnered considerable attention for their applications in diagnostics and therapeutics, owing to their excellent photophysical and photochemical properties. In this work, three novel cyclometalated iridium(III) complexes tethered to multiple guanidinium moieties were designed as luminescent molecular glues. Protein-binding studies showed that the complexes exhibited high binding affinity toward bovine serum albumin (BSA). One of the complexes was utilized to modify glutathione (GSH)-responsive, doxorubicin (DOX)-loaded BSA nanoparticles (DOX/^{ss}BNPs). Notably, the functionalization of DOX/^{ss}BNPs with the complex changed the surface charge from negative to positive. Upon incubation with GSH, the size of Ir-DOX/^{ss}BNPs decreased significantly, attributable to the efficient release of DOX. The positively charged Ir-DOX/^{ss}BNPs showed increased cellular uptake in HeLa cells, which was further demonstrated to be important to their performance in combined chemo-photodynamic therapy. The results illustrated that these luminescent iridium(III)-based molecular glues can be used for intracellular drug delivery and combined chemo-photodynamic therapy.

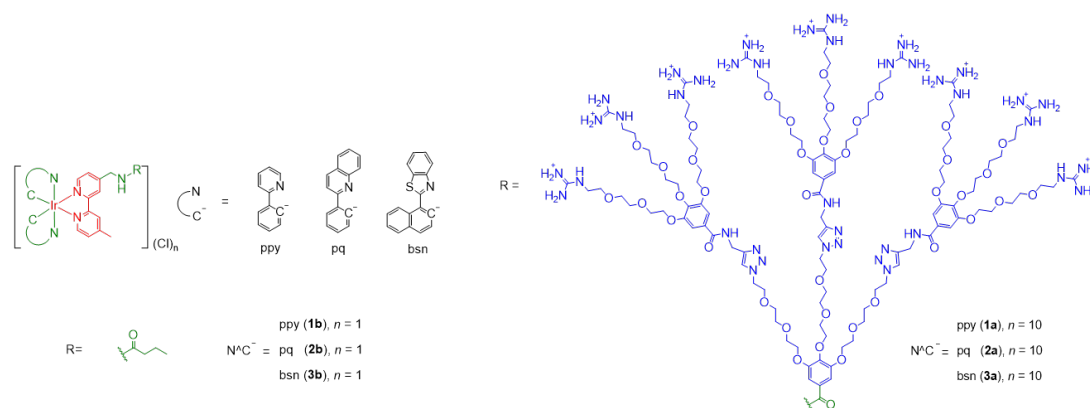


Figure 49. Structures of complexes **1a – 3a** and **1b – 3b**.

Aknowlegments

We thank the Hong Kong Research Grants Council (Project No. CityU 11301121, CityU 11317022, CityU 11309423, and C7075-21GF) and the Hong Kong Research Grants Council and National Natural Science Foundation of China (Project No. N_CityU104/21) for financial support.

References

- [1] K. K.-W. Lo. *Acc. Chem. Res.* **2020**, 53, 32 – 44.
- [2] N. B. Hentzen; R. Mogaki; S. Otake; K. Okuro; T. Aida. *J. Am. Chem. Soc.* **2020**, 142, 8080 – 8084.

Iron(III) Complexes with Luminescence Lifetimes of up to 100 Nanoseconds

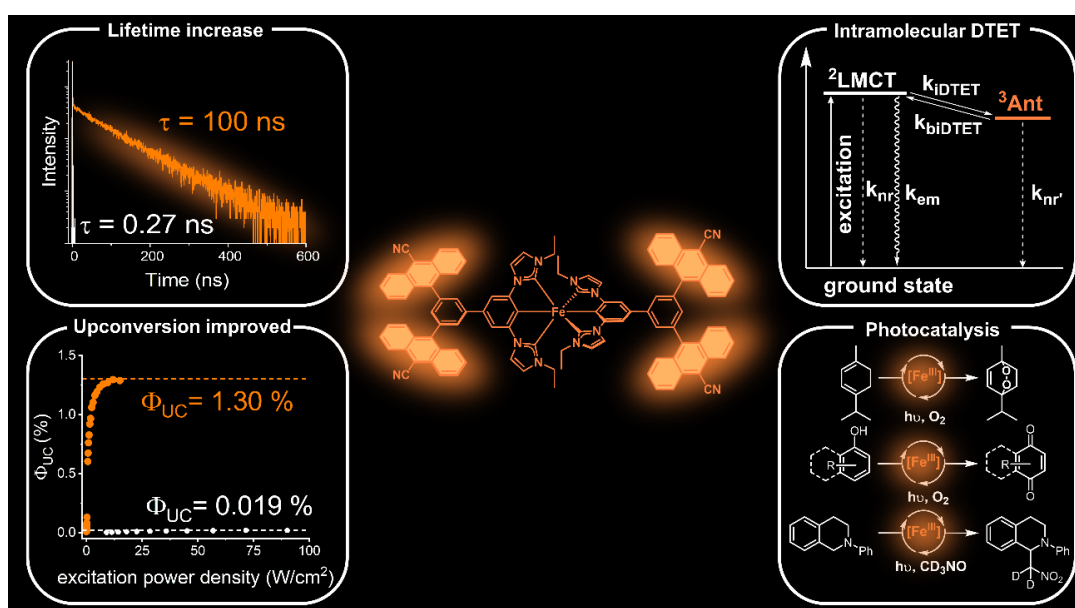
J. Wellauer,¹ B. Pfund,¹ I. Becker,² F. Meyer,² A. Prescimone,¹ and O. S. Wenger^{1,*}

¹Department of Chemistry, University of Basel, CH-4056 Basel. E-mail: joel.wellauer@unibas.ch

²University of Göttingen, Institute of Inorganic Chemistry, D-37077 Göttingen

Although photophysical research has uncovered about a dozen luminescent iron(III) complexes so far, most display LMCT excited-state lifetimes limited to the subnanosecond range, usually too short lived to enable efficient bimolecular photochemical reactions.^{1,2}

In this work, we introduce a new series of iron(III) complexes with excited-state lifetimes ranging from 1 to 100 nanoseconds. Key to this advancement was the use of anthracene chromophores, which serve as triplet energy reservoirs to slow down the decay of the ²LMCT state via reversible intramolecular doublet–triplet energy transfer (DTET). This strategy extended the excited-state lifetime by roughly 350-fold compared to the parent complex, reaching a record lifetime of 100 nanoseconds for the longest lived complex.³ As a result, red-to-blue photon upconversion efficiency improved by a factor of 70, and benchmark photoredox reactions proceeded with significantly higher yields. Altogether, these findings mark a step forward in designing iron-based systems with photophysical and photochemical properties that can compete with those of noble metal complexes.



Acknowledgments

O.S.W. acknowledges funding by the Swiss National Science Foundation (grant number 200020_207329).

References

- [1] F. Glaser, A. Aydogan, B. Elias, L. Troian-Gautier, *Coord. Chem. Rev.* **2024**, 500, 215522.
- [2] J. Wellauer, F. Ziereisen, N. Sinha, A. Prescimone, A. Velić, F. Meyer, O. S. Wenger, *J. Am. Chem. Soc.* **2024**, 146, 11299–11318.
- [3] J. Wellauer, B. Pfund, I. Becker, F. Meyer, A. Prescimone, and O. S. Wenger, *J. Am. Chem. Soc.* **2025**, 147, 8760–8768.

A novel cyclometalated Co^{III} triazolylidene photosensitiser complex displaying low-temperature emission and improved light harvesting

M. White,^a Z. Yao,^b P. A. Scattergood,^a D. A. W. Ross,^a A. Yartsev,^b P. Persson^b, I. M. Dixon,^c & P. I. P. Elliott^a

a University of Huddersfield, UK; *b* Lund University, Sweden; *c* Toulouse University, France
mary.white@hud.ac.uk

Throughout the development of photosensitiser transition metal (TM) complexes based upon Earth-abundant metals, focus has largely steered towards iron to replace rare and expensive metals such as ruthenium and iridium.^[1] Cobalt TM complexes, however, have been comparatively unexplored despite their ability to produce a larger ligand field splitting than those of Fe^{II}.^[2-4] Although emissive ³MLCT states have not been reported, it has been shown that the relatively high oxidation state of Co^{III} can induce ligand fields strong enough to allow lowest energy ³MC state photoactivity.^[2] Furthermore, recent findings reveal how decay of Co^{III} ³MC states operates within the Marcus inverted region.^[3] With this rationale, Co^{III} TM architecture design can be exploited increase the driving force for ground state recovery within this region and produce longer ³MC state lifetimes.^[3] The recently reported complex [Co^{III}(ImP)₂]⁺ (**1**) exhibits emission at 758 nm at 77 K which assigned to a ³MC state.^[4] In this work, we explore the photophysical properties of a novel triazolylidene cyclometalated Co^{III} complex in a joint experimental and computational density functional theory investigation. The novel triazolylidene cyclometalated Co^{III} complex (**2**) is targeted due to the superior electron donation properties of triazoles to improve ligand field splitting. Complex **2** similarly displays low temperature emission which shows a blue-shift in emission but is accompanied by significantly improved light harvesting absorption in the visible region.

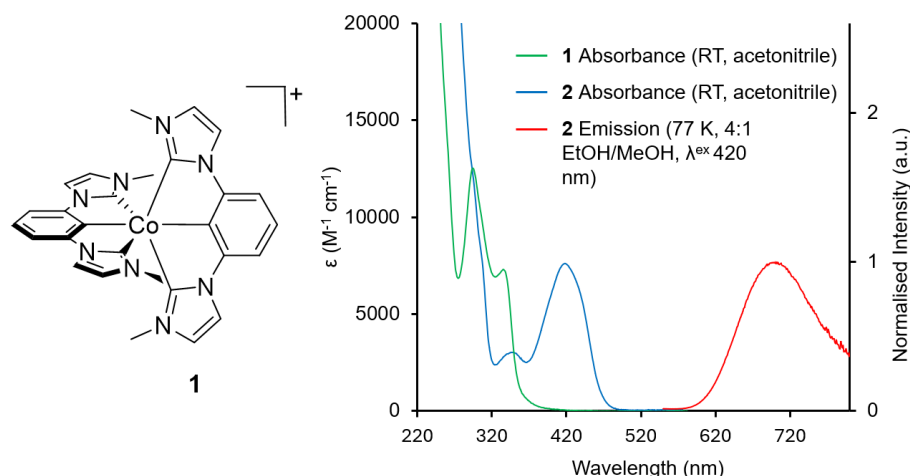


Figure 50. Chemical structure of [Co^{III}(ImP)₂]⁺ (**1**, left); UV-Vis absorption spectra **1** and of the novel Co^{III} triazolylidene complex **2**, and normalised emission spectrum of **2** (right).

Aknowlegments

Thanks to the Leverhulme Trust for funding this research (grant number RPG-2022-128).

References

- [1] C. Wegeberg, O. S. Wenger, *JACS Au* **2021**, 1, 1860-1876
- [2] S. Kaufhold *et al.*, *Am. Chem. Soc* **2021**, 143, 1307-1312
- [3] A. Y. Chan *et al.*, *Science* **2023**, 382, 191-197
- [4] A. Krishna *et al.*, *Inorg. Chem* **2025**, 64, 1401-1409

Exploring the photophysical behaviours of imidazolylidene vs. triazolylidene Fe^{III} ‘abnormal’ carbene complexes

M. White,^a Z. Yao,^b P. A. Scattergood,^a D. A. W. Ross,^a A. Yartsev,^b P. Persson^b, I. M. Dixon,^c & P. I. P. Elliott^a

a University of Huddersfield, UK; *b* Lund University, Sweden; *c* Toulouse University, France
mary.white@hud.ac.uk

Improving the photo-induced properties of first row transition metal (TM) complexes has been, and remains to be, a principal focus across photophysics.^[1] Over the past decade, continued research has resulted in longer-lived excited state lifetimes of ferrous and ferric TM complexes through destabilisation of low-lying metal-centred (MC) states, which ultimately lead to fast and non-radiative deactivation.^[1,2,3] The employment of strongly electron-donating *N*-heterocyclic carbene (NHC) ligands has been one notable design strategy to raise MC state energies sufficiently to inhibit deactivation of desired charge transfer states.^[2,3] Complex **1**, [Fe^{III}(ImP)₂]⁺, utilises imidazole-based NHCs in addition to a cyclometallating framework to further increase ligand field strength.^[2,3] Photoexcitation into the lowest energy energy absorption of **1** band at 585 nm results in red emission appearing at 750 nm from a ²LMCT excited state with a lifetime of 240 ps.^[2,3] In this work, we explore the photophysical properties of a novel triazolylidene cyclometalated Fe^{III} complex, **2**, in a joint experimental and computational density functional theory investigation. Targeted due to the superior electron-donation properties of triazolylidene moieties to elicit a stronger ligand field splitting, our work will be contrasted to the findings of the imidazole-based **1**.

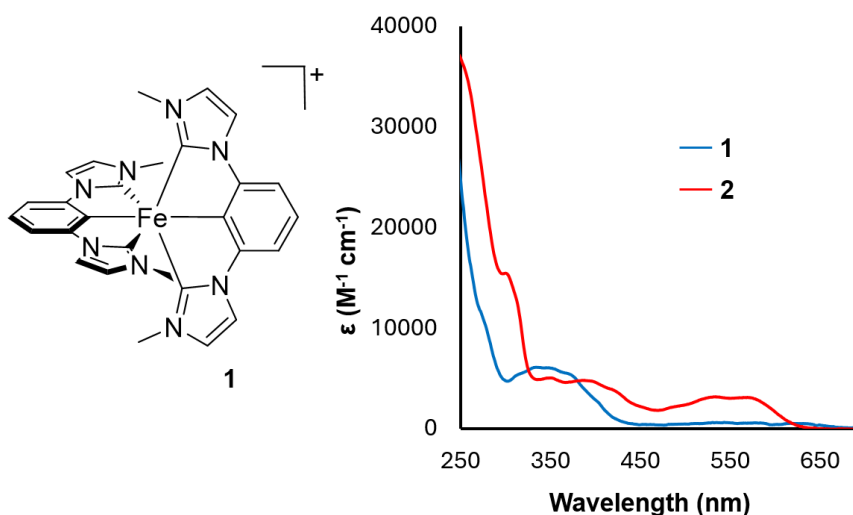


Figure 51. Chemical structure of [Fe^{III}(ImP)₂]⁺ (**1**, left), UV-Vis absorption spectra of **1** and of the novel Fe^{III} triazolylidene complex **2** (right).

Aknowlegments

Thanks to the Leverhulme Trust for funding this research (grant number RPG-2022-128).

References

- [1] C. Wegeberg, O. S. Wenger, *JACS Au* **2021**, 1, 1860-1876
- [2] J. Steube *et al.*, *Nat. Chem* **2023**, 15, 468-474
- [3] C. E. Johnson *et al.*, *Chem. Sci* **2023**, 14, 10129-10139

Selectively Targeting DNA Structure with Regio-pure Phthalocyanines: A Photophysical Study

E.R. Windle,¹ D. Graczyk,¹ D. MacKay,² P. Malakar,³ R. M. Edkins,² S.J. Quinn¹

1. School of Chemistry, University College Dublin, Dublin 4, Ireland.

2. Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, UK.

3. Central Laser Facility, STFC Rutherford Appleton Laboratory, UK

eleanor.windle@ucdconnect.ie

Phthalocyanines are promising photodynamic therapy (PDT) sensitizers with strong absorbance in the biological window and whose photophysical properties are determined by the aggregation state.^[1] Picosecond transient absorbance (TA) spectroscopy reveals the regio-pure Zn(II) phthalocyanine (**1**) to be monomeric and luminescent in DMSO with a long-lived triplet lifetime ($\tau = 200 \mu\text{s}$) suitable for PDT but to form soluble aggregates in aqueous solution with rapid non-radiative decay ($\tau = 80 \text{ ps}$) suitable for photothermal therapy (PTT). With good potential for both PDT and PTT, **1** is a promising dual-activity photosensitizer. The interaction between **1** and a library of nucleic acids has been studied to determine the impact on the aggregation state and photophysical behavior, in order to explore how binding to biomacromolecules may influence the phototherapeutic mechanism.^{[2],[3]} Despite the cationic nature, **1** is highly selective for guanine-rich DNA sequences capable of forming quadruplexes with very limited interaction with double-stranded B-DNA. In the presence of guanine-rich DNA, effective aggregate disruption with a time-dependency (Figure 1b) and an extended triplet lifetime in the microsecond range is observed. CD spectroscopy and time-resolved infrared spectroscopy indicate the ability of **1** to chaperone changes in quadruplex conformation (Figure 1d) and induce the formation of parallel quadruplex structures. In addition, **1** is efficiently disrupted by the cytosine-rich i-motif for which ligands are rarely reported in the literature. The selectivity of **1** for unusual DNA structures compared to related molecules indicates the importance of position and nature of the substituents and highlights the potential of **1** as a DNA-targeting photosensitizer.

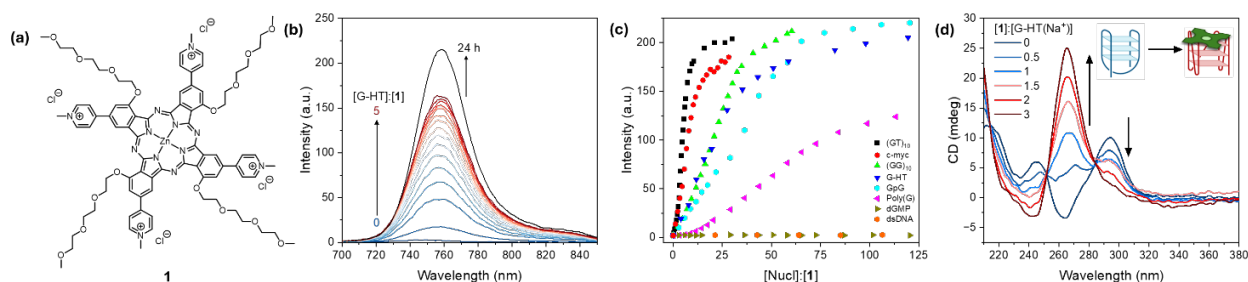


Figure 52. (a) Structure of **1**. (b) Emission spectra of **1** with addition of G-HT quadruplex. (c) Emission intensity of **1** with addition of nucleic acids. (d) Change in CD spectra of G-HT in the presence of **1**.

Acknowledgements

This project was funded by a Government of Ireland Postgraduate Scholarship (GOIPG/2022/1362) and the ultrafast studies at the CLF were funded by the STFC.

References

- [1] D.A. Bunin, A.G. Martynov, D.A. Gvozdev and Y.G. Gorbunova, *Biophys. Rev.*, **2023**, 15, 983-998.
- [2] C. Rennie, E. Sitch, J. Hillis and R. Edkins, *ChemRxiv* (preprint). **2022**, DOI:10.26434/chemrxiv-2022-r25k8
- [3] E.R. Windle, C.C. Rennie, R.M. Edkins and S.J. Quinn, *Chem. Eur. J.*, **2025**, 31, e202403095.



Transparent WO₃ Films with Organized Mesopores and Oriented Crystallinity as a Robust Photoanode for Visible-Light-Driven Water Oxidation at Neutral pH

Debraj Chandra, Yuta Tsubonouchi, Zaki N. Zahran and Masayuki Yagi

Department of Materials Science and Technology, Faculty of Engineering, Niigata University, 8050 Ikarashi-2, Niigata 9050-2181, Japan. yagi@eng.niigata-u.ac.jp

Photoelectrochemical (PEC) water splitting is one of the most promising clean and sustainable energy-providing systems, in which green H₂ fuel is produced by utilizing abundant solar light. A critical requirement for PEC devices is a competent photoanode material for water oxidation. WO₃ photoanodes have attracted much attention owing to their visible light response (band gap, $E_g = 2.6\text{--}2.8$ eV). However, WO₃ photoanodes usually suffer from obstruction associated with separation, migration and reaction of the photon-generated holes during water oxidation. Herein, we present synthesis of efficient WO₃ photoanodes through nanstructure control, band gap engineering and crystal-facet design. First ever thermal crystallization in a small mesopore system (ca. 2-3 nm pores) of WO₃ photoanode has been achieved by employing a unique in situ surfactant-thermal-carbonization method, using a laboratory-made structure directing agent (SDA) hexadecyl-2-pyridinylmethylamine (PAL16).¹ Besides, nanorod morphologies of N₂-intercalated pure monoclinic WO₃ has been obtained for improvement of visible light response, using hydrazine as N₂ source as well as a SDA.² Again, the transformation of WO₃ nanowires into active facets exposed hexagonal prisms has been demonstrated by simple tuning the synthesis temperature in presence of hydrazine. Single crystalline hexagonal prisms WO₃ gave preferentially exposed (002) and (020) crystal-facets on the top-flat and side-rectangle surfaces, that exhibited 3.7-fold higher PEC water oxidation performance than the polycrystalline WO₃ nanowires.³ However, these photoanodes were prepared by squeeze of WO₃ paste over FTO substrates as a nontransparent thin layer. A highly transparent crystalline WO₃ photoanode with well-organized mesoporous structure (ca. 7 nm pores) has been directly prepared on FTO electrode from a homogeneous aqueous solution derived from tungsten precursor and a block copolymer SDA.⁴ The strong adherent of mesoporous WO₃ film on FTO provided, 1) high surface area to increase the number of active sites, 2) organized nano-sized pore walls that reduce the hole migration length required for surface reaction and 3) good electron transport in a thin transparent WO₃ layer without compromising the light absorption. The integrated system of WO₃ photoanode with a CoO_x co-catalyst gave high and stable photocurrent (98% photocurrent retained after 30 h, giving Faradaic efficiency O₂ evolution >90%) for PEC water oxidation under neutral pH conditions, which is rare for most of the reported WO₃ photoanodes.

References

- [1] D. Chandra, K. Saito, T. Yui, M. Yagi, *Angew. Chem. Int. Ed.* 52, 12606 (2013).
- [2] D. Chandra, D. Li, M. Yagi, et. al., *ACS Sustainable Chem. Eng.* 7, 17896 (2019).
- [3] D. Chandra, T. Katsuki, M. Yagi, et. al., *ACS Appl. Mater. Interfaces* 15, 20885 (2023).
- [4] D. Chandra, K. Ouchi, M. Yagi, et. al., *submitted*, (2024).

Dimensionally-Controlled Coordination Polymer Eu(III) Complexes

Kotaro Yakuwa¹, Junpei Yuasa¹

1. Tokyo University of Science. E-mail: 1324704@ed.tus.ac.jp (Kotaro Yakuwa)

Eu(III) complex binding antenna ligands exhibits red emission through energy transfer from the antenna ligand to Eu(III) ion. Besides, Eu(III) complexes often formed unpredictable fascinating structures with unique emission properties.^[1-3] In this work, we proposed a unique coordination polymer structure of Eu(III) complex with long lifetime and high quantum efficiency.

First, we synthesized β -diketonate ligand to fabricate the coordination polymer Eu(III) complex. The single crystal suitable for X-ray diffraction analysis was successfully obtained. The X-ray diffraction analysis revealed that Eu(III) complex formed a 2D-sheet coordination polymer (**Figure 1**).^[4]

We measured emission quantum efficiency and emission decay of the Eu(III) complex in the solid state, revealing that 2D-sheet coordination polymer exhibited the bright red luminescence at the solid state (**Figure 2**).

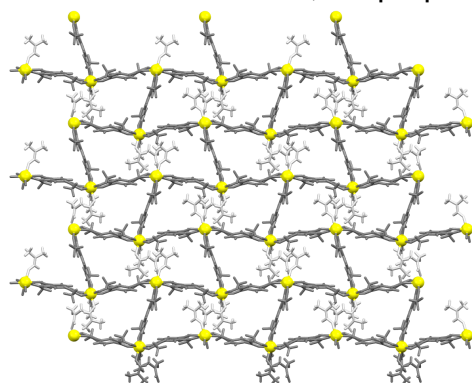


Figure 53. The packing structure of Eu(III) complex (yellow: Europium, gray: atoms including ligand, light gray: solvent (*N, N*-dimethylformamide))

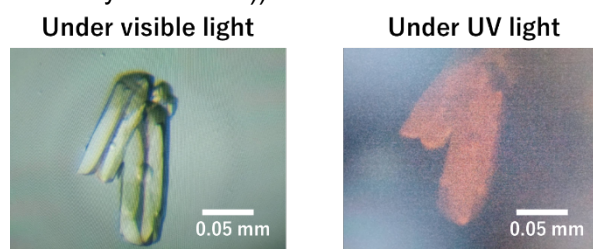


Figure 2. The picture of Eu(III) complex under visible(left) and UV (right) light.

References

- [1] E. S. Andreiadis, R. Demadrille, D. Imbert, J. Pécaut, M. Mazzanti, *Chem. Eur. J.* **2009**, 15 (37), 9458–9476.
- [2] K. Nakamura, Y. Hasegawa, H. Kawai, N. Yasuda, N. Kanehisa, Y. Kai, T. Nakamura, S. Yanagida, Y. Wada, *J. Phys. Chem. A* **2007**, 111 (16), 3029–3037
- [3] Y. Kitagawa, F. Suzue, T. Nakanishi, K. Fushimi, Y. Hasegawa, *Dalt. Trans.* **2018**, 47 (21), 7327–7332.
- [4] Y.-B. Dong, M. D. Smith, R. C. Layland, H.-C. A Zur Loye, *Chem. Mater.* **2000**, 12 (4), 1156–1161.

MCD and MCPL Studies on Octahedral $[\text{Mo}_6\text{I}_8\text{Y}_6]^{2-}$ Clusters in the Excited Triplet States

H. Yanagikawa,¹ T. Tomikawa,² Y. Kitagawa,² Y. Hasegawa,² K. Lang,³ K. Ishii.¹

¹Institute of Industrial Science, the University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo, 153-8505, Japan

²Faculty of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo, Hokkaido, 060-8628, Japan

³Institute of Inorganic Chemistry of the ASCR, Husinec-Řež 1001, 250 68 Řež, Czech Republic
E-mail: h-yanagi@iis.u-tokyo.ac.jp

Metal clusters have attracted considerable attention, because their properties and functionalities, which greatly depend on the geometrical arrangement, are expected to outperform mononuclear complexes. Especially, octahedral hexanuclear molybdenum (Mo) clusters have been traditionally studied for several decades in terms of their phosphorescence properties because of the large spin-orbit coupling on Mo ions.^{1,2} Furthermore, the photofunctions based on excited triplet states, such as phosphorescent probes or photosensitizers for photodynamic therapy are reported.³

Recently, the spin-forbidden transitions from the singlet ground (S_0) state to the excited triplet (T_1 and/or T_2) states were investigated by applying magnetic circular dichroism (MCD) spectroscopy to porphyrins with a heavy metal ion. Here, the dispersion-type Faraday A term owing to the highly symmetric π -conjugated system allows us to analyze the degenerate excited triplet states and their orbital angular momenta.^{4,5}

In this study, we investigated the excited triplet states of three $[\text{Mo}_6\text{I}_8\text{Y}_6]^{2-}$ clusters (Figure 1) by using MCD and magnetic circularly polarized luminescence (MCPL) spectroscopy. Typically, the Mo cluster **1** showed a broad absorption band and its MCD Faraday A term at 400 nm, which indicates the degeneracy of the excited singlet states in the highly symmetric $[\text{Mo}_6\text{I}_8\text{Y}_6]^{2-}$ cluster. In the highly concentrated solution, although only a broad shoulder band at 600 nm was observed in the electronic absorption spectrum, a distinct Faraday A term was observed in the corresponding MCD spectrum. Also, we successfully observed the intense, negative MCPL signal for the phosphorescence at 700 nm. The sign of MCPL was consistent with that of MCD, indicating these transitions correspond to $S_0 \leftrightarrow T_1$. To our knowledge, this is the first demonstration of the usefulness of MCD and MCPL for investigating the excited triplet states of metal clusters.

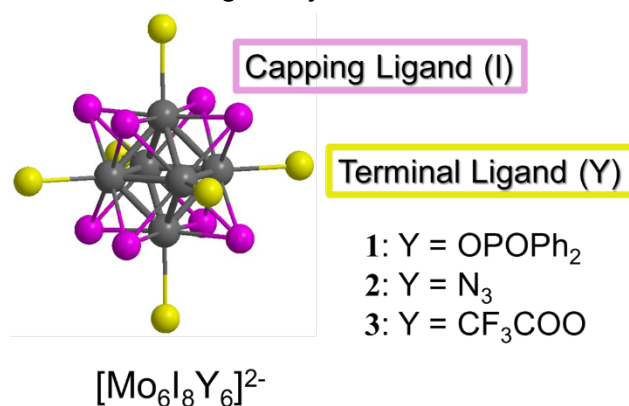


Figure 1. Molecular structures of $[\text{Mo}_6\text{I}_8\text{Y}_6]^{2-}$ clusters.

References

- [1] A. W. Maverick, H. B. Gray, *J. Am. Chem. Soc.*, **1981**, 103, 1298.
- [2] Y. Saito, H. K. Tanaka, Y. Sasaki, T. Azumi, *J. Phys. Chem.*, **1985**, 89, 4413.
- [3] K. Kirakci, M. A. Shestopalov, K. Lang, *Coord. Chem. Rev.*, **2023**, 481, 215048.
- [4] K. Murata, K. Ishii, *Eur. J. Inorg. Chem.*, **2017**, 44, 5103.
- [5] K. Ishii, J. Wada, K. Murata, *J. Phys. Chem. Lett.*, **2020**, 11, 9828.

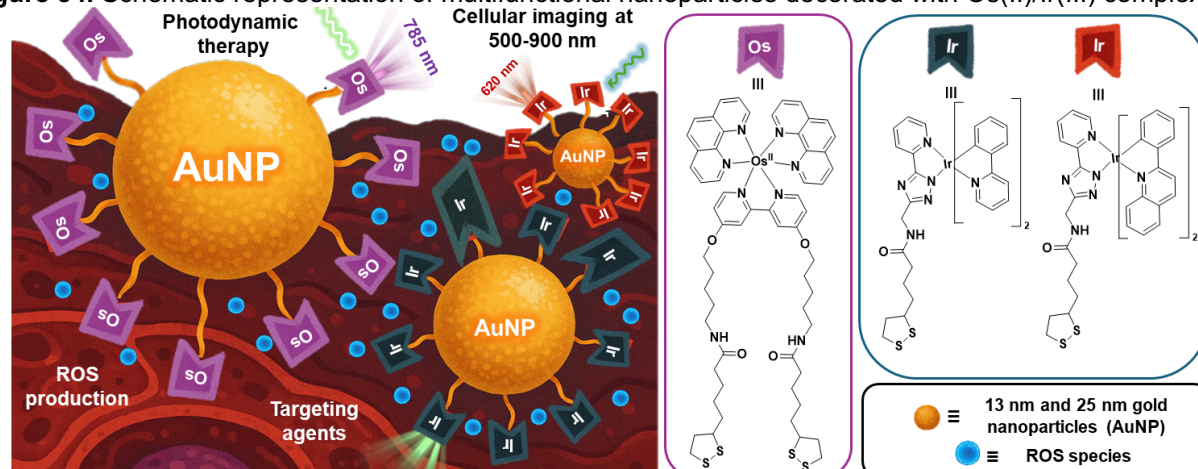
Luminescent gold nanoparticles decorated with photoactive metal complexes for cellular imaging and photodynamic therapy

Borys V. Zakharchenko,^{1#} Luke S. Watson,¹ Elnaz Yaghini,² Alexander J. MacRobert,³
Michael J. Hannon,¹ Nikolas J. Hodges,³ Zoe Pikramenou^{1*}

¹School of Chemistry, University of Birmingham, UK; ²Dept. of Surgical Biotechnology, Faculty of Medical Sciences, University College London, UK; ³School of Biosciences, University of Birmingham, UK; [#]b.zakharchenko@bham.ac.uk

Gold nanoparticles, AuNP, are popular multimodal probes for cellular imaging and photothermal therapy. Surface functionalization of AuNP offers an innovative approach to deliver anticancer agents in cells and increase drug penetration and targeting^[1]. We have been interested in the introduction of luminescent metal complexes on the surface of AuNP to increase water solubility of metallo agents and deliver therapeutic agents in a localised approach.^[2] Osmium(II) complexes containing phenanthroline ligands have attractive properties for potential theranostic agents^[3] given their anticancer activity, their redox potentials favourable for biological transformations within cancer cells and their luminescence in the near infrared (NIR) region. Cyclometalated iridium(III) complexes, with their high photostability, quantum yields, tunable photophysical properties, and targeting capabilities^[4], are excellent candidates for imaging and mitochondria-targeting agents. We have designed various molecular designs with optimal emission properties, focusing on a structure incorporating appropriately substituted phenyl-quinoline/pyridine and 3-(2-pyridyl)-1,2,4-triazole with dithiolane anchors for attaching to AuNP surface as the ancillary ligand coordinated in a heteroleptic neutral Ir(III) complex (Fig.1). The Ir complexes form stable, water-soluble the nanoparticles of 13 and 25 nm, bearing 900 and 2700, the Ir complexes per AuNP, respectively. The novel iridium coated nanoparticles we report exhibit strong luminescence at 510 and 620 nm and have a characteristic long luminescent lifetimes of hundreds of nanoseconds. Additionally, we have developed AuNP decorated with the Os(II) complex that are water-soluble, luminescent in the NIR region, localize in cytoplasmic and perinuclear compartments of lung and breast cancer cells. Time-resolved studies of singlet oxygen emission confirmed the dual functionality of the Os-based nanoprobe for both imaging and cancer therapy.

Figure 54. Schematic representation of multifunctional nanoparticles decorated with Os(II)/Ir(III) complexes.



References. [1] A.B. Caballero, L. Cardo, S. Claire...& M.J. Hannon, *Chem Sci.* **2019**, *10*, 9244-9256; [2] A. N. Dosumu, S. Claire, L.S. Watson, N. J. Hodges, *JACS Au* **2021**, *1* (2), 174-186 [3] L. S. Watson, J.S. Hughes, T. Rafik...& Z. Pikramenou, *Nanoscale* **2024**, *16*, 16500-16509; [4] S.M.King, S. Claire, R.I. Teixeira...& Z. Pikramenou, *J. Am. Chem. Soc.* **2018**, *40* (32), 10242-10249.



Put a cage on it: Luminescent metal complexes in confined space

C. Zehe¹, N. Quadrio², L. Arnal Valles², L. Menduti², A. Lazaro³, I. Rimoldi², G. Facchetti², L. De Cola^{1,2}

¹Department of Biochemistry and Molecular Pharmacology, Istituto di Ricerche Farmacologiche Mario Negri IRCCS, Italy

²Department of Pharmaceutical Sciences DISFARM, Università degli Studi di Milano, Italy

³Institute of Functional Interfaces, Karlsruhe Institute of Technology KIT, Germany

The use of metal complexes as imaging agents for aqueous systems is beneficial because of their good photostability, long phosphorescence lifetime, large Stokes shift and long wavelength emission in the red spectral region, which is necessary for biological sensing due to lower cell autofluorescence and increased tissue penetration depth in this region.^[1] However their use has been restricted due to their limited water solubility for bright neutral Ir(III) compounds,^[2] stability for charged systems such as Cu(I) compounds^[3] and due to the triplet nature of the excited state by oxygen quenching. Such issues are also faced when the excited state is created by charge recombination (electroluminescence) or by electrochemiluminescence (ECL), where one electrode is replaced by a sacrificial electron donor or acceptor, a coreactant. For ECL Ru(II) and more recently Ir(III) complexes are the choice for highly sensitive detection of analytes at low concentration in a range of different fields including biological assays and environmental monitoring.^[4] Iridium complexes are indeed promising candidates for ECL assays due to their bright, energy tunable,^[4b] phosphorescence emission, long phosphorescence lifetimes as well as good photostability and thermal stability.^[5] However, as for photoluminescence, the emission of Iridium complexes is greatly quenched by the presence of molecular oxygen in solution and solubility is restricted by the neutral character of the brightest of them.

This work demonstrates that encapsulating Iridium complexes into porous silica nano materials and in particular in nanocages^[6] can provide a universal method to retain luminescent properties and improve compatibility in aqueous media even if the complexes are completely water insoluble. The effect of encapsulation on the photophysics and molecular arrangement is explored. We observe multi-fold increase of the luminescence intensity and a remarkable elongation of PL lifetime upon encapsulation compared to air-saturated aqueous solution. In addition such complexes remain accessible to electrons and small molecules due to the morphology of such a single pore open structure allowing their luminescence to be produced via electrochemiluminescence.

Acknowledgement: This project has received funding from the European Union's Horizon Europe EIC Pathfinder Open programme under Grant Agreement N. 101046787 (ECLIPSE).

References

- [1] N. A. Yusoh, M. R. Gill, X. Tian, *Chem Soc Rev* **2025**.
- [2] X. Yang, Y. Xu, X. Huang, J. Hang, W. Guo, Z. Dai, *Anal Chem* **2023**, 95, 4543-4549.
- [3] M. Zhao, A. Y. Chen, D. Huang, Y. Zhuo, Y. Q. Chai, R. Yuan, *Anal Chem* **2016**, 88, 11527-11532.
- [4] aL. Li, Y. Chen, J. J. Zhu, *Anal Chem* **2017**, 89, 358-371; bE. Longhi, J. M. Fernandez-Hernandez, A. Iordache, R. Frohlich, H. P. Josel, L. De Cola, *Inorg Chem* **2020**, 59, 7435-7443.
- [5] J. M. Fernandez-Hernandez, E. Longhi, R. Cysewski, F. Polo, H. P. Josel, L. De Cola, *Anal Chem* **2016**, 88, 4174-4178.
- [6] aK. Ma, Y. Gong, T. Aubert, M. Z. Turker, T. Kao, P. C. Doerschuk, U. Wiesner, *Nature* **2018**, 558, 577-580; bP. Picchetti, G. Moreno-Alcantar, L. Talamini, A. Mourgout, A. Aliprandi, L. De Cola, *J Am Chem Soc* **2021**, 143, 7681-7687.



High-Efficiency Photoinduced Charge Separation in Iron N-Heterocyclic Carbenes

M. Zhang,^a J. Schwarz,^b O. Prakash^b A. Ilic,^b K. Wärnmark,^b R. Lomoth^a

a. Department of Chemistry – Ångström Laboratory, Uppsala University, SE-75120 Uppsala, Sweden.

b. Center for Analysis and Synthesis, Department of Chemistry, Lund University, SE-22100 Lund, Sweden

Email: minli.zhang@kemi.uu.se

Iron N-heterocyclic carbenes (FeNHCs) have, in recent years, emerged as novel photoactive compounds and attracted tremendous attention for their potential in offering interesting excited-state reactivities.^[1] Symmetry-breaking charge separation (SBCS) in molecular systems has been widely investigated from a fundamental perspective and in view of potential applications in photovoltaics and photocatalytic applications.^[2] However, the scarcity of bimolecular SBCS cases and the demand of solvation processes to assist the SBCS in multichromophoric assemblies has limited the application of SBCS reactions. It has been proven that certain Fe(III) N-heterocyclic carbene compounds provide exceptional properties that are capable of oxidizing or reducing the complex in its ground state by its ²LMCT excited state. Bimolecular SBCS of a Fe(III)NHC complex was recently demonstrated in fluid solution^[3] and the intrinsic driving force for charge separation makes these chromophores promising candidates for SBCS in the solid state.^[4] Herein, the bimolecular SBCS study of several FeNHCs will be presented. The ultrafast spectroscopy and photoconductivity studies show that high-efficiency photoinduced charge separation can be achieved in FeNHC solids despite their differences in the excited-state lifetimes and the SBCS driving forces, which provide new insight into the consideration of the potential applications for FeNHCs.

Acknowledgments

Thanks to the Swedish Research Council (VR, 2020-05058), the Foundation for Strategic Research (SSF, EM16-0067), and the Knut and Alice Wallenberg Foundation (KAW2018.0074) for financial support on research. Thanks to C.F. Liljewalch Scholarship Foundation for financial support on traveling.

References

- [1] K. S. Kjær, N. Kaul, O. Prakash, P. Chábera, N. W. Rosemann, A. Honarfar, O. Gordivska, L. A. Fredin, K. E. Bergquist, L. Häggström, T. Ericsson, L. Lindh, A. Yartsev, S. Styring, P. Huang, J. Uhlig, J. Bendix, D. Strand, V. Sundström, P. Persson, R. Lomoth, K. Wärnmark. *Science* **2019**, 363 (6424), 249–253; L. H. M. Groot, A. Ilic, J. Schwarz, K. Wärnmark. *Journal of the American Chemical Society* **2023**, 145, 17, 9369–9388.
- [2] L. Estergreen, A. R. Mencke, D. E. Cotton, N. V. Korovina, J. Michl, S. T. Roberts, M. E. Thompson and S.E. Bradforth, *Accounts of Chemical Research* **2022**, 55, 1561-1572; X. Zhao , R. M. Young , C. Tang , G. Wu , K. R. Peinkofer , Y. Han , S. Yang , Y.-K. Xing , H. Han , H. Wu , X. Li , Y. Feng , R. Zhang , C. L. Stern , M. R. Wasielewski and J. F. Stoddart , *Chem* **2025**, 11 , 102248.
- [3] N. Kaul and R. Lomoth, *Journal of the American Chemical Society* **2021**, 143, 10816-10821.
- [4] M. Zhang, C. E. Johnson, A. Ilic, J. Schwarz, M. B. Johansson and R. Lomoth, *Journal of the American Chemical Society* **2023**, 145, 19171-19176.

The Characteristic of Photo-Induced ³MLCT Emission Behavior for Ru-(Cyclometalated) Chromophores

L.-T. Zhuo,^a M.-K. Tsai^{*b} and Y. J. Chen^{*a}

^a Department of Chemistry, Fu-Jen Catholic University, New Taipei City 24205, Taiwan, ROC, e-mail : qq10120@gmail.com

^b Department of Chemistry, National Taiwan Normal University, Taipei City 11677, Taiwan, ROC

This study presents a rare report on the 77K observations of Ru-(cyclometalated) (Ru-CM) phosphorescent chromophores in mixed ligand [Ru(bpy)₂(CM)]⁺-type complexes specifically [Ru(bpy)₂(TBPZ)]⁺ and [Ru(bpy)₂(DBPZ)]⁺, where bpy = 2,2'-bipyridine, TBPZ = Tribenzo[a,c,i]phenazine, DBPZ = dibenzo[a,c]phenazine. Their electrochemistry and photophysical parameters were also characterized. In the cyclic voltammogram scan, the first reduction potential in the negative region corresponds to the reduction of the CM^{1/2} of TBPZ and DBPZ moieties for [Ru(bpy)₂(CM)]⁺. The observed absorption spectra show a low-energy metal-to-ligand charge transfer (MLCT) band, which attributed to contributions from both Ru-CM and Ru-bpy chromophore moieties based on the DFT modeling. The 77K phosphorescence spectra and computational modeling of the target [Ru(bpy)₂(CM)]⁺ with polycyclic aromatic CM ligand in this study characterize the Ru-CM phosphorescent chromophore. This contrasts with the Ru-bpy phosphorescent chromophore observed in [Ru(bpy)₂(CM)]⁺ complexes featuring low-ring-count polycyclic aromatic CM ligands.¹⁻³

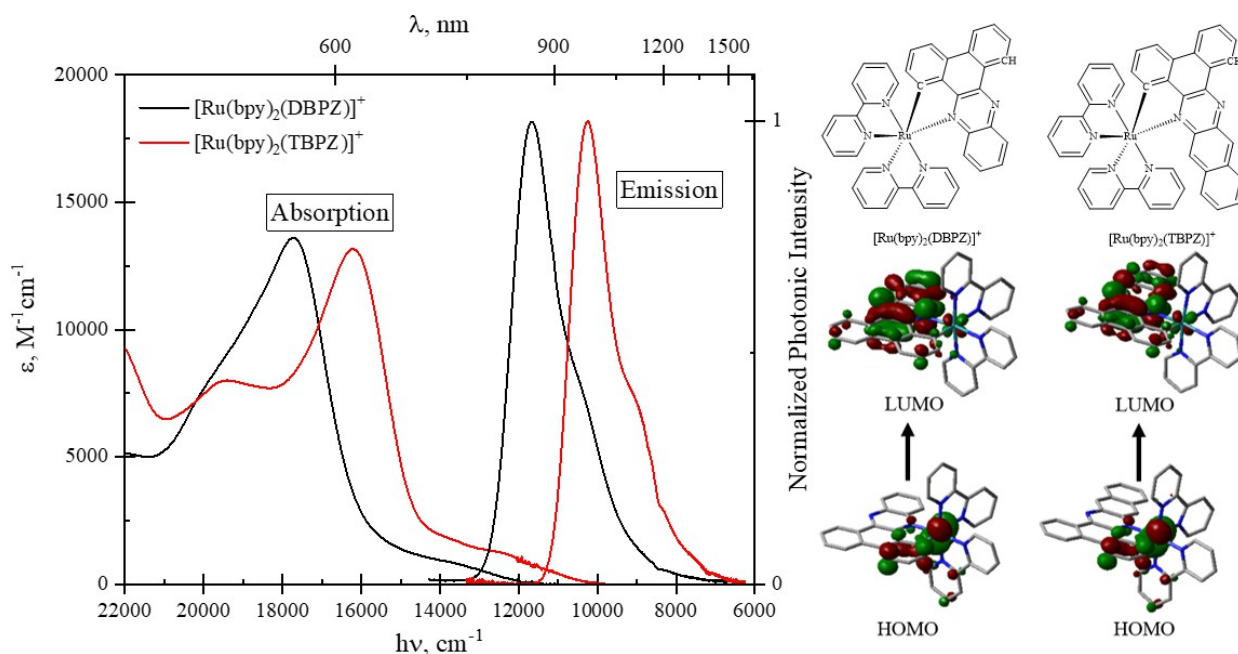


Figure 1. The 298K absorption spectra in CH₃CN and 77K emission spectra in butyronitrile glasses. (left panels), and structure of HOMO and LUMO (right panels) of Sn state for [Ru(bpy)₂(DBPZ)]⁺ and [Ru(bpy)₂(TBPZ)]⁺.

References

- [1] M. L. Muro-Small et al., *Eur. J. Inorg. Chem.* **2012**, 2012 (25), 4004.
- [2] X. Z. Zhang et al., *J. Phys. Chem. A* **2019**, 123 (44), 9431.
- [3] Y. R. Chih et al., *ACS Omega* **2022**, 7 (51), 48583.

Quantum Chemical Studies on a Heterodinuclear Rotaxane: Towards Biomimetic Photocatalysis

K. P. Zois^{a,b}, M. Müssler^c, M. Semwal^d, L. Blechschmidt^d, L. Zedler^d, A. K. Mengele^c, B. Dietzek-Ivanšić^d, S. Rau^c, L. González^a

^a Faculty of Chemistry, Institute of Theoretical Chemistry, University of Vienna, Währinger Str. 17, 1090 Vienna, Austria, konstantinos.pantelis.zois@univie.ac.at

^b Vienna Doctoral School in Chemistry (DoSChem), University of Vienna, Währinger Str. 42, 1090 Vienna, Austria

^c Institute of Inorganic Chemistry I, Ulm University, Albert-Einstein-Allee 11, 89081 Ulm, Germany

^d Institute of Physical Chemistry, Friedrich Schiller University Jena, Helmholtzweg 4, 07743 Jena, Germany

The combination of photoredox-active and catalytically competent moieties in one molecular framework is highly sought-after and in this context, bridging ligands containing alkyne moieties present an ideal platform for efficient photoinduced electron-transfer processes. [1] However, due to the intrinsic reactivity of alkynes, under irradiation, a way to protect these bridging ligand is to be found. Therefore, embedding the dimetallic photocatalyst in a soft-matrix macrocycle offers an attractive solution.

Our primary interest is to understand the photophysics of a Ru-Rh dyad, embedded in a curcubit[7]uril ring – forming a supramolecular rotaxane photocatalyst – towards the realisation of efficient biomimetic photocatalysis, for instance, the reductive hydrogenation of NAD⁺. Quantum chemical methods, such as Density Functional Theory (DFT) and GFN2-xTB, have been used in order to study the structural characteristics of the system and their implications for catalysis. TD-DFT calculations have also been used to shed light on the excited states of the system and its mono- and doubly-reduced analogues.

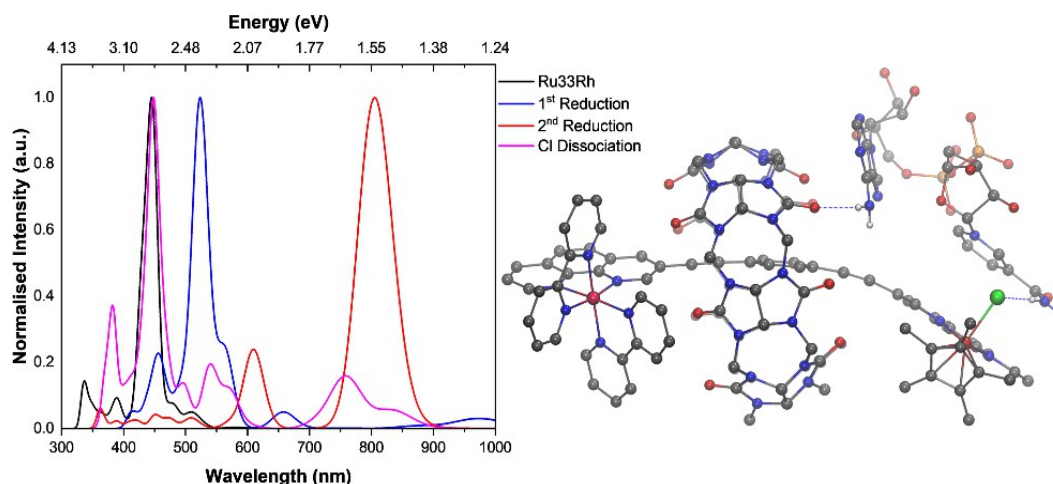


Figure 1. Computed UV-Vis spectra of the dimetallic dyad, for different oxidation states, along with a DFT-optimised geometry of the rotaxane molecule, during the catalytic cycle of NAD⁺ reductive hydrogenation.

Acknowledgements

This project is funded by the Austrian Science Fund (FWF, project no. I6116) and the Deutsche Forschungsgemeinschaft (DFG, project TRR234 ‘Catalight’, project no. 364549901, projects A1, C3). The University of Vienna is thanked for continuous support.

References

- [1] L. Zedler, P. Wintergerst, A. K. Mengele, C. Müller, C. Li, B. Dietzek-Ivanšić, S. Rau, *Nat Commun* **2022**, *13*, 2538

List of Participants

First name	Surname	Affiliation	Email address
Jibin Alex	Abraham	Charles University in Hradec Králové	abrahamji@faf.cuni.cz
Marta Erminia	Alberto	University of Calabria	marta.alberto@unical.it
Mary Angella	Alfred	Charles University	alfredm@faf.cuni.cz
Alessandro	Aliprandi	University of Padova	alessandro.aliprandi@unipd.it
Alessandro	Amadeo	University of Perugia - University of Messina	alessandroamadeo00@gmail.com
Michael	Andrews	Royal Society of Chemistry	andrewsm@rsc.org
Sergio	Aranda Ruiz	University of Zurich	sergio.aranda@chem.uzh.ch
Amine	Assel	University of Messina	assel.amine@gmail.com
Ally	Aukauloo	Université Paris-Saclay	ally.aukauloo@universite-paris-saclay.fr
Sujoy	Baitalik	Jadavpur University	sbaitalik@hotmail.com
Maria Vittoria	Balli	University of Bologna	mariavittoria.balli2@unibo.it
Andrea	Barbieri	ISOF-CNR- Bologna	andrea.barbieri@isof.cnr.it
Martyna	Bartusiak	Dublin City University	martyna.bartusiak2@mail.dcu.ie
Filippo Piero	Battaglia	University of Bologna	filippo.battaglia2@unibo.it
Stefan	Bednarik	Charles University in Hradec Králové	bednaris@faf.cuni.cz
Elisabetta	Benazzi	University of Padova	elisabetta.benazzi@unipd.it
Curtis	Berlinguette	University of British Columbia	cberling@chem.ubc.ca
Anagha Raghavendrachar	Bidarahalli	AGH University of Krakow	anagha@agh.edu.pl
Jack	Biddulph	Dublin City University	jack.biddulph3@mail.dcu.ie
Oussama	Bindech	Laboratory of Quantum Chemistry of Strasbourg	obindech@unistra.fr
Claudia	Bizzarri	Tor Vergata University of Rome	claudia.bizzarri@uniroma2.it
Sergey	Bokarev	Technical University of Munich	sergey.bokarev@tum.de
Olga	Bokareva	Leibniz Institute for Catalysis (LIKAT)	olga.bokareva@catalysis.de
Ivana Lidia	Bonaccorsi	University of Messina	ivanalidia.bonaccorsi@unime.it
Alberto	Bossi	SCITEC-CNR-Milano	alberto.bossi@cnr.it
Greta	Bucyte	Light Conversion	greta.bucyte@lightcon.com

Alejandro	Cadranel	FAU Erlangen-Nürnberg	ale.cadranel@fau.de
Sebastiano	Campagna	University of Messina	campagna@unime.it
Ambra Maria	Cancelliere	University of Messina	acancelliere@unime.it
Andrea	Cannizzo	University of Bern	andrea.cannizzo@unibe.ch
Jakob Tillmann	Casanova	University of Bern	jakob.casanova@unibe.ch
Felix	Castellano	North Carolina State University	fncastel@ncsu.edu
Paola	Ceroni	University of Bologna	paola.ceroni@unibo.it
Cecilia	Cerretani	University of Copenhagen	cece@chem.ku.dk
Noémie	Chantry	UCLouvain	noemie.chantry@uclouvain.be
Pritha	Chatterjee	University of Kanpur	prithac20@iitk.ac.in
Yuan Jang	Chen	Fu Jen Catholic University	054971@mail.fju.edu.tw
Jie Ying	Chen	Fu Jen Catholic University	gaydog987@gmail.com
Mihaela	Cibian	Université du Québec à Trois-Rivières (UQTR)	mihaela.cibian@uqtr.ca
Simon	Clausing	Johannes Gutenberg University Mainz	Simon.Clausing@uni-mainz.de
Javier	Concepcion	Brookhaven National Laboratory	jconcepc@bnl.gov
Tim	Connell	Deakin University	t.connell@deakin.edu.au
Marta	Costa Verdugo	DIPC (Donostia International Physics center)	marta.costa@dipc.org
Laura	Cuevas Contreras	University of Granada	lauracc@ugr.es
Samira	Dabelstein	University of Rostock	samira.dabelstein@uni-rostock.de
Janusz	Dabrowski	Uniwersytet Jagiellonski	jdabrows@chemia.uj.edu.pl
Elena	Dallerba	Curtin University	elena.dallerba@curtin.edu.au
Ana	de Bettencourt-Dias	University of Nevada	abd@unr.edu
Luisa	De Cola	University of Milan and Istituto Mario Negri	luisa.decola@unimi.it
Jiri	Demuth	Charles University	demuthj1@faf.cuni.cz
Emily	Derham	Dublin City University	emily.derham5@mail.dcu.ie
Jesús	Díaz Burrueco	University of Granada	jesdb@ugr.es
Benjamin	Dietzek-Ivansic	Leibniz Institute of Surface Engineering	benjamin.dietzek@leibniz-ipht.de
Luis Guilherme Alves	do Nascimento	University of São Paulo	luis_nascimento@usp.br
Conor	Doran	University of Auckland	cdor231@aucklanduni.ac.nz
Florian	Döttinger	Universität Basel	f.doettinger@unibas.ch
Federico	Droghetti	University of Ferrara	drgfrc@unife.it

Laura	Duncan	Durham University	laura.l.duncan@durham.ac.uk
Nils	Düsterhues	Universität Paderborn	nils.duesterhues@uni-paderborn.de
Alexander	Eith	FSU Jena	alexander.eith@uni-jena.de
Elkhansa	Elbashier	University of Otago	elbel670@student.otago.ac.nz
Svetlana	Eliseeva	Centre de Biophysique Moléculaire, CNRS	svetlana.eliseeva@cnrs-orleans.fr
Paul	Elliott	University of Huddersfield	p.i.elliott@hud.ac.uk
Othmane	Essahili	Mohammed VI Polytechnic University	othmane.essahili@um6p.ma
Mona	Farhadi Rodbari	University of Ulm	mona.farhadi-rodbari@uni-ulm.de
Mikhail	Filatov	Technological University Dublin	mikhail.filatov@tudublin.ie
Greta	Fogar	University of Trieste/Leiden Institute of Chemistry	greta.fogar@phd.units.it
Antonio	Francés-Monerris	ICMol - Universitat de València	antonio.frances@uv.es
Paul	Francis	Deakin University	paul.francis@deakin.edu.au
Yoann	Fréroux	Université de Rennes	yoann.freroux@univ-rennes.fr
Daniel	Friedewald	JMU Würzburg	daniel.friedewald@uni-wuerzburg.de
Dennis	Fritzler	Universität Konstanz	dennis.fritzler@uni-konstanz.de
Maurilio	Galletta	CNR - IMM Messina	maurilio.galletta@cnr.it
Elena	Galoppini	Rutgers University	galoppin@newark.rutgers.edu
Damiano	Genovese	University of Bologna	damiano.genovese2@unibo.it
Salvatore	Genovese	University of Perugia - University of Messina	salvatore.genovese1@studenti.unime.it
Federica	Giorgianni	University of Perugia - University of Messina	giorgiannifederica1@gmail.com
Felix	Glaser	Université catholique de Louvain	felix.glaser@uclouvain.be
Ksenija	Glusac	University of Illinois-Argonne National Laboratory	glusac@uic.edu
Rebeca	Gomez Castillo	Max Planck Institute CEC	rebeca.gomez-castillo@cec.mpg.de
Iván Alonso	González	Universidad Tecnológica Metropolitana	igonzaalezp@utem.cl
Keith	Gordon	University of Otago	keith.gordon@otago.ac.nz
Daniel	Graczyk	University College Dublin	daniel.graczyk@ucdconnect.ie
Robertas	Grigutis	Light Conversion	robertas.grigutis@lightcon.com
Véronique	Guerchais	CNRS University of Rennes	veronique.guerchais@univ-rennes1.fr
Alexey	Gusev	Ultrafast Systems	alex@ultrafast.systems
Kristoffer	Haldrup	Technical University of Denmark	hald@fysik.dtu.dk
Garry	Hanan	Université de Montréal	garry.hanan@umontreal.ca

Yasuchika	Hasegawa	Hokkaido University	hasegaway@eng.hokudai.ac.jp
Maximilian	Henning	Paderborn University	maximilian.henning@upb.de
David	Herbert	University of Manitoba	david.herbert@umanitoba.ca
Masanari	Hirahara	Osaka Institute of Technology	masanari.hirahara@oit.ac.jp
Teruyuki	Honda	Kyushu University	honda.teruyuki.699@s.kyushu-u.ac.jp
Shota	Hosoya	Hokkaido University	shota111018@eis.hokudai.ac.jp
Kazuyuki	Ishii	The University of Tokyo	k-ishii@iis.u-tokyo.ac.jp
Osamu	Ishitani	Hiroshima University	iosamu@hiroshima-u.ac.jp
Nicolas	Issot	Université de Toulouse	nicolas.issot@univ-tlse3.fr
Ren	Itagaki	Kyoto University	itagaki.ren.75h@st.kyoto-u.ac.jp
Munetaka	Iwamura	University of Toyama	miwamura@sci.u-toyama.ac.jp
Moritz	Jahn	Johannes Gutenberg University Mainz	moritz.jahn@uni-mainz.de
Pengyue	Jin	University of Konstanz	pengyue.jin@uni-konstanz.de
Tao	Jin	University of Basel	tao.jin@unibas.ch
Amelia	Kacperkiewicz	University of Manitoba	kacperka@myumanitoba.ca
Hajime	Kamebuchi	Osaka Metropolitan University	hkamebuchi@omu.ac.jp
Michael	Karnahl	TU Braunschweig	michael.karnahl@tu-braunschweig.de
Chizuru	Kasahara	University Jena	chizuru.kasahara@uni-jena.de
Christoph	Kerzig	Johannes Gutenberg University Mainz	ckerzig@uni-mainz.de
Alina	Koba	Ulm University	alina.koba@uni-ulm.de
Henriette	Kolbinger	JGU Mainz	henriette.kolbinger@uni-mainz.de
Athul	Krishna	Universitat Paderborn	athul@mail.uni-paderborn.de
Sandra	Kronenberger	Johannes Gutenberg University Mainz	skrone@uni-mainz.de
Prashant	Kumar	University College London	prashant.kumar@ucl.ac.uk
Stephan	Kupfer	Friedrich Schiller University Jena	stephan.kupfer@uni-jena.de
Claudio	La Falce	University of Messina	claudiolafalce94@gmail.com
Giuseppina	La Ganga	University of Messina	glaganga@unime.it
Jana	Lapesova	Charles University	lapesovja@faf.cuni.cz
Christopher	Larsen	University of Auckland	christopher.larsen@auckland.ac.nz
Theodore	Lazarides	Aristotle University of Thessaloniki	tlazarides@chem.auth.gr
Giuliana	Lazzaro	University of Messina	giuliana.lazzaro@unime.it

Simon	Liedtke	Lund University	simon.liedtke@compchem.lu.se
Yu Hui	Lin	Fu-Jen Catholic University	annlove60504@gmail.com
Sophia	Lipinski	Technical University of Munich	sophia.lipinski@tum.de
Khaoula	Lmcharrag	Charles University	lamchark@faf.cuni.cz
Patrick	Loftus	Dublin City University	patrick.loftus7@mail.dcu.ie
Jannik	Löseke	University Paderborn	loesekej@mail.uni-paderborn.de
Franziska	Lux	University Paderborn	franziska.lux@uni-paderborn.de
Xiao	Ma	The University of Tokyo	maxiao22@iis.u-tokyo.ac.jp
David	MacMillan	Princeton University	dmacmill@princeton.edu
David	Magri	University of Malta	david.magri@um.edu.mt
Tamar	Maisuradze	Friedrich Schiller University Jena	tamar.maisuradze@uni-jena.de
Francesca	Mancini	University of Bologna	francesca.mancini27@unibo.it
Andrea	Mantovani	University of Ferrara	mntndr2@unife.it
Edoardo	Marchini	University of Ferrara	mrcdrd@unife.it
Max	Massi	Curtin University	m.massi@curtin.edu.au
Martina	Mazzaferro	University of Messina	martina.mazzaferro@studenti.unime.it
Nathan	McClenaghan	University of Bordeaux / CNRS	nathan.mcclenaghan@u-bordeaux.fr
James	McCusker	Michigan State University	jkm@chemistry.msu.edu
Sherri	McFarland	The University of Texas at Arlington	sherri.mcfarland@uta.edu
Isobel	Meikle	University of Sheffield	imeikle1@sheffield.ac.uk
Gerald	Meyer	UNC Chapel Hill	gimeyer@email.unc.edu
Martina	Milani	University of Ferrara	martina.milani@unife.it
Kiyoshi	Miyata	Kyushu University	kmiyata@chem.kyushu-univ.jp
Evan	Moore	The University of Queensland	egmoore@uq.edu.au
Pablo	Msellem	Mario Negri Institute, Milano	pamsellem@marionegri.it
Marius	Müßler	Ulm University	marius.muessler@uni-ulm.de
Sandra Anila	Nair	Ulm University	sandra.anila-nair@uni-ulm.de
Akinobu	Nakada	Kyoto University	nakada@scl.kyoto-u.ac.jp
Francesco	Nastasi	University of Messina	fnastasi@unime.it
Mirco	Natali	University of Ferrara	mirco.natali@unife.it
Nidhi	Nehra	Charles University in Hradec Králové	nehra@faf.cuni.cz

Veronika	Novakova	Charles University in Hradec Králové	veronika.novakova@faf.cuni.cz
Stephen	O'Sullivan	Dublin City University	stephen.osullivan63@mail.dcu.ie
Tomohiro	Ogawa	Kyushu University	togawa@chem.kyushu-univ.jp
Ken	Onda	Kyushu University	konda@chem.kyushu-univ.jp
Kerstin	Oppelt	University of Zürich	kerstin.oppelt@uzh.ch
Chandrani	Pal	IIT Kanpur	cpchem20@iitk.ac.in
Ashis Kumar	Patra	Indian Institute of Technology Kanpur	akpatra@iitk.ac.in
Michael	Pattuwege	Deakin University	mlpattu@hotmail.com
Teresa	Paviglianiti	Università degli Studi di Messina	pvgttrs00c57h224f@studenti.unime.it
Yann	Pellegrin	CEISAM - CNRS	yann.pellegrin@univ-nantes.fr
Marta	Penconi	CNR - SCITEC-Milano	marta.penconi@cnr.it
Sandrine	Perruchas	Institut des Matériaux de Nantes	sandrine.perruchas@cnrs-imn.fr
Petter	Persson	Lund University	petter.persson@compchem.lu.se
Robin	Perutz	University of York	robin.perutz@york.ac.uk
Stephane	Petoud	Center for Molecular Biophysics	Stephane.petoud@cnrs-orleans.fr
Waldemar	Pichór	AGH University of Krakow	pichor@agh.edu.pl
Martin	Pižl	University of Chemistry and Technology Prague	pizlma@vscht.cz
Mary	Pryce	Dublin City University	mary.pryce@dcu.ie
Fausto	Puntoriero	University of Messina	fpuntoriero@unime.it
Mariet Sibi	Puthanagady	Friedrich Schiller University	mariet.puthanagady@uni-jena.de
Nicolò	Quadrio	University of Milan	nicolo.quadrio@unimi.it
Emily	Race	University of Sheffield	elrace1@sheffield.ac.uk
Jeffrey	Rack	University of New Mexico	jirack@unm.edu
Enrico	Rampazzo	University of Bologna	enrico.rampazzo@unibo.it
Sven	Rau	Ulm University	sven.rau@uni-ulm.de
Vincent	Robert	Laboratory of Quantum Chemistry of Strasbourg	vrobert@unistra.fr
Jonathan	Rochford	University of Massachusetts Boston	jonathan.rochford@umb.edu
Leon David	Rodrigues	Charles University	rodrigule@faf.cuni.cz
Federica	Ruani	ISOF-CNR	federica.ruani@cnr.it
Evgenia	Ryndin	Ulm University	evgenia.ryndin@uni-ulm.de
Arindam	Saha	University of Montreal	arindam.saha@umontreal.ca

Abhijit	Saha	Indian Institute of Technology Kanpur	asaha@iitk.ac.in
Ken	Sakai	Kyushu University	ksakai@chem.kyushu-univ.jp
Antonio	Santoro	University of Messina	antonio.santoro@unime.it
Luca	Schleicher	JGU Mainz	Ischleic@students.uni-mainz.de
Till	Schmidt-Raentsch	University of Goettingen	till.schmidt-raentsch@uni-goettingen.de
Stefano	Scoditti	Donostia International Physics Center	stefano.scoditti@dlpc.org
Kaito	Segawa	Kyushu University	segawa.kaito.148@s.kyushu-u.ac.jp
Mohini	Semwal	Friedrich Schiller University	mohini.semwal@uni-jena.de
Indranil	Sen	Dortmund University	indranil.sen@tu-dortmund.de
Mathias	Senge	The University of Dublin	sengem@tcd.ie
Luis	Senz	JGU Mainz	luis.senz@uni-mainz.de
Scolastica "Lella"	Serroni	Università degli Studi di Messina	sserroni@unime.it
Georgina	Shillito	Friedrich Schiller University Jena	georgina.shillito@uni-jena.de
Kazuteru	Shinozaki	Yokohama City University	shino@yokohama-cu.ac.jp
Baldeep	Sidhu	University of Manitoba	sidhub34@myumanitoba.ca
Alessandro	Sinopoli	University of Messina	alessandro.sinopoli@unime.it
Simon Nicholas	Smith	University College Dublin (UCD)	simon.smith@ucd.ie
Simon	Soldner	Universität Würzburg	simon.soldner@uni-wuerzburg.de
Fumika	Sueyoshi	Kyushu University	sueyoshi.fumika.622@s.kyushu-u.ac.jp
Licheng	Sun	Westlake University/KTH Stockholm	panzhuoying@westlake.edu.cn
Paulina	Szoldra	AGH University of Krakow	szoldra@agh.edu.pl
Kazuma	Takahara	University of Hyogo	takahara@sci.u-hyogo.ac.jp
Alexander N.	Tarnovsky	Bowling Green State University	atamov@bgsu.edu
Luise	Thomisch	Friedrich Schiller University Jena	luise.thomisch@uni-jena.de
Mark	Thompson	University of Southern California	met@usc.edu
Toranosuke	Tomikawa	Hokkaido University	lelysblanc871@eis.hokudai.ac.jp
Simon	Torres Gonzalez	Universität Paderborn	simon.torres.gonzalez@uni-paderborn.de
Ludovic	Troian-Gautier	UCLouvain	Ludovic.Troian@uclouvain.be
Stefanie	Tschierlei	TU Braunschweig	s.tschierlei@tu-bs.de
Kiyoshi	Tsuge	University of Toyama	tsuge@sci.u-toyama.ac.jp

Florent	Urbain	Université libre de Bruxelles	florent.urbain@ulb.be
Abha	Valavalkar	Leibniz Institute of Photonic Technology	abha.valavalkar@leibniz-ipht.de
Renske	van der Veen	Helmholtz Center Berlin for Materials and Energy	renske.vanderveen@helmholtz-berlin.de
Benjamin	Van Kuiken	European XFEL	benjamin.van.kuiken@xfel.eu
Ana Karem	Vega Salgado	UCLouvain	ana.vegasalgado@uclouvain.be
Barbara	Ventura	ISOF-CNR, Bologna	barbara.ventura@isof.cnr.it
Marco	Villa	University of Bologna	marco.villa11@unibo.it
Antonin	Víček	J. Heyrovsky Institute Prague/ QMU London	a.vlcek@qmul.ac.uk
Dorothee	Wagner	University of Basel	dorothee.wagner@unibas.ch
Cui	Wang	University of Konstanz	cui.wang@uni-konstanz.de
Jiahao	WANG	City University of Hong Kong	jwang884-c@my.cityu.edu.hk
Mengfei	Wang	ICReDD, Hokkaido University	wang.mf@icredd.hokudai.ac.jp
Christina	Wegeberg	University of Southern Denmark	wegeberg@sdu.dk
Tanja	Weil	Max Planck Institute for Polymer Research	officeweil@mpip-mainz.mpg.de
Julia	Weinstein	the University of Sheffield	Julia.Weinstein@Sheffield.ac.uk
Joël	Wellauer	University of Basel	joel.wellauer@unibas.ch
Oliver	Wenger	University of Basel	oliver.wenger@unibas.ch
Mary	White	University of Huddersfield	mary.white@hud.ac.uk
Eleanor	Windle	University College Dublin	eleanor.windle@ucdconnect.ie
Michael	Wolf	University of British Columbia	mwolf@chem.ubc.ca
Frank	Würthner	University of Würzburg	wuerthner@uni-wuerzburg.de
Masayuki	Yagi	Niigata University	yagi@eng.niigata-u.ac.jp
Kotaro	Yakuwa	Tokyo University of Science	1324704@ed.tus.ac.jp
Hirohisa	Yanagikawa	The University of Tokyo	h-yanagi@iis.u-tokyo.ac.jp
Hartmut	Yersin	University of Regensburg	hartmut.yersin@ur.de
Elizabeth	Young	Lehigh University	ery317@lehigh.edu
Borys	Zakharchenko	University of Birmingham	b.zakharchenko@bham.ac.uk
Clara	Zehe	Mario Negri Institute, Milano	cZehe@marionegri.it
Minli	Zhang	Uppsala University	minli.zhang@kemi.uu.se
Li-Ting	Zhuo	Fu-Jen Catholic University	qq10120@gmail.com
Konstantinos P.	Zois	University of Vienna	konstantinos.pantelis.zois@univie.ac.at