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/

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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

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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 hold, 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. Wasgestian)
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) *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.*
1989	Santa Barbara, USA (Peter Ford, Richard Watts) *The logo of ISPPCC (octahedron) was introduced. Coordination Chemistry Reviews starts publishing ISPPCC proceedings, a tradition never interrupted.*
1991	Fribourg, Switzerland (Alexander von Zelewsky, Peter Belser)
1993	Sendai, Japan (Hiroshi Kobayashi, Takeshi Ohno, Masaoki Furue)
1995	Krakow, Poland (Zofia Stasicka, Grazyna Stochel) *ISPPCC incorporates the existing "Symposium on the Photochemical and Thermal Reactions of Coordination Compounds (SPTROCC)" which took place in Europe.*
1997	Saint Michael's College, Colchester, USA (Josh van Houten)
1999	Lipari, Italy (Sebastiano Campagna, Scolastica Serroni, Francesco Barigelletti)
2001	Veszprém, Hungary (Attila Horwath, Otto Horwath)
2004	Hong Kong, China (Vivian W.-W. Yam, Chi-Ming Che) *initially planned for 2003.*

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 *rosticcerie*, 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@chantillycafè.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**
8:30	Registration y-ISPPCC
9:40-09:50	**opening**
09:50-10:05	Yoan Fréroux
10:05-10:20	Marius Müßler
10:20-10:35	Jie Ying Chen
10:35-10:50	Xiao Ma
10:50-11:05	Noémie Chantry
11:05-11:35	*Coffee break*
11:35-11:50	Laura Duncan
11:50-12:05	Martin Pižl
12:05-12:20	Dorothee S. Wagner
12:20-12:35	Federico Droghetti
12:35-12:50	Stefano Scoditti
12:50-14:00	*Lunch time*
14:00-14:15	Emily L. Race
14:15-14:30	Marta Costa Verdugo
14:30-14:45	Li-Ting Zhuo
14:45-15:00	Amelia Kacperkiewicz
15:00-15:15	Eleonor Windle
15:15-15:30	Elena Dallerba
15:30-16:00	*Coffee break*
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

time	**July 8**
9:00-9:15	Francesca Mancini
9:15-9:30	Oussama Bindech
9:30-9:45	Fumika Sueyoshi
9:45-10:00	Minli Zhang
10:00-10:15	Elkhansa Elbashier
10:15-10:30	Andrea Mantovani
10:30-11:00	*Coffee break*
11:00-11:15	Baldeep Sidhu
11:15-11:30	Hirohisa Yanagikawa
11:30-11:45	Nicolò Quadrio
11:45-12:00	Arindam Saha
12:00-12:15	Greta Fogar
12:15-12:30	Yu Hui Lin
12:30-13:45	*Lunch time*
13:45-14:00	Federica Ruani
14:00-14:15	Felix Glaser
14:15-14:30	Luis G. Alves do Nascimento
14:30-14:40	**Closing remarks**

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 $[Ru(tpm)(prbim)(NH_3)]^{2+}$ 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** (***University of Basel)*** Synthetic control over excited-state behavior of Nickel(II) complexes
yOC-9	12:20-12:35	**Federico Droghetti** (*University of Ferrara*) Light-driven CO_2 reduction with a heptacoordinated Iron(II) polypyridine complex
yOC-10	12:35-12:50	**Stefano Scoditti** (*DIPC, University of Calabria, PMAS*) 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** *(University of Messina)*		
yOC-11	14:00-14:15	**Emily L. Race** (*University of Sheffield*) 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** (*DIPC, PMAS*) Photochemical behavior of Ruthenium(II) complexes in Choline Geranate (CAGE) ionic liquids
yOC-13	14:30-14:45	**Li-Ting Zhuo** (*Fu Jen Catholic University*) 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** (*University of Manitoba*) 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** (*University College Dublin*) Contrasting excited state processes of Zn(II) and Cu(II) phthalocyanines
yOC-16	15:15-15:30	**Elena Dallerba** (*Curtin University*) Unveiling the potential of Iridium complexes in tissue imaging
15:30-16:00		**Coffee Break**

Session 4

Chair: Arindam Saha *(Université de Montréal)*, Martina Mazzaferro *(University of Messina)*

yOC-17	16:00-16:15	**Chizuru Kasahara** (*University Jena*) [FeFe]-H_2ase mimicking complex bearing two organic photosensitisers for photocatalytic H_2 evolution
yOC-18	16:15-16:30	**Sophia Lipinski** (*Technical University of Munich*) Diphosphine design enables rainbow emitting Ag(I) complexes for light-emitting electrochemical cells
yOC-19	16:30-16:45	**Edoardo Marchini** (*University of Ferrara*) 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** (*Lund University)* Reaction-diffusion simulations of photoredox processes in solution
yOC-21	17:00-17:15	**Ana Karem Vega Salgado** (*Université Catholique de Louvain*) Key factors influencing cage escape in photoinduced electron transfer
yOC-22	17:15-17:30	**Sergio Aranda** (*University of Zurich*) Unveiling the activation pathway of the CO_2 reduction catalyst trans-(Cl)-[Ru(X,X'- dimethyl-2,2'-bipyridine)$(CO)_2Cl_2$] by direct spectroscopic observation
yOC-23	17:30-17:45	**Othmane Essahili** (*Mohammed VI Polytechnic University*) Sustainable luminescent materials for next-generation smart building integration

Tuesday, July 8th

Session 5

Chair: Federica Giorgianni *(University of Messina)*

yOC-24	9:00-9:15	**Francesca Mancini** (*University of Bologna*) 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** (*Université de Strasbourg*) 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** (*Kyushu University*) Photocatalytic H_2 evolution by pyridinium-tethered mononuclear and dinuclear Platinum complexes
yOC-27	9:45-10:00	**Minli Zhang** (*Uppsala University*) High-efficiency photoinduced charge separation in Iron N-heterocyclic carbenes
yOC-28	10:00-10:15	**Elkhansa Elbashier** (*University of Otago*) Altering the optical properties of Zn-porphyrin through β-substitutions
yOC-29	10:15-10:30	**Andrea Mantovani** (*University of Ferrara*) Comparison of Iridium sensitizers employed in the photoelectrochemical generation of added-value organics
10:30-11:00		**Coffee Break**
Session 6 **Chair: Salvatore Genovese** *(University of Messina)*		
yOC-30	11:00-11:15	**Baldeep K. Sidhu** (*University of Manitoba*) 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** (*University of Tokyo*) Novel spectroscopic approaches to evaluate the excited triplet states of metal complexes using magnetic circular dichroism
yOC-32	11:30-11:45	**Nicolò Quadrio** (*University of Milan*) Plastics detection using hydrogels functionalized with switchable Iridium complexes
yOC-33	11:45-12:00	**Arindam Saha** (*Université de Montréal*) 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** (*University of Trieste, Leiden University*) Sn^{IV}-porphyrins conjugates as bio-inspired models for artificial photosynthesis
yOC-35	12:15-12:30	**Yu-Hui Lin** (*Fu Jen Catholic University*) 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** *(University of Messina)*		
yOC-36	13:45-14:00	**Federica Ruani** (*ISOF-CNR*) 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** (*Université Catholique de Louvain*) Welcome to the dark side: photoactive Iron complexes with microsecond excited-state lifetimes
yOC-38	14:15-14:30	**Luis G. A. do Nascimento** (*University of São Paulo*) 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

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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.

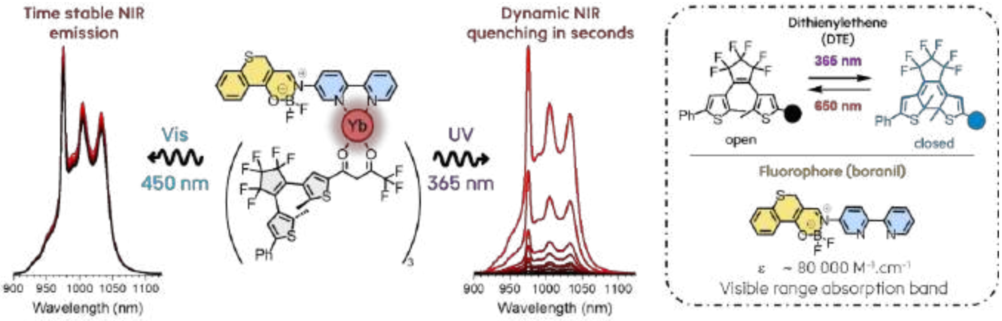

Figure 1. An Ytterbium(III) complex combining a photochromic dithienylethene ligand and a fluorophore as an antenna provides efficient luminescence switching with non-destructive readout behaviour.

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

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

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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 heterodinculear 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.

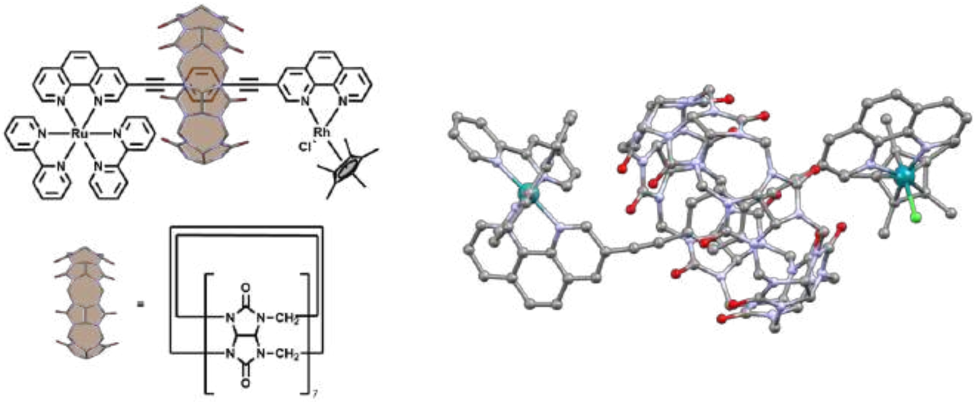

Figure 1: Molecular depiction & DFT structure of Hetero[2]Rotaxane.

Acknowledgments

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Characteristics of photoinduced Quenching $[Ru(tpm)(prbim)(NH_3)]^{2+}$ Ions: Density Functional Modeling and Efficient Metal Center State Quenching Mechanisms

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We synthesized the photoinduced quenching complex, $[Ru(tpm)(prbim)(NH_3)]^{2+}$ to investigate the excited-state relaxations between triplet metal-to-ligand charge-transfer (^{3}MLCT) and metal-center (^{3}MC) 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 $Ru(tpm)(prbim)(NH_3)]^{2+}$ 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 $[Ru(tpm)(prbim)(NH_3)]^{2+}$ suggests that the transition from ^{3}MLCT to ^{3}MC states occurs via modifications in metal-ligand bond lengths, providing insight into the quenching mechanism.

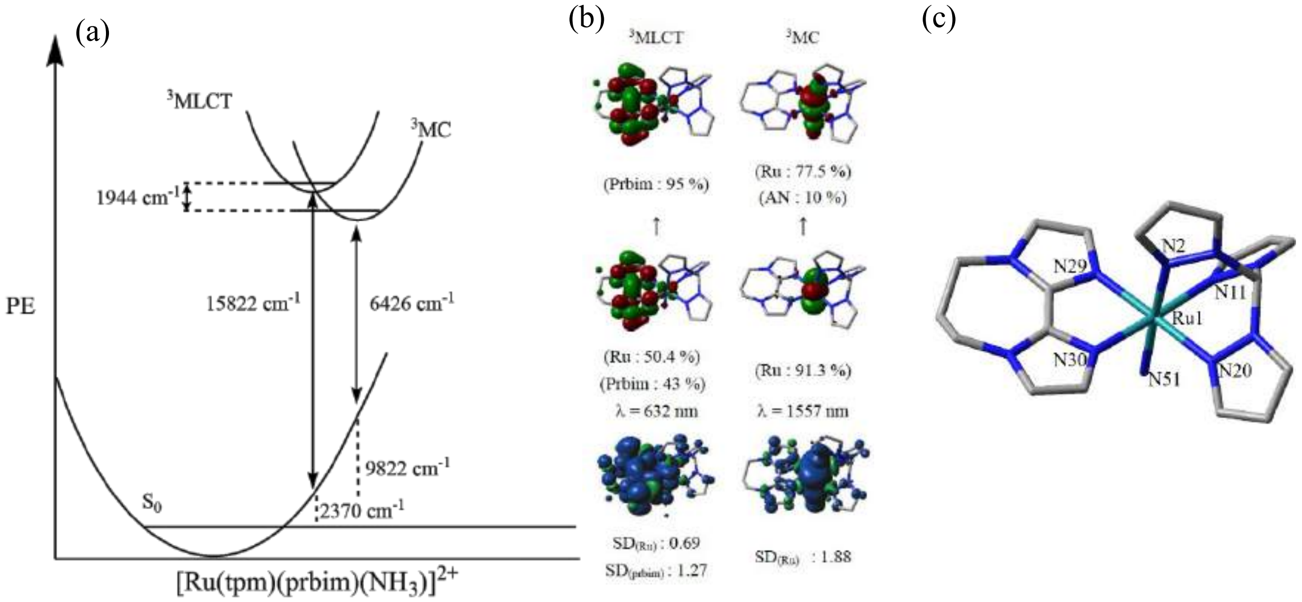

Figure 1. Illustration of the computational model for the relaxation of the ^{3}MLCT and ^{3}MC excited states for the target complex $[Ru(tpm)(prbim)(NH_3)]^{2+}$: (a) potential energy diagram illustrating the energy gap between the ^{3}MLCT and ^{3}MC excited states. (b) Natural Transition Orbitals (NTOs) of the ^{3}MLCT and ^{3}MC 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

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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)$_2$(H$_2$dcbpy)] (**Figure 1a**).[2] Figure 1b shows typical confocal laser phosphorescence microscopy images overlapped with transmitted light microscopy images for [Pt(CN)$_2$(H$_2$dcbpy)] 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)$_2$(H$_2$dcbpy)] induced by MeOH vapor.

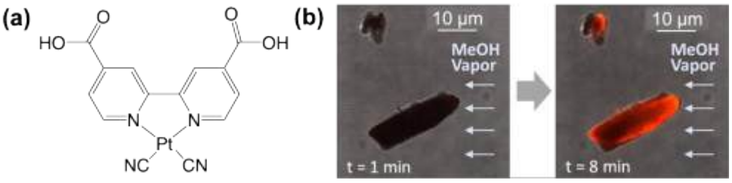

Figure 1. (a) Molecular structure of [Pt(CN)$_2$(H$_2$dcbpy)] and (b) confocal laser phosphorescence microscopy images overlapped with transmitted light microscopy images of its particle before and after exposure to MeOH vapor.

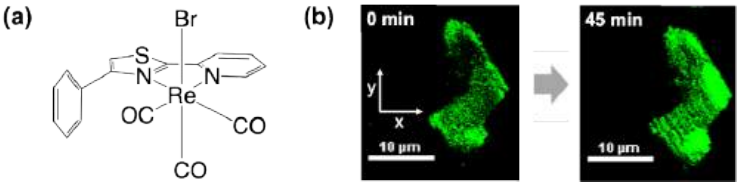

Figure 2. (a) Molecular structure of *fac*-[Re(CO)$_3$Br(ppt)] and (b) confocal laser phosphorescence microscopy images of its particle before and after exposure to CHCl$_3$ vapor.

In *fac*-[Re(CO)$_3$Br(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 CHCl$_3$ 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.

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

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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.

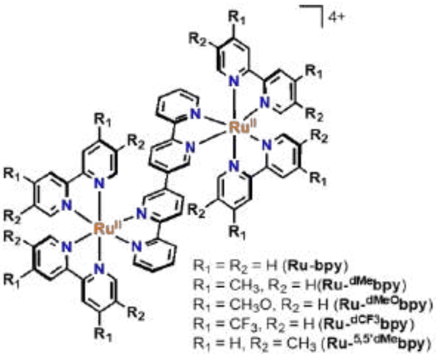

Figure 1: Structure of the complexes

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'''-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.

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The Development of Sulfur-Containing, APTRA-Derived Fluorescent Probes with Specific Zn^{2+} Binding

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The divalent cations Mg^{2+}, Ca^{2+} and Zn^{2+} 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 Mg^{2+} detection, *o*•aminophenol•N,N,O-triacetate (APTRA) is a commonly used binding unit, despite the fact it also binds to Ca^{2+} and Zn^{2+} (Figure 1).[2]

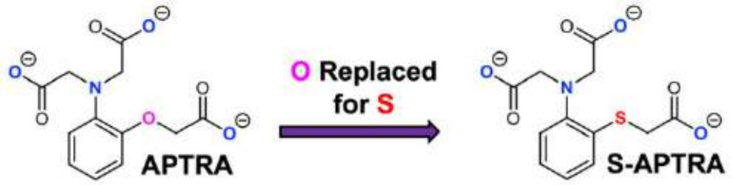

Figure 1. Structures of APTRA (left) and S-APTRA (right).

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 Zn^{2+} very strongly, and with high selectivity over Mg^{2+} and Ca^{2+} (**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 Zn^{2+} binding, with no interference from either Mg^{2+} or Ca^{2+} (**Figure 2**). It also has the advantage of improved water solubility compared to many of the other reported Zn^{2+} probes, whilst the high (pentadentate) denticity prevents the formation of ternary complexes with endogenous biological molecules, allowing the sole detection of free Zn^{2+} *in vivo*, This renders S-APTRA-Rosamine a reliable and selective Zn^{2+} probe, with potential application in cellular imaging.

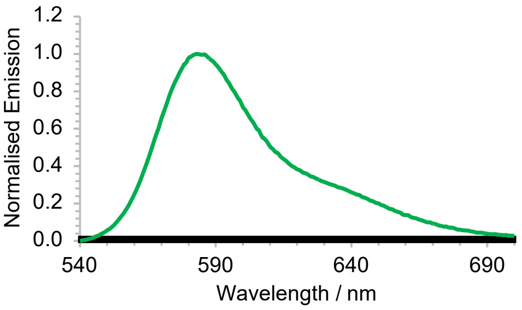

Figure 2. Emission spectrum of S•APTRA-rosamine (black) and in its Zn^{2+}-bound forms (green) in aqueous buffer solution (50 mM HEPES, 100 mM KCl, pH 7.21).

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

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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 $[Ru(\alpha\text{-diimine})_2(dppz)]^{2+}$, 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.

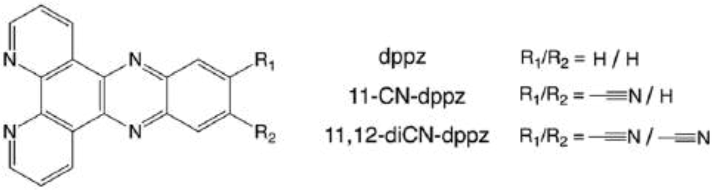

Figure 1. Structures of investigated dppz ligands in $[Ru(tap)_2(dppz\text{-}R_1,R_2)]^{2+}$.

Acknowledgments

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

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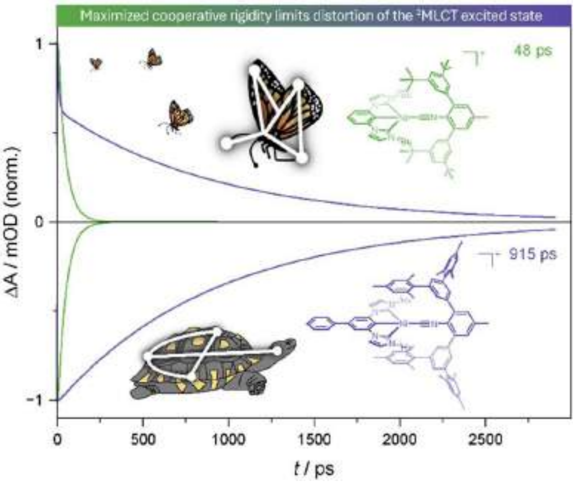
Conventionally, photochemical reactions occur only from the lowest excited state of the photoactive species while higher excited states relax on a ps timescale, and the additional energy is lost, limiting photochemical reactivity.[1,2] Here we present a molecular design strategy to slow the relaxation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

From the excited ^{3}MLCT state, square planar Ni^{II} complexes undergo molecular distortion and fast deactivation into low lying ^{3}MC 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 ^{3}MLCT 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.



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Light-Driven CO_2 Reduction with a Heptacoordinated Iron(II) Polypyridine Complex

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The growing necessity to mitigate human-induced CO_2 emissions has driven research toward innovative approaches for converting them into value-added products. Recent findings in designing molecular catalysts for the CO_2 reduction reaction (CO_2RR) 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 CO_2 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]

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

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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 (^{3}MC), where the coordination environment and the tridentate ligand play a crucial role in the photodissociation pathway.

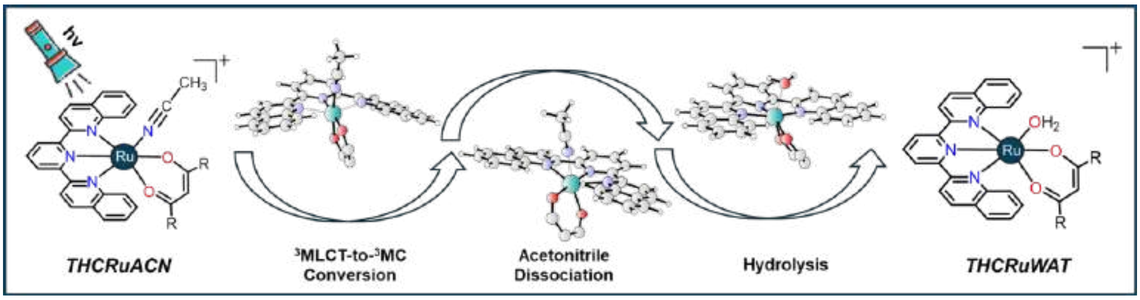

Figure 1. Mechanism of Photodissociation of THCRuACN complex.

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

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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).

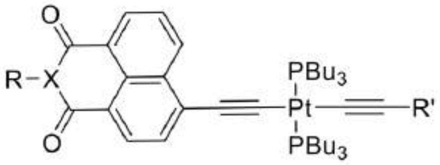

Figure 1. *trans*-(4-ethynyl-1,8-naphthalic anhydride)Pt(PBu_3)$_2$R.

Acknowledgments

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

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

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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 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 ^{3}MC (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.

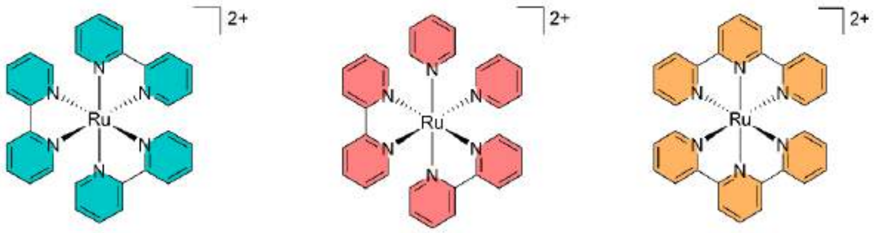

Figure 1. Structure of the ruthenium compounds used in this study

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).

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

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This is a rare report of Ru-(Cyclometalated), Ru-CM, phosphorescent chromophore in the mixed ligand $[Ru(bpy)_2(CM)]^+$, type complexes for $[Ru(bpy)_2(TBPZ)]^+$, where bpy 2,2'-bipyridine, TBPZ = Tribenzo[a,c,i]phenazine. The $[Ru(bpy)_2(TBPZ)]^+$ 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 $TBPZ^{-1/-2}$. 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 $[Ru(bpy)_2(ppy)]^+$ (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 $[Ru(bpy)_2(TBPZ)]^+$ exhibits the Ru-CM phosphorescent chromophore

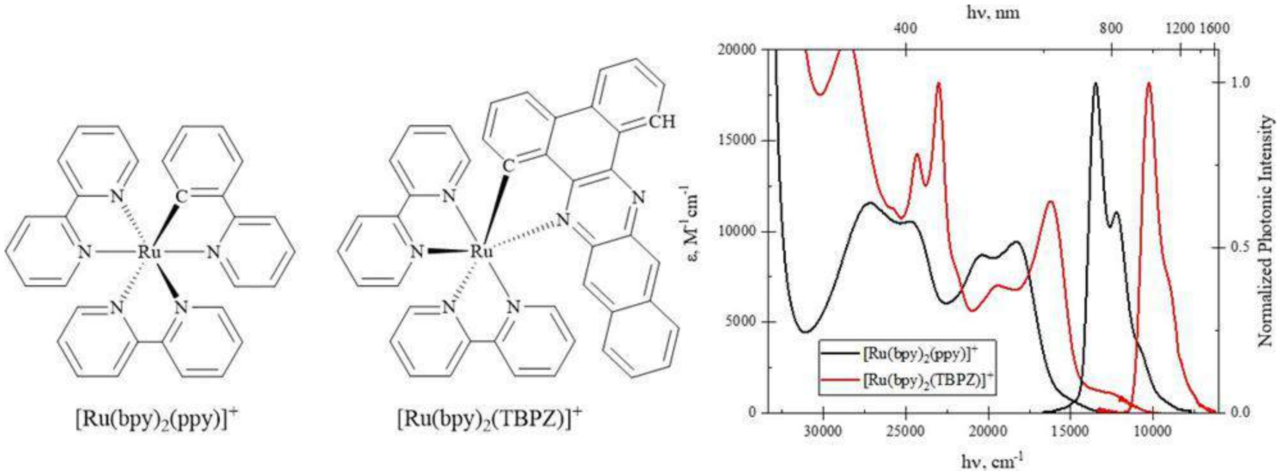

Figure 1. The 298K absorption spectra in CH_3CN and 77K emission spectra in butyronitrile glasses. (right panels), and structure of $[Ru(bpy)_2(ppy)]^+$ and $[Ru(bpy)_2(TBPZ)]^+$ (left panels).

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.

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

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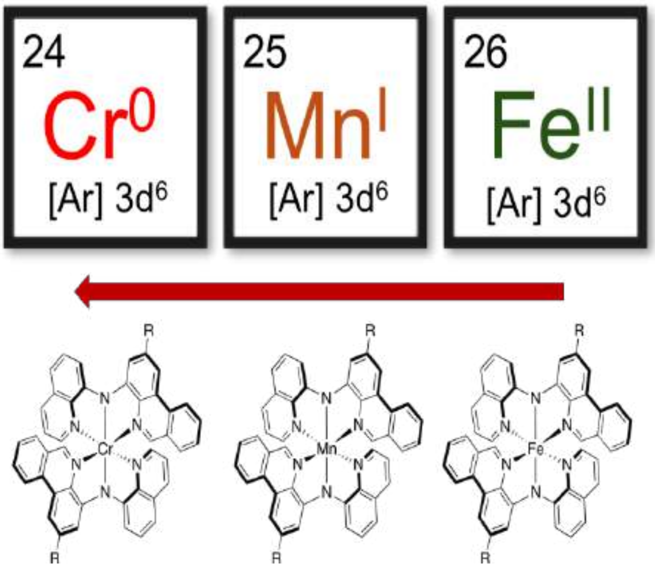
Coordination chemistry allows one to combine the unique influence of metals on the physical properties of molecules with the ability to further tune these properties using ligand design. Accordingly, coordination complexes can be applied in light emitting diodes, artificial photosynthesis schemes and 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.



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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.

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

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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 regiopure 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 S_1 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 H_2O compared to D_2O. 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 ($\tau = 1$ 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.

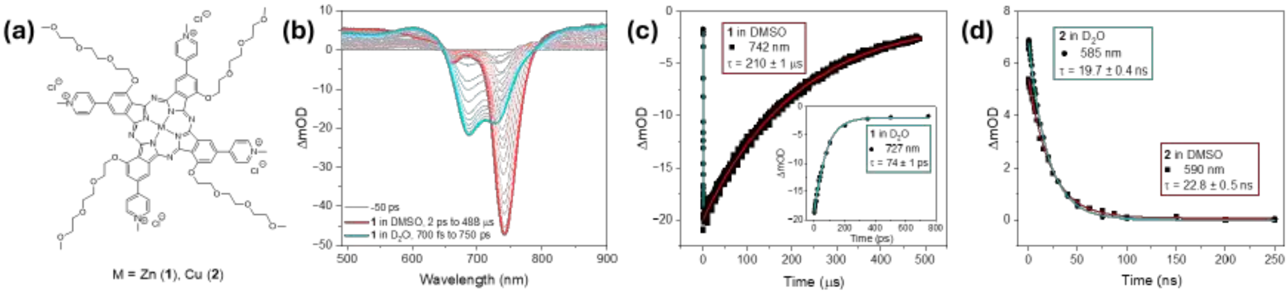

Figure 1. (a) Structure of **1** and **2**. (b) TA spectra of **1** in DMSO and D_2O. Recovery of (c) ground state bleach band of **1** and (d) transient band of **2** in DMSO and D_2O.

Acknowledgments

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Unveiling the Potential of Iridium Complexes in Tissue Imaging

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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.

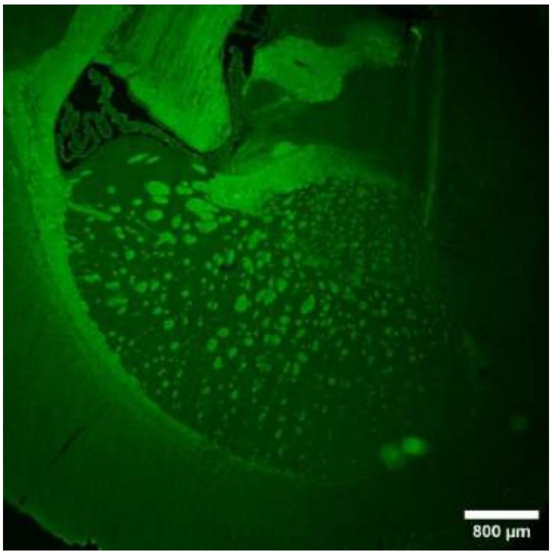

Figure 1. Microscopy image showing the staining of mouse brain tissue using an Ir(III) luminescent probe.

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.

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[FeFe]-H_2ase mimicking complex bearing two organic photosensitisers for photocatalytic H_2 evolution

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Photocatalytic H_2 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 $[(\mu\text{-S})_2Fe_2(CO)_6]$, the mimic of [FeFe]-$H_2$ase's catalytic centre (**CAT**), as the enzyme is known to exhibit remarkable H_2 production.[1] Thereby, applications of $[(\mu\text{-S})_2Fe_2(CO)_6]$ derivatives for photocatalytic H_2 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.

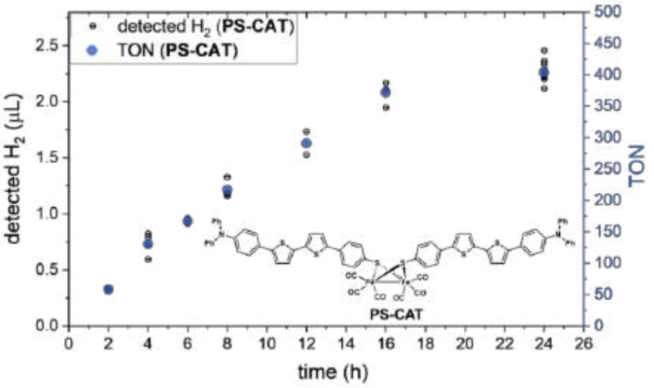

Figure 1. Molecular structure and photocatalytic activity of PS-CAT. The reactions were performed under 455 nm irradiation in the presence of 1, 3-dimethyl-2-phenylbenzimidazoline in N-Methyl-2-pyrrolidone.

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

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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, d^{10} 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 (λem = 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.

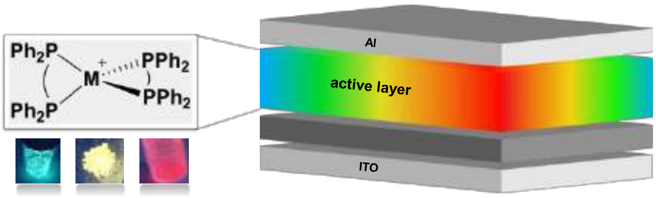

Figure 1. Diphosphine design toward rainbow emitting homoleptic cationic Ag(I) complexes for LECs.

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

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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 TiO_2 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.

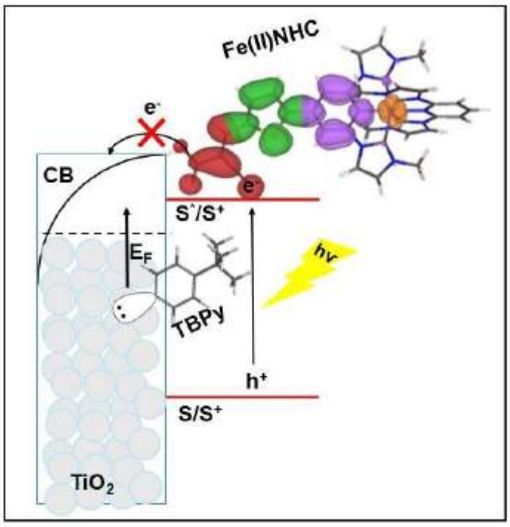

Figure 1. Schematic representation of an Fe(II)-SSC, with the absorption of TBPy onto TiO_2 also depicted.

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Reaction-Diffusion Simulations of Photoredox Processes in Solution

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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.

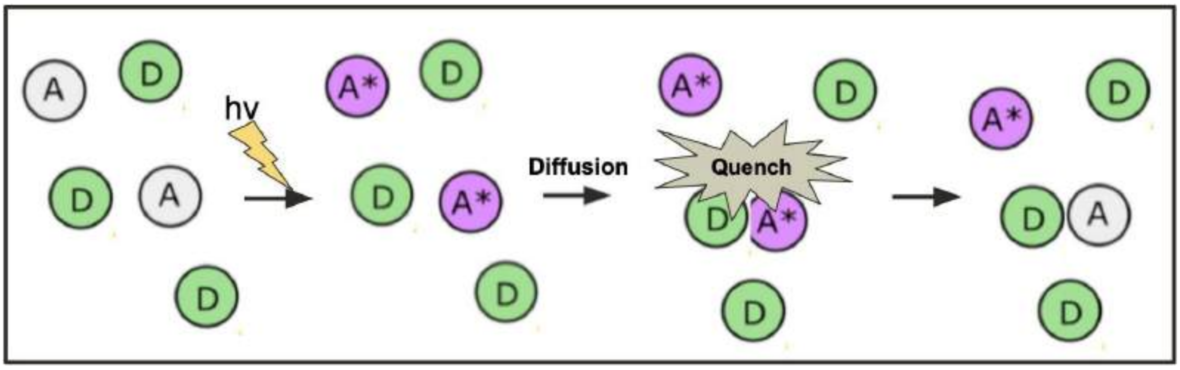

Figure 1: Collision quenching of donor and excited acceptor.

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Key factors influencing cage escape in photoinduced electron transfer.

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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 $9x10^7$ to $1.5x10^{10}$ $M^{-1}s^{-1}$ 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

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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]

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We report on the activation pathway *(Figure 1)* of a series of CO_2 reduction catalyst, Trans-(Cl)-[Ru(X,X’-dimethyl-2,2’-bipyridine)$(CO)_2Cl_2$, 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 $Ru(bpy)_3Cl_2$. 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.

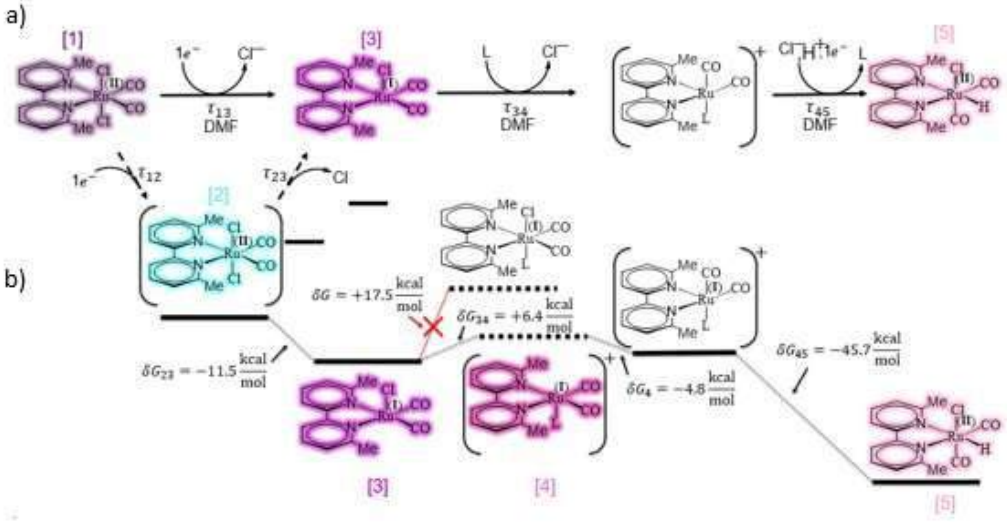

Figure 1. Proposed mechanism for Ru6dmb as a catalyst, Rubp3 and BNAH system based on a) experimental TRIR measurements and b) DFT calculations.

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Sustainable Luminescent Materials for Next-Generation Smart Building Integration

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In this work, five phenanthroline derivatives substituted with different methyl groups have been selected to synthesize βdiketonate-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

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Supramolecular interaction in Ru-Co and Ru-Fe complexes for efficient solar-driven hydrogen evolution and CO_2 reduction

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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 $[Ru(bpy)_2CN_2]$ within the field of solar energy conversion, focusing on its application to molecular hydrogen evolution and CO_2 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 $[Ru(bpy)_2CN_2]$ and hexadentate polypyridyl cobalt and iron complexes. [3,4]

Spectroscopic titrations were employed to monitor changes in absorbance, luminescence intensity, and lifetimes of the $[Ru(bpy)_2CN_2]$ complex upon addition of the catalyst. Our results demonstrate the successful formation of 1:1 supramolecular adducts, exhibiting a high association constant (K_{ass} □ 10^5 M^{-1}), which results in efficient static quenching of the ruthenium complex emission. The photocatalytic system comprises the $[Ru(bpy)_2CN_2]$ 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 CO_2 reduction in the presence of the iron complex.

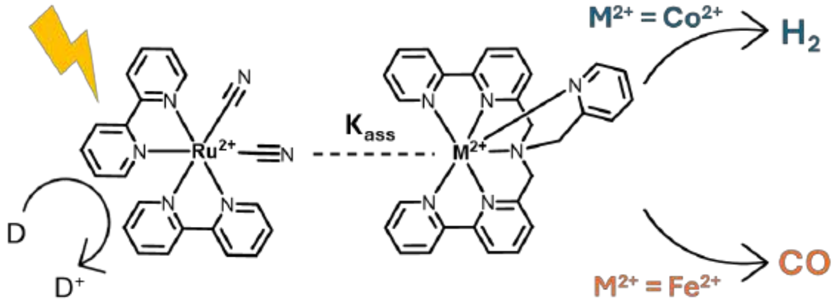

Figure 1. Schematic representation of the photo-driven hydrogen evolution and CO_2 reduction mechanisms through Ru-Co and Ru-Fe supramolecular interactions.

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

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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.

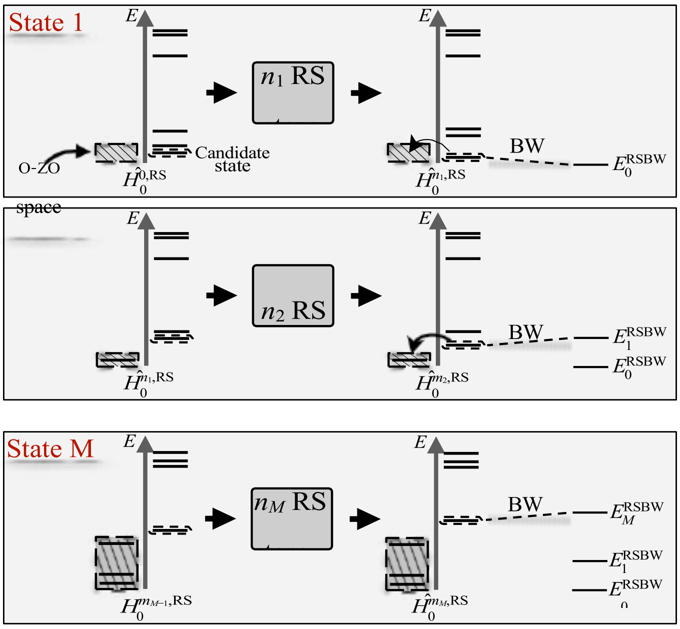

Figure 1. The diagram illustrates the calculation of a specific states using the RSBW approach. Initially, the Optimized Zero-Order (OZO) space is empty, and the first candidate is the lowest-energy zero-order state. After several Rayleigh-Schrödinger treatments, the candidate state becomes a reliable 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.

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Photocatalytic H_2 Evolution by Pyridinium-tethered Mononuclear and Dinuclear Platinum Complexes

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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 H_2 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 H_2 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]

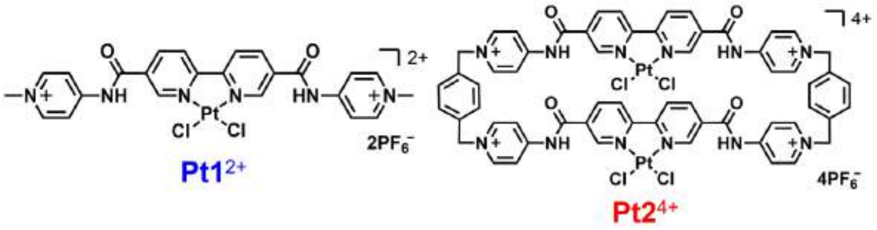

Figure 1. The structures of **Pt1**$^{2+}$ and **Pt2**$^{4+}$.

In this study, we synthesized new mononuclear and dinuclear platinum photocatalysts (**Pt1**$^{2+}$, **Pt2**$^{4+}$, **Figure 1**) to evaluate the role of dinucleating ligand installed in **Pt2**$^{4+}$. 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. **Pt1**$^{2+}$ and **Pt2**$^{4+}$ were successfully characterized by ^{1}H NMR and ESI-TOF-MS and elemental analysis. It was found that **Pt1**$^{2+}$ and **Pt2**$^{4+}$ show photocatalytic activity for H_2 evolution in the presence of EDTA (**Figure 2**). The difference in their photocatalytic activity was investigated by photochemical and electrochemical technique.

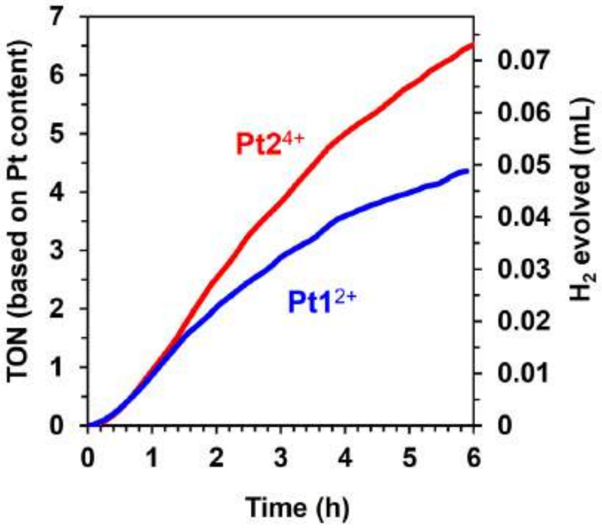

Figure 2. Photocatalytic H_2 evolution activities of **Pt1**$^{2+}$ (0.05 mM) or **Pt2**$^{4+}$ (0.025 mM) in an aqueous acetate buffer (pH = 5.0, 0.1 M) containing 20 vol % TFE and EDTA (30 mM) under Ar. Irradiated by Xe lamp (λ > 400 nm, 300 mW cm^{-2}).

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

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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 ^{2}LMCT 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

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

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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 $mM^{-1}cm^{-1}$) 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.

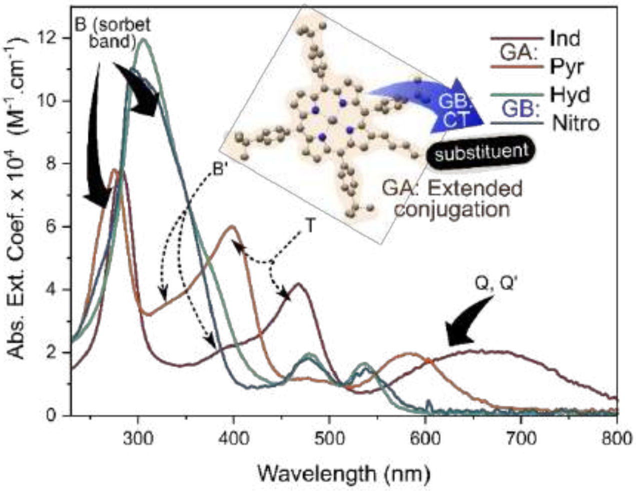

Figure 1. UV-Vis spectra of the four Zn-porphyrins, indicating the main electronic transitions.

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

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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 TiO_2 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.

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

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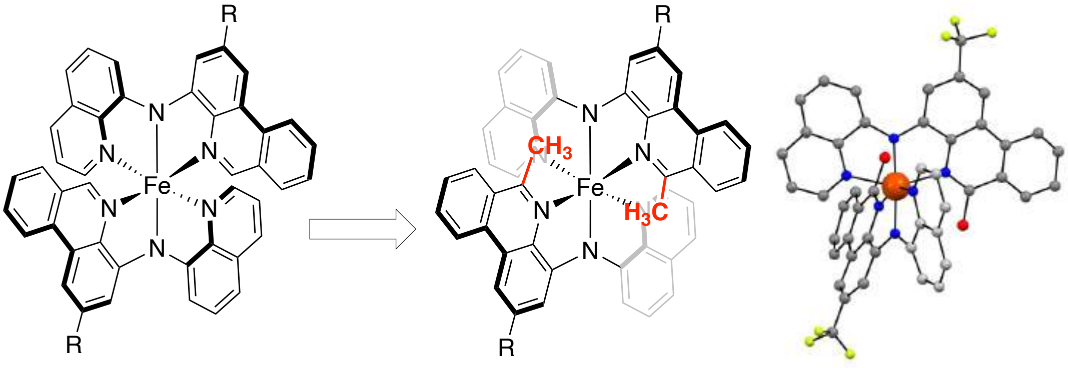
Iron coordination complexes have long been sought as a sustainable replacement for precious metal sensitizers in applications that exploit photo-generated excited states, from luminescent materials to photoredox catalysis to dye-sensitized solar cells. The main shortcoming of iron-based dyes is their 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.



all low-spin Fe(II) **high-spin Fe(II)**

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

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

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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]

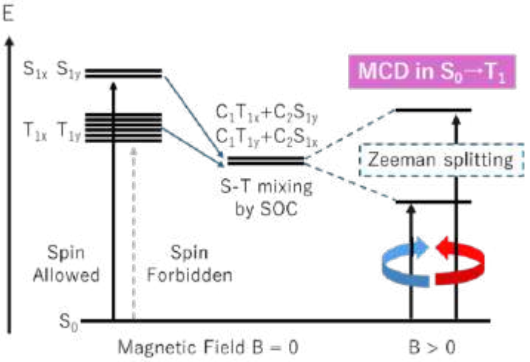

Figure 1. The mechanism of MCD Faraday *A* term in spin-forbidden $S_0 \to T_1$ transition.

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 $S_0 \to T_1$ absorption band, a Faraday *A* term for the $S_0 \to T_1$ 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 $S_0 \to T_1$ transition but also for the $S_0 \to T_2$ transition, which allows us to directly observe the nonluminescent, short-lived T_2 state.[4]

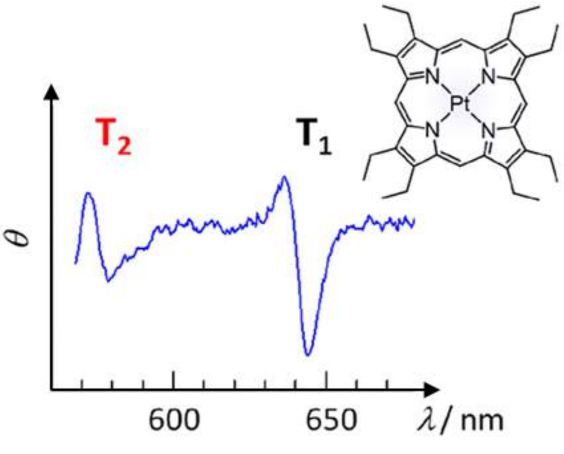

Figure 2. The MCD Faraday A term of excited triplet states in PtOEP.[4]

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 $S_0 \to T_1$ 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.

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Plastics detection using Hydrogels Functionalized with Switchable Iridium Complexes

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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 exited 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.

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

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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 $^1\pi$- π * and intra-ligand charge-transfer (^{1}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]

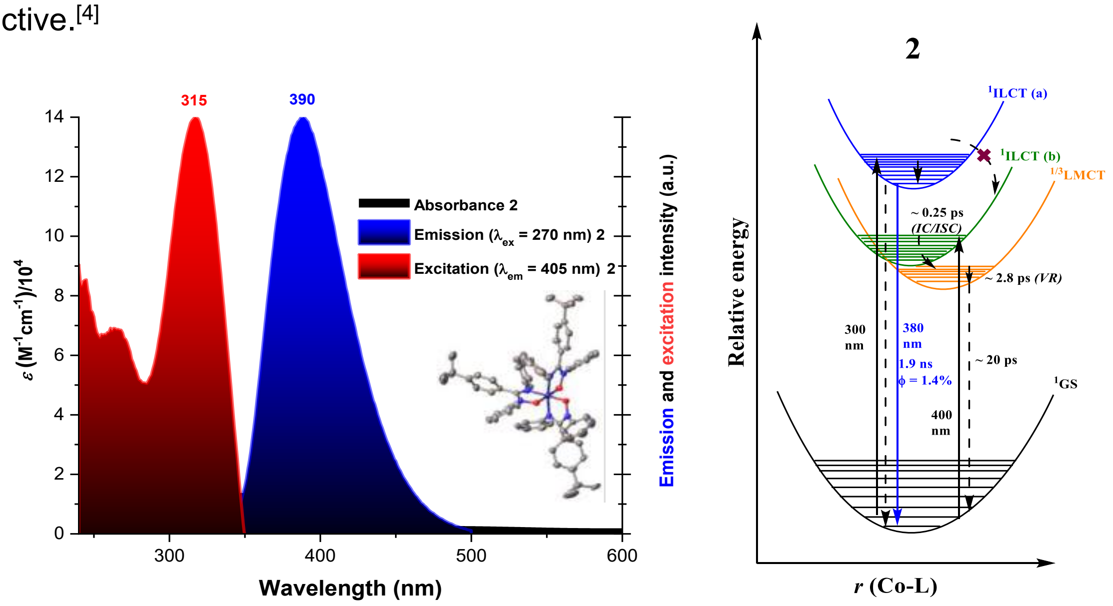

Figure 1. Graph showing the absorbance and emission spectra for one of the Anti-Kasha Co(III) complexes (left) and schematic for the decay pathway (right)

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.

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

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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 is 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]

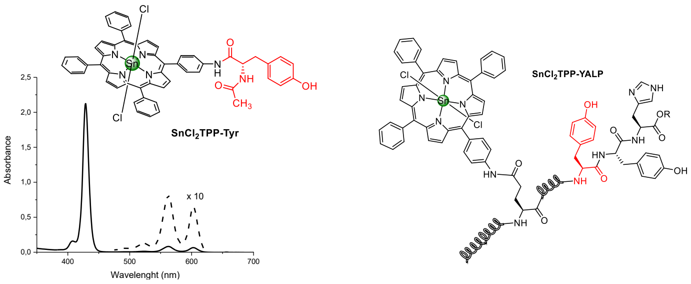

Figure 1. Example of a Sn^{IV}-porphyrin/amino acid conjugate for PCET studies (**SnCl$_2$TPP-Tyr**) and schematic representation of a Sn^{IV}-porphyrin/YALP conjugate for transmembrane unidirectional ET studies (**SnCl$_2$TPP-YALP**).

Acknowledgments

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

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Examine 77 K Phosphorescence of [Os(bpy)2(en)]2+: ADF Modeling and Spin-Orbit Coupling Mediated Intensity Stealing

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In early studies, the basic optical properties of the $[Os(bpy)_3]^{2+}$ 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 $[Os(bpy)_2(en)]^{2+}$ 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 singletto-triplet transitions. Based on the properties of the $[Os(bpy)_3]^{2+}$ 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 $[Os(bpy)_2(en)]^{2+}$ 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]

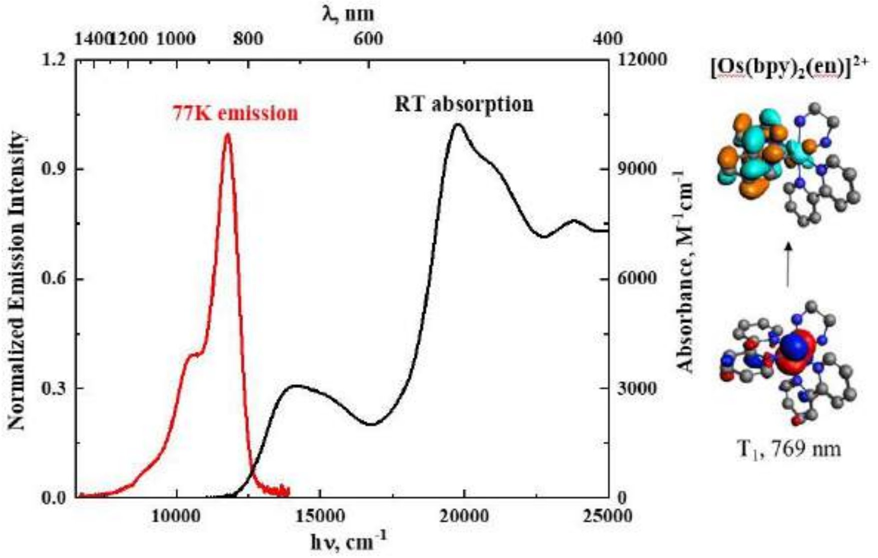

Figure 1. The 77 K emission spectra (red line, in butyronitrile) and the 298 K absorption spectra (black line, in CH_3CN) of the $[Os(bpy)_2(en)]^{2+}$ ion are shown in the left panel, along with the T_1 natural transition orbitals (NTOs) displayed in the right panel.

Aknowlegments

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

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

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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 (CH_2Cl_2 and toluene) and discuss the photophysical behavior of the formed complex. Interestingly, the solvent polarity strongly affects the photophysical response of the system.

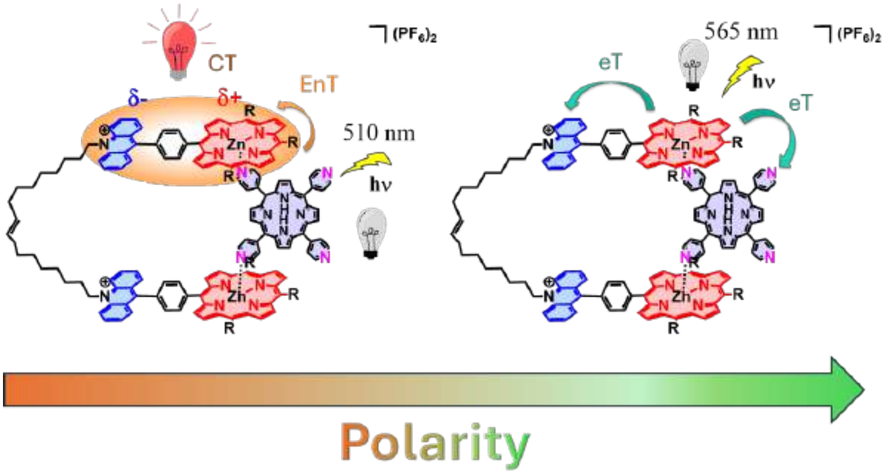

Figure 1. Effect of solvent polarity on photoinduced processes occurring in the host-guest complex.

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").

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Welcome to the Dark Side:

Photoactive Iron Complexes with Microsecond Excited-State Lifetimes

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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.

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

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Rhenium(I) complexes are promising candidates for artificial photosynthesis studies, mainly focused on CO_2 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*-$[Re(CO)_3(phen)(NI)]PF_6$, 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 CO_2 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 oxidating potential of complex **1** is that on the excitation wavelength ($\lambda_{exc} = 350$ 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 $\lambda_{exc} = 430$ 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 $NI^{-\bullet *}$ 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.

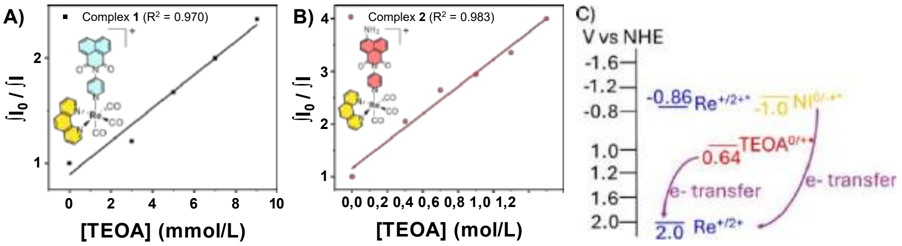

Figure 1. Stern-Volmer plots of the reductive quenching of the excited state of complexes **1** (A) and **2** (B) by TEOA in deaerated DMF at different concentrations (the complexes structures are in the figure) (B); Schematic energy diagram of the reductive quenching of the complex **1** excited state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

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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. Vlcek	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	ISPPCC registration	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**		**Lunch time**
14:00	ISPPCC registration	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
		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	Opening	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	PL1: J. McCusker	16:40-17:10	*Coffee Break*			16:10 -16:30	OR21: S. Baitalik	16:10 -16:40	*Coffee Break*
17:00-17:20	IN1: A. Cadranel	17:10-17:30	IN5: O. Ishitani	17:00	excursions	16:30-17:00	*Coffee Break*	16:40-17:00	OR30: AK Patra
17:20-17:40	OR1: E. Moore	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	OR2: J. Weinstein	17:50-18:10	OR8: A. Bossi						
		18:10 -18:30	OR9: C. Kerzig					17:20-18:00	closing
19:00	*Welcome Cocktail*	18:30-20:00	POSTER-1 (even)			20:30	*Social Dinner*		

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

26th ISPPCC PROGRAM

<table>
<tr><th colspan="3">Tuesday July 8 2025</th></tr>
<tr><td>11:00 – 15:30</td><td colspan="2">Registration (Trifiletti Theater)</td></tr>
<tr><td>16:00 -16:20</td><td colspan="2">Opening</td></tr>
<tr><td colspan="3">Chair: Antonin Vlcek (J. Hyerovsky Institute, Prague and Queen Mary University London)</td></tr>
<tr><td>16:20 – 17:00</td><td>PL1</td><td>James K. McCusker (Michigan State University)
Probing Reaction Coordinates for Ligand Field-state Interconversion Dynamics</td></tr>
<tr><td>17:00 – 17:20</td><td>IN 1</td><td>Alejandro Cadranel (Friedrich-Alexander-Universität Erlangen-Nürnberg and Universidad de Buenos Aires)
High-Energy MLCT States in Ru Polypyridines for Solar-Energy Conversion</td></tr>
<tr><td>17:20 – 17:40</td><td>OR1</td><td>Evan Moore (University of Queensland, St. Lucia, Australia)
Synergistic Hetero-TTA: Fact or Fiction?</td></tr>
<tr><td>17:40 – 18:00</td><td>OR2</td><td>Julia Weinstein (The University of Sheffield)
Ultrafast structural and spin dynamics in Copper(I) diimine phosphine complexes from femtosecond optical and X-ray spectroscopies</td></tr>
<tr><td>19:00</td><td colspan="2"><i>Welcome Party</i></td></tr>
</table>

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 Universitat 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 Vlcek** (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 $Fe(CN)_6$ → $Fe(CN)_5H_2O$ 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 $^1O_2$ 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	0R16	**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	***Coffee Break***	
17:00 – 18:30	**POSTER SESSION 2 (odd numbers)**	
20:30	***Social Dinner***	

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/Magnetoptical 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*

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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 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.

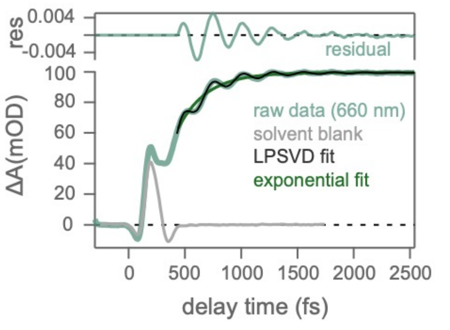

Figure 1. *Ultrafast time-resolved absorption data at 660 nm for $[Co(pyrro\text{-}bpy)_3]^{3+}$ (where pyrro-bpy is 4,4′-di-pyrrolidine-2,2′-bipyridine) in CH_3CN solution following ca. 45 fs excitation into the lowest energy ${}^1A_1 \rightarrow {}^1T_1$ ligand-field absorption at 480 nm.*

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

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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 com plexes 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 $T_1 \rightleftarrows S_1$ (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 the100s 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 ~1 cm^{-1} to ~3 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.

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Nanodiamond Sensors to Control Cellular Function

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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.

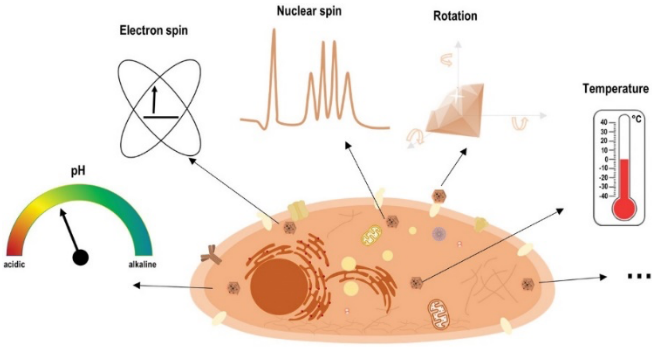

Figure 1. Detecting and manipulating intracellular signals[1]

Acknowledgments

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

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

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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 ($[Febpy_3]^{2+}$) and, in combination with TRIR, their initial evolution ($ReCl(CO)_3(bpy)$ and $W(C{\equiv}NAryl)_6$). Finally, we will discuss in a greater detail the Ir–Ir bond formation upon $^1(d\sigma^* \rightarrow p\sigma)$ 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 Commenius program, grant CZ.02.01.01/00/22_008/0004617.

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Supramolecular Engineering of Ruthenium Catalysts toward High Water Oxidation Activity

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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]

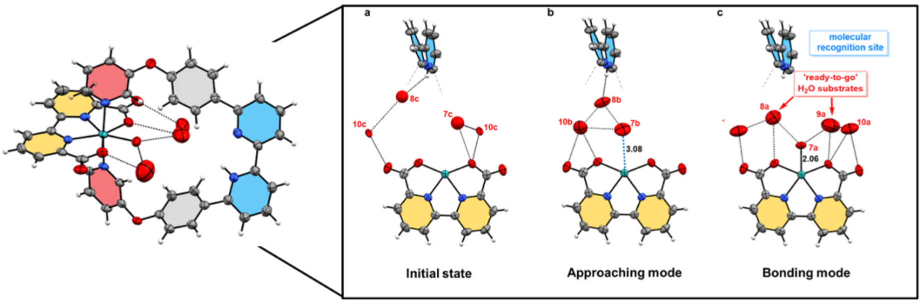

Figure 2. Single crystal “snapshot” of Ru(bda) catalyst with pocket of organized water molecules.

References

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

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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]

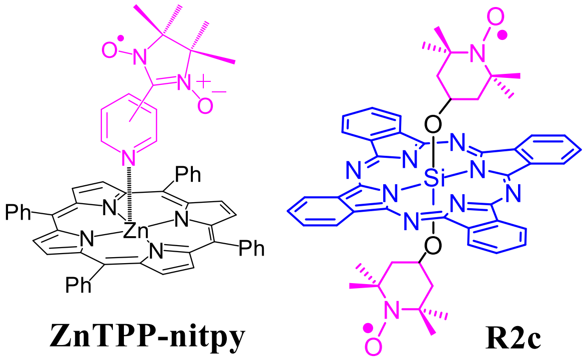
ZnTPP-nitpy
R2c

Figure 3. Molecular structures of ZnTPP-nitpy and R2c

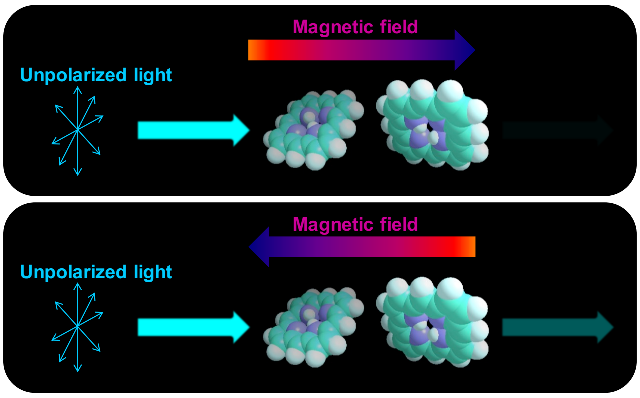

Figure 2. Magneto-chiral dichroism (MChD)

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Ligand-Based Oxidative and Reductive Catalysis for Water Oxidation and Fuels Generation From CO_2

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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, CO_2 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 CO_2 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 CO_2 reduction to formate. The formyl and dihydroquinoxalinide intermediates, generated by an ET-PCET mechanism, are the culprits in the hydride transfer to CO_2. 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 $[M(bpy)_2(bi\text{-}bimH_2)]^{n+}$ 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.

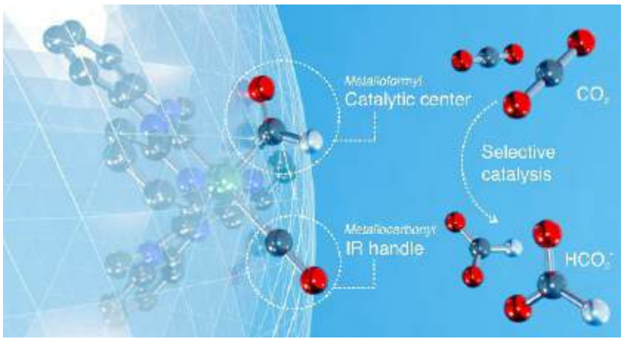

Figure 1. Ligand-Based CO_2 Reduction to Formate.

Aknowlegments

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

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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 absorption[5] 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]

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

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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 to 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.

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

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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

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Stimuli-responsive Flexible Lewis Pair Functionalized Coordination Complexes

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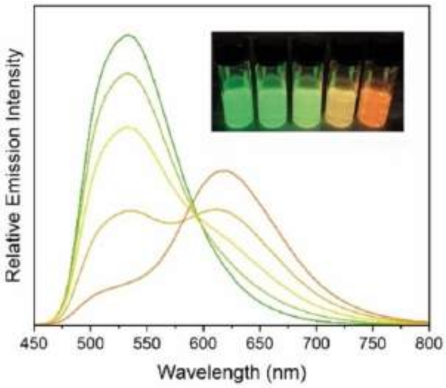
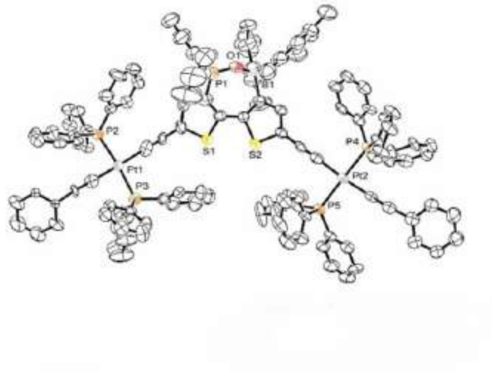
Coupling photo- and electroactive metal complexes to stimuli-responsive organic molecules results in intriguing new properties in these systems which can be leveraged for diverse applications in chemical sensing, bioimaging, and photopatterning. Flexible Lewis pair (FlexLPs) are systems that encompass 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.





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Signal amplification in electrochemiluminescent biosensors

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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 $[Ru(bpy)_3]^{2+}$ 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 $[Ru(bpy)_2(bpy\text{-}S\text{-}S\text{-}R)]^{2+}$, a $[Ru(bpy)_3]^{2+}$ 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.

Acknowlegments

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Lanthanoid Sensitisation from Re(I) Triangular Assemblies

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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.

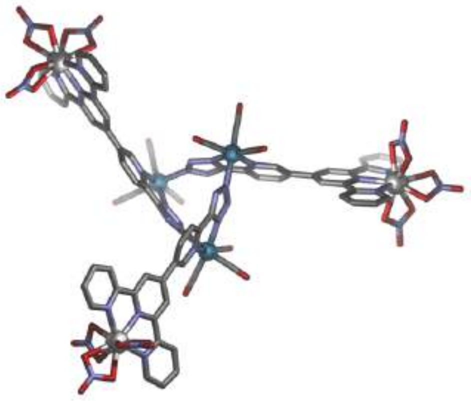

Figure 1. DFT model structure for the Re(I) tricarbonyl tetrazolato triangular assembly, featuring Eu(III) cations bound to the external terpyridine ligands.

Aknowlegments

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Light-Triggered Metallodrugs: Harnessing Excited State Dynamics for Phototherapy

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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 CO_2 Reduction

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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 (C_3N_4) [5]. Our molecular-based TiO_2 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 (CO_2) reduction into value-added fuels. By insisting in the use of aqueous reaction platforms, our initial challenge was to gain a sufficiently high CO_2 reduction selectivity versus water reduction even in fully aqueous media. A high selectivity in CO_2 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 CO_2-to-HCOOH conversion are still limited, especially when photo-driven in aqueous media. Our recent studies successfully unveiled the mechanism of CO_2 reduction to formate which undergoes via the M-H attack on CO_2, directly ends up with the release of formate [11,12]. Remarkably, the water-soluble $[Rh^{III}Cp^*(\text{dihydroxy-bpy})Cl]^+$ family was found to be the first example showing the water-induced switching in selectivity for the CO_2-to-HCOOH conversion [12].

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Photocatalytic events for CO_2 reduction and Oxygen Atom Transfer

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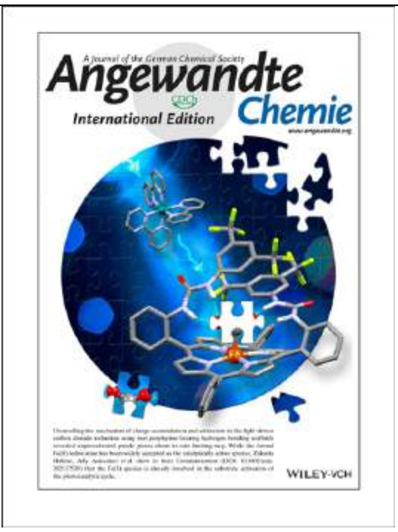
We found that the light-driven CO_2 reduction using an iron porphyrin holding urea groups as hydrogen bonding donor in the second coordination sphere of the catalyst lead to a multifold increase in TON and TOF compared to both non-substituted **TPPFe**, reaching one of the highest values in molecular photocatalysis and importantly with water as proton source. In contrast to the classic photocatalytic scheme where Fe^0 is argued to be the species to react with CO_2, we evidenced that the RDS herein resides in the formation of the **[UrFe^I-CO_2]** adduct. The added urea functionality plays an important role in the binding and activation of CO_2 at the Fe^I state enabling the faster photocatalytic conversion.[1]

Coupling a photoredox module and a bio-inspired non-heme model to activate O_2 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 (MVc+) can convey an electron to O_2 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]



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

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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

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

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To generate solar fuels, such as green H_2, green MeOH, or green NH_3 by the reduction of respective H_2O, CO_2, or N_2, 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 CO_2, 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.

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

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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 CO_2 reduction.

Aknowlegments

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

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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 (^{3}ILCT) 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.

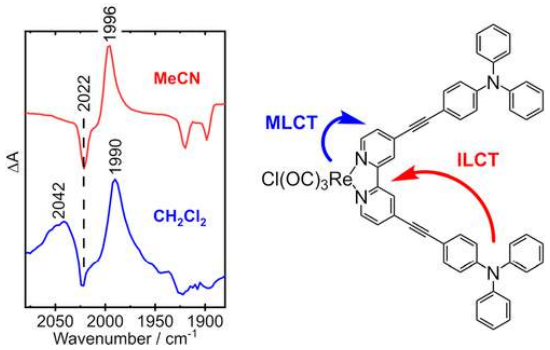

Figure 1. Switching the excited state for a metal complex using solvent as probed by time-resolved infrared spectroscopy.

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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

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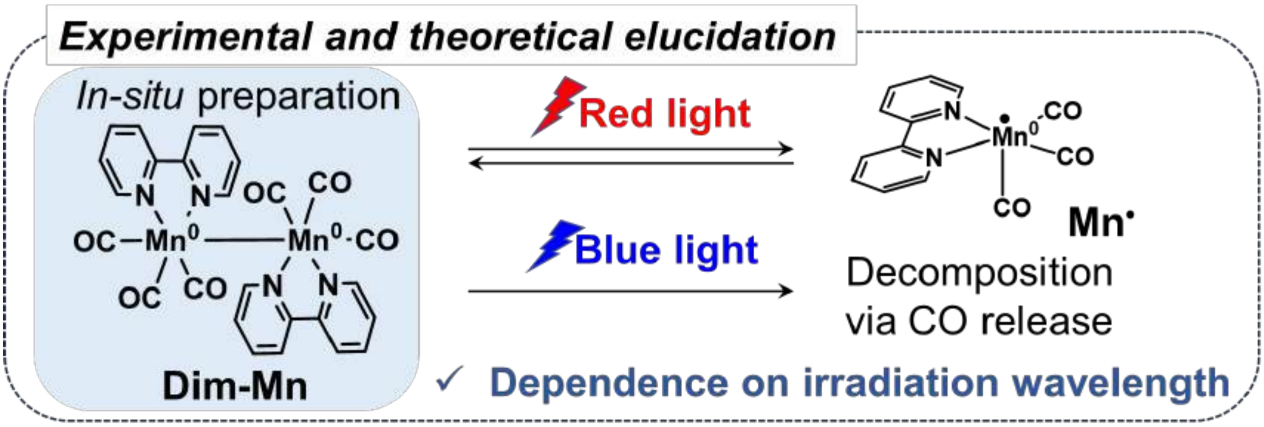
fac-$[Mn^{I}(diimine)(CO)_3(L)]^{0/+}$ has attracted significant attention as a catalyst for the photocatalytic reduction of CO_2.[1] However, in such photocatalytic systems, the photoexcitation of Mn complexes and reaction intermediates induces their decomposition, which lowers the durability of these 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-CO_2-TEOA**) as the catalyst, $[Os^{II}(4,4'\text{-dimethyl-bpy})(5,5'\text{-dimethyl-bpy})_2]^{2+}$ (**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 $[Mn^{0}_2(bpy)_2(CO)_6]$ (**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 $[Mn^{0}_2(bpy)_2(CO)_6]$ (**Dim-Mn**)



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

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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.

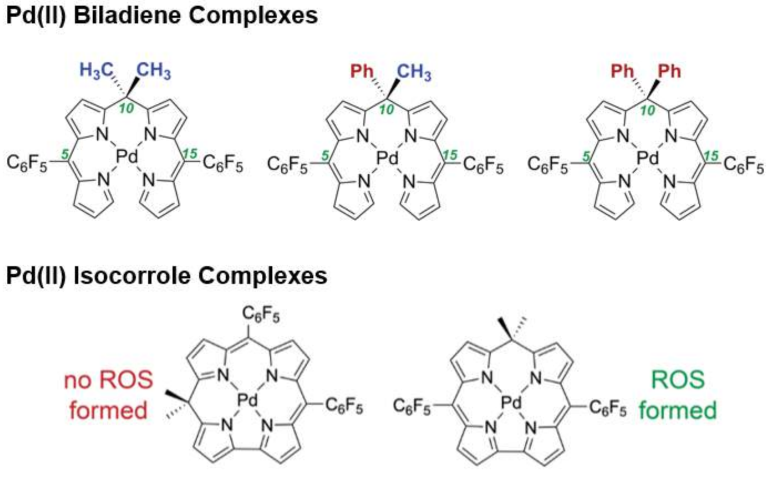

Figure 2. Molecular structures of the non-aromatic designer tetrapyrroles presented in this talk.

New metal complexes in luminescence, photocatalysis and charge accumulation

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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.

IN8

Gated Pathway for Photoinduced Interfacial Electron Transfer

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

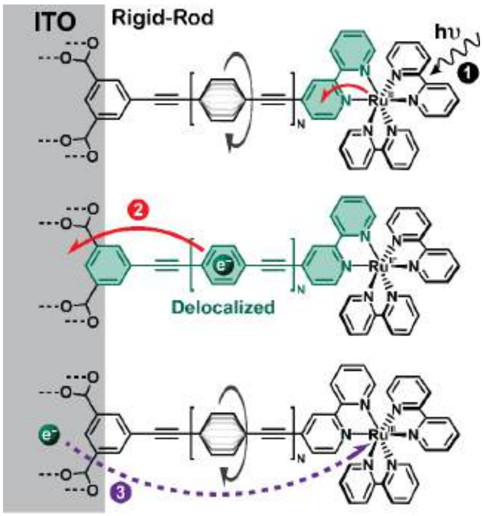

Figure 3. Mechanism for light initiated (1) “gated” electron transfer (2) that promotes long distance transfer to an oxide surface while inhibiting the unwanted charge recombination reaction (3).

Acknowledgments

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Electrochemistry of electrode/graphene nanoribbon hybrid materials

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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.

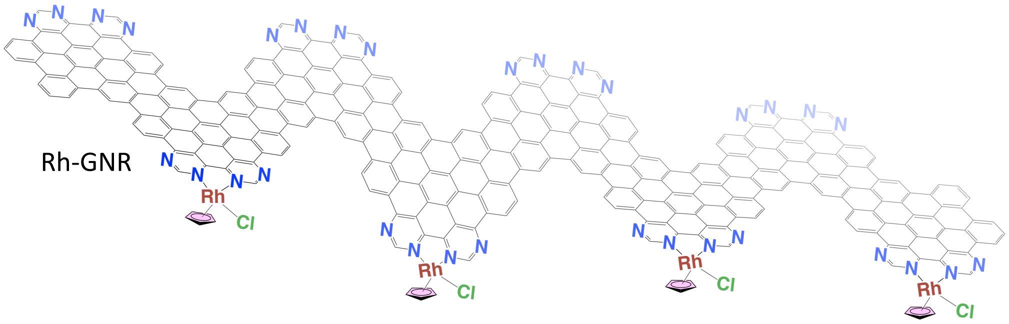

Figure 4. Structure of Rh-coordinated graphene nanoribbons.

Aknowlegments

Thanks to NSF for support.

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Photophysical characterization and structure determination of DNA-stabilized silver nanoclusters

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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.

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A New Look at the Magneto-Optical Activity of Metalloporphyrins

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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 pentafluorphenyl 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

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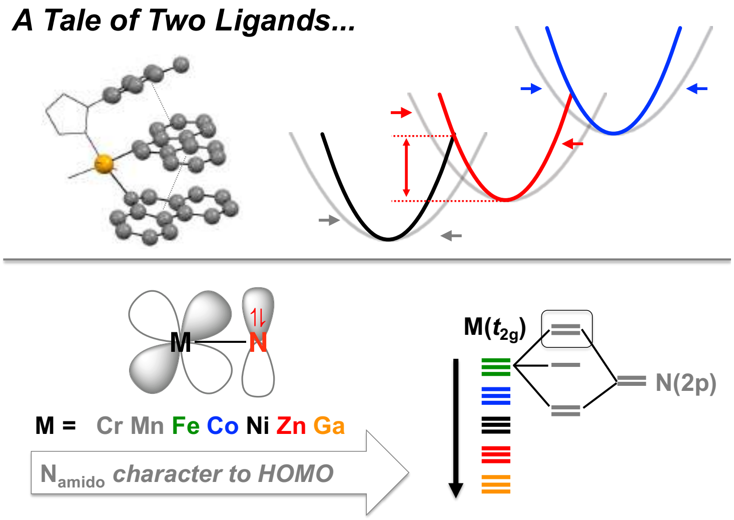
Photoactive transition metal coordination complexes play an outsized role in modern photochemistry, owing primarily to their ability to absorb visible light and generate useful, long-lived excited states. Ligand design is key to efforts to control both light absorption and the properties of excited states–including 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.



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Synergistic Hetero-TTA: Fact or Fiction?

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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.

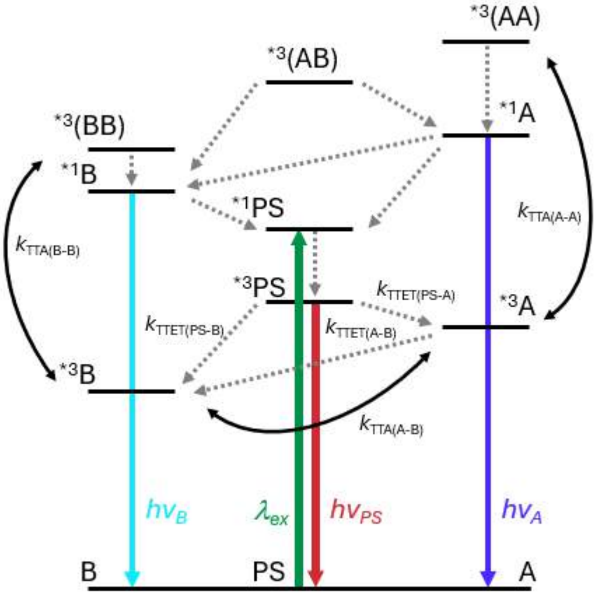

Figure 1. A simplified Jablonski diagram showing the different excited states and processes involved in homo- and hetero-TTA. S = sensitizer, A = annihilator (or mediator), B = annihilator.

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

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OR2

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

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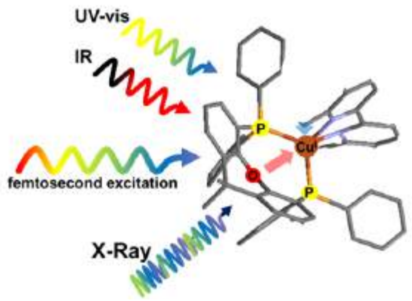
Transition metal complexes have been used in a plethora of light-driven processes and applications for decades. In the quest for cheaper, scalable photosensitizers and photocatalysts, much recent research turned toward complexes of 1st or 2nd row transition metals. To this end, (bis)diimine complexes 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

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Photoactivation Dynamics of Abundant Transition Metal Complexes

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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 stated 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.

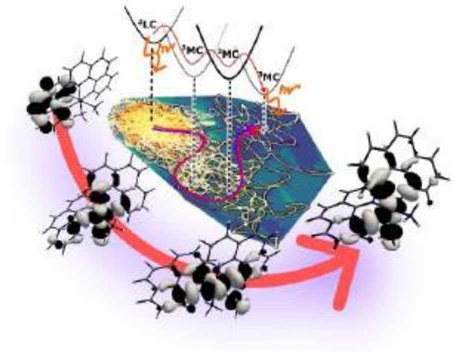

Figure 2. Photoactivation dynamics of transition metal complexes involve multidimensional motion to activate internal conversion and intersystem crossing paths.

Aknowlegments

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

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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 an 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

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Maximizing Photon to Product Efficiency in Photoredox Catalysis

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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. $[\mathrm{PC}^{\bullet-}:\mathrm{D}^{\bullet+}]$), 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.

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Luminescence Changeable Lanthanide-mixed Coordination Polymers for CO_2-storage

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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 CO_2 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)benzamilde). This study demonstrates a luminescence changeable CO_2-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]

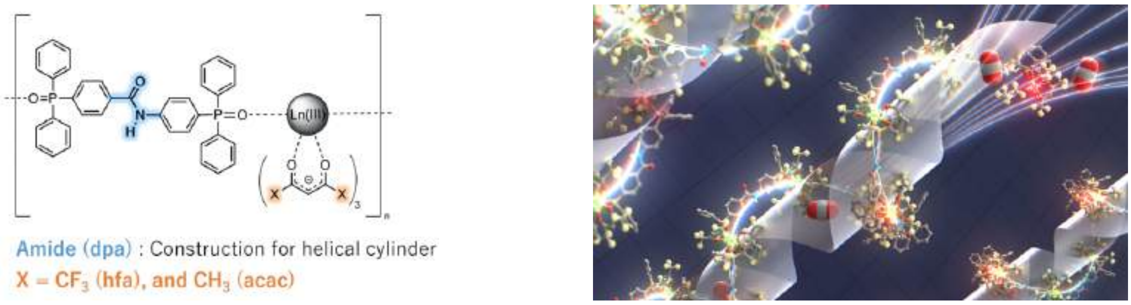

Figure 3. Chemical structure and $C0_2$ capture image of Eu(III)/Tb(III) mixed coordination polymer

Aknowlegments

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

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

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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 (^{2}LMCT) 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 $\{[\mathrm{Re}^{\mathrm{I}}]^{+} + \mathrm{D}^{\bullet+}\}$ and it highlights the complex competition between kinetic factors controlling the fundamental dynamics of the charge separated pairs inside the solvent cage.

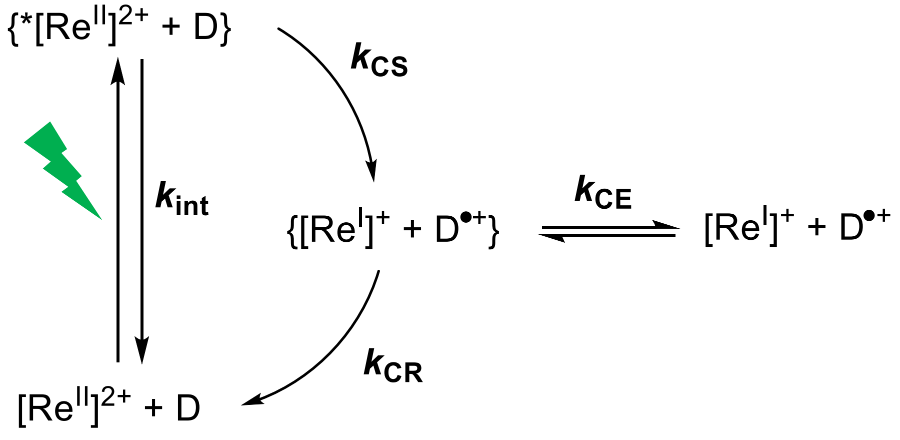

Figure 4. Photocycle between a rhenium(II) complex, $[\mathrm{Re}]^{2+}$, and the electron donor, D. k_{int} = intrinsic decay rate of excited $[\mathrm{Re}]^{2+}$; k_{CS} = rate of charge separation; k_{CR} = rate of charge recombination; k_{CE} = rate of cage escape.

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

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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 (**5**a-c/**6**a-c) to a IL one (**5**d/**6**d).

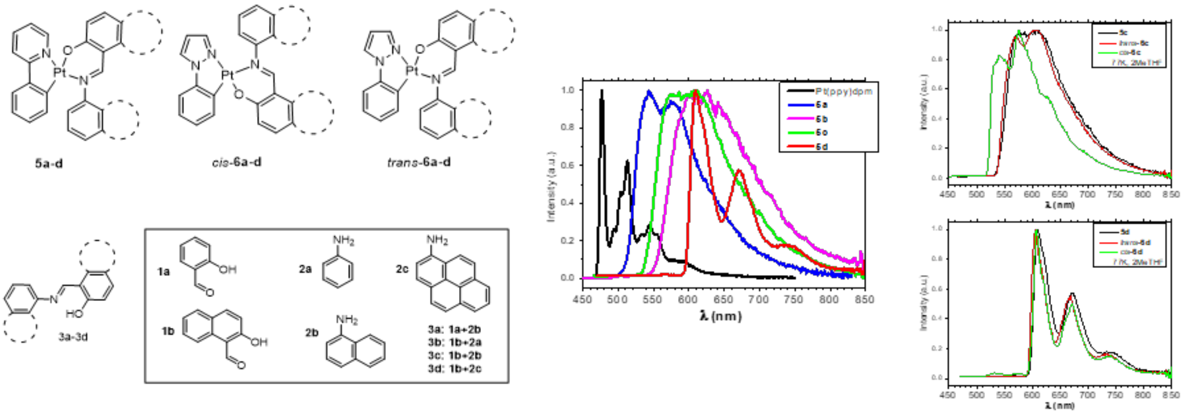

Figure 5. Structure of the studied Pt(C^N)(O^N) complexes; summary of the optical emissions

Aknowlegments

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

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

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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.

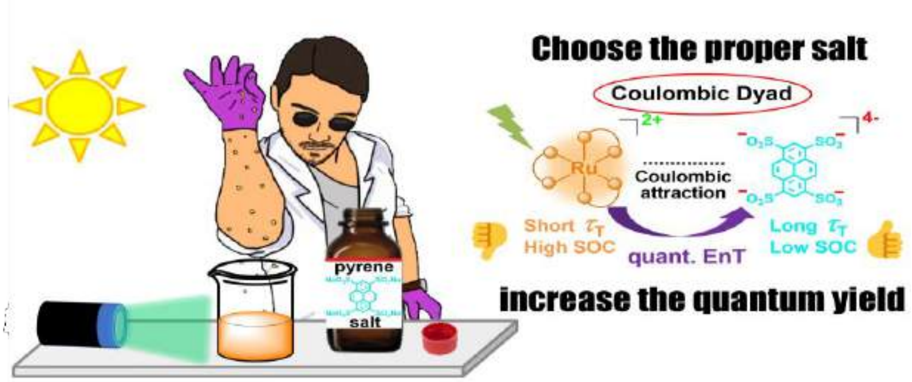

Figure 1. Straightforward preparation of a coulombic dyad for more efficient photocatalytic reactions.

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Structural characterization of the $Fe(CN)_6$ ➔ $Fe(CN)_5H2O$ photo-aquation process

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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 $[Fe(CN)_6]^{4-}$ following photoexcitation at 320 nm: $[Fe(CN)_6]^{4-}$ + *hv* ➔ $[Fe(CN)_6]^{4-*}$ ➔ $[Fe(CN)_5]^{3-}$ + CN^- ➔ $[Fe(CN)_5H_2O]^{3-}$ + 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.

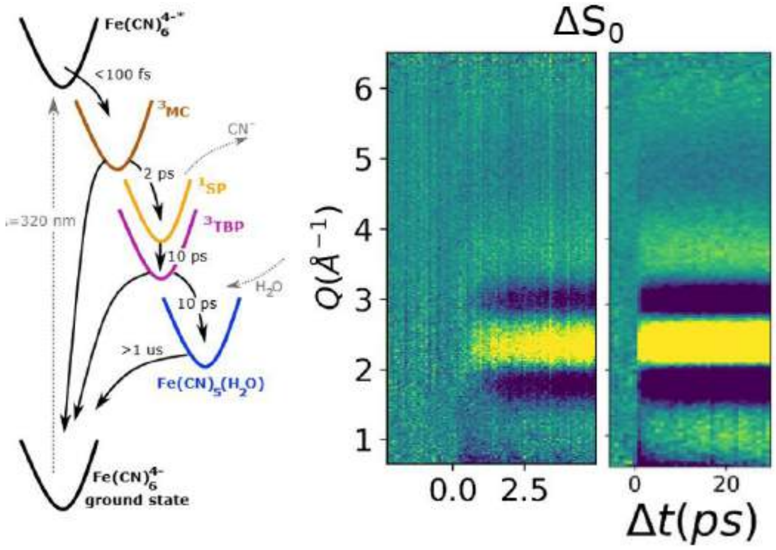

Figure 1. Schematic reaction scheme for the $[Fe(CN)_6]^{4-}$ + hν ➔ $[Fe(CN)_5H_2O]^{3-}$ photo-aquation reaction (left) and a 2D representation of the acquired TR-XSS data ($\Delta S(Q,\Delta t)$, right) showing how the reaction progresses on several different time scales with a concordant change in the X-ray scattering as the molecular structures change.

Acknowlegments

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Redox-Driven Photoselective Self-Assembly

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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]

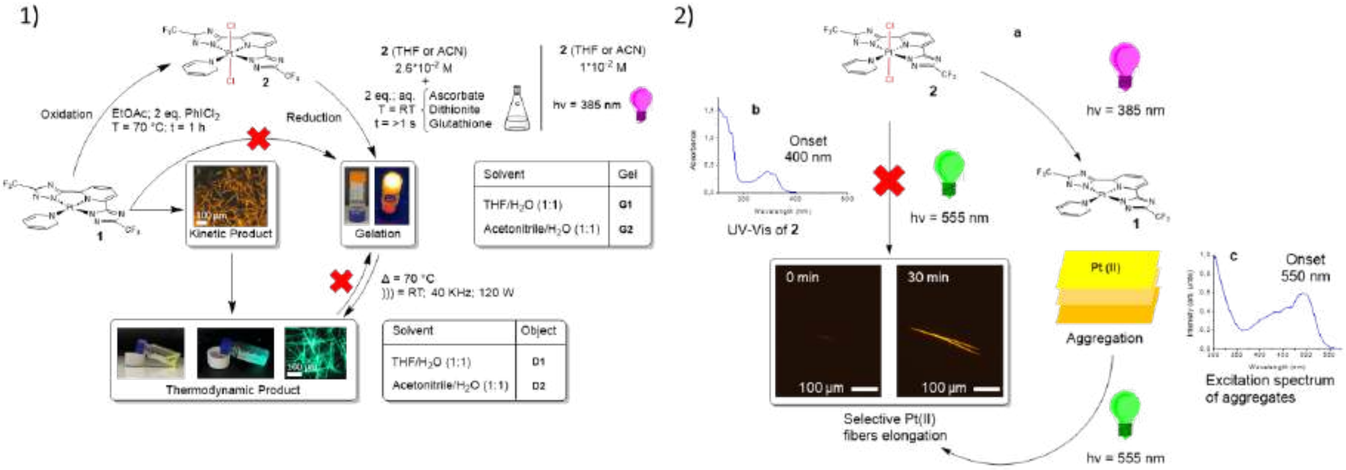

Figure 6. 1) Self-assembly pathway selection by photo or chemical reduction. 2) Photoselective elongation of Pt(II) fibers

Aknowlegments

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π Covalency in the Halogen Bond

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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

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

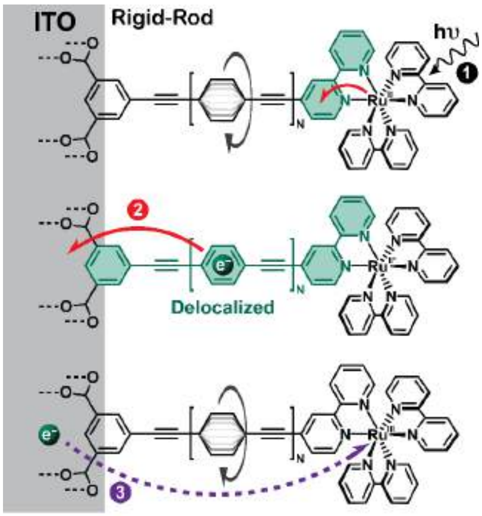

Figure 7. Mechanism for light initiated (1) "gated" electron transfer (2) that promotes long distance transfer to an oxide surface while inhibiting the unwanted charge recombination reaction (3).

Acknowledgments

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Elucidating Chemical Engineering Principles for Achieving High Emission and $^1O_2$ Photogeneration Quantum Yields with Homoleptic Cu(I) Complexes

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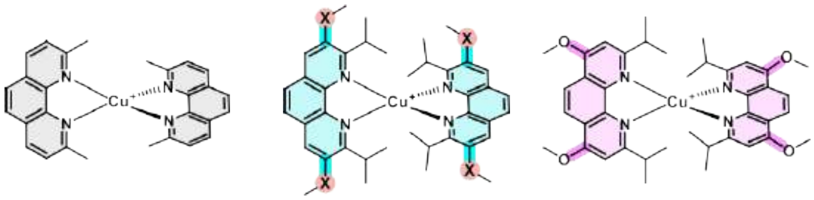
McMillin and colleagues elucidated the photochemical properties of homoleptic copper(I) complexes with the general formula CuL_2^+ in the late 1970s.[1] By utilizing the sterically constrained neocuproine (ncup, Figure 1) as a ligand, they demonstrated that it was possible to enhance the excited-state 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 CuL_2^+ 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 $^1O_2$ 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.



$Cu(ncup)_2^+$ ($\Phi < 0.1\%$)

X = O : **C1** ($\Phi = 6.7\%$)
X = S : **C2** ($\Phi = 1.3\%$)

C3 ($\Phi = 0.7\%$)

Figure 1. Structures of the seminal $Cu(ncup)_2^+$ complex and of the new complexes developed.

Acknowledgement

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

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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 d^6 Ru(II) & Ir(III) ions with their emissive and photoreactive ^{3}MLCT states. This includes the exploitation of microsecond lifetime ^{2}MC states of Cr(III) complexes[2] and the previously overlooked and remarkably long-lived highly photooxidising ^{3}MC states of cobalt(III) ions.[3] The now famous d^5 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 ^{2}LMCT 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.

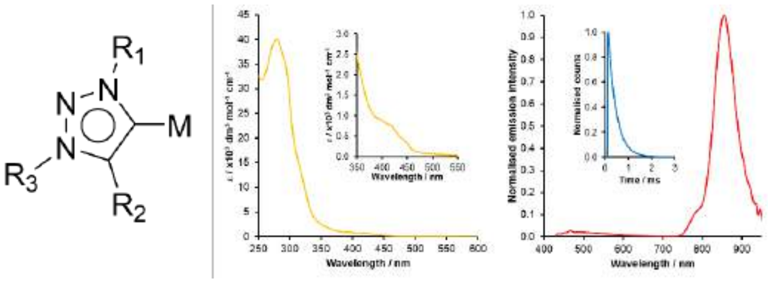

Figure 8. Generic structure of a 1,2,3-triazolylidene donor complex and absorption and emission data for a first transition series metal ion triazolylidene complex.

Acknowledgements

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

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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 ^{3}MC dissociative states.

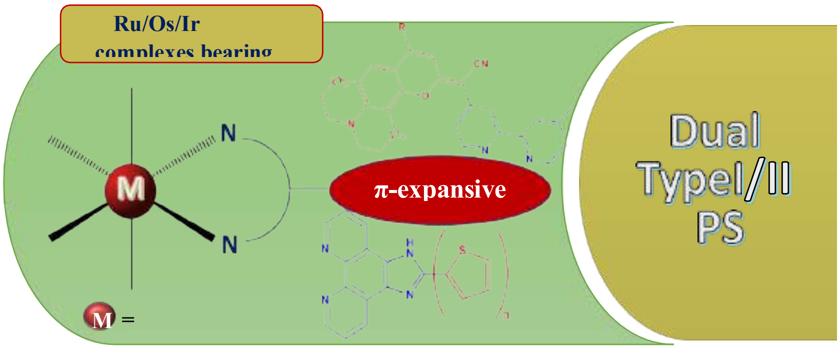

Figure 1.

Acknowledgments

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

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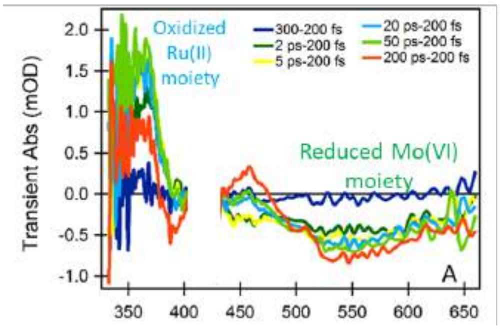
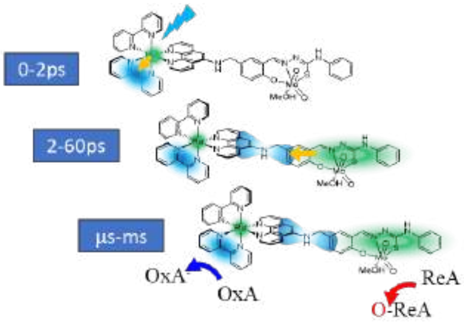
In this study we shed light on the underlying mechanisms of photo-induced oxidation-enhancement (PIOE) in biomimetic mono- and bi-metallic molybdenum photo-catalysts. In particular Ru(II)-Mo(VI) dyads show enhanced photo-activation of oxidative catalysis of Mo(VI), with respect to isolated Mo(VI) complexes.[1]





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 µs 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.

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

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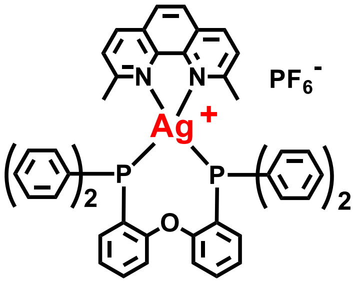
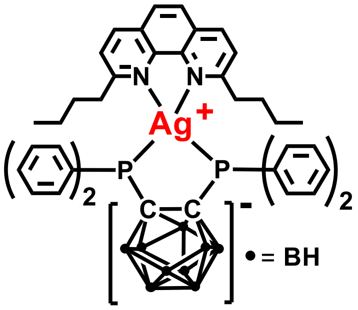
Photophysical properties of Ag(I) complexes can be modified drastically by ligand variation. By designing compound **1**, a heteroleptic Ag(I) complex of 2,9-dimethylphenanthroline (dmp) and a neutral diphosphine (DPEphos), an extremely long-lived phosphorescence of τ(phos) = 110 ms (PMMA doped 1 wt%, Φ_{PL}(phos) ≈ 50 %, λ_{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 (P_2-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}LL'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 Φ_{PL}(TADF) = 100 % (neat powder, λ_{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.



$[Ag(dmp)(DPEphos)]^+PF_6^-$

Compound 1



$Ag(dbp)(P_2$-nCB)

Compound 2

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Chiral metal complex for asymmetric photocatalysis

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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.

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OR20

Conformational Engineering and Atropisomerism as Photosensitizer Design Principles

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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

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

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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.

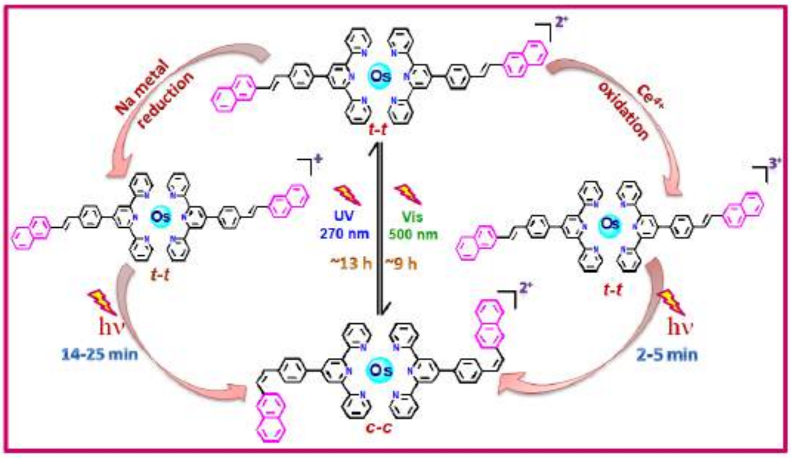

Figure 1. Multistep switching via oxidation-reduction and reversible *t-t*⇌*c-c* isomerization.

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

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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 metallacrowns (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 N_2-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.

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

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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]

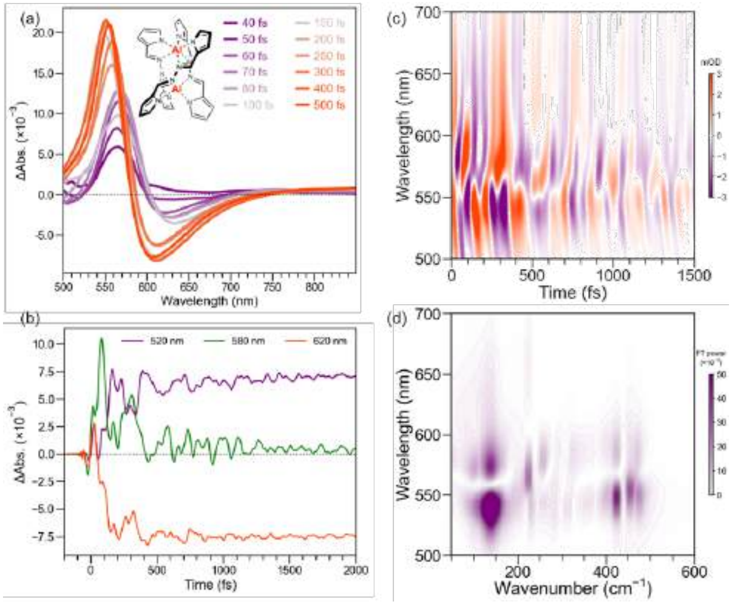

Figure 9. (a) Transient absorption with 10-fs pump pulse centered at 400 nm. (inset) The chemical structure of the Al complex (ALPHY), (b) beat signal observed at each wavelength, (c) beat signal obtained by population change subtraction, (d) beat map of the observed coherent oscillations as a function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

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

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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.

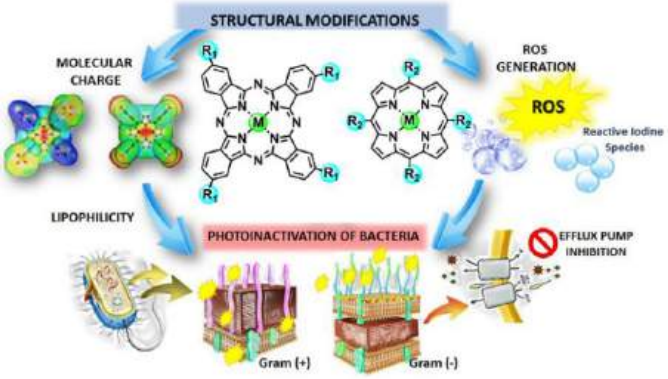

Figure 10 *Schematic representation of PDI using the aforementioned families of photosensitizers.*

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 (ΦΔ 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 TiO_2 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.

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Photocatalytic Reduction of CO_2 to HCOOH using a Porphyrin-Rhenium Dyad

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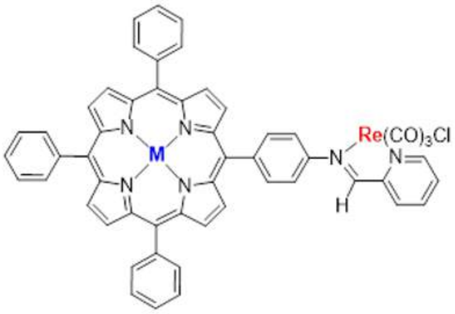
One approach to address increasing greenhouse gas emissions is photocatalytic carbon dioxide (CO_2) reduction into valuable C1 chemicals. Porphyrins, which absorb in the visible region of the spectrum are promising materials for photocatalytic CO_2 reduction. While a number of organometallic – porphyrin dyads have been reported for selective photocatalytic reduction of CO_2 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 (H_2PorRe) and zinc porphyrin-rhenium tricarbonyl (ZnPorRe) dyad (shown below) for intramolecular photocatalytic CO_2 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 predomiant product, with negligible amounts of CO detected. Photocatalysis in this dyadleadign 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 **H_2PorRe**, 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.

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Understanding mechanochromism in CuX-L hybrid coordination polymers

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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.

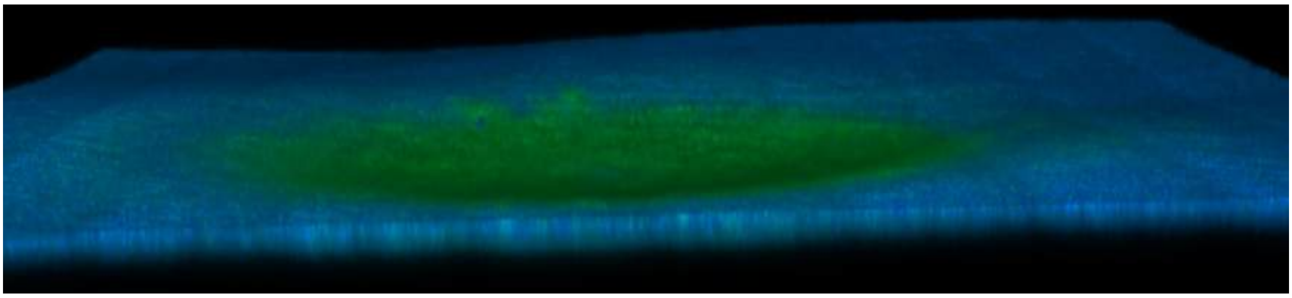

Figure 11. Confocal image of mechanically stressed polymer coating containing CuX-L HCP

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.

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Luminescence mechanochromism of copper-based materials

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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.

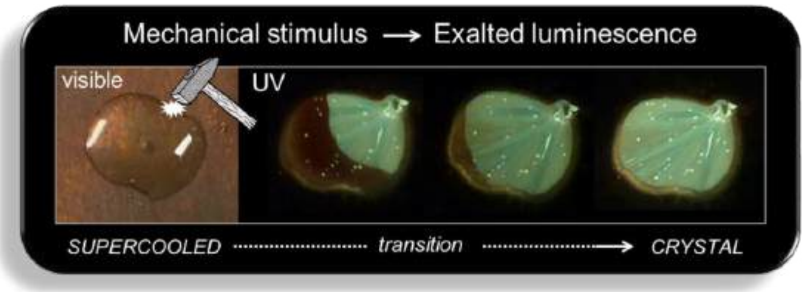

Figure 1. Photos of the supercooled liquid phase at room temperature under visible light and after mechanical stimulation (hammer) under UV showing the progressive photoluminescence switching.

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.

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Light-driven Catalysis of the CO_2 Reduction Reaction using Heptacoordinated Cobalt and Iron Complexes

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Conversion of solar energy into chemical fuels, via the CO_2 reduction reaction (CO_2RR), represents a promising solution to the global energy problem. Direct conversion of CO_2 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 CO_2RR 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. H_2 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.

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

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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]

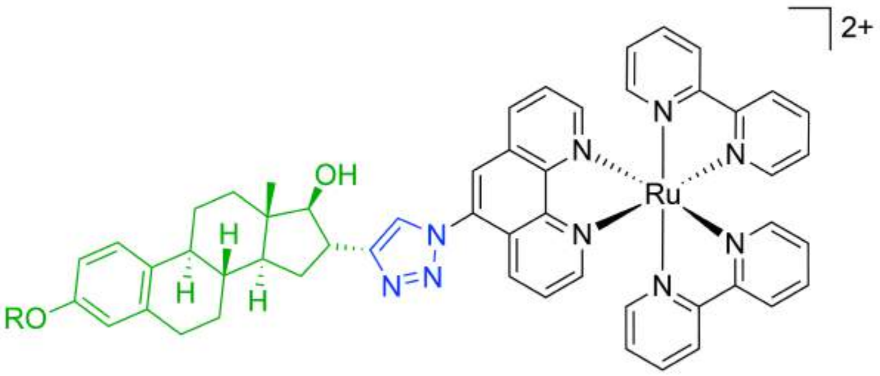

Figure 1. The estrogen-$Ru(bpy)_3$ conjugates described in this study.

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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

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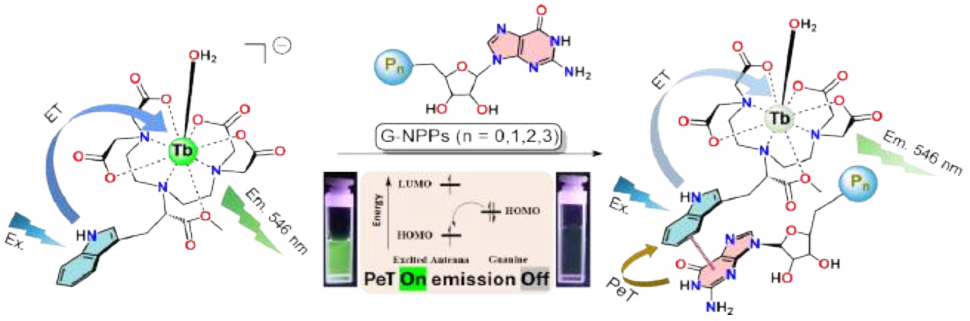
The nucleoside phosphates (NPP) are important physiological phosphates that are vital in energy storage, transfer and consumption, DNA synthesis, phosphorylation, molecular recognition, cellular transduction, and regulation in crucial enzyme activities, etc.[1,2] Therefore, designing sensitive and selective 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 4*f*→4*f* 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.



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Highly efficient artificial photocatalysts mimicking Photosystem 1

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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 NADH$_2^+$ 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 containg an alkynyl linkage providing for very efficient electronic coupling already in the ^{1}MLCT 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.

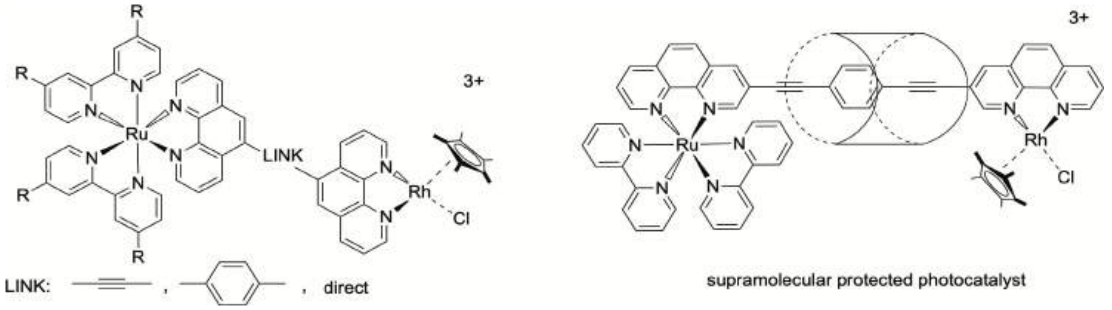

Figure 1. Photocatalysts for visible light driven formation of NADH$_2^+$ and efficient protected novel catalyst

Acknowledgments

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

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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**	*Design, Synthesis, and Photophysical Properties of ABAC-Type Low-Symmetry Zinc Phthalocyanine*
P2	Mary Angelia	**Alfred**	*If Yes, Activate; Else Stay Quenched - PET Controlled Switchable Silicon Phthalocyanines for Photodynamic Therapy of Cancer*
P3	Alessandro	**Amadeo**	*GelOx: The breathing gel*
P4	Sergio	**Aranda**	*Mechanistic Insights into Solvent and Structural Variations of a Homogeneous Catalyst* $Ni(bpet)(SCN)_2$ *for* CO_2 *Reduction*
P5	Amine	**Assel**	*Exploring Coumarin–Boron Monofluoride Complexes: Synthetic Approaches, Fluorescence Properties, and In Silico Medicinal Chemistry Insights*
P6	Maria Vittoria	**Balli**	*Ruthenium complexes as electrochemiluminescent labels for advancing PCR-free nucleic acids detection*
P7	Andrea	**Barbieri**	*Design and Characterization of Lanthanide complexes for Down-Shifting Luminescent Conversion Layers in Perovskite Solar Cells*
P8	Martyna	**Bartusiak**	*TAS and TRIR Spectro-Electrochemical Studies of a Ruthenium–Naphthalene Diimide Ester Complex: Charge Transfer Dynamics and Excited Sates Populated in Solution and on a NiO Surface*
P9	Filippo Piero	**Battaglia**	*Synthesis of cobalt complexes catalytic for visible light-assisted hydrogen production with innovative molecular-based hybrid photoelectrodes design*
P10	Stefan	**Bednarik**	*Self-assembly of tetrapyrazinoporphyrazines into J-aggregates*

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

P24	Tim	**Connell**	*Maximizing Photon to Product Efficiency in Photoredox Catalysis*
P25	Marta	**Costa Verdugo**	*Photochemical Behavior Of Ruthenium(II) Complexes In Choline Geranate (CAGE) Ionic Liquids*
P26	Laura	**Cuevas**	*"CrIII Complex–DNA Interaction as a Source of Induced Circularly Polarized Luminescence and Photodamage"*
P27	Samira	**Dabelstein**	*Femtosecond-spectroscopy of novel Fe(III)-complexes demonstrating a reservoir effect*
P28	Elena	**Dallerba**	*Unveiling the Potential of Iridium Complexes in Tissue Imaging*
P29	Jiri	**Demuth**	*J-dimers of phthalocyanine analogues and how to use them*
P30	Emily	**Derham**	*Photodegradation of Herbicides Using Boron Dipyrromethane (BODIPY) Polymers*
P31	Jesús	**Díaz-Burrueco**	*Pyrazole-based IrIII complexes as effective antennas to sensitize EuIII-based emission in ultrasmall NaGdF4:Eu nanoparticles*
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26th ISPPCC

POSTER
ABSTRACTS

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

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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).

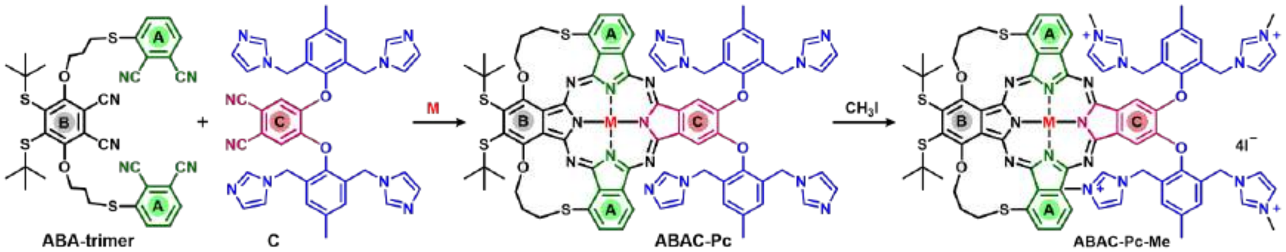

Figure 1. Synthesis of ABAC-Pc via cyclisation of an ABA-trimer with phthalonitrile (C) in the presence of a metal template (M), followed by quaternization to yield ABAC-Pc-Me.

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*).

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

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Conventional chemotherapeutic treatment of cancer poses a threat to healthy cells, presenting the need for selective cell death. Although photodynamic therapy[1] 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 bridge[2] 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).

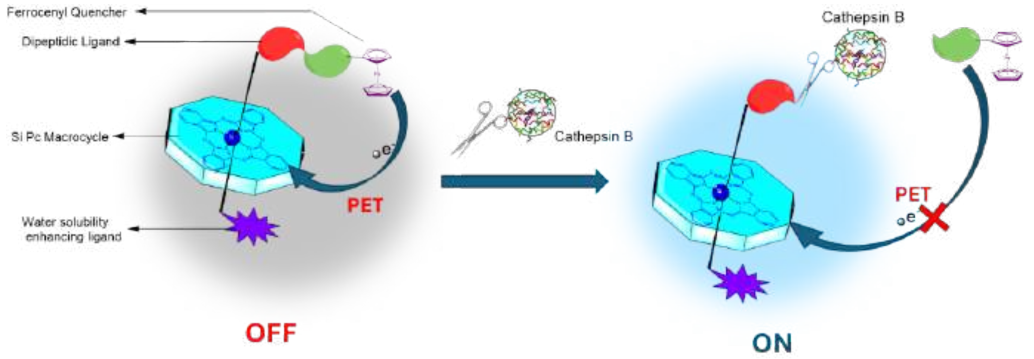

Figure 2. Schematic functioning of the antibody-drug conjugate with the cleavable Valine-Citrulline ligand.

Acknowledgments

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GelOx: The breathing gel

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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.

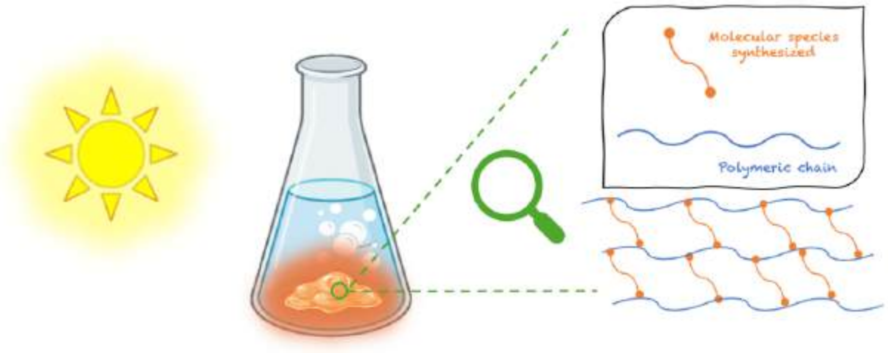

Figure 3. *Scheme of photosynthetic system embedded in an hydrogel matrix.*

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Mechanistic Insights into Solvent and Structural Variations of a Homogeneous Catalyst Ni(bpet)(SCN)$_2$ for CO$_2$ Reduction

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In the field of catalytic organometallic chemistry, complexes such as Ni(bpet)X$_2$ [1] have demonstrated promising activity as reductants for CO$_2$ 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 CO$_2$ 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 H$_2$ evolution from CO$_2$ 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.

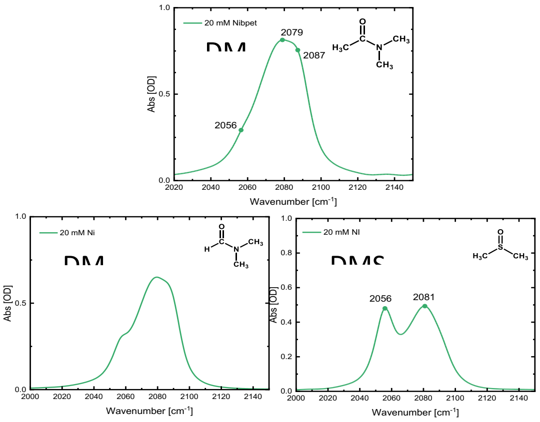

Fig 1. Metal-NCS vibration dependent on solvent.

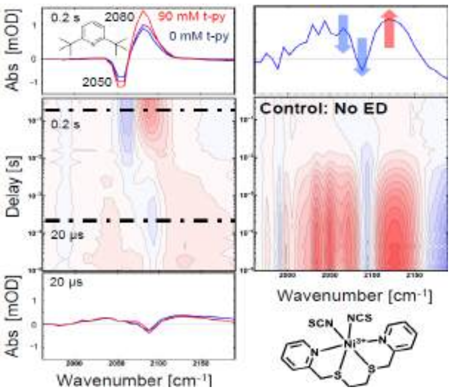

Fig 2. Left panel is a TRIR base dependence, right panel is a back electron transfer.

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Exploring Coumarin–Boron Monofluoride Complexes: Synthetic Approaches, Fluorescence Properties, and *In Silico* Medicinal Chemistry Insights

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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 H_2O 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

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Ruthenium complexes as electrochemiluminescent labels for advancing PCR-free nucleic acids detection

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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 complexes[2] 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.

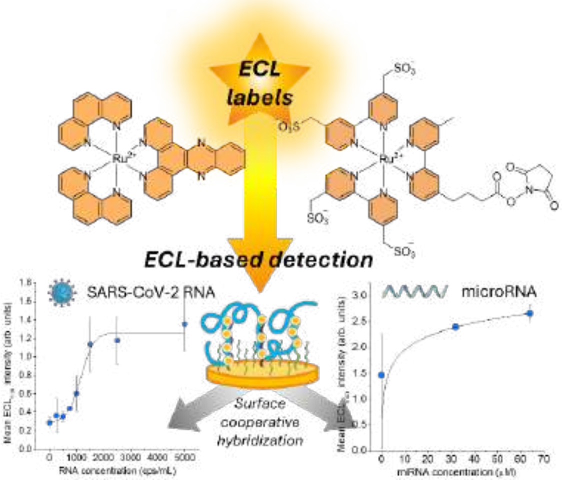

Figure 4. Schematic representation of the ECL biosensor detection approach.

Acknowledgments
The European Union's Horizon Europe EIC Pathfinder Open program "ECLIPSE" (Grant Agreement No. 101046787) is acknowledged for financial support.

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Design and Characterization of Lanthanide complexes for Down-Shifting Luminescent Conversion Layers in Perovskite Solar Cells

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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 (Ln = 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]

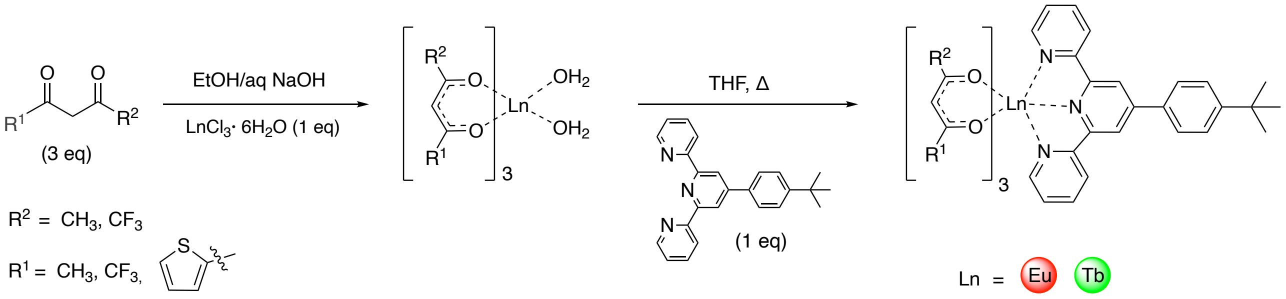

Figure 5. General synthetic procedure for the preparation of the luminescent lanthanide complexes.

Aknowlegments

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TAS and TRIR Spectro-Electrochemical Studies of a Ruthenium–Naphthalene Diimide Ester Complex: Charge Transfer Dynamics and Excited Sates Populated in Solution and on a NiO Surface

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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 **$[Ru(dceb)_2(phen\text{-}NDI)]^{2+}$** (dceb = 4,4′-di-carboxyethyl-2,2’-bipyridine; phen = 1,10-phenanthroline, NDI = naphthalene diimide), further as **$Ru(dceb)\text{-}NDI^{2+}$**, 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 ν(C=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 Ru → 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 C=O groups at 1721, 1700 and 1686 cm^{-1} deplete, together with the ester carbonyl at 1729 cm^{-1}. New transient ν(C=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 Ru → 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 **$Ru(dceb)\text{-}NDI^{2+}$** and $[Pt(DMSO)_2I_2]$ in the presence of triethylamine (TEA) as a sacrificial electron donor and a TON_{H_2} = 100 obtained.

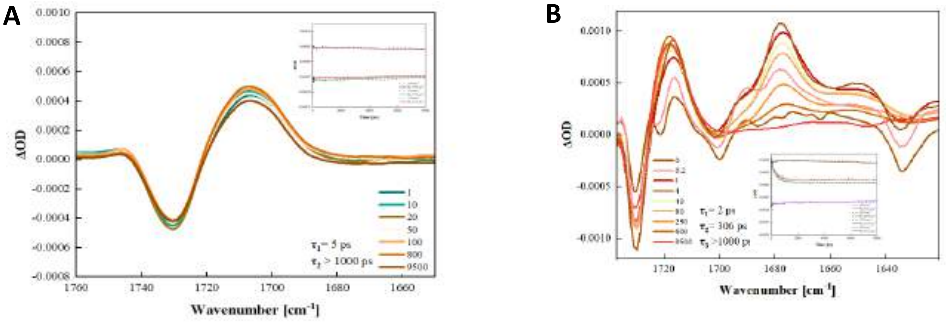

Figure 1 (A) TRIR spectrum of **$Ru(dceb)\text{-}NDI^{2+}$** upon excitation at 420 nm and (inset) decay trace obtained in the TRIR. (B) TRIR spectrum of **$Ru(dceb)\text{-}NDI^{2+}$** upon excitation at 365 nm and (inset) decay trace obtained in the TRIR.

Acknowledgments

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SYNTHESIS OF COBALT COMPLEXES CATALYTIC FOR VISIBLE LIGHT-ASSISTED HYDROGEN PRODUCTION WITH INNOVATIVE MOLECULAR-BASED HYBRID PHOTOELECTRODES DESIGN

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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

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Self-assembly of tetrapyrazinoporphyrazines into J-aggregates

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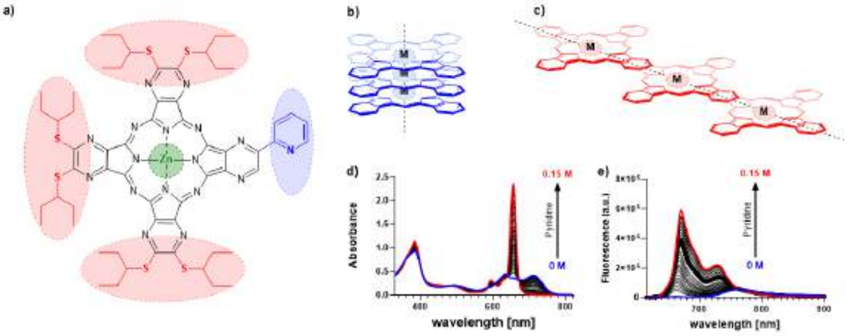
Phthalocyanines (Pcs) are synthetic macrocyclic dyes composed of four isoindoline units linked by azomethine bridges, structurally close to porphyrins. Their extended 18 π-conjugated system endows them with unique photophysical properties, making them valuable in various applications such as fluorescence 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

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On the Mechanism of Photodriven Hydrogenations of N_2 and other substrates by Hantzsch Ester: Photoinduced generation of weak N−H pyridinyl bonds in the presence of a suitable buffer.

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Hantzsch ester (HEH$_2$) 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 HEH$_2$ to reduce N_2 to NH_3 (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 HEH$_2$ 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 HEH$_2$ for efficient proton-coupled reductions. We show that varying the irradiation wavelength during N2R confirms the necessity of HEH$_2$ excitation for NH_3 production. Additionally, while other buffer systems and dihydropyridines can support N2R, the HEH$_2$ and Col-buffer combination is particularly privileged. Mechanistic studies reveal that HEH$_2$ 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 HEH$_2^{\bullet+}$ is rapidly deprotonated by Col to generate HEH•. Net irradiation of HEH$_2$ 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$^{\bullet}$ 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 HEH$_2$ and Col-buffer systems.

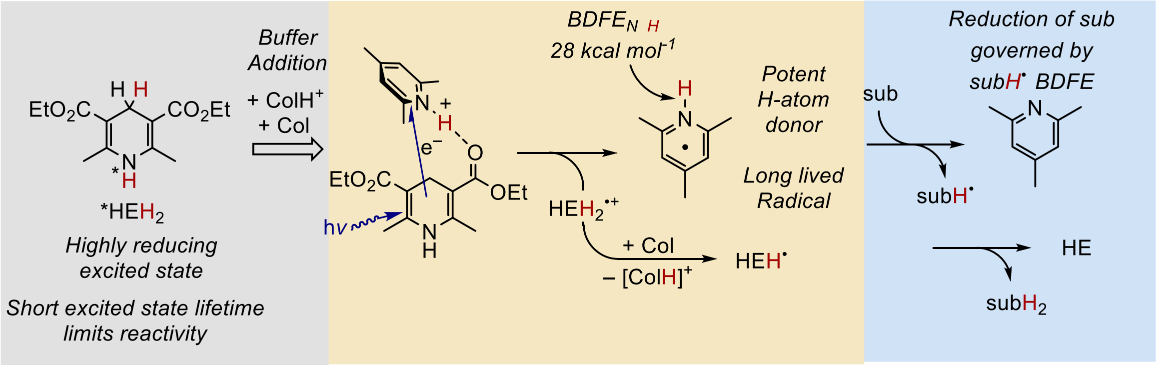

Figure 6. Mechanism behind production of HEH• and ColH•, both potent hydrogen-atom donors functional for small molecule reduction, after net irradiation of HEH$_2$ in the presence of Col/[ColH]OTf.

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Developing Copper Vanadate for Enhanced Photoelectrochemical Performance

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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 $\mu A\ cm^{-2}$ 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.

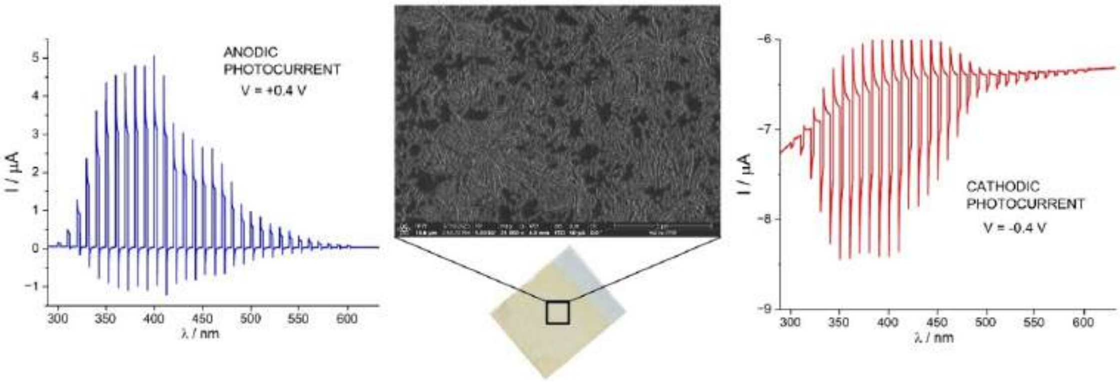

Figure 1. The layer of copper vanadate on ITO and its photocurrent spectra recorded on different potentials.

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.

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Time-resolved infrared spectroelectrochemical studies of two rhenium naphthalimide complexes

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Photocatalysis is the process by which a compound (photocatalyst) uses the energy absorbed from incident light to catalyse a reaction, CO_2 reduction for instance. Photocatalytic CO_2 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 CO_2 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 CO_2 reduction.

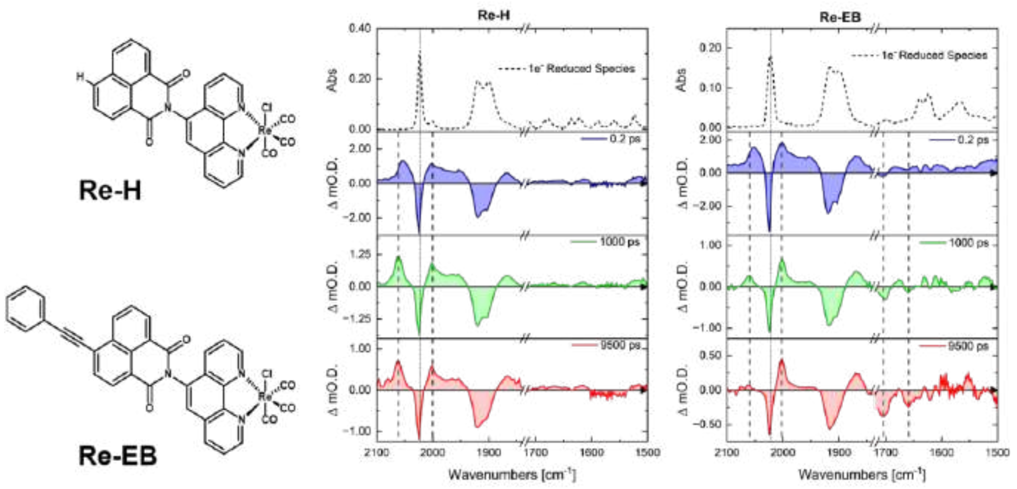

Figure 7. TRIR-SEC spectra of the 1e$^-$ reduced species of **Re-H** and **Re-EB** in DCM following 420 nm excitation. The signals marked by the dashed lines indicate the concurrent population of MLCT-like (blue-shifted) and ILCT-like (red-shifted) excited-states.

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Diimine Ligands in Heteroleptic Cu(I) Complexes: A Path to Efficient Solar Energy Utilization

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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 CO_2 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.

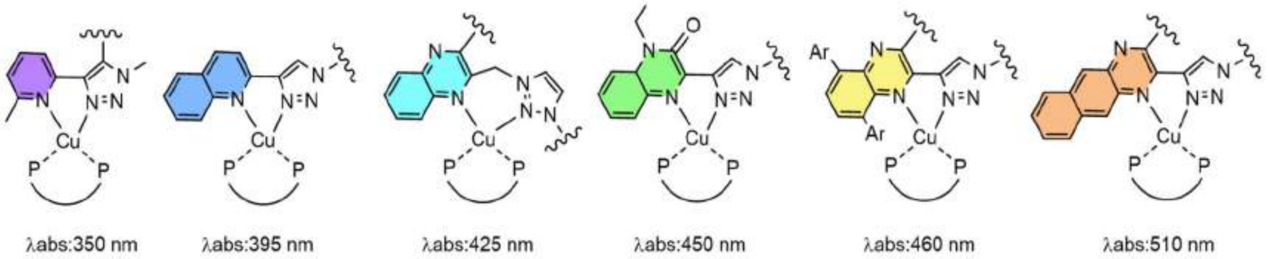

Figure 8. Schematic structures of the heteroleptic Cu(I) complexesand the influence of the diamine on the UV-vis absorption.

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Theoretical X-ray spectroscopy and ultrafast dynamics in transition metal complexes

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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].

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Excited-State Dynamics in Cobalt(III) Polypyridyl Complexes

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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

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Investigating Anti-Kasha dynamics with quantum-mechanically derived force-fields and non-adiabatic molecular dynamics.

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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.

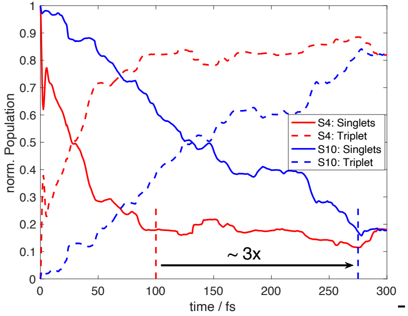

Figure 9: Non adiabatic molecular dynamics from states S4 and S10, grouped by total Singlet and Triplet populations, calculated by SHARC. According to experimental and computational evidence, the excitation of S4 and S10 induce Kasha and anti-Kasha responses from the system, respectively. The latter is evident from the remarkable extension of the single states population.

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

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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.

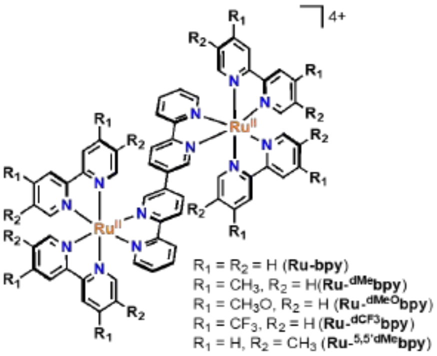

Figure 10: Structure of the

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.

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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

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In this work, we have introduced a phenyl-terpyridine (ptpy) ligand in octahedral Ru(II) core of $[Ru(ptpy)(L\text{-}L)Cl]^+$ 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: $[Ru(ptpy)(L\text{-}L)Cl](PF_6)$, ([**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 $^1O_2$ generation, while [**3**] and [**4**] solely exhibited poor to moderate $^1O_2$ production. The interplay of excited states leading to these behaviors was rationalized from the lifetimes of the ^{3}MLCT excited states using transient absorption spectroscopy, suggesting intricate relaxation dynamics and $^1O_2$ 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 $^1O_2$-mediated PDT mechanisms, while [**4**] primarily can be utilized as PDT agent.

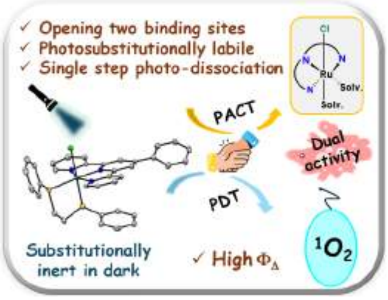

Figure 1. Schematic representation depicting the dual functional activity of the complex upon light exposure.

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Characteristics of Relaxations for Low-Energy Triplet Excited States of $[Ru(tpm)(prbim)(L)]^{2+}$ Ions (L= NH_3 and CH_3CN): Density Functional Modeling and Efficient Metal Center State Quenching Mechanisms

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We synthesized the photoinduced quenching complexes, $[Ru(tpm)(prbim)(L)]^{2+}$ (L = NH_3 and CH_3CN), to explore the excited-state relaxations between triplet metal-to-ligand charge-transfer (^{3}MLCT) and metal-center (^{3}MC) 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 $[Ru(tpm)(prbim)(L)]^{2+}$ 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 $[Ru(tpm)(prbim)(NH_3)]^{2+}$ show a transformation into those of $[Ru(tpm)(prbim)(AN)]^{2+}$, and the ^{3}MC states (triplet d-d excited state characters) of DFT modeling of the complex supports the observed quenching mechanism. Furthermore, the DFT modeling of $[Ru(tpm)(prbim)(NH_3)]^{2+}$ suggests a possible mechanism of $^3\text{MLCT} \rightarrow {}^3\text{MC}$ by adjustments in metal-ligand bond lengths.

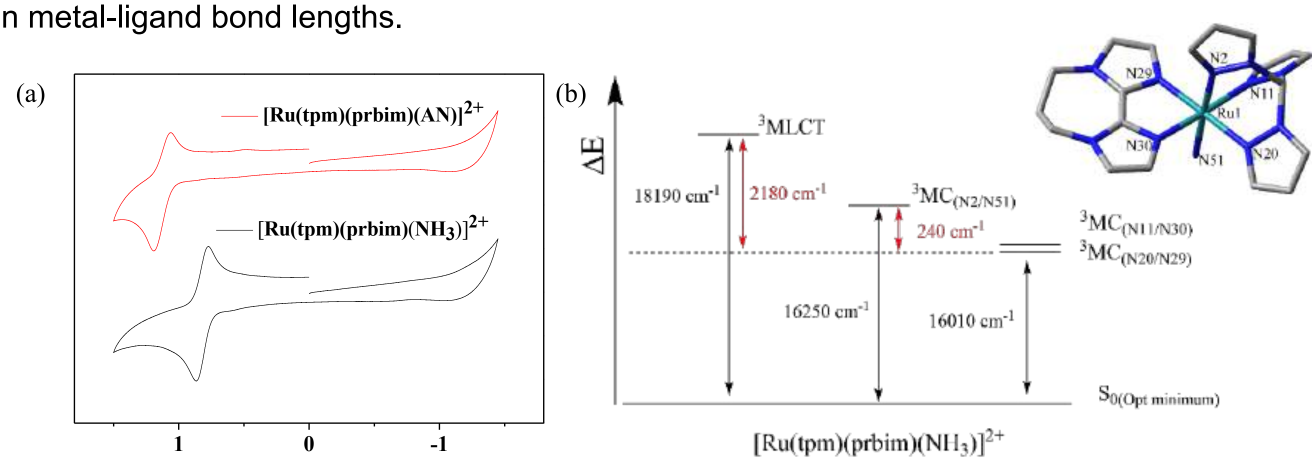

Figure 11. Left panel: Cyclic voltammograms (CV) of the target complexes do not exhibit reduction wave and show the oxidation wave for $Ru^{2+/3+}$; right panel: The Jablonski diagram illustrates the excited-state relaxation processes and energy gap between the ^{3}MLCT and ^{3}MC states for $[Ru(tpm)(prbim)(NH_3)]^{2+}$, 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

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The 77 K observations and computational modeling of Ru-bpy and Ru-pz phosphorescent chromophores in $[Ru(NH_3)_4(bpy)]^{2+}$ [1-3] and $[Ru(NH_3)_5(pz)]^{2+}$ [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], $\phi_{em(p)}$ ($k_{RAD(p)}$) [$h\nu_{em(max)}$], are 5.5×10^{-4} (12 ms^{-1}) [12400 cm^{-1}] and 0.5×10^{-4} (0.8 ms^{-1}) [11720 cm^{-1}] for $[Ru(NH_3)_4(bpy)]^{2+}$ and $[Ru(NH_3)_5(pz)]^{2+}$, respectively. The fifteen-fold difference in the $k_{RAD(p)}$ ratio between $[Ru(NH_3)_4(bpy)]^{2+}$ and $[Ru(NH_3)_5(pz)]^{2+}$ 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 ($S_{3(T)}$) and triplet emitting state (T_e) at triplet geometry for $[Ru(NH_3)_5(pz)]^{2+}$ has very low SOCM-IS contributions, which contrasts with those for $[Ru(NH_3)_4(bpy)]^{2+}$ (see Figure 1), where ADF refers to the Amsterdam Density Functional system.

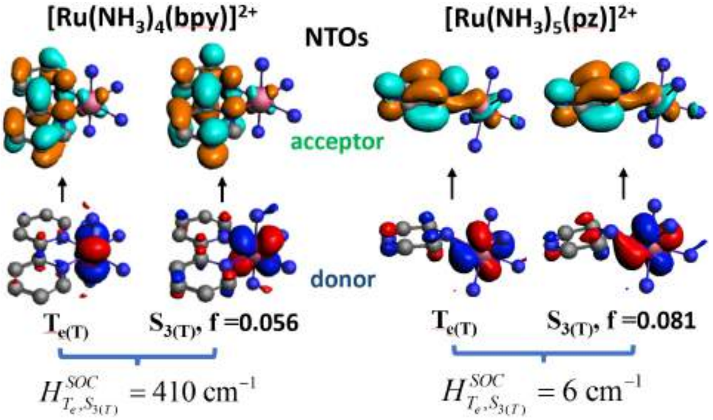

Figure 1. Comparisons of calculated SOC amplitudes between triplet emitting- (T_e) and most intense $S_{3(T)}$ states for $[Ru(NH_3)_4(bpy)]^{2+}$ (left) and $[Ru(NH_3)_5(pz)]^{2+}$ (right) ions. The natural transition orbitals (NTOs) of T_e and $S_{3(T)}$ at the triplet geometry, obtained from ADF modeling for both ions, display the characteristics of metal-to-ligand charge-transfer, and indicate that the SOC configurations of T_e and $S_{3(T)}$ represent the different donor-Ru(dπ) orbital for $[Ru(NH_3)_4(bpy)]^{2+}$ and the nearly identical composition of donor-Ru(dπ) orbital for $[Ru(NH_3)_5(pz)]^{2+}$.

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Structure – Properties Relationships in Coordination Complexes of *N,N'*-Disubstituted Amidine Oxide (AMOX) Ligands

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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

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Efficient Ferredoxin Reduction by Red-Light Generated Silicon Phthalocyanine Radicals

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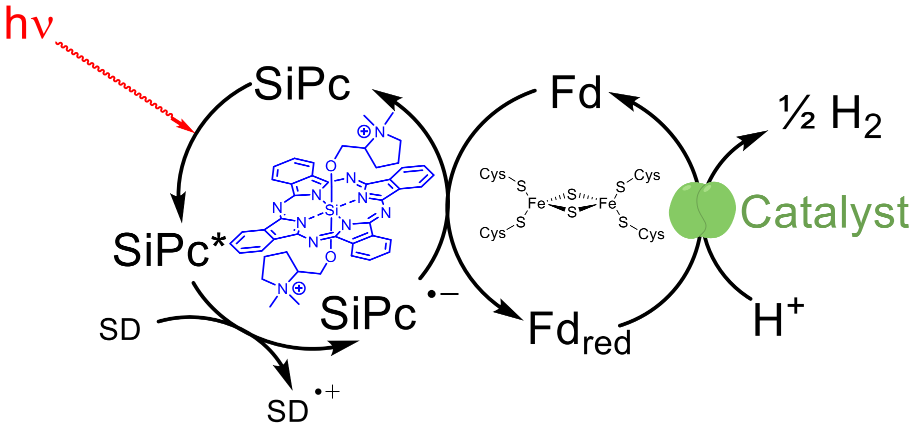

Figure 12. Envisioned photocatalytic cycle

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 $SiPC^{\bullet-}$. 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.

Acknowlegments

The authors would like to thank Vincent Artero for providing cobaloxime samples.

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Maximizing Photon to Product Efficiency in Photoredox Catalysis

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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. $[\mathrm{PC}^{\bullet -}{:}\mathrm{D}^{\bullet +}]$), 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.

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

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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 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 ^{3}MC (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.

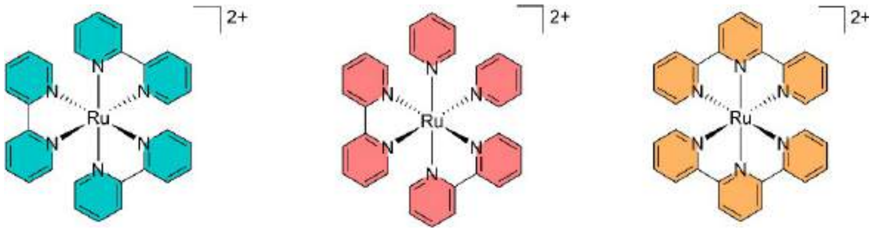

Figure 1. Structure of the ruthenium compounds used in this study

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).

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Cr^{III} Complex–DNA Interaction as a Source of Induced Circularly Polarized Luminescence and Photodamage

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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 $[Cr(dqp)_2]Cl_3$ 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 Proyects C-EXP-140-UGR23 and PID2022-138090NB-C21.

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Femtosecond-spectroscopy of novel Fe(III)-complexes demonstrating a reservoir effect

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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).

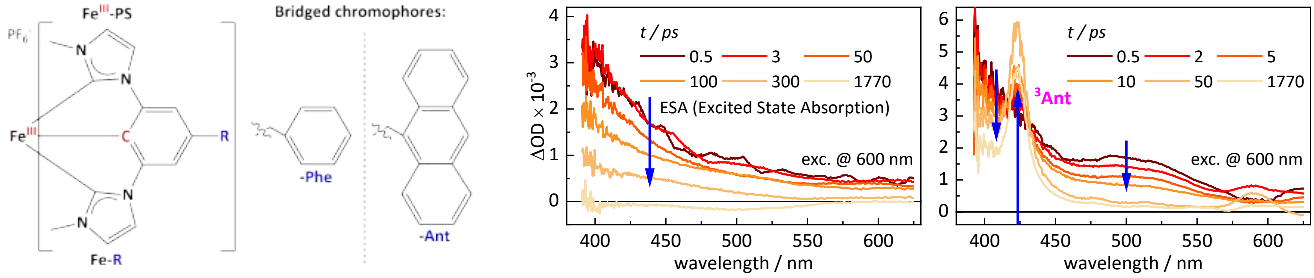

Figure **Left:** Molecular structure of the investigated photosensitizers. **Right:** Ultrafast transient-absorption-spectra at the given delay-times of phenyl-derivative (Fe-Phe) and of the anthracenyl-derivative (Fe-Ant). The complexes are dissolved in acetonitrile and optically excited at 600 nm. 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.

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Unveiling the Potential of Iridium Complexes in Tissue Imaging

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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.

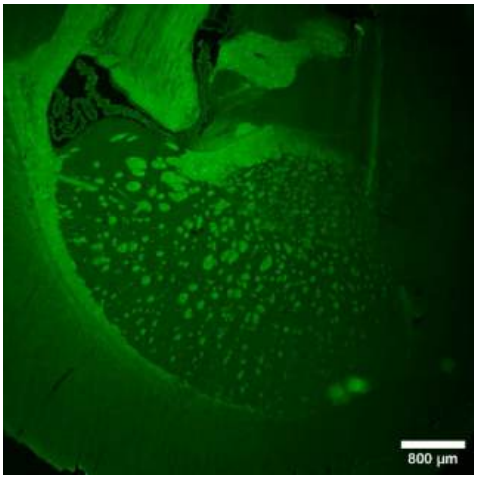

Figure 14. Microscopy image showing the staining of mouse brain tissue using an Ir(III) luminescent probe.

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.

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J-dimers of phthalocyanine analogues and how to use them

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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 oktakis(dialkylamino) AzaPcs to alkylsulfanyl to compare the influence of electron effects of peripheral substitution on the stability of J-dimers.

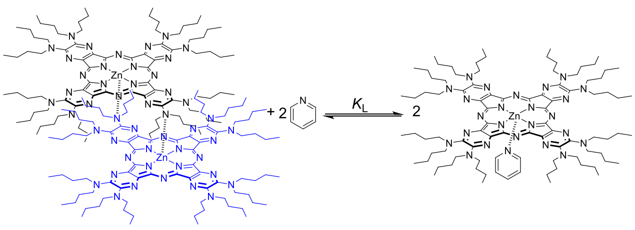

Fig. 1 Dissolution of J-dimer by pyridine.

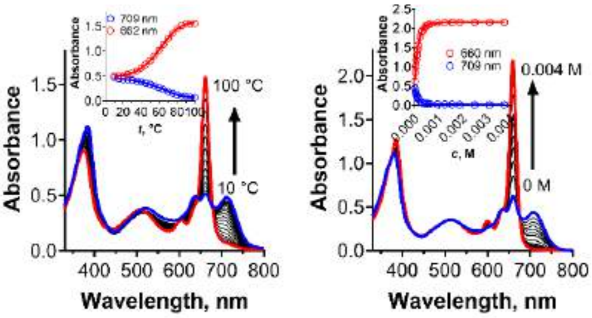

Fig. 2 Changes in absorption spectra during temperature experiments or titration of AzaPc by pyridine (blue – dimer, red – monomer).

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Photodegradation of Herbicides Using Boron Dipyrromethane (BODIPY) Polymers

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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.

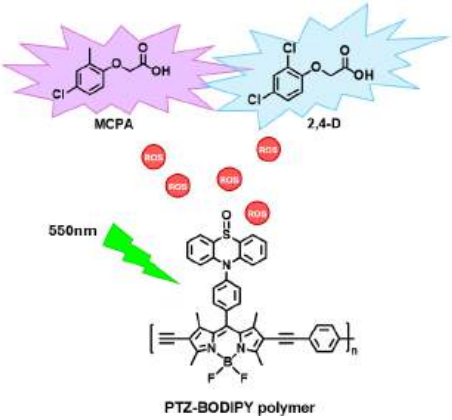

Figure 15. *Schematic of herbicide degradation using a PTZ-BODIPY polymer.*

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Pyrazole-based Ir^{III} complexes as effective antennas to sensitize Eu^{III}-based emission in ultrasmall NaGdF$_4$:Eu nanoparticles

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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 NaGdF$_4$ nanoparticles functionalized with pyrazole-based photoluminescence Ir^{III} complexes.

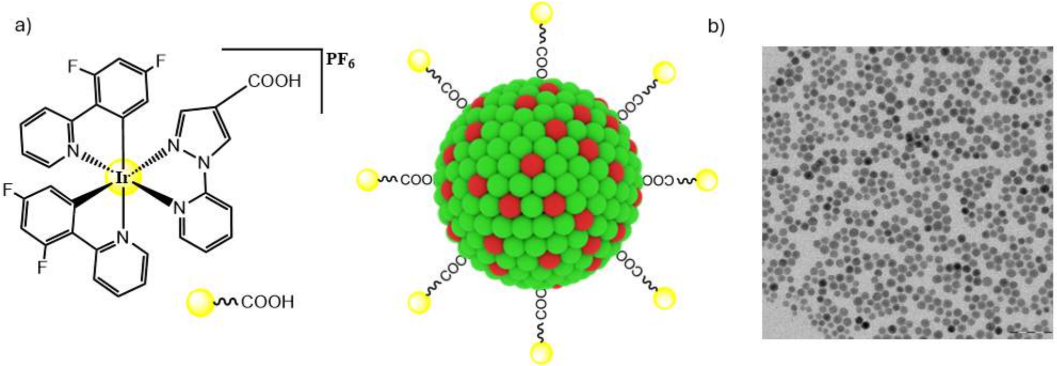

Figure 16. a) Schematic representation of emissive Ir^{III} complex and NaGdF$_4$:Eu@Ir composite. b) TEM image of NaGdF$_4$:Eu nanoparticles.

Aknowlegments

Thanks to the project PID2022-138090NB-C21, MICIN/AEI/10.13039/501100011033/FEDER.

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

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Rhenium(I) complexes are promising candidates for artificial photosynthesis studies, mainly focused on CO_2 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*-$[Re(CO)_3(phen)(NI)]PF_6$, 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 CO_2 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 oxidating potential of complex **1** is that on the excitation wavelength ($\lambda_{exc} = 350$ 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 $\lambda_{exc} = 430$ 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 $NI^{-\bullet*}$ 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.

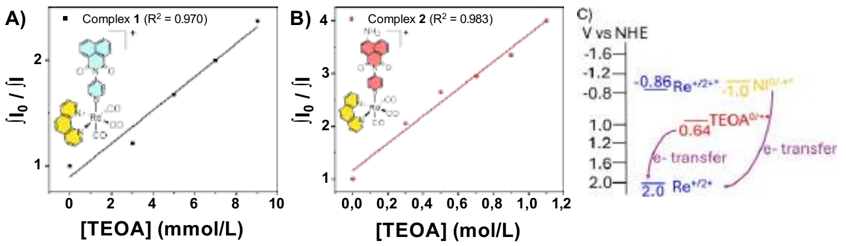

Figure 1. Stern-Volmer plots of the reductive quenching of the excited state of complexes **1** (A) and **2** (B) by TEOA in deaerated DMF at different concentrations (the complexes structures are in the figure) (B); Schematic energy diagram of the reductive quenching of the complex **1** excited state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

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Efficiency and Distance Dependency of Doublet-Triplet Energy Transfer Processes

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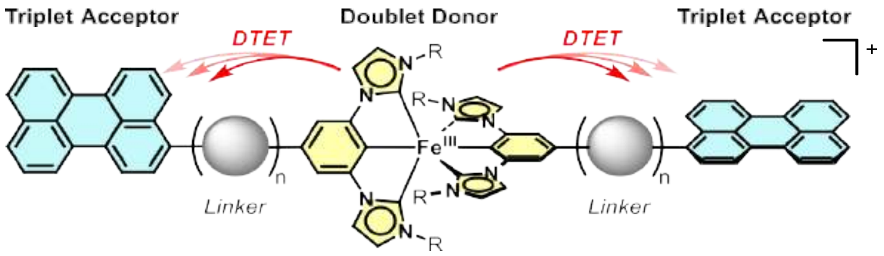
In Nature photoinduced electron and energy transfer processes are prevalent. Under the premise of elaborating a deep understanding of photosynthesis and to enable its artificial imitation, such processes are investigated for example using transition metal complexes. In this context, recent breakthroughs 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.

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Mn(I) isocyanide complexes with benzothiadiazole motifs: unravelling the excited-state manifold using RIXS

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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]

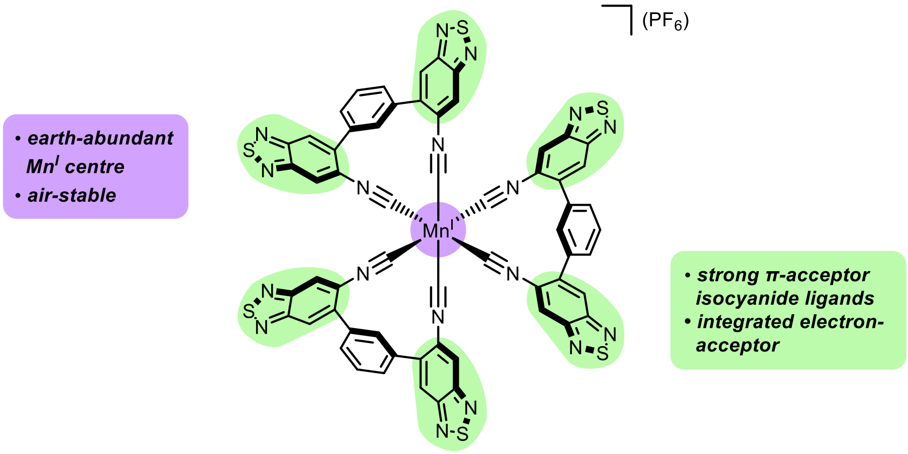

Figure 1. Structure of Mn(I) isocyanide complex incorporating benzothiadiazole moieties.

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.

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Light-Driven CO_2 Reduction with a Heptacoordinated Iron(II) Polypyridine Complex

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The growing necessity to mitigate human-induced CO_2 emissions has driven research toward innovative approaches for converting them into value-added products. Recent findings in designing molecular catalysts for the CO_2 reduction reaction (CO_2RR) 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 CO_2 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].

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The Development of Sulfur-Containing, APTRA-Derived Fluorescent Probes with Specific Zn^{2+} Binding

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The divalent cations Mg^{2+}, Ca^{2+} and Zn^{2+} 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 Mg^{2+} detection, *o*-aminophenol-N,N,O-triacetate (APTRA) is a commonly used binding unit, despite the fact it also binds to Ca^{2+} and Zn^{2+} (Figure 1).[2]

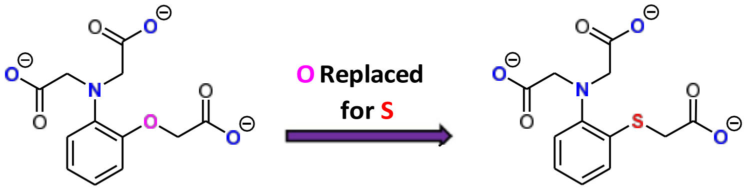

Figure 1 - Structures of APTRA (left) and S-APTRA (right).

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 Zn^{2+} very strongly, and with high selectivity over Mg^{2+} and Ca^{2+} (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 Zn^{2+} binding, with no interference from either Mg^{2+} or Ca^{2+} (Figure 2). It also has the advantage of improved water solubility compared to many of the other reported Zn^{2+} probes, whilst the high (pentadentate) denticity prevents the formation of ternary complexes with endogenous biological molecules, allowing the sole detection of free Zn^{2+} *in vivo*, This renders S-APTRA-Rosamine a reliable and selective Zn^{2+} probe, with potential application in cellular imaging.

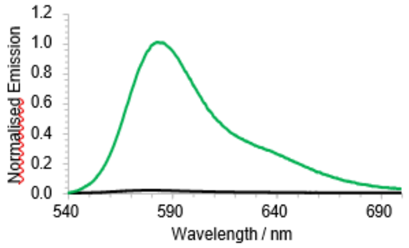

Figure 2 - Emission spectrum of S-APTRA-rosamine (black) and in its Zn^{2+}-bound forms (green) in aqueous buffer solution (50 mM HEPES, 100 mM KCl, pH 7.21).

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Accessing the reservoir effect in Iron^{III}-complexes *via* electron withdrawing linker-groups

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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 ^{2}LMCT 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 ^{2}LMCT-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 ^{2}LMCT states and provide accessible ^{3}Chrom-states to enable a reservoir effect (Fig. 1, right).[2] Therefore, this approach promises to significantly prolong the observable ^{2}LMCT-lifetimes and increase the catalytic activity compared to $[Fe(ImP)_2]^+$.

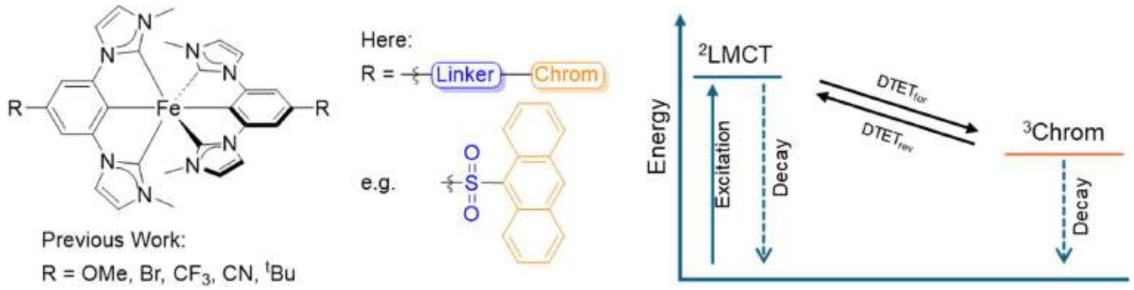

Figure 1. Structure of $[Fe(ImP)_2]^+$ based complexes with varied substituents and a possible sulfone- anthracene linker system(left).[1][3] Schematic representation of a possible triplet-reservoir in equilibrium with a ^{2}LMCT-state via DTET (right).[2]

Aknowlegments

Thanks to the Fonds der Chemischen Industrie and the BMBF for financing this work.

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Understanding multi-timescale effects in a light-driven overall water splitting system

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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

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Photoluminescence lifetime stability studies of β-diketonate europium complexes based phenanthroline derivatives in Luminesence Solar Concentrators LSCs films

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Abstract: In this work, five phenanthroline derivatives substituted with different methyl groups have been selected to synthesize βdiketonate-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

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Photophysical Characterization of Ru and Os Phenazine-Based Polypyridine Complexes as Potential Photosensitizers for Photodynamic Therapy

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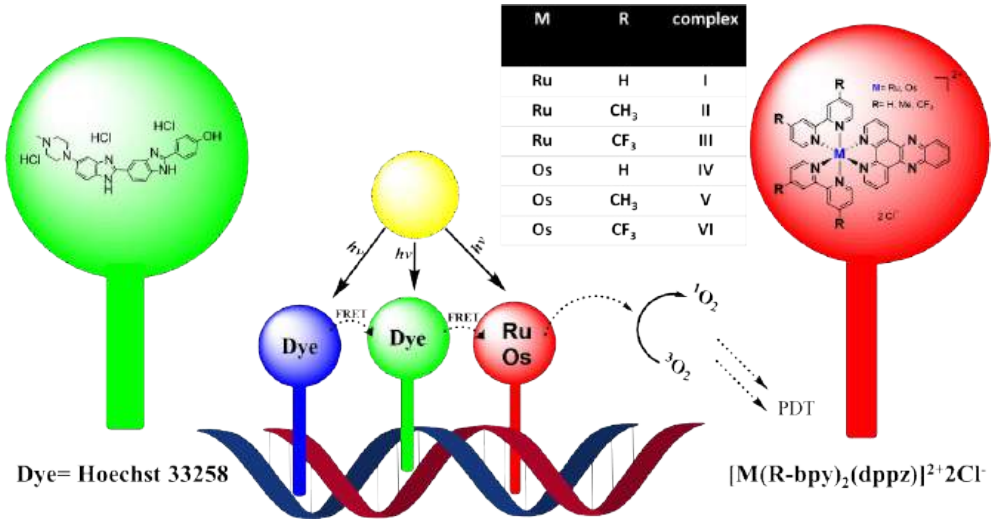
Ruthenium (Ru) and Osmium (Os) polypyridyl complexes are promising agents for site-specific photodynamic therapy (PDT) due to their tunable photophysical properties, strong DNA intercalation, and ability to generate ROS upon light activation[1,2]. Here, we introduce a DNA-templated light-harvesting system combining Ru/Os dipyridophenazine (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)$_2$(dppz)]$^{2+}$ confirm intercalation[3], 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.



M	R	complex
Ru	H	I
Ru	CH_3	II
Ru	CF_3	III
Os	H	IV
Os	CH_3	V
Os	CF_3	VI

Scheme 1: Graphical abstract of research project

Acknowledgments

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Enhancement of Intersystem Crossing in Asymmetrically Substituted BODIPY Dyes

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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 (^{1}CT) state formed by electron transfer between the subunits. A promising alternative for achieving high triplet yields is reducing the singlet-triplet energy gap ($\Delta E_{S\text{-}T}$), 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 $\Delta E_{S\text{-}T}$, enabling efficient ISC via the $S_1 \rightarrow T_2$ pathway. A comprehensive study of asymmetrical BODIPYs (**aBDP**s) 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. **aBDP**s 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.

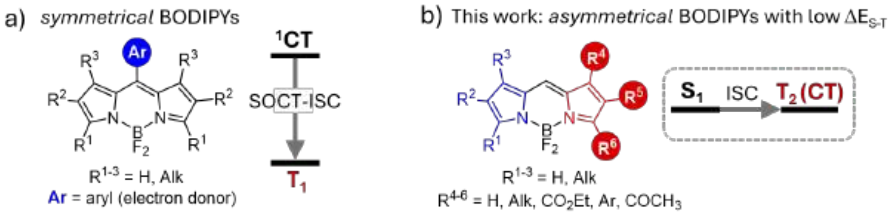

Figure 1. General structures of a) symmetrical BODIPY donor-acceptor dyads undergoing the SOCT-ISC process and b) asymmetrical BODIPY dyes forming triplet excited states via the $S_1 \rightarrow T_2$ pathway.

Aknowlegments

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

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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 is 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]

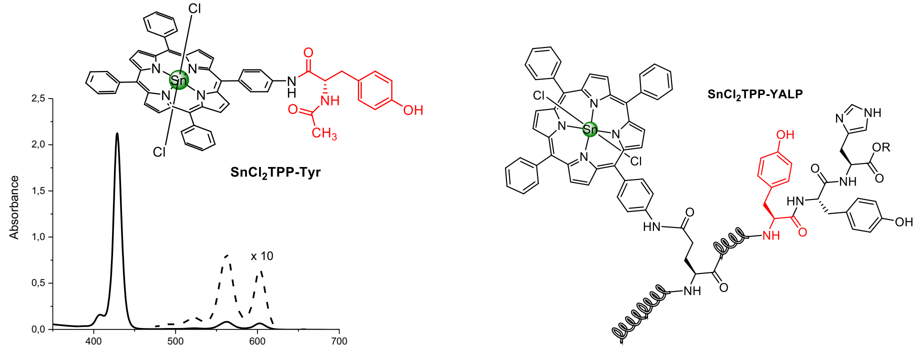

Figure. Example of a Sn^{IV}-porphyrin/amino acid conjugate for PCET studies (**SnCl$_2$TPP-Tyr**) and schematic representation of a Sn^{IV}-porphyrin/YALP conjugate for transmembrane unidirectional ET studies (**SnCl$_2$TPP-YALP**).

Acknowledgments

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A Computational Approach to Emergent Photoactivated Anticancer Therapies Based on Transition Metal Complexes

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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 O_2 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

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Electrochemiluminescence of Earth Abundant Transition Metal Complexes

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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.

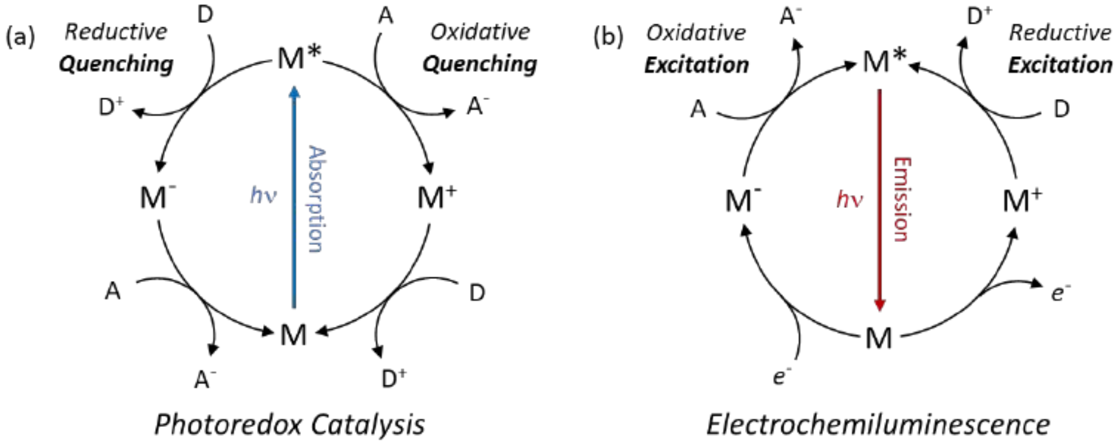

Figure 2. Generalized electron-transfer reaction pathways for (a) photoredox catalysis and (b) ECL, where M is the photocatalyst or luminophore, D is an electron donor (reductant), A is an electron acceptor (oxidant).

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New antennae for photoswitchable luminescent lanthanide(III) complexes

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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.

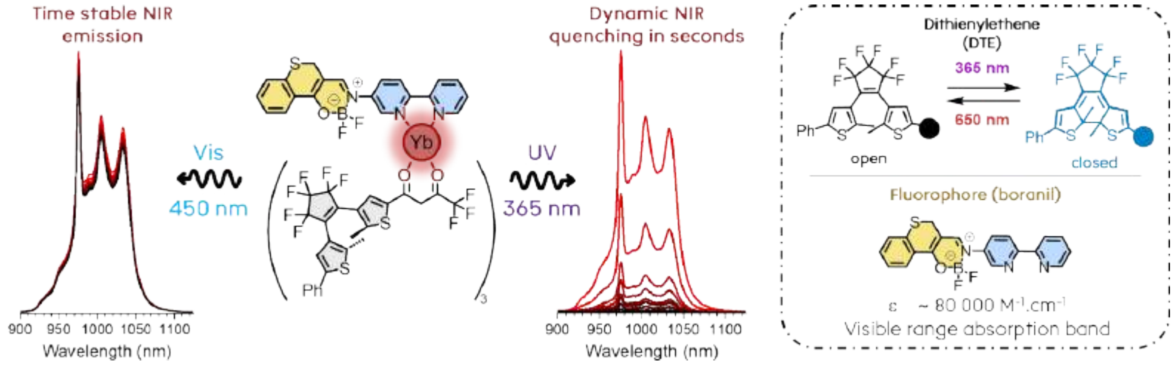

Figure 1. An Ytterbium(III) complex combining a photochromic dithienylethene ligand and a fluorophore as an antenna provides efficient luminescence switching with non-destructive readout behaviour.

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.

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Harnessing an Oxide Relay Pathway in a Molecular Cleft for Light-Driven Water Oxidation

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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.

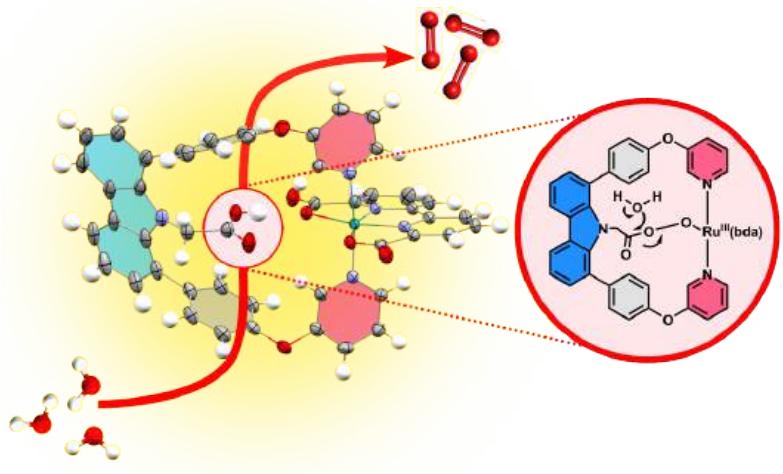

Figure 3. Photocatalytic water oxidation proceeding via the oxide relay pathway.

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Antenna effects on the photophysics of luminescent dinuclear chromium(III) complexes

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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, **Cr_2-ref** and **Cr_2-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 **Cr_2-ref** and **Cr_2-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. **Cr_2-An** shows broader near-infrared luminescence bands with slightly lower energy than **Cr_2-ref**. With the luminescence lifetime of above 100 ns in solution at room temperature, **Cr_2-An** acts as a suitable photosensitizer for green-to-blue photon upconversion with anthracene-based annihilators.

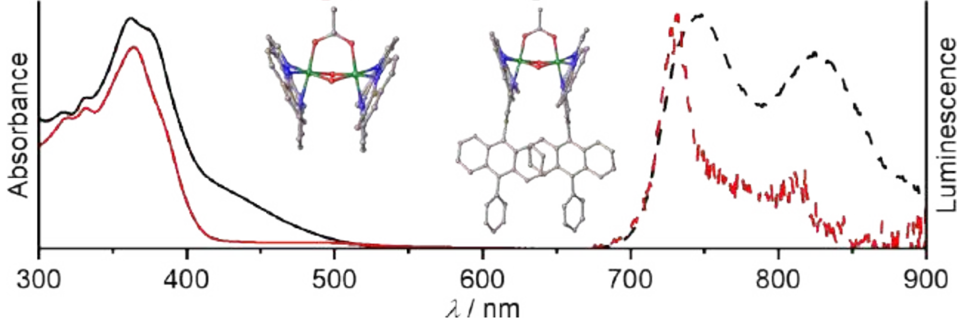

Figure 1. Absorption (solid traces) and luminescence (dashed traces) spectra for **Cr_2-ref** (red) and **Cr_2-An** (black) with the corresponding crystal structures.

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Molecular deactivation dynamics of two photoactive iron (III) complexes

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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**).

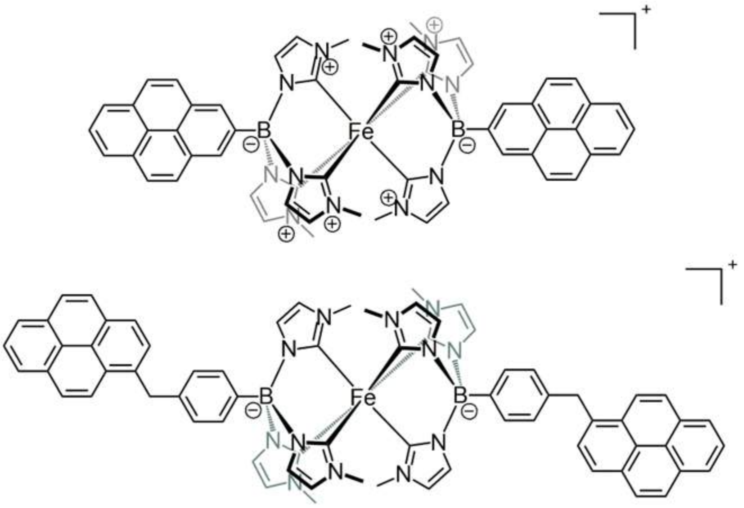

Figure 1. *Structure of the two iron (III) complexes.*

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Towards biohybrid systems for water photo-oxidation: design and synthesis of photo- and redox-active molecular components

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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.

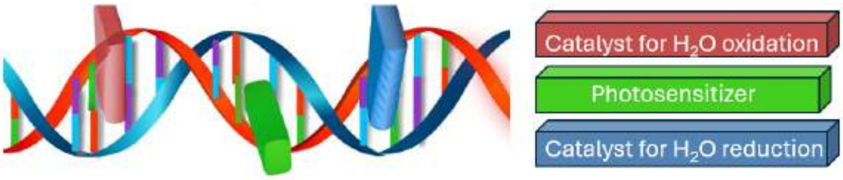

Figure 4. Schematization of the supramolecular assembly goal of the project [3]

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Welcome to the Dark Side:

Photoactive Iron Complexes with Microsecond Excited-State Lifetimes

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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.

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Resolving Mechanistic Pathways in Bioinorganic Catalysis via Ultrafast X-ray Spectroscopy

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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"

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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)]BF_4 (Cu1-2) and [Ag(Me-dpa)(Xantphos)]BF_4 (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 (^{1}H, ^{19}F, ^{31}P, ^{11}B), 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.

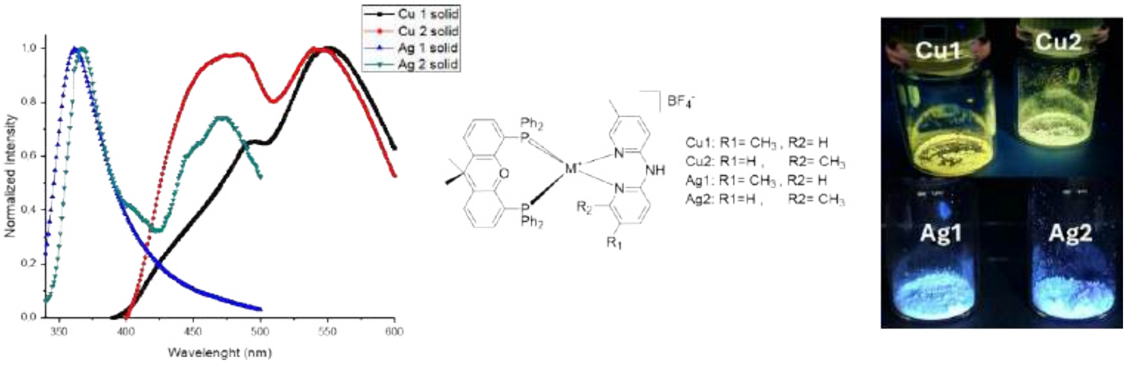

Figure 1. Photoluminescence in the solid state (left) of the complexes series Cu1-2 and Ag 1-2 (middle) and respective picture of the powder (right)

Aknowlegments: Thanks to project FONDECYT N° 1230199

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Synthesis, DNA Binding Interactions & Time Resolved Spectroscopy of Ru(II) – Pteridinyl Complexes

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Octahedral transition metal polypyridyl complexes with π-extended intercalating ligands such as dipyridophenazine (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 [Ru(phen)$_2$(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.

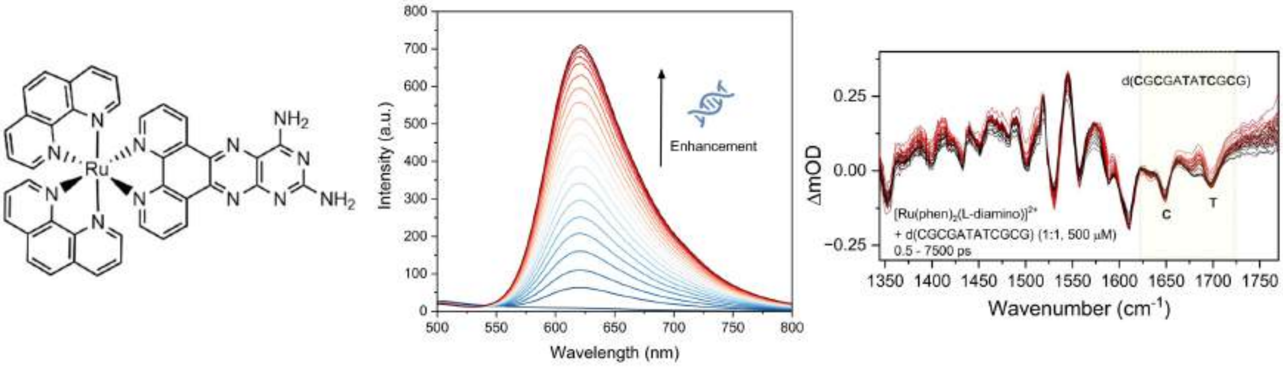

Figure 1. Example of a Ru(II)-pteridinyl complex, luminescence enhancement of [Ru(phen)$_2$(L-diamino)]$^{2+}$ *vs.* st-DNA, and TRIR spectra of the complex in the presence of a DNA dodecamer.

Acknowledgements

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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

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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 d^8 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]

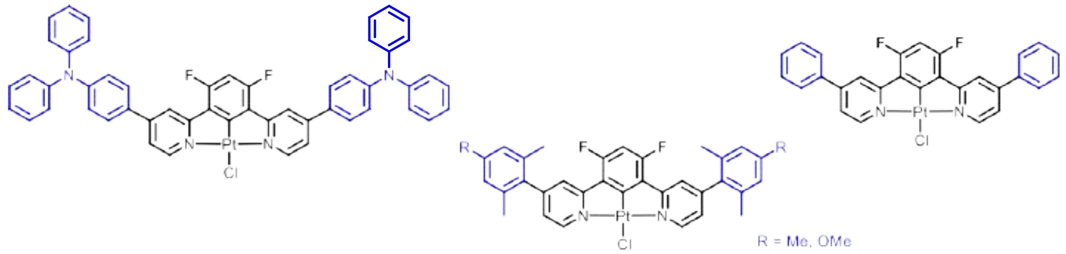

Figure 1. Selected exemples of functionalized Pt(II) complexes

In this context, we found that introducing bulky π-delocalized groups at the 4-position of the pyridine rings in Pt(F_2dpyb)Cl {F_2dpybH = 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]

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X-ray Scattering From Molecular Dynamics Simulations of Photoactivated Molecules in Aqueous Solution

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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 Δt=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.

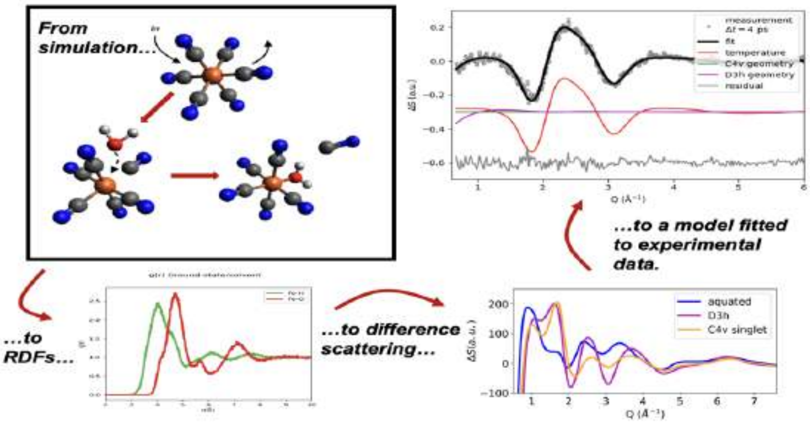

Figure 1: *Overview of the Iron(II)hexacyanide photoaquation,*

Aknowlegments

Thanks to DANSCATT for supporting the beamtime activities, as well as to Novo Nordisk Foundation for project funding (grant number NFF20OC0061740).

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Low-Temperature Emission of Cyclometalated Cobalt(III) Complexes Linked to Organic Chromophores

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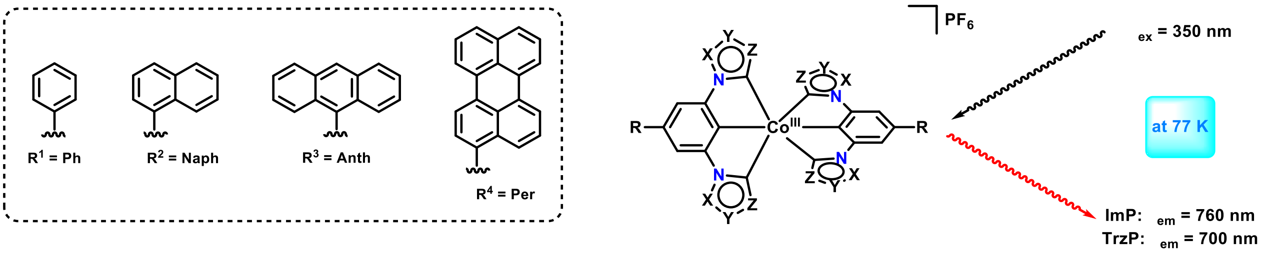
With the aim of developing new sustainable strategies that reduce the use of fossil fuels, one approach uses photosensitisers which are excited by light absorption and subsequently trigger chemical reactions.[1] These photosensitisers are predominantly based on ruthenium, osmium and iridium. However, 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 ^{3}MC 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.



[Co(ImP^R)$_2$]PF$_6$: X, Y = CH; Z = NCH$_3$
[Co(TrzP^R)$_2$]PF$_6$: X = N; Y = NCH$_3$; Z = C(CH$_2$)$_2$CH$_3$

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Light- and Redox-Controlled ON/OFF Switching in PCET

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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_{1obs}) and a pH dependent electron exchange between **2**(Ru^{III}-OH) and **1**(Ru^{II}) (k_{2obs}). Notably, at pH 8–10, the redox potentials of **1** and **2** differed significantly (>0.25 V), slowing theS 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.

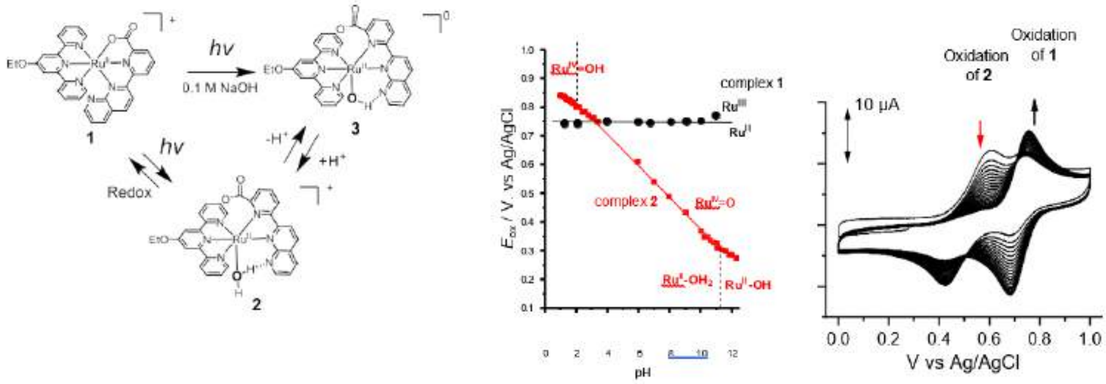

Figure 1. Left: Stimuli responses among **1**, **2**, and **3**. Center: Pourbaix diagram of **1** (black) and **2** (red). Right: Cyclic voltammograms of **2** at pH 7 from 1st to 20th scans. C_{Ru}: 0.5 mM, scan rate: 1 V/s.

Acknowledgments
We thank Prof. S. Masaoka (Osaka Univ.) and M. Kondo (Inst. Sci. Tokyo) for X-ray crystallography.

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Excited-State Characterization of Novel Iron (II) Isocyanide Complexes Using Ultrafast Spectroscopy

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Iron (II) complexes are attractive earth-abundant alternatives to Ru(II) or Ir(III) systems, in which long-lived ^{3}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}MLCT states via low-lying ^{3}MC states, as seen in $[Fe(bpy)_3]^{2+}$.[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)).

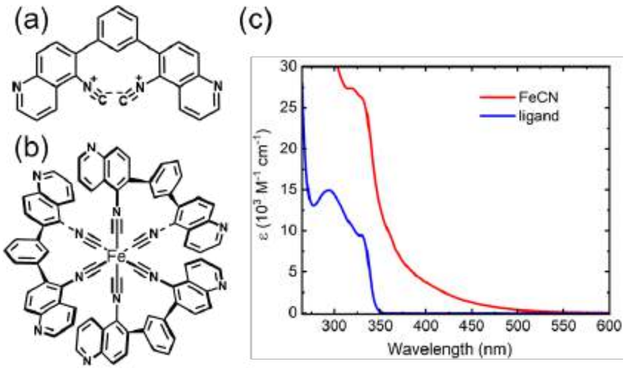

Fig. 1. (a) Novel isocyanide ligand. (b) Molecular structure of the iron isocyanide complex (FeCN). (c) UV–vis absorption spectra.

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.

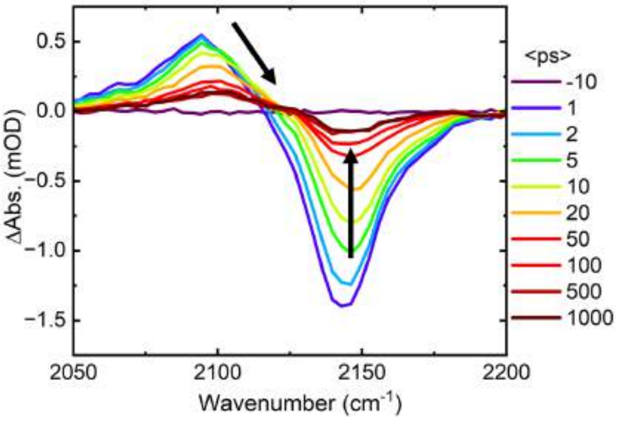

Fig. 2. TR-IR spectra of FeCN in THF (excitation wavelength = 400 nm).

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Energy Loop-Induced Nonlinear Emission in a Eu(III) Complex via the $^7F_1$ State Generated through a Radiative Pathway

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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, $[Eu(hfa)_3(2,7\text{-POpy})]_n$ (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.

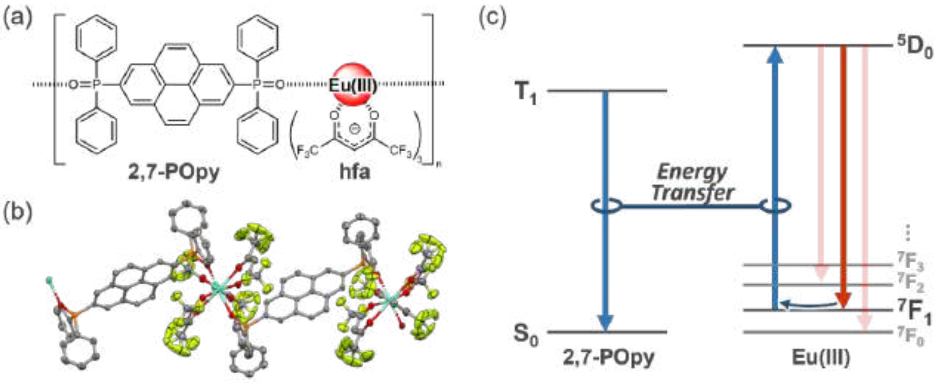

Figure 5. (a) Molecular structure, (b) crystal structure, (c) Schematic photosensitized emission mechanism of the coordination polymer **$[Eu(hfa)_3(2,7\text{-POpy})]_n$**.

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Phase-Migrating Z-Scheme Charge Transportation Enables Photocatalytic Molecular Conversions Harnessing Water as an Electron Source

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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 H_2O/DCE biphasic solution with Fc as an electron donor, a photoredox catalyst, and benzyl bromide (Bn-Br) undergoes reductive coupling to form dibenzyl (Bn_2) 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 Bn_2 and O_2 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]

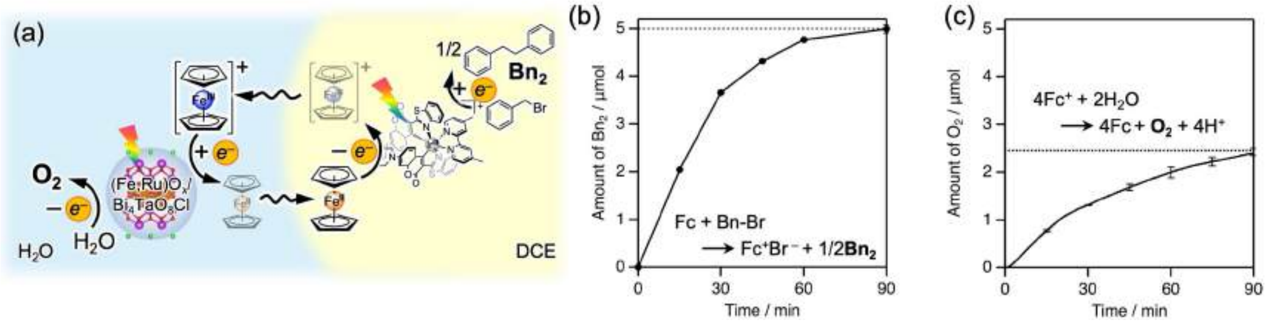

Figure 1. (a) Conceptual scheme of a biphasic Z-scheme photocatalytic system using Fc^+/Fc as a phase- migrating electron mediator. Time course of half reactions of (b) Bn_2 formation using photoredox catalyst and Fc as an electron donor in a H_2O/DCE (2:1, *v*/*v*) biphasic solution under exposure to visible-light (*À* = 470 nm), and (b) O_2 evolution using photogenerated Fc^+ by Bn_2 production as an electron acceptor and a semiconductor photocatalyst under exposure to visible-light (*À* = 430 nm) by a stepwise one. The dashed line shows the upper limit of Bn_2 and O_2 evolution expected from the amount of Fc added to these solutions.

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CPL inducement and energy transfer in Eu(III) complexes by chiral transition metal complexes observed by steady-state and time-resolved CPL spectroscopy

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Figure 1. $[Eu(pda)_2]^-$

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 $^5D_0 \rightarrow {}^7F_1$ 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: τ_1 (~6 μs), τ_2 (~60-50 μs), and τ_3 (100-700 μs). The shorter lifetime components of τ_1 and τ_2 are attributed to $[Eu(pda)_2]^-$ associated with the $[Co(en)_3]^{3+}$, where energy transfer from Eu^{3+} 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 τ_1 component is opposite to that of the τ_2 one, and that of the τ_3-component is very close to 0. These results indicate that the solution includes two types of CPL-exhibiting species (τ_1 and τ_2 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 homo-allosteric effect. These features demonstrate the potential of $[Eu(pda)_2]^-$ for a sensing probe molecule using steady-state and time-resolved CPL spectroscopy.

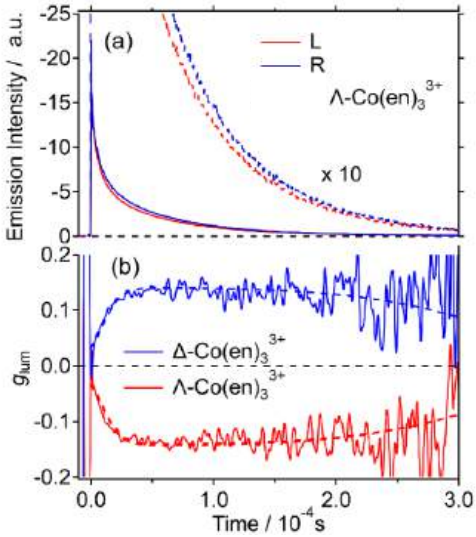

Figure 2. Time-resolved circularly polarized luminescence of $[Eu(pda)_2]^-$. (λ_{ex} = 355 nm) Temporal profiles of (a) I_L and I_R and (b) g_{lum} (0 - 0.3 ms, [Eu] = 0.1 mmol/ dm^3, [Co] = 0.5 mmol/ dm^3)

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Organic Functionalization of Thiomolybdates for HER – Enabling the Design of Photocatalytic Dyads

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Thiomolybdates are a promising class of molecular catalysts for photocatalytic or electrocatalytic hydrogen evolution reaction (HER). [1] The prototype cluster $[Mo_3S_{13}]^{2-}$ 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.

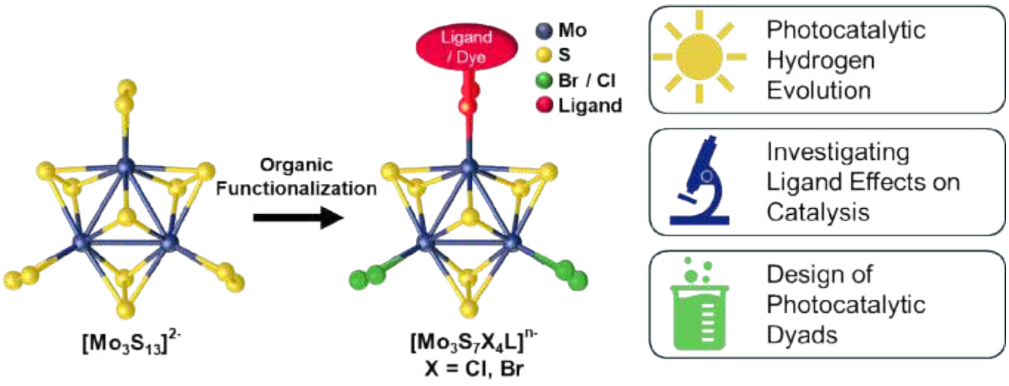

Figure 1. Simplified reaction scheme on the functionalization of $[Mo_3S_{13}]^{2-}$ with organic ligands / dye molecules and overview of main objectives.

Acknowledgments

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Luminescent Fe (III) Complex Sensitizes Triplet-Triplet Annihilation Upconversion and Catalyzes Photopolymerization

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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 3d^5 Fe(III) complex [Fe(phtmeimb)$_2$]PF$_6$ with tridentate scorpionate ligands (Figure 1) shows multiple nanoseconds luminescence lifetime from the ^{2}LMCT excited state in solution at room temperature,[4] making it a promising photosensitizer for sTTA-UC.

In this work, we use [Fe(phtmeimb)$_2$]PF$_6$ 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.

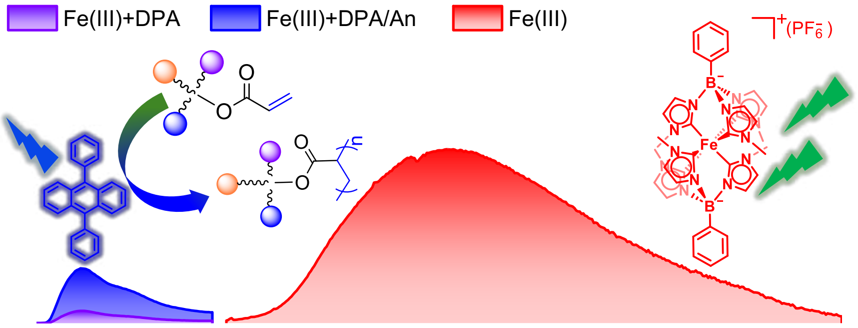

Figure 6. Green-to-blue photon upconversion sensitized by a luminescent Fe(III) complex and the upconversion-driving photocatalytic polymerizations

Aknowlegments

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Making Mo(0) a Competitive Alternative to Ir(III) in Phosphors and Photocatalysts

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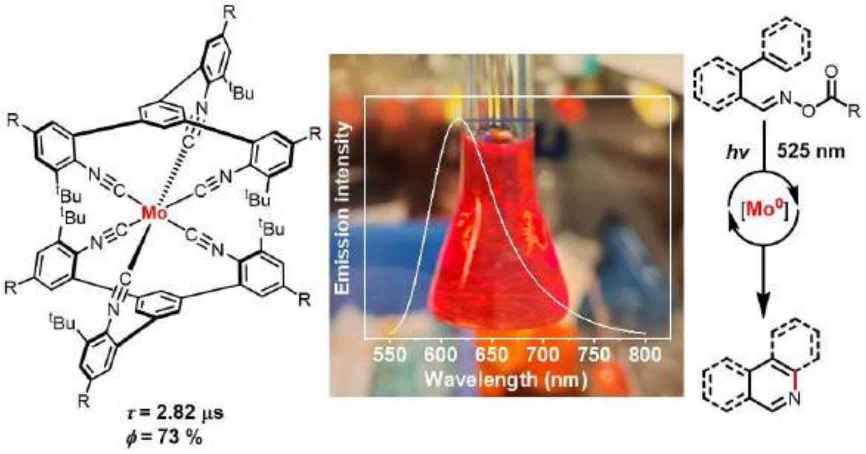
The critical rarity and cost of iridium(III) in phosphorescent lighting and photoredox catalysis drive the pursuit of Earth-abundant alternatives.[1] Here, we present a new class of molybdenum(0) complexes featuring facially coordinating, tripodal arylisocyanide ligands that deliver exceptional photophysical and redox properties[2]. 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*-$[Ir(ppy)_3]$—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 $MoCl_4(THF)_2$ 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]



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

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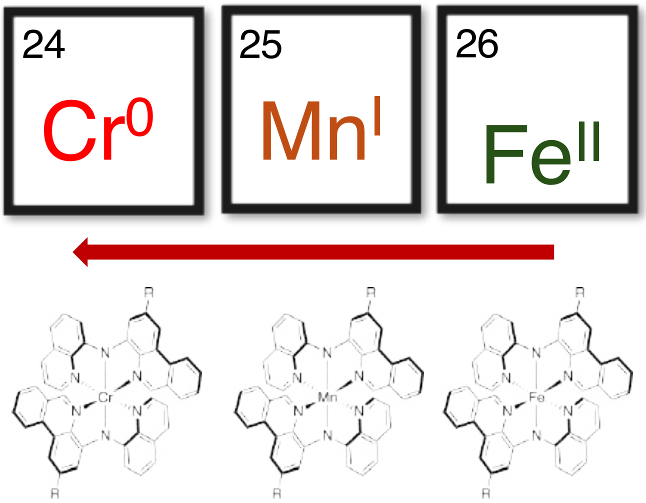
Coordination chemistry allows one to combine the unique influence of metals on the physical properties of molecules with the ability to further tune these properties using ligand design. Accordingly, coordination complexes can be applied in light emitting diodes, artificial photosynthesis schemes and 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 (:NR_2) 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.



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Control of emission wavelength by pH and proton conductivity of cis-Pt(II)-NHC bis(pyridylacetylide) complexes loaded in highly proton-conductive membrane

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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, [(^{i}Pr-NHC)Pt^{II}(C≡C-*n*Py)$_2$] (**Pt-*n*Py**; ^{i}Pr-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 [(^{i}Pr-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.

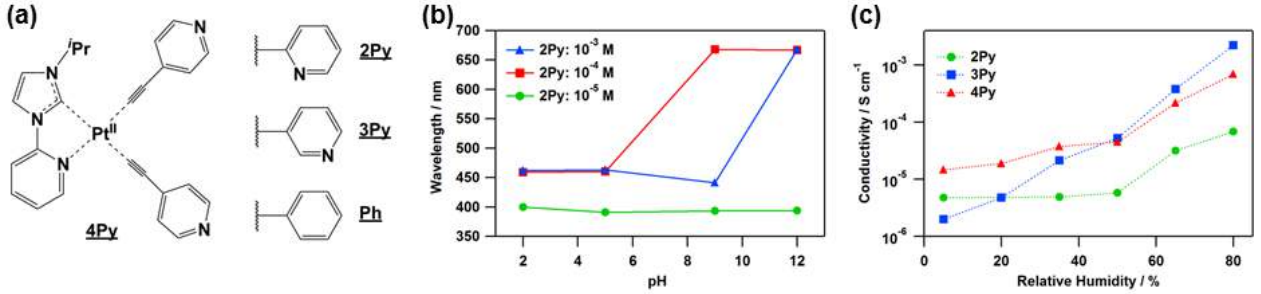

Figure 7. (a) Molecular structure of **Pt-*n*Py**, (b) pH and concentration dependence of emission wavelength in **Pt-2Py**@Nafion, and (c) humidity dependence of proton conductivity of the films (10^{-1} M).

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Dye-sensitized solar cells based on Cu(I) complexes containing catechol anchor groups that operate with aqueous electrolytes

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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-TiO_2 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.

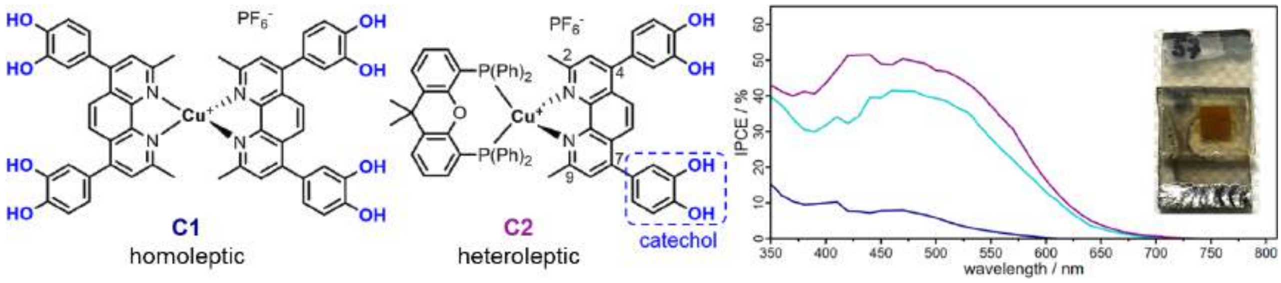

Figure 1. Molecular structures of the homoleptic Cu(I) complex **C1** and its heteroleptic counterpart **C2** (left) and the incident photon-to-current efficiencies (IPCE, right) of the assembled DSSCs based on **C1** (dark blue) and **C2** (magenta).

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[FeFe]-H_2ase mimicking complex bearing two organic photosensitisers for photocatalytic H_2 evolution

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Photocatalytic H_2 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 $[(\mu\text{-S})_2Fe_2(CO)_6]$, the mimic of [FeFe]-$H_2$ase's catalytic centre (**CAT**), as the enzyme is known to exhibit remarkable H_2 production.[1] Thereby, applications of $[(\mu\text{-S})_2Fe_2(CO)_6]$ derivatives for photocatalytic H_2 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.

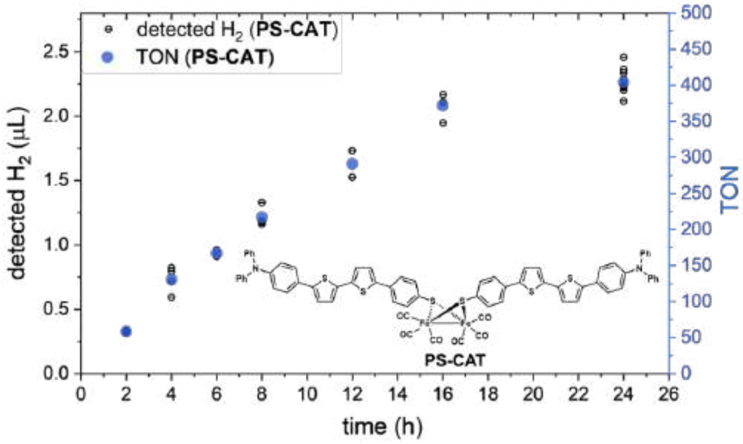

Figure 8. Molecular structure and photocatalytic activity of **PS-CAT**. The reactions were performed under 455 nm irradiation in the presence of 1, 3-dimethyl-2-phenylbenzimidazoline in N-Methyl-2-pyrrolidone.

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Cell and reactor design for space and time resolved *operando* multi-spectroscopic analysis integration

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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 µXRF mapping. Generated knowledge on degradation can also give an insight into possible repair and self-regulating mechanisms.

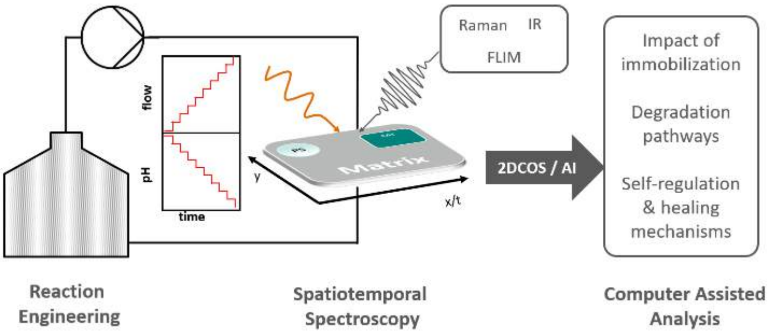

Figure 9. Key objectives overview: combining reaction engineering concepts with spectroscopic insights for generation of high resolution data.

Aknowlegments

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How to get 200% H_2 with 25% less energy input using molybdenumsulfide clusters as photocatalysts for HER

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Molecular metal sulfides, or thiomolybdates, are promising molecular catalysts for the photocatalytic or electrocatalytic hydrogen evolution reaction (HER).[1] In particular, the prototype cluster $[Mo_3S_{13}]^{2-}$ 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.

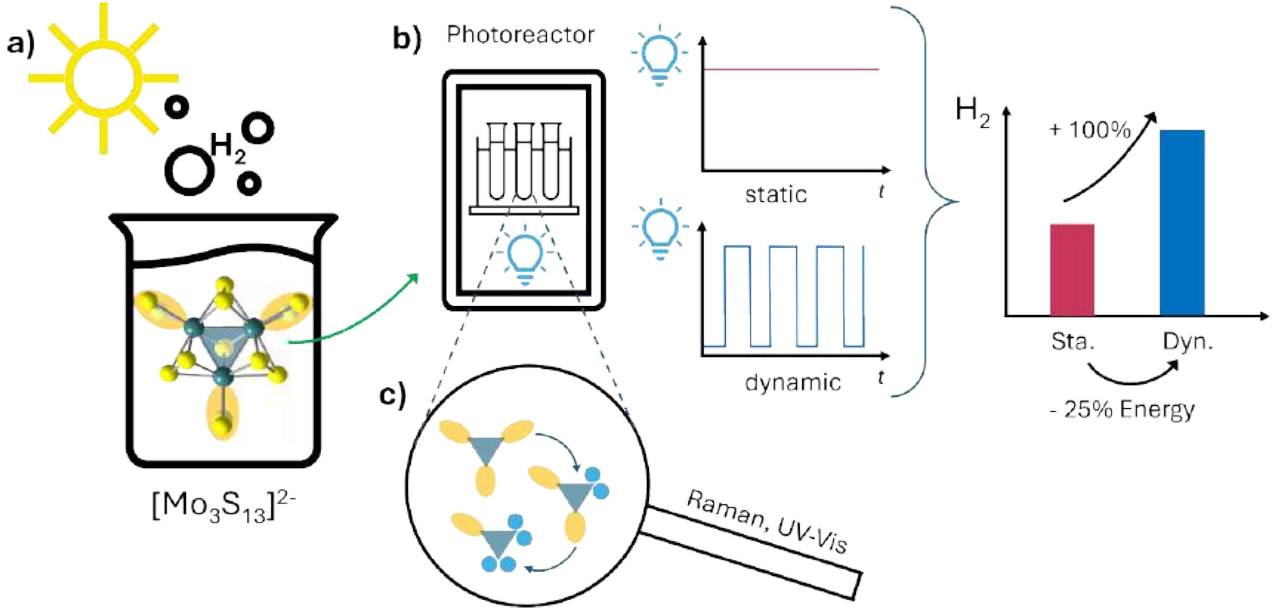

Figure 1. a) Molecular molybdenum sulfide cluster can evolve hydrogen in a suited system using sun light; b) in a phtotreactor the different factor settings are simulated and with the optimized setting the double amount of hydrogen can be measured with 25% less energy input; c) Using UV-Vis and Raman spectroscopy to investigate mechanistic steps during the catalysis.

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Light Induced Cobalt Stabilized Highly Delocalized Radical for Hydrogen Production

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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]

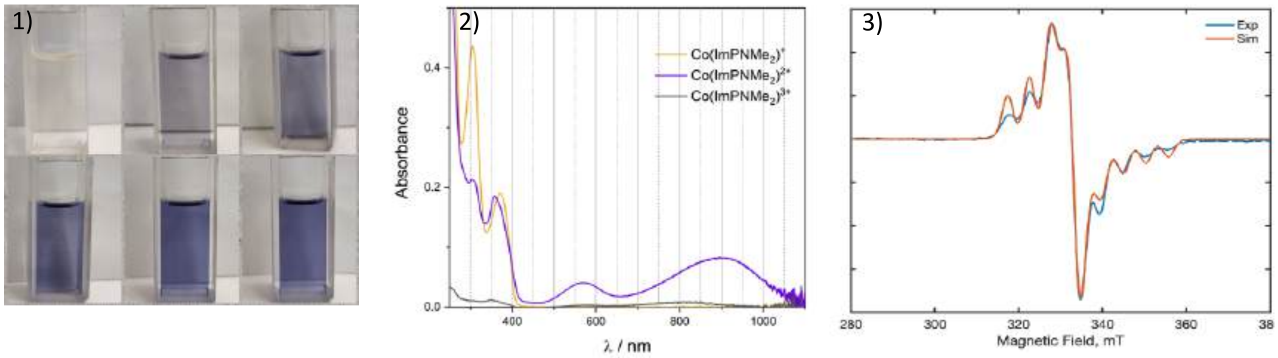

Figure 10). Photo-oxidation of 1 mM solution of [Co(ImPNMe$_2$)$_2$]$^+$ in $C_2H_2Cl_4$, pictures taken in 2 min intervals. **Figure 2).** SEC-UV-Vis spectra of 1 mM solution of [Co(ImPNMe$_2$)$_2$]$^+$in DCM-MeCN. **Figure 3).** Experimental and simulated EPR spectrum measured in a 28 mM frozen solution of [Co(ImPNMe$_2$)$_2$]$^+$ in $C_2H_2Cl_4$.

Combining these two ideas, we have synthesized a light induced radical system by modifying a very recently reported cyclometalated system based on cobalt ([Co(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)

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Novel Manganese(I) Complex with a 190 ns Metal-to-Ligand Charge Transfer Lifetime and Luminescence

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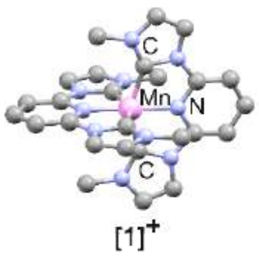
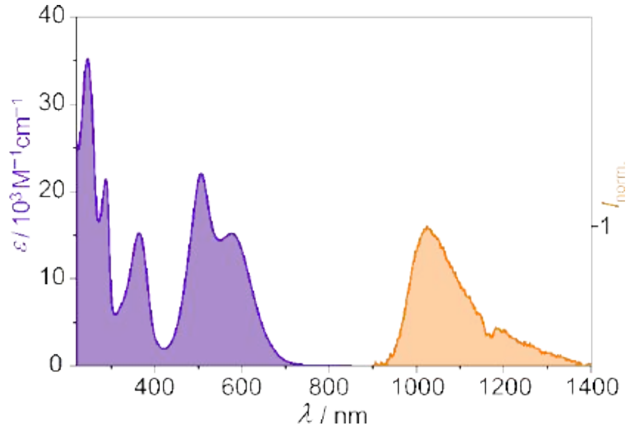
In recent decades high interest for emissive and photoactive transition metal complexes has emerged, due to their attractive properties in lighting[1] and photocatalysis[2]. Whereas precious metal complexes, such as $[Ru(bpy)_3]^{2+}$ or $Ir(ppy)_3$, have dominated this field,[3] the focus of recent investigations has shifted towards earth-abundant first-row metal centres such as manganese.[4] Precious metal complexes with the d^6 valence configuration typically exhibit luminescence from their triplet metal-to-ligand charge transfer (^{3}MLCT) 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 polyisonitrile 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]



[1]$^+$



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 ^{3}MLCT 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]

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Photoproduction of carbon monoxide and singlet oxygen by visible-light-driven Re(I)-based PhotoCORMs

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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 ($^1O_2$) 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 $^1O_2$ 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 $^1O_2$ 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 $^1O_2$ are further investigated by optimizing the involved triplet excited states (^{3}MLCT and ^{3}MC) in selected complexes.[3] This exploration aims to assess their energy transfer ability to $^3O_2$ compared to the population of dissociative ^{3}MC 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.

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Towards photoactive 3d transition metal complexes – A computational perspective

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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 scare 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 $3d^6$ 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]

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DESIGN AND STUDY OF NEW PHOTO-ELECTROCHEMICAL CELLS FOR H_2 PRODUCTION

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Solar energy, although abundant, suffers from intrinsic intermittency. A promising approach to overcome this limitation involves its conversion into hydrogen (H_2), 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.

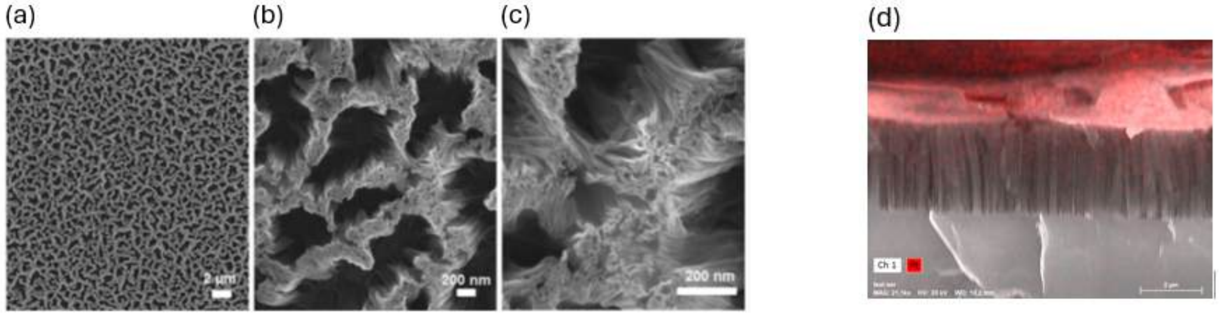

Figure 11. The top panel reports the SEM image of the Si NW array acquired under different magnifications of a) 10, b) 100, and c) 300 kX, respectively. [2] d) Cross section of the Si NW after deposition of nano Pt.

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.
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Improved Photoinduced Electron Transfer in Azaphthalocyanine-Ferrocene System upon Formation of a Charge-Transfer Complex

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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.

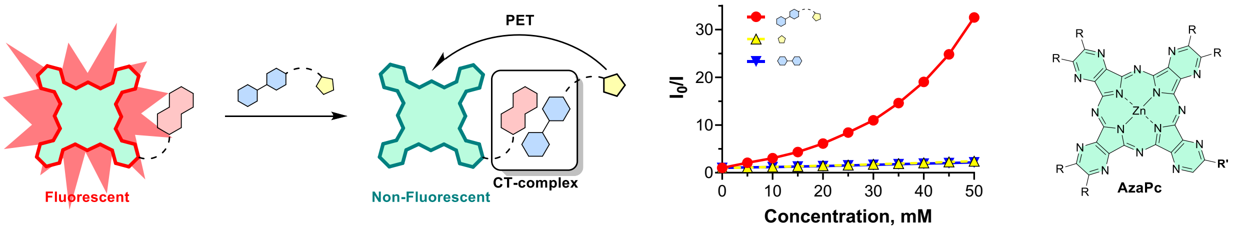

Figure 12. Schematic representation (left) of the principle of the fluorescence quenching by PET (AzaPc – green, ferrocene quencher – yellow) enhanced by formation of a CT-complex (red – electron-rich, blue – electron-poor); Stern-Volmer plot for the designed quencher and its components individually (middle); general structure of a low symmetrical AzaPc derivative (right).

Aknowlegments

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Fluorescent metal-organic frameworks as an effective alternative for heavy metal detection in aqueous environment

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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 Cu^{2+} 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.

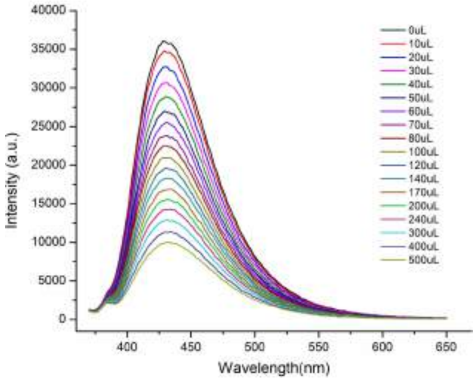

Figure 1. Fluorescence titration of an aqueous suspension of Zr-MOF (0.1 mg mL^{-1}) upon gradual addition of a 10^{-4} M aqueous solution of $CuCl_2$ (λ_{exc} = 340 nm).

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Shaping light-driven reactivity: from heteroleptic to homoleptic Ru(II) bisamide complexes for H_2 evolution

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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

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Reaction-Diffusion Simulations of Photoredox Processes in Solution

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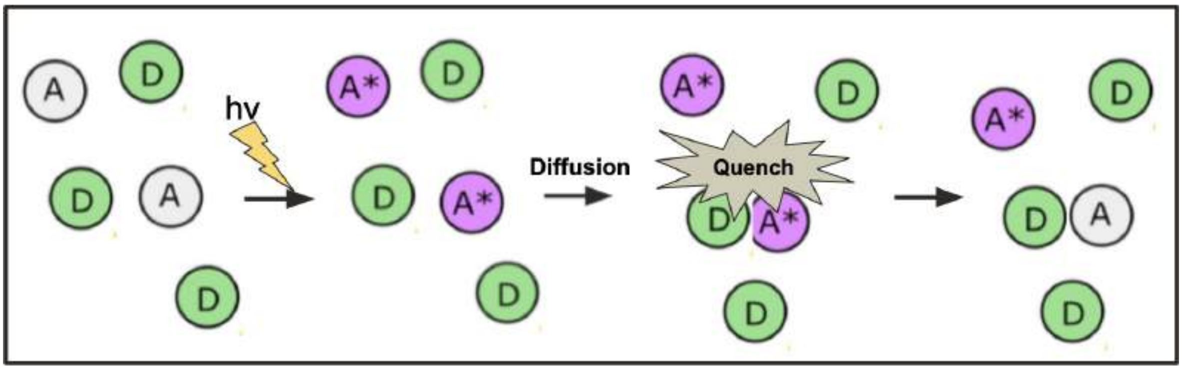
A computational method to simulate bimolecular quenching reactions in solution using coarse-grained reaction-diffusion dynamics is presented and applied to quenching of molecular photosensitizers in solutions.[1,2,3,4] The simulations are implemented to describe photoinduced reactions involving explicit 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



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The Swedish Research Council (VR, 2021-05313), the Knut and Alice Wallenberg (KAW, 2016.0059) foundation, the Swedish e-Science initiative eSSENCE, 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.

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P80

Characteristics of 77 K Emission for Phosphorescent Os-bpy Chromophore: ADF Modeling and Spin-Orbit Coupling Mediated Intensity Stealing

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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.

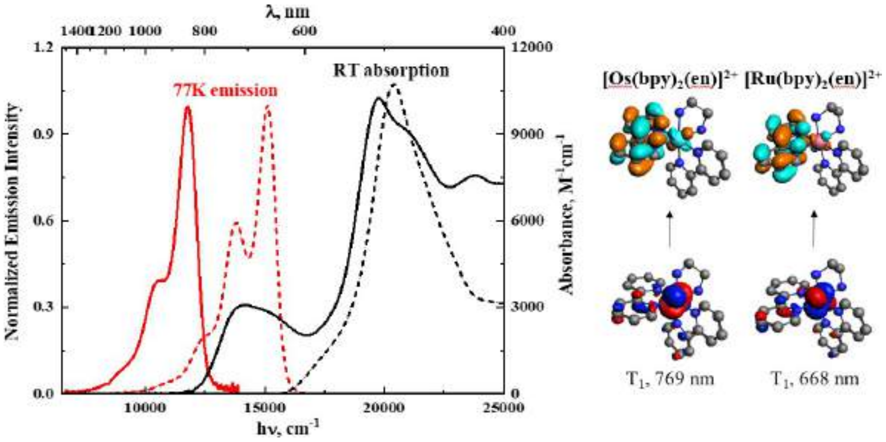

Figure 1. Comparison of the 298 K absorption spectra (black curve, in CH_3CN) and the 77 K emission spectra (red curve, in butyronitrile) of $[Ru(bpy)_2(en)]^{2+}$ (dashed lines) and $[Os(bpy)_2(en)]^{2+}$ (solid lines) in the left panel, along with the T_1 natural transition orbitals (NTOs) shown in the right panel.

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Structure-Property Relationships for Heteroleptic Ag(I) Complexes for Light-Emitting Electrochemical Cells

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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, d^{10} 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 ($[Ag(N^\wedge N)(P^\wedge P)]^+$).[4] For instance, in powder state, the nature of the excited states (*e.g.* changes from $^{1/3}$MLCT/$^{1/3}$LLCT to $^{1/3}$LC) 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.

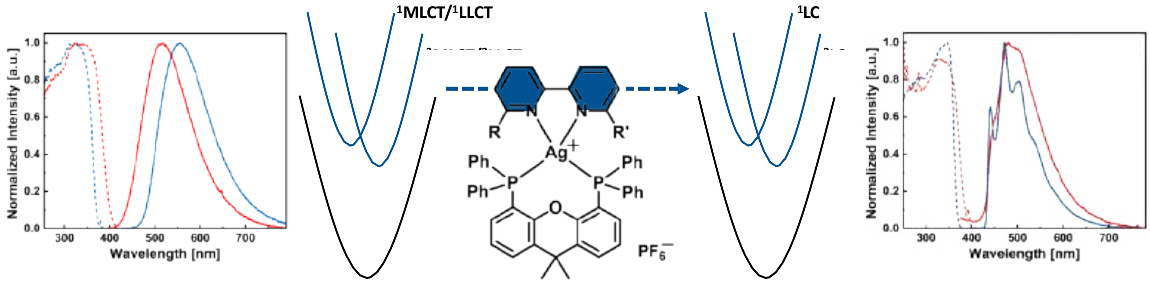

Figure 1. Impact of minor molecular changes on the nature of the excited states.

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Fluorescent J-dimers of Phthalocyanines

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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 applications[3] 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.

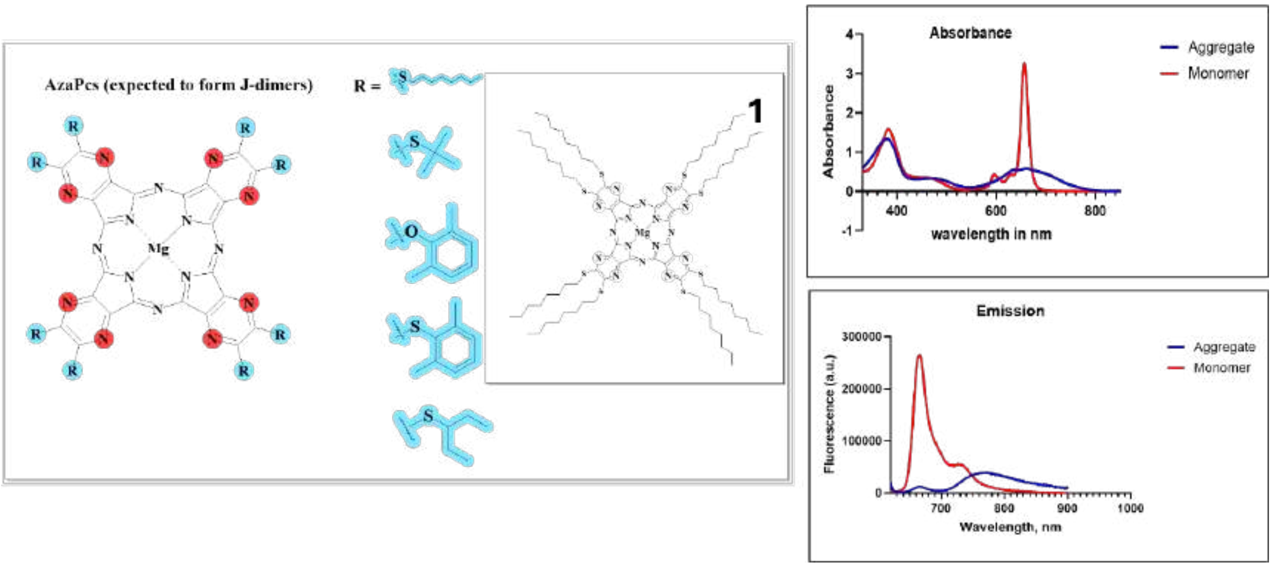

Figure 13. Schematic representation of the target AzaPcs that are expected to form J-dimers, and absorbance and emission spectras of 1.

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Investigating the Photophysical Properties and Activity of a Zinc Porphyrin Appended Polyethylenimine Polymer Towards Solar Driven Water Splitting

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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 H_2 gas as a clean source of energy, releasing only H_2O as a by-product of combustion.[1] Herein, the activity of a branched polyethylenimine polymer towards the photocatalytic reduction of H_2O to H_2 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 H_2 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.

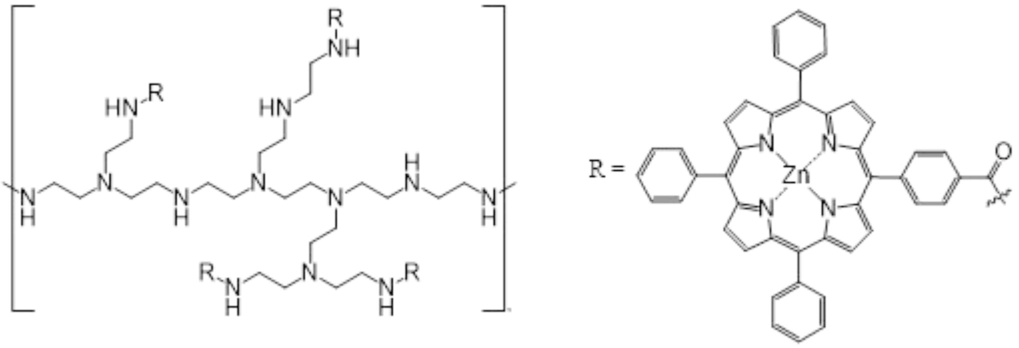

Figure 1. Structure of PEI-ZnTPP.

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Effect of electronic parameters and distortion on the inverted Marcus behavior of bidentate Co^{III} photocatalysts

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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.

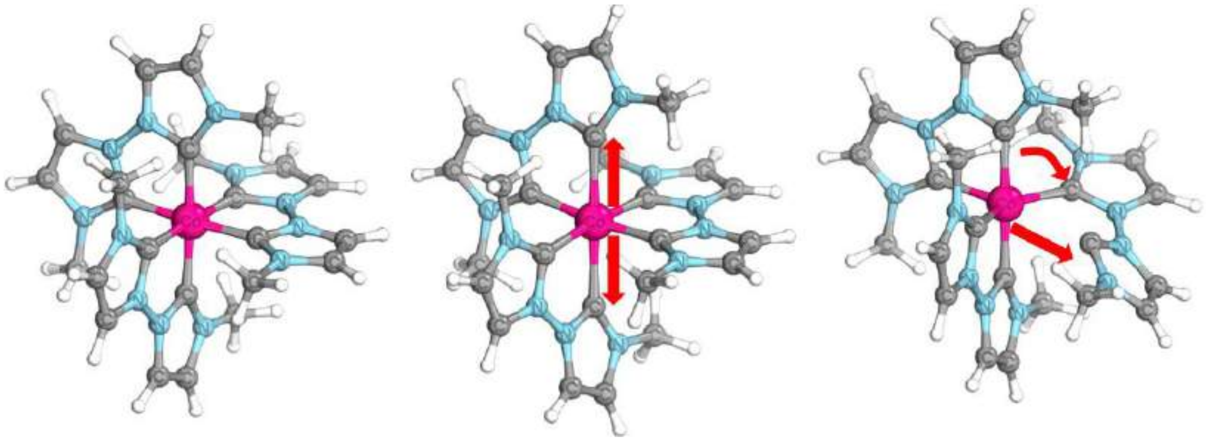

Figure 1. Visualization of the singlet (left), triplet (middle) and crossing point (right) structures. The observed distortions are highlighted using arrows. The triplet structure exhibits an elongation along one axis consistent with expectations for a partially occupied d_{z^2} orbital, while the crossing point structure exhibits an distortion towards a trigonal-bipyramidal structure.

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Photocatalytical Reactions using Co^{III}(ImP)- and Fe^{II}(ImP)-complexes

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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 TC™ 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.

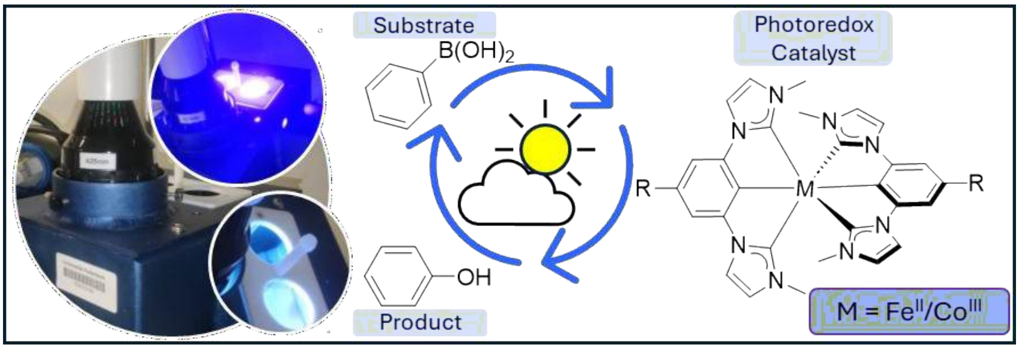

Figure 1. Schematic representation of the investigated photoredox catalytic reaction utilizing Fe(II) and Co(III) complexes as catalysts

Aknowlegments

Thanks to my workgroup for their support for this project.

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Microscopic studies of vapochromic behaviors in molecular crystals of [Re(CO)$_3$Br(ppt)]

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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)$_3$Br(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 CHCl$_3$ 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 CHCl$_3$ 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 CHCl$_3$ vapor. CHCl$_3$-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.

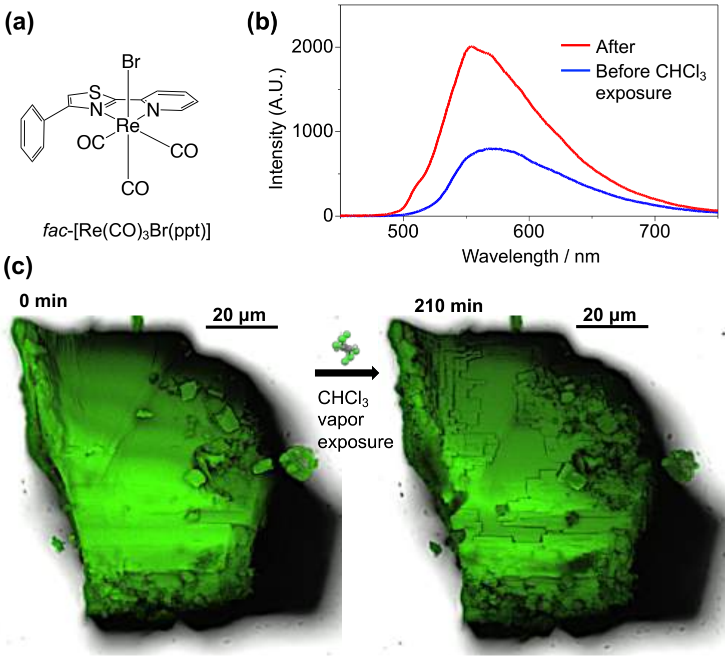

Figure 1. (a) Molecular structure of *fac*-[Re(CO)$_3$Br(ppt)], (b) emission spectra of *fac*-[Re(CO)$_3$Br(ppt)] before and after exposure to CHCl$_3$ vapor, and (c) top view of three-dimensional confocal laser phosphorescence microscopy images overlapped with transmitted light microscopy images of a ~100 µm-sized crystal, 0 min and 210 min after CHCl$_3$ vapor exposure.

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FERROCENE-BASED MOLECULAR LOGIC GATES BASED ON PHOTOINDUCED ELECTRON TRANSFER

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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 corrosion[8] and lab-on-a-molecule systems for detecting a congregation of biologically relevant analytes.[9]

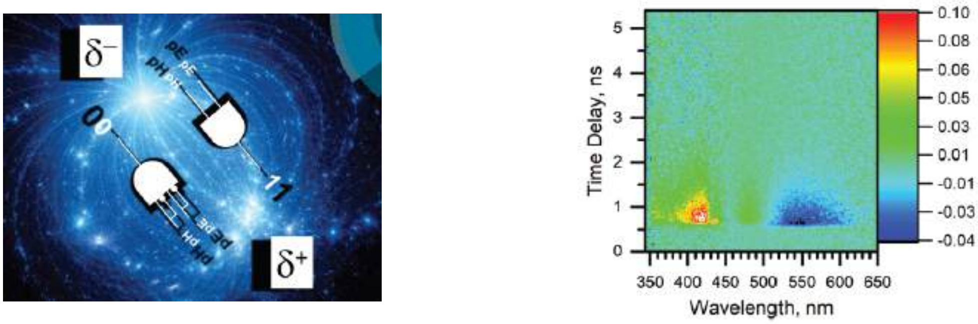

Figure 14. Front cover image of two logic gates in an electrical field and a transient absorption map of a fluorescent molecular logic gate for acid and oxidant.

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Theoretical Insights and Struggles on The Series of 3d^6 Metal Complexes

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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 3d^6 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.

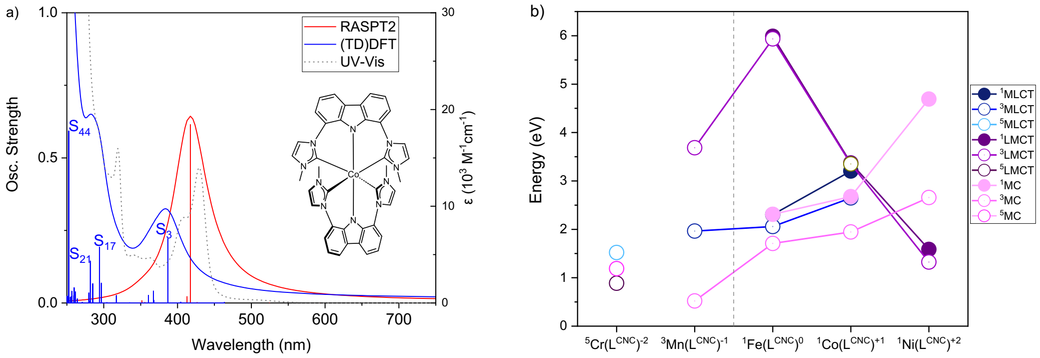

Figure 15. a) Simulated absorption spectra at RASPT2 and TD-DFT levels of theory, b) energy trends of the $^{1/3}$MC, $^{1/3}$MLCT/ILCT, $^{1/3}$LMCT states for the series of isoelectronic 3d metal complexes.

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Supramolecular interaction in Ru-Co and Ru-Fe complexes for efficient solar-driven hydrogen evolution and CO_2 reduction

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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 $[Ru(bpy)_2CN_2]$ within the field of solar energy conversion, focusing on its application to molecular hydrogen evolution and CO_2 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 $[Ru(bpy)_2CN_2]$ and hexadentate polypyridyl cobalt and iron complexes [3-4].

Spectroscopic titrations were employed to monitor changes in absorbance, luminescence intensity, and lifetimes of the $[Ru(bpy)_2CN_2]$ complex upon addition of the catalyst. Our results demonstrate the successful formation of 1:1 supramolecular adducts, exhibiting a high association constant ($K_{ass} \sim 10^5\ M^{-1}$), which results in efficient static quenching of the ruthenium complex emission.

The photocatalytic system comprises the $[Ru(bpy)_2CN_2]$ 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 CO_2 reduction in the presence of the iron complex.

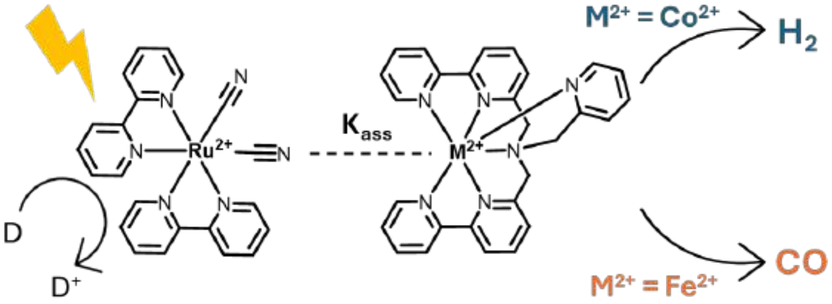

Figure 16. Schematic representation of the photo-driven hydrogen evolution and CO_2 reduction mechanisms through Ru-Co and Ru-Fe supramolecular interactions.

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

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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 TiO_2 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.

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

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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 TiO_2 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.

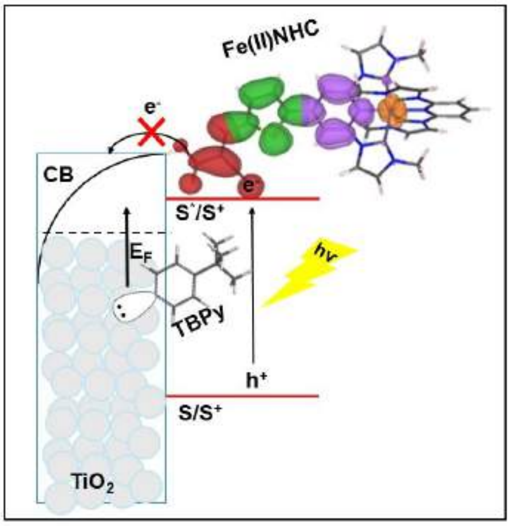

Figure 17. Schematic representation of an Fe(II)-SSC, with the absorption of TBPy onto TiO_2 also depicted.

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A novel water-dispersible microemulsion of a supramolecular copolymer for drug delivery systems

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Supramolecular polymers[1] 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 nanoparticles[3] created by incorporating **H**/**G1** and **H**/**G1**/**G2** polymers into water-dispersible CTAB, highlighting their potential for biomedical applications.

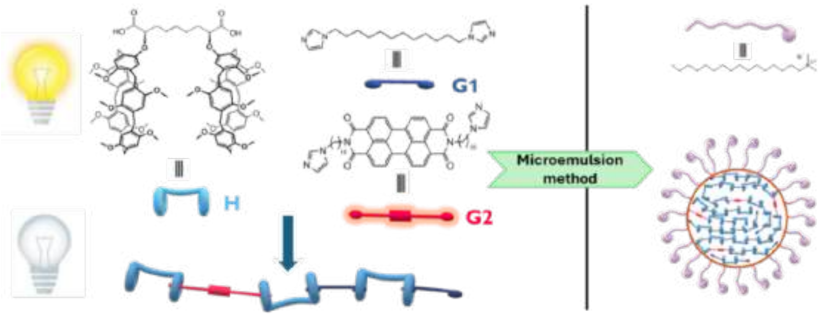

Figure 18. Mechanism of supramolecular polymer formation and its dispersion in water medium.

Aknowlegments

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Dynamic processes in photoactive metal-containing rotaxanes

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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.

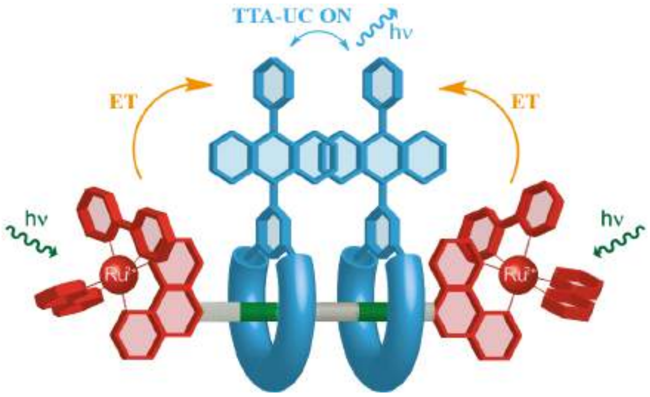

Figure 19. Cartoon representing intra-rotaxane triplet fusion leading to upconverted (TTA-UC) light output.

Acknowledgements

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Photochemistry, electron transfer and catalysis mapped by a combination of ultrafast laser and X-ray spectroscopies

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Copper(I) diimine complexes have been studied since the late 1970s due to their interesting electron dynamics and structural distortions. Heteroleptic [Cu(I)(diimine)(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 adaptions 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.

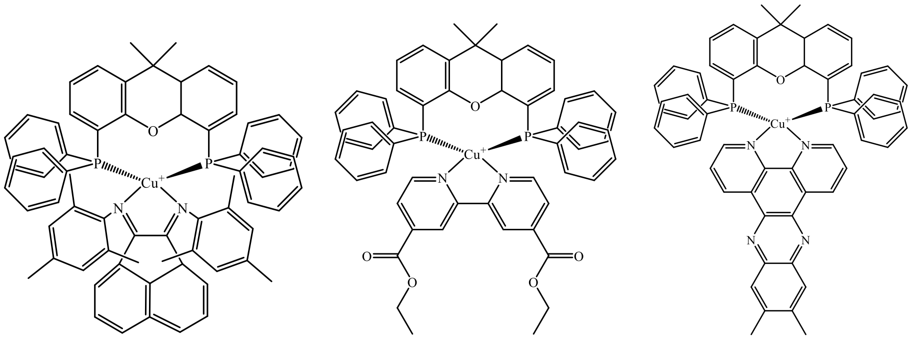

Figure 20. Structures of photosensitising heteroleptic Copper(I) complexes.

Aknowlegments

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Charge transfer dynamics in molecular-based photoanodes for solar fuels production

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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 (TiO_2).[1] The chromophore absorbs light and injects electrons into the TiO_2 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/TiO_2 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 quenching [2] 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]

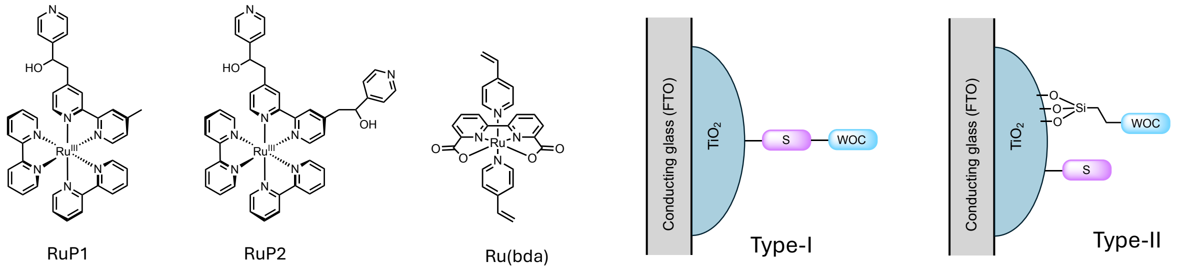

Figure 21. *Structures of the sensitizers (S) and catalyst (WOC) and photoanodes possible configurations.*

Acknowlegment: This project received funding from PRIN MUR project "Photogen" (Prot. 2022AWXS83).

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Red and NIR emitting Zn(II)-salen complexes for sensing and biological applications

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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

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"If you like it you should put a ring on it"

Rotaxanes as supramolecular protective motifs in reductive heterodinuclear photocatalysis

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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 heterodinculear 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.

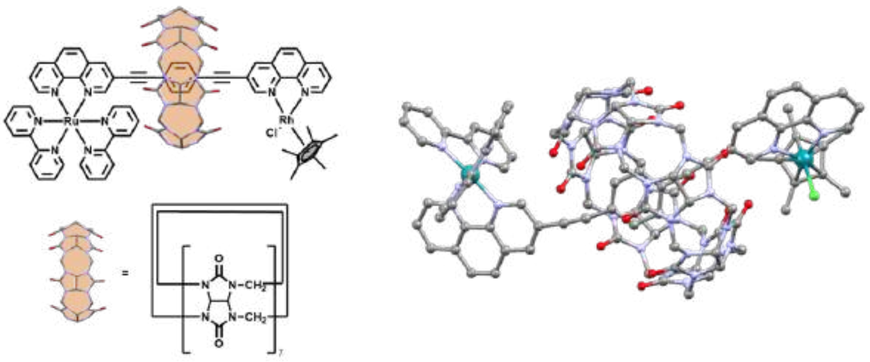

Figure 22: Molecular depiction & DFT structure of Hetero[2]Rotaxane.

Acknowledgments

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

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Tuning the photophysical properties of π-extended Cu-bibenzimidazole complexes

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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.

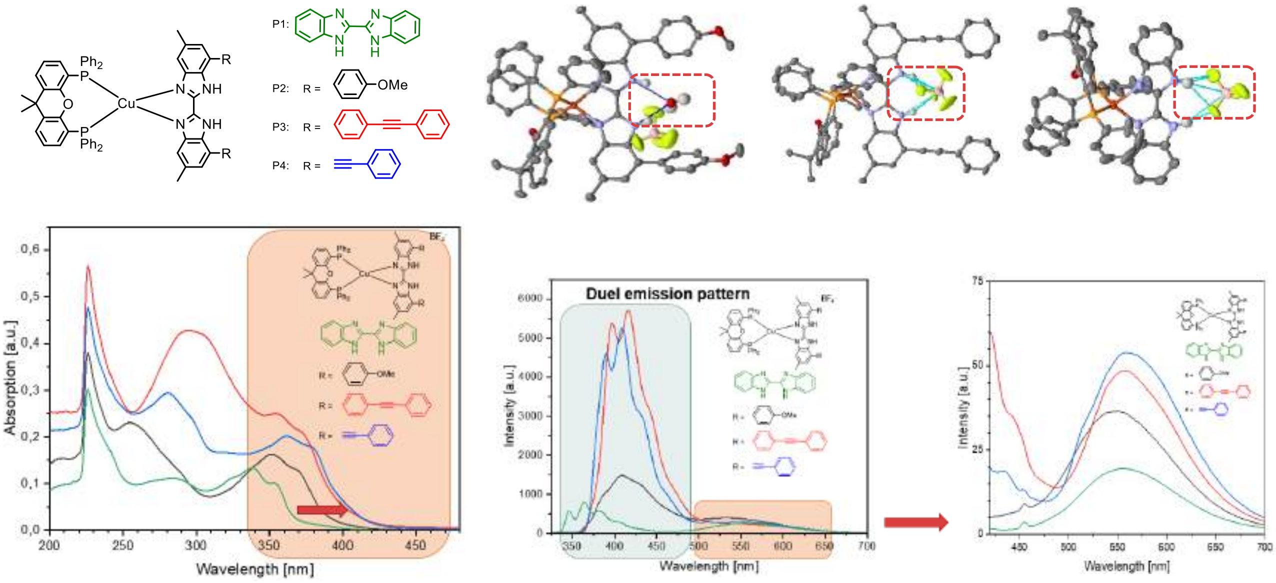

Figure 1: Novel copper-based PS with bibenzimidazole ligands, X-ray structure of different Cu(I) complexes, UV-vis and emission spectroscopic data.

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Conjugated polymer photocatalysts with a built-in metal complex for CO_2 reduction

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Reductive conversion of CO_2 into energy-added molecules has been an important subject in various fields including materials chemistry, catalysis, electrochemistry, and photochemistry, from viewpoints of both decreasing CO_2 concentration and gaining energy and carbon resources. Among the various methods and schemes proposed, visible-light-driven CO_2 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 CO_2 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 CO_2. Hence, the design principle, that maximizes the synergy between the conjugated skeleton and catalyst moiety, is strongly desired for achieving efficient photocatalytic CO_2 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 CO_2 reduction.[1-3]

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Benzothiazole-Quinoline based sensor for selective detection of Fe^{3+} ions and its applications

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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 Fe^{3+} 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 Fe^{3+} ions at 380 nm ($\lambda_{ex.}$ = 320 nm). The detection limit of **4HBTHQTz** with Fe^{3+} is found to be 0.64 μM, 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 Fe^{3+} 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 Fe^{3+} ions.

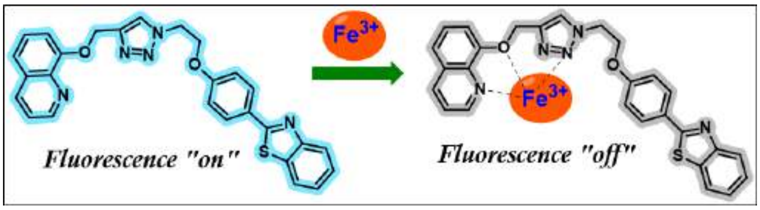

Figure 23. Representation of 4HBTHQTz.

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Tunning Electron-Accepting Properties of Phthalocyanines for Charge Transfer Processes

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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.

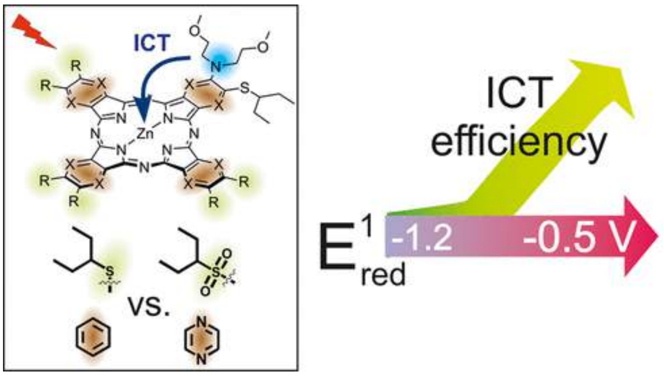

Figure 24. Schematic representation of the project.

Acknowledgments

The project was done thanks to the financial support from the Ministry of Education, Youth and Sports under the ERC CZ programme (LL2318).

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Exploration of Molecular Design to Achieve Nanosecond Excited States in Fe(II) Complexes Towards Long-Lived Triplet States

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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 d^6 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 ^{3}MLCT 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.

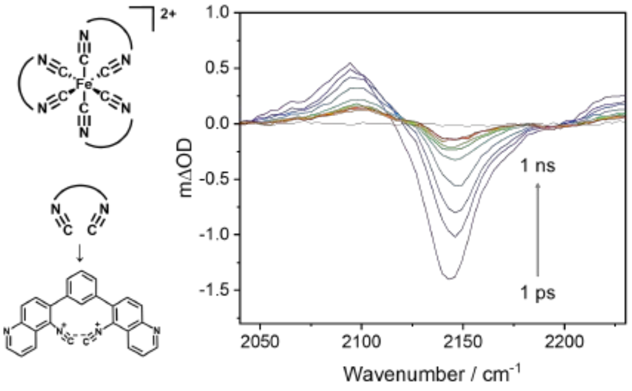

Figure 25. Molecular structure of Fe(II) isocyanide complex and its TR-IR spectra of C-N stretching modes (λ_{ex} = 400 nm)

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Time-Resolved Spectroscopic Studies on Reaction Mechanism in Complex Artificial Photosynthesis Systems

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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 CO_2 reduction (Fig. 1a) [1-5], the role of exciplex states in hybrid photocatalysts composed of a metal complex and a semiconductor nanoparticle for CO_2 reduction (Fig. 1b) [6], the electron transfer processes from a photosensitizer to an electrode in dye-sensitized photoelectrochemical cells (DSPEC) for H_2O oxidation (Fig. 1c), and the photoexcited processes at an electrode under the applying voltage in DSPEC for CO_2 reduction (Fig. 1d).

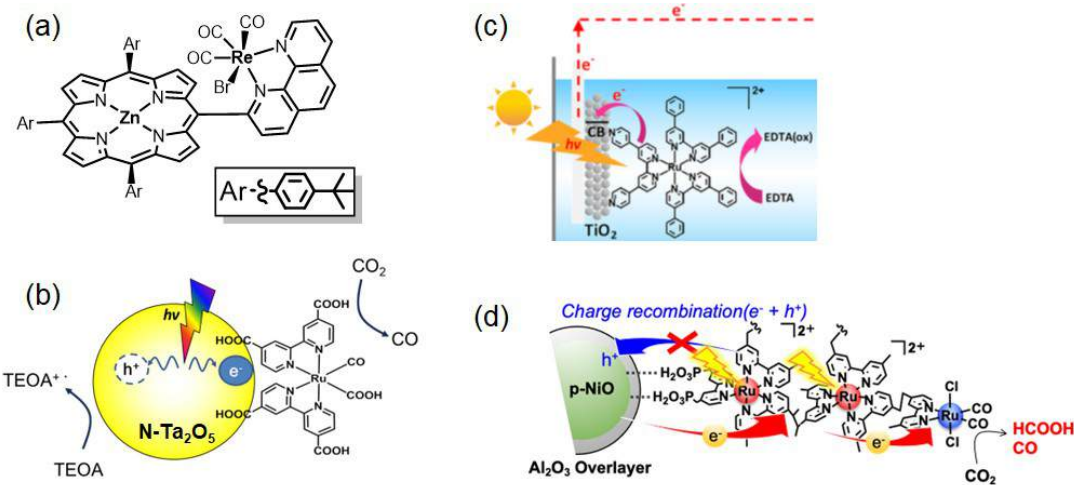

Figure 1. Complex artificial photosynthesis systems we studied using time-resolved spectroscopic methods: (a) dyad photocatalyst for CO_2 reduction, (b) hybrid photocatalyst for CO_2 reduction, (c) hybrid photoanode for H_2O oxidation, and (d) hybrid photocathode for CO_2 reduction.

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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

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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 µs 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.

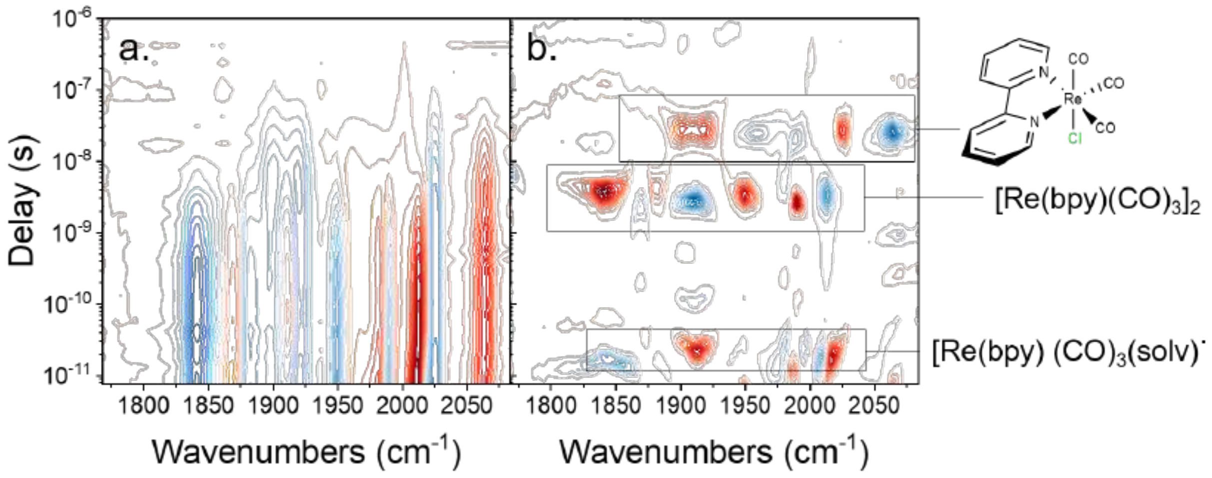

Figure 26. a. tr-IR of pre-reduced Re(bpy)(CO)$_3$Cl b. Lifetime density plot of a. and assignment of different reduction intermediates by their excited state lifetime [1].

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.

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Boron Dipyrromethenes (BODIPYs) for Antimicrobial Photodynamic Therapy (aPDT)

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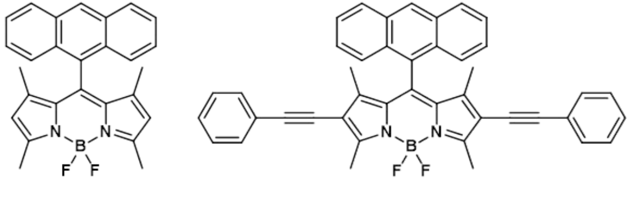
The prevalence of multidrug resistant (MDR) microbes due to the overuse and misuse of antibiotics has put an enormous strain on healthcare systems worldwide and will continue to grow into a much more significant problem if no alternative treatments are found for these pathogens. As 10,000,000 people 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.



BDP-1 BDP-2

Figure 27. Structures of BODIPYs discussed throughout the abstract.

Acknowledgements

Financial support from SFI (19/FFP/6882 award) is gratefully acknowledged.

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Conformational Switching of a Nano-Size Urea-bridged Zn(II)Porphyrin Dimer by External Stimuli

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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···π and π···π 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.

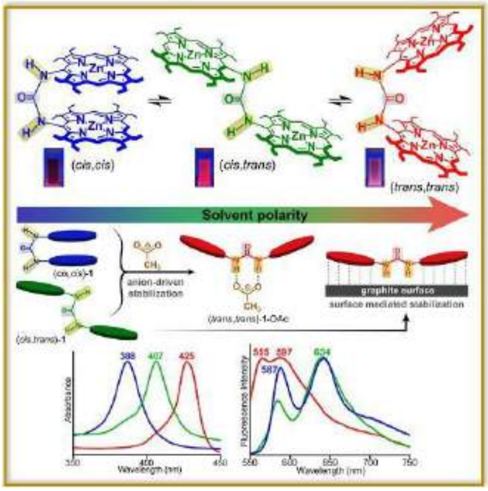

Figure 1. Three possible conformers of a urea-bridged Zn(II)porphyrin dimer and their selective stabilization investigated through advanced spectroscopic methods.

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We thank IIT Kanpur for providing all the facilities and support and Prof. Thiruvancheril G. Gopakumar for his help in performing the AFM studies.

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Near-Infrared Electrochemiluminescence from Chromium(III) Complexes in Mixed Annihilation Systems

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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).

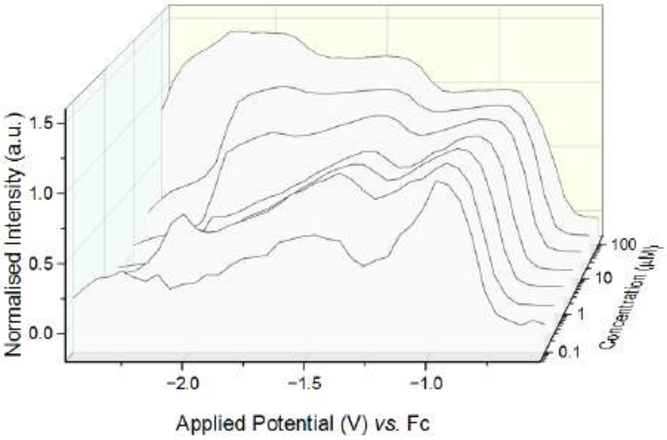

Figure 28. Normalised ECL intensity *versus* applied reduction potential and Cr(III) concentration, generated by 'spooling' ECL, for a Cr(III)/Ir(III) mixed annihilation ECL system.

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Disaggregation Kinetics of TPPS J-Aggregates under Mild Acidic to Neutral pH: The Synergistic Role of Albumin and Gold Nanoclusters

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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.

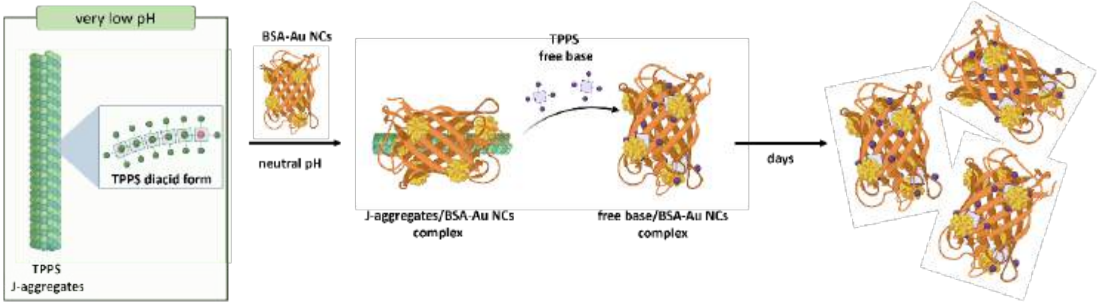

Figure 29. Visual summary of the stepwise disassembly of TPPS J-aggregates stabilized by a protein–gold nanocluster hybrid system. *Created in https://BioRender.com*

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Single Active Ligand in Iridium Complexes for Near Infrared Phosphorescent OLEDs

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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.

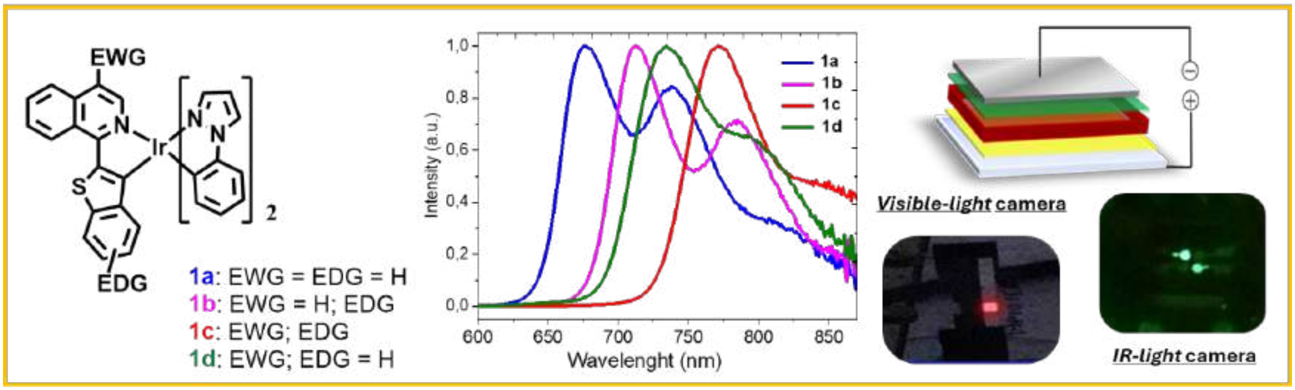

Figure 30. *Near-Infrared (NIR) emitters and their PhOLEDs.*

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).

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3D printed hybrid photocatalytic cement composites

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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 TiO_2-cement path on the surface of the cementitious underlays instead of incorporating TiO_2 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 TiO_2 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 TiO_2 nano-powder in the cement matrix. Increasing the amount of TiO_2 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

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Ultrafast time-resolved infrared spectroelectrochemistry

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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 minigrid 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.

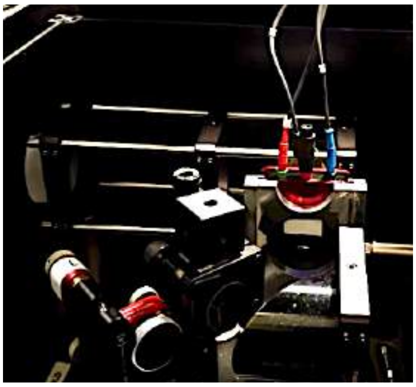

Figure 31. TRIR OTTLE cell.

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

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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 $(tbbpy)_2Ru(tpphz)PtI_2$ surrounded with a polymeric system, PDha-g-AMPS-g-$mPEG_{1000}$. 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.

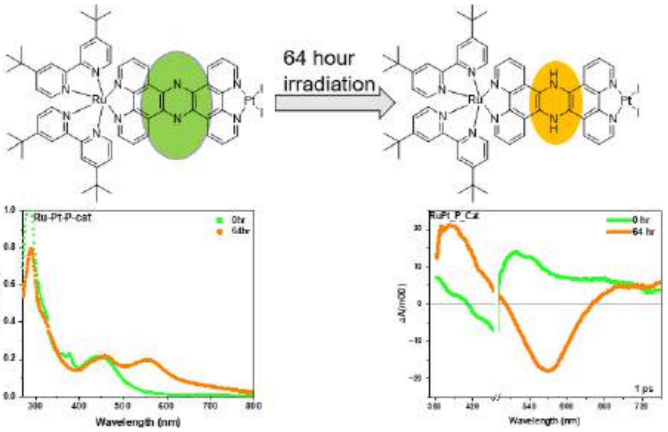

Figure 1. UV-Vis and TA spectra at 0 and 64 hr of irradiation showing formation of doubly hydrogenated bridge (inactive form) via mono hydrogenated bridge (active form) from the initial species.

Acknowledgments

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Plastics detection using Hydrogels Functionalized with Switchable Iridium Complexes

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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 exited 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.

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Ultrafast Laser Control of Photochemical Reactions in Light-Harvesting Transition Metal Complexes

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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.

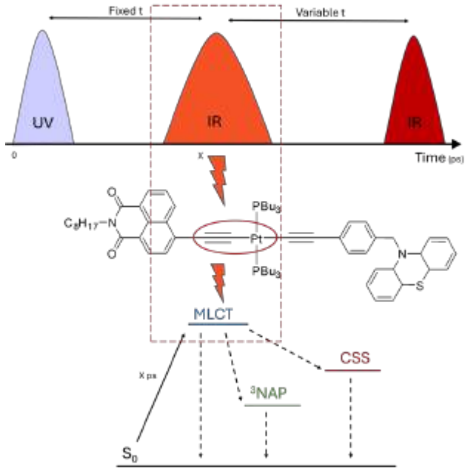

Figure 32. The mechanism of IR perturbation for electron transfer control.

Aknowlegments

We thank the University of Sheffield, the EPSRC and the Lord Porter Laser Laboratory.

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Prolonging Ru(bpy)$_3^{2+}$ Luminescence Lifetime in Silica Nanoparticles via Energy Reservoir Mechanism

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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) polypyrydine 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 μs.

Inspired by this energy reservoir mechanism, we report a self-organized SNPs system prepared with a reverse microemulsion strategy containing the Ru(bpy)$_3^{2+}$ 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)$_3^{2+}$, 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.

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Spectroscopies from perturbation theories

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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.

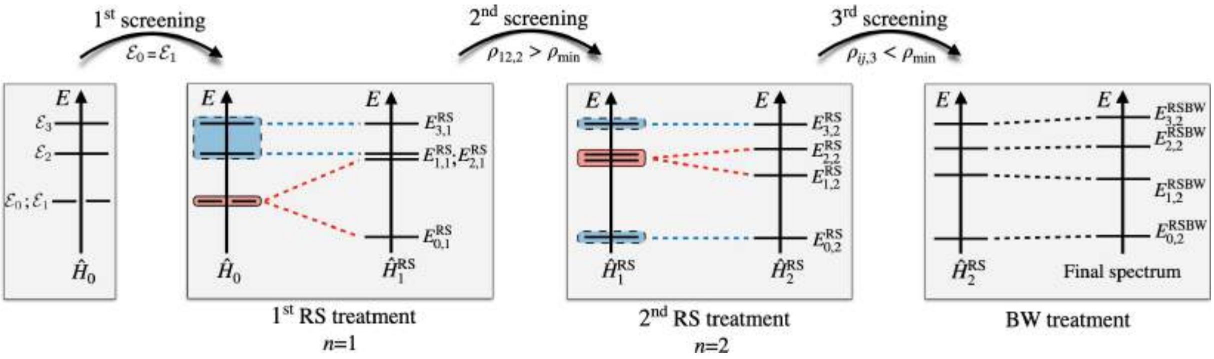

Figure 1. For perturbation scheme expansion to converge, the partitioning is determinant. The method uses a step-by-step partitioning that allows for the accurate description of energy states.

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Pulse Radiolysis Time-Resolved Infrared Spectroscopic Studies of Mn(I) and Re(I) Tricarbonyl CO_2 Reduction Catalysts

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The catalytic conversion of CO_2 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 CO_2 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 CO_2 reduction can give rise to disparate product distributions, primarily related to competing two-electron reduction pathways for CO, HCO_2^- and H_2 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 CO_2 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 CO_2 reduction catalysts, combining PR-TRIR analysis with more conventional photochemical and spectro-electrochemical techniques.[2-5]

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Synthesis Of Low-Symmetrical Silica-Phthalocyanines With Axial Modification For Photodynamic Therapy

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Photodynamic therapy (PDT) is an effective form of cancer therapy involving a photochemical reaction with a photosensitizer (PS), light and molecular oxygen[1]. 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 positions[2]. 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.

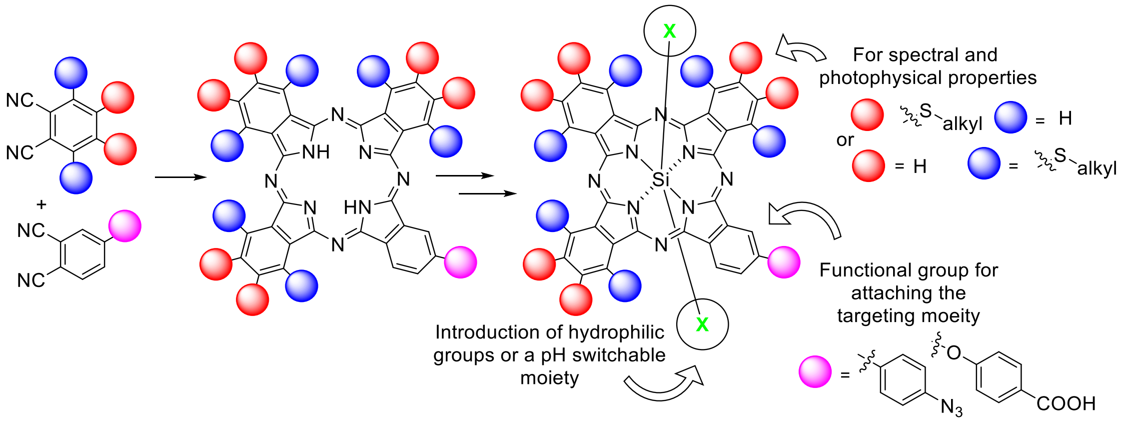

Figure 33. Developed method toward low-symmetrical SiPcs

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From ruthenium to iron: New perspectives on DNA-intercalating metal complexes

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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.

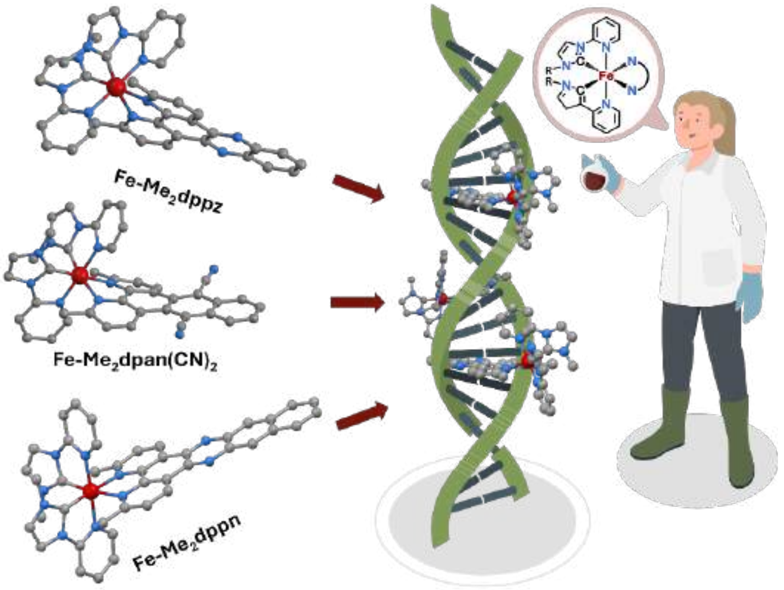

Figure 34: Molecular structures of the investigated DNA-intercalating iron complexes (left) and a conceptual representation of DNA-intercalated iron–dppz complexes.

Aknowlegments

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Fine-tuning the Excited State Dynamics of Ruthenium(II) Polypyridyl Complexes with Benzazole-Substituted 8-Hydroxyquinolines

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A series of structurally related bistridentate heteroleptic Ru(II) polypyridyl complexes: $[Ru^{II}(ttpy)(8\text{-}HQL^{S/N/O})]^+$ (**Ru1-Ru3**) were synthesized, where **ttpy** = *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 $^1O_2$ generation ability, these heteroleptic Ru(II) complexes demonstrated potential as photocatalysts for oxidation of organic substrates.

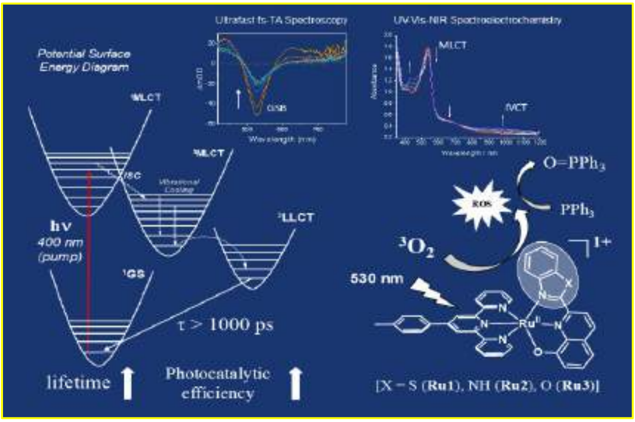

Figure 1. Systematic variation in five membered ring heterocycles of 8-hydroxyquinoline ligand backbone impacting on the overall excited state lifetime and dynamics of the heteroleptic bis(tridentate)Ru(II) polypyridyl complexes.

Acknowledgments
We thank IIT Kanpur for infrastructures and providing High Performance Computing (HPC-2013) facility for the DFT calculations.

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Anti- Kasha emission from Co(III)-Amidine-*N*-oxide complexes: photophysics and reactivity

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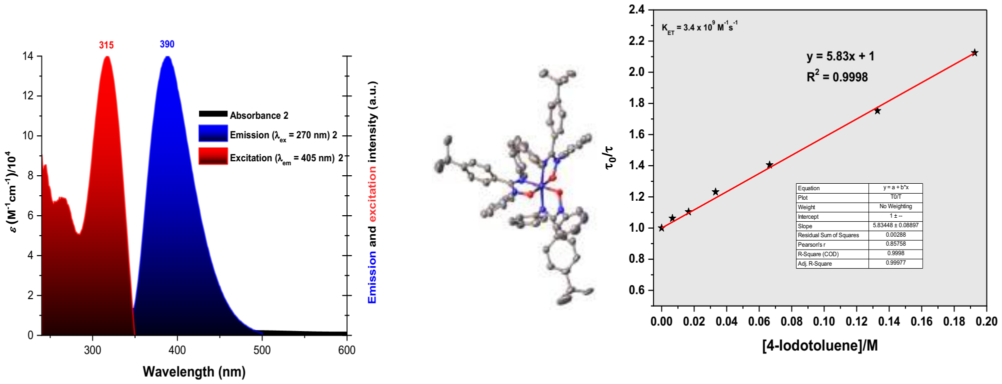
The photophysical properties of 3d metal complexes remain a fascinating field of study, particularly when transitioning from the rare 2nd and 3rd row metal complexes towards their 1st row congeners.[1-3] Here, we present a series of novel photoactive Co(III) metal complexes based on amidine-*N*-oxide ligands. These complexes exhibit unusual anti-Kasha type singlet emissions. Contrary to the widely accepted Kasha emitters[1-3] which emit from the lowest-lying excited state, these complexes show room temperature fluorescence from higher-lying states consisting of an admixture of $^1\pi$-π^* and intra-ligand charge-transfer (^{1}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]



Equation	y = a + b*x
Plot	T0/T
Weight	No Weighting
Intercept	1 ± --
Slope	5.83448 ± 0.08897
Residual Sum of Squares	0.00288
Pearson's r	0.85758
R-Square (COD)	0.9998
Adj. R-Square	0.99977

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

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Light-driven Catalytic Activity and Deactivation Processes of Thio(oxo)molybdate Hydrogen Evolution Reaction Catalysis

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Thiomolybdates and thiooxomolybdates function as molecular catalysts for light-driven or electrocatalytic hydrogen evolution reaction (HER).[1] The well-known prototype cluster $[Mo_3S_{13}]^{2-}$ has undergone numerous studies regarding catalytic activity and deactivation processes.[2] However, for other thiomolybdates such as $[Mo_2S_{12}]^{2-}$ and thiooxomolybdates like $[Mo_2O_2S_6]^{2-}$ 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 $[Mo_2S_{12}]^{2-}$ or $[Mo_2O_2S_6]^{2-}$ 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.

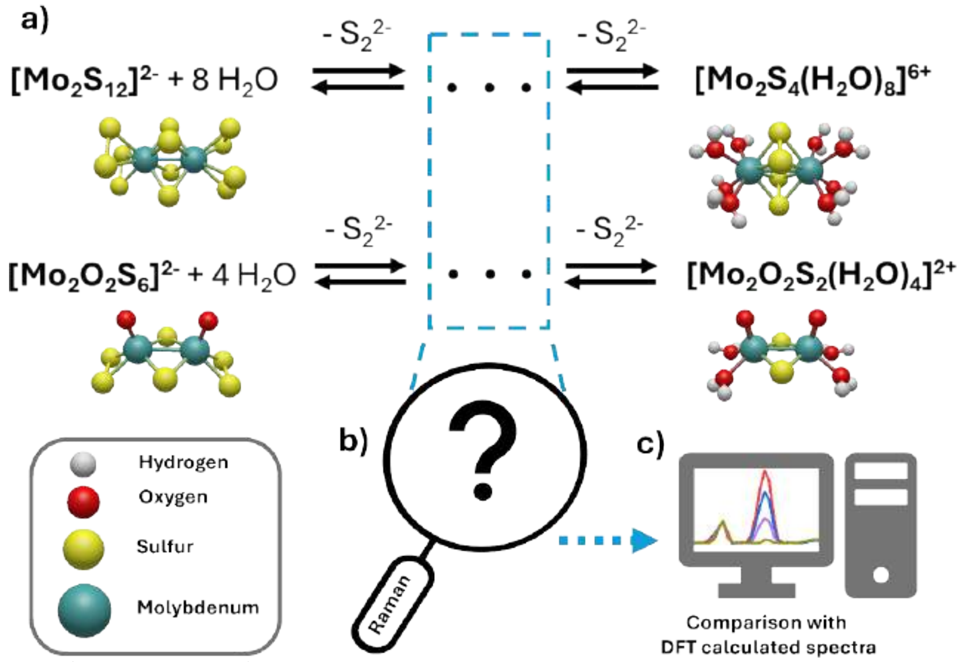

Figure 1. a) $[Mo_2S_{12}]^{2-}$ and $[Mo_2O_2S_6]^{2-}$ might undergo ligand exchange with the solvent (water) over a certain period. b) Possible ligand exchange is monitored using Raman spectroscopy. c) The resulting spectra and their kinetics are evaluated and compared to DFT calculated spectra.

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Metallonitrenes As Key Intermediates In C–N bond Formation

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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 leadas 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.

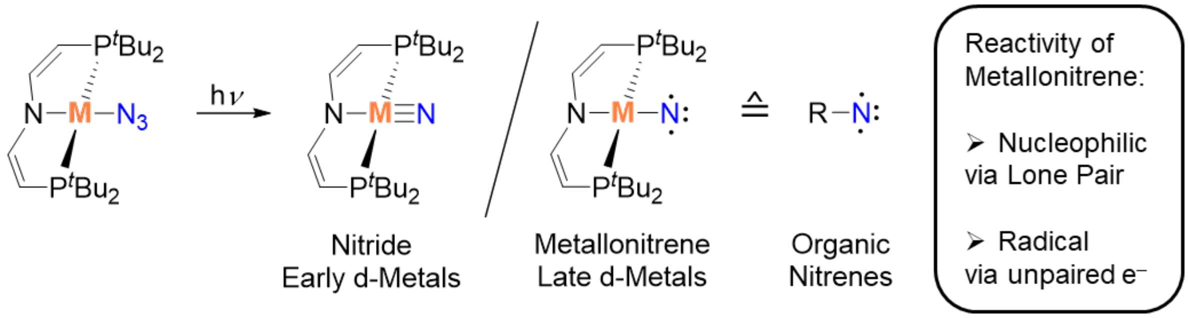

Figure 36. Irradiation of azide complexes can lead to nitrides ($M\equiv N$) or metallonitrenes (M–N), depending on the metal. The latter are similar to organic nitrenes with respect to electronic structure and reactivity.

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Computational Insights into the Photodissociation Mechanism of Terpyridine-Based Ruthenium(II) Complexes

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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. ^{3}MLCT or ^{3}LC) enables the efficient generation of reactive oxygen species (ROS), which induce cellular oxidative stress. Conversely, PACT requires ^{3}MLCT-^{3}MC conversion and the subsequent population of ^{3}MC 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 ^{3}MLCT–^{3}MC 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 ^{3}MLCT state, as complexes with higher ^{3}MLCT–^{3}MC 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 **Ru$_1$** and **Ru$_2$** (Figure 1), to rationalize how the ^{3}MLCT–^{3}MC conversion, acetonitrile release, and subsequent water coordination at the Ru center influence the photochemical efficiency of these prospective PACT agents.

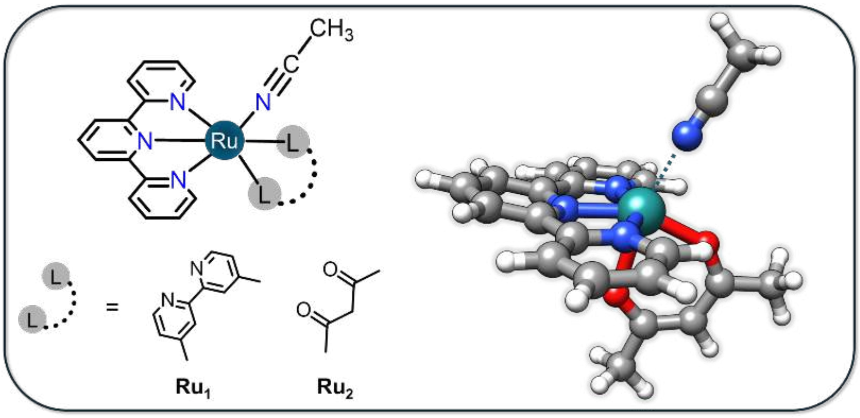

Figure 37. Structure of **Ru$_1$** and **Ru$_2$** complexes and transition state structure of the acetonitrile release of **Ru$_2$**

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Control of Emission Efficiency and Color by Mixed Crystals of Platinum(II) and Palladium(II) Complexes in One-dimensional Chain

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Square-planar Pt(II) complexes with the $5d^8$ electronic configuration often exhibit ^{3}MMLCT emission in the visible region due to Pt···Pt interactions arising from the one-dimensional stacked structures. In contrast, Pd(II) complexes with the $4d^8$ electron system form very weak Pd···Pd interactions, and there are extensively few examples of ^{3}MMLCT emission.[1] We recently developed a cyclometalated Pd(II) complex with the Pd···Pd interaction, $K[Pd(CN)_2(dFppy)]\cdot H_2O$ (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 ^{3}MMLCT excited state in the stacked column between **Pd-dFppy** and **Pt-dFppy**. However, the ^{3}MMLCT 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.

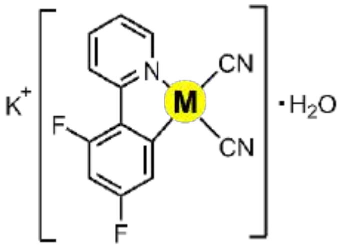

Fig. 1 Structural formula of $K[M(CN)_2(dFppy)]\cdot H_2O$ (M = Pt, Pd)

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.

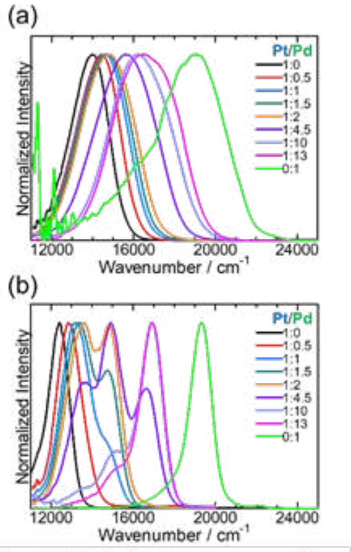

Fig. 2 Emission spectra at (a) RT and (b) 77 K (λ_{ex} = 350 nm).

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Unraveling Solvent Polarity Effects in Thermally Activated Delayed Fluorescence Through Time-Resolved Spectroscopy

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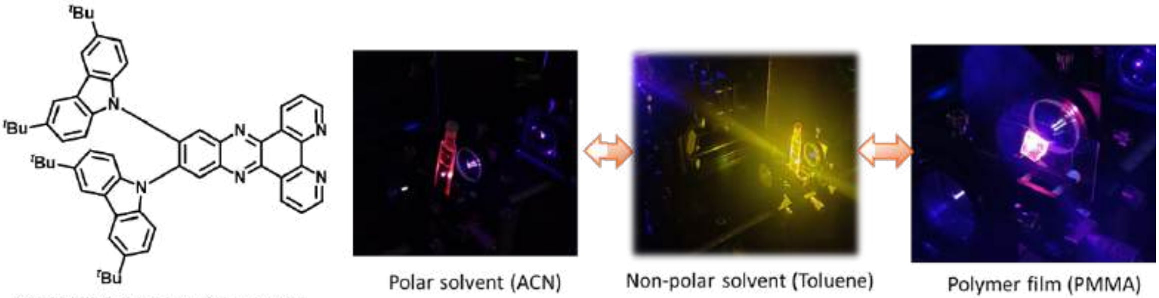
Thermally activated delayed fluorescence (TADF) has emerged as an effective approach to harvest triplet state for organic light-emitting diodes (OLEDs) due to their ability to achieve fluorescence via reverse intersystem crossing (RISC)[1,2] This study presents a comprehensive investigation into the photophysics of a TADF-active organic chromophore namely Cbzdppz (Figure 1). Our fs-transient absorption measurements reveal photoexcitation of Cbzdppz leads to the formation of a singlet charge-transfer state (^{1}CT) 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 ^{1}CT 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 Cbzdppz 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 ^{1}CT 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).



11,12-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)dipyrido[3,2-*a*:2',3'-*c*]phenazine

Polar solvent (ACN)

Non-polar solvent (Toluene)

Polymer film (PMMA)

Figure 1: Emission Enhancement of Cbzdppz: 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).

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Conformation Dependent Emission and Circularly Polarized TADF in Linear CDP Copper (I) Complexes

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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}CDP$_2$Cu]X {X – Br and PF$_6$} showing orange to deep red emission ranges from 605 to 715 nm in solution, in powders, and in rigid polystyrene film. Comparing [^{Me}cAAC$_2$Cu]PF$_6$, 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 0.71×10^5 s^{-1} in solution state and remarkable dissymmetry factor $\pm 1.5 \times 10^{-2}$ in polystyrene film.

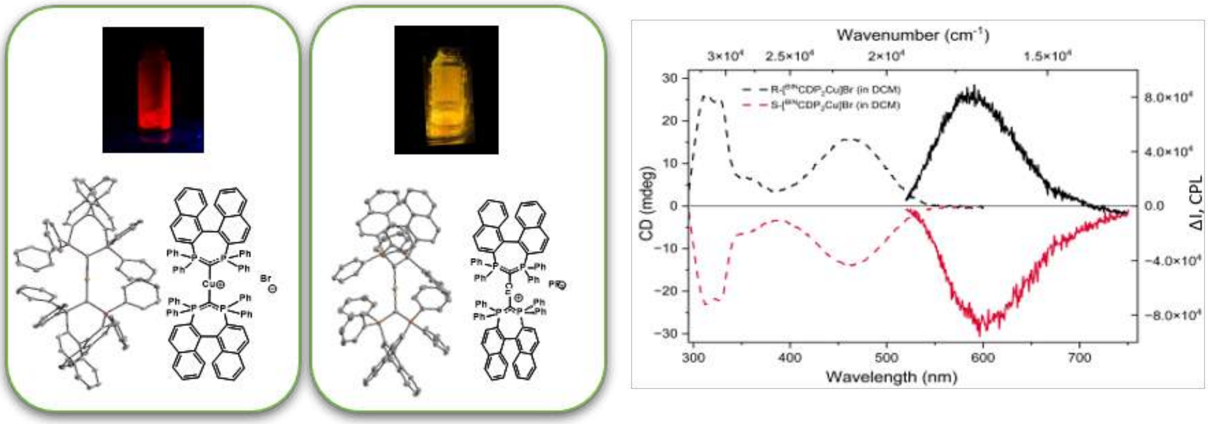

Figure 38. Conformational dependent emission and circularly polarized Luminescence Property

Aknowlegments

Financial support by the Deutsche Forschungsgemeinschaft (DFG STE1834/4-2) is gratefully acknowledged.

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Temperature Dependency of the Light-Driven Hydrogen Evolution Reaction using Thiomolybdate Clusters

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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 $[Mo_3S_{13}]^{2-}$ 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.

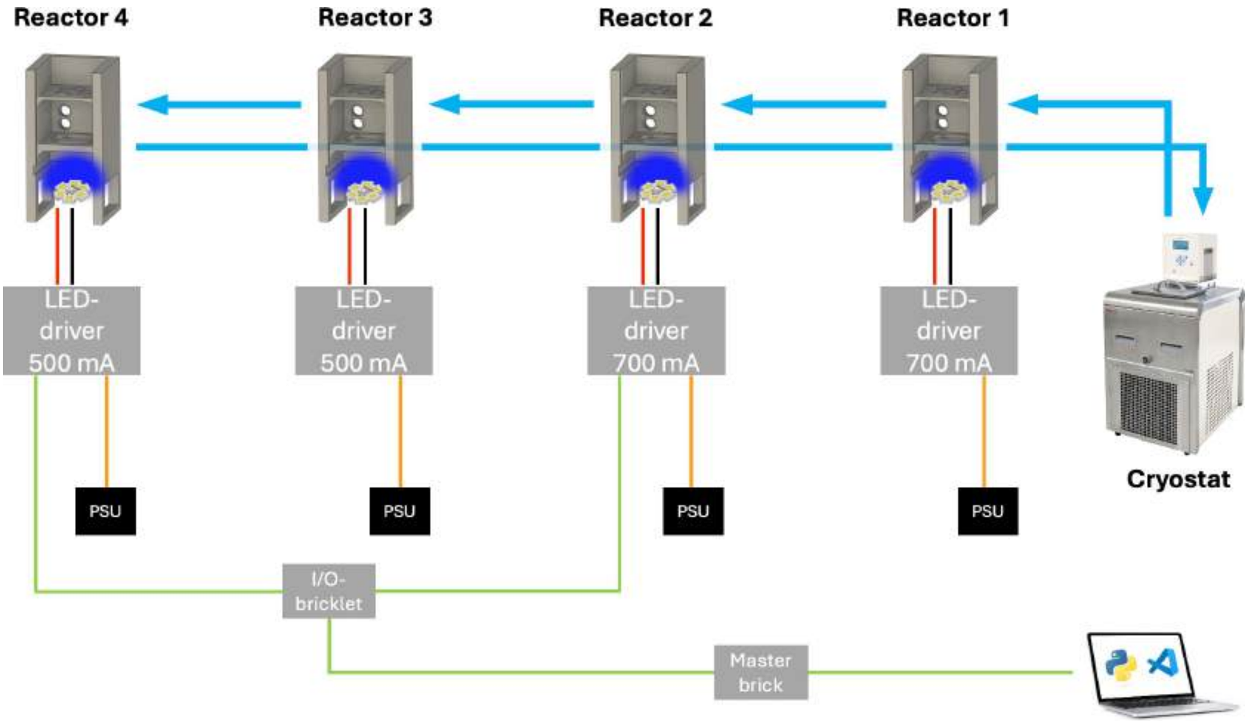

Figure 1. The setup of the four photoreactors. The temperature control unit inside the reactors is tempered by a cryostat. The LEDs are powered through a LED driver. The dynamic irradiation is achieved by using an I/O-bricklet to pulse the LEDs at the desired frequency with the desired ON/OFF-ratio.

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Excited state processes in a supramolecular photocatalyst – a quantum computational investigation

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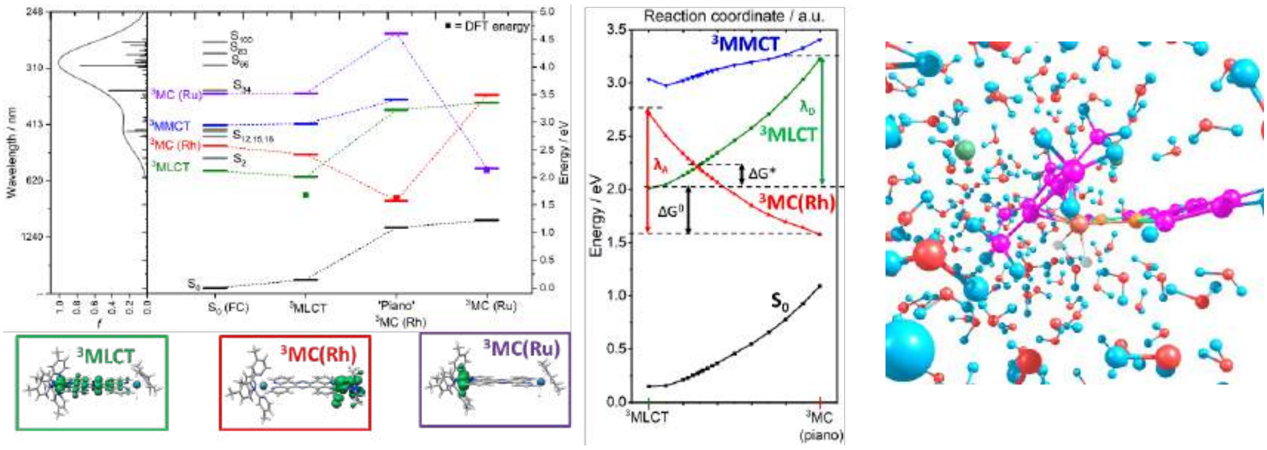
The photophysical properties of a model supramolecular photocatalyst are investigated using a suite of quantum computational methodologies. The photocatalyst, denoted **RutpphzRhCp*** is comprised of a Ru(II) photosensitiser, a highly conjugated bridging moiety and a Rh(III) catalytic centre.[1] Previous 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 (H_2O, 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, ^{3}MLCT, ^{3}MC$_{(Rh)}$ and ^{3}MC$_{(Ru)}$ geometries; Centre: Marcus potential energy curves of the ^{3}MLCT and ^{3}MC$_{(Rh)}$ states; Right: Snapshot of catalytic centre calculated in an explicit solvent environment.



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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-d$_4$

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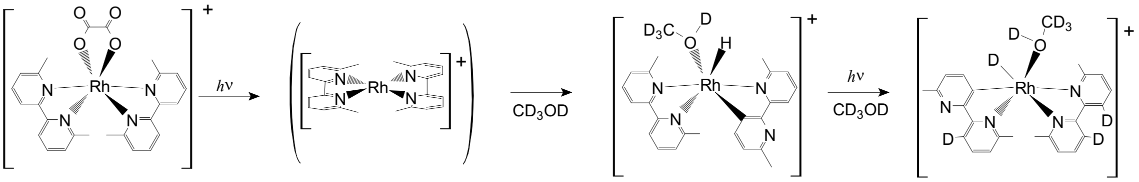
Photoirradiation to bis(6,6'-dimethyl-2,2'-bipyridine)(oxalato)rhodium(III) ($[Rh(N^\wedge N)_2(ox)]^+$) caused the dissociation of ox followed by the formation of unprecedented Rh(III) complex $[Rh^{III}(N^\wedge N)(C^\wedge N)(H)(CD_3OD)]^+$ (C^N = [6,6'-dimethyl-2,2'-bipyridine]-3-yl-κC^3,κ$N^{1'}$) with Rh–H and Rh–C σ bonds in CD_3OD. Although $[Rh^{III}(N^\wedge N)(C^\wedge N)(H)(CD_3OD)]^+$ was converted to $[Rh^{I}(N^\wedge N)_2]^+$ by further photoirradiation, the auto-cyclometallation due to the steric hindrance between methyl groups of N^N ligands reproduced the Rh(III) complex. Surprisingly, the resultant Rh(III) complex was $[Rh(N^\wedge N)(C^\wedge N^D)(D)(CD_3OD)]^+$, whose H atoms in Rh–H bond and at 3, 3'-positions of N^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.

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

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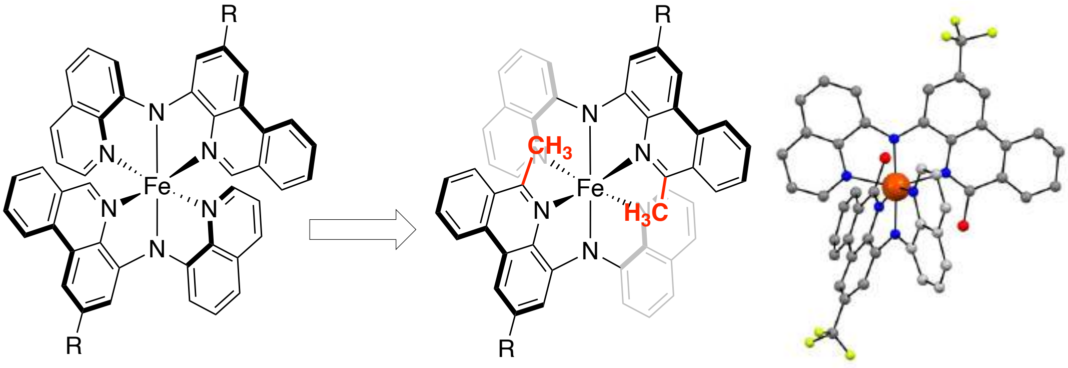
Iron coordination complexes have long been sought as a sustainable replacement for precious metal sensitizers in applications that exploit photo-generated excited states, from luminescent materials to photoredox catalysis to dye-sensitized solar cells. The main shortcoming of iron-based dyes is their 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.



all low-spin Fe(II) **high-spin Fe(II)**

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 CO_2 Reduction to Liquid Fuel via Modified UiO-66 Photocatalysts

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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 CO_2 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 m^2/g for Cu@UiO-66 to 1532 m^2/g for Ni@UiO-66, directly impacting CO_2 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 $\mu mol \cdot g^{-1} \cdot h^{-1}$, far surpassing the base UiO-66 (0 $\mu mol \cdot g^{-1} \cdot h^{-1}$), while Cu@UiO-66 achieved the highest ethanol production at 12.45 $\mu mol \cdot g^{-1} \cdot h^{-1}$. [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 CO_2 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.

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Synthesis and Resolution of *tris*-Heteroleptic Ruthenium Polypyridyl Complexes as Chiral DNA Binding Luminescent Probes

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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 ($\Delta RT_{(\Lambda\text{-}\Delta)}$ > 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 (λ_{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.

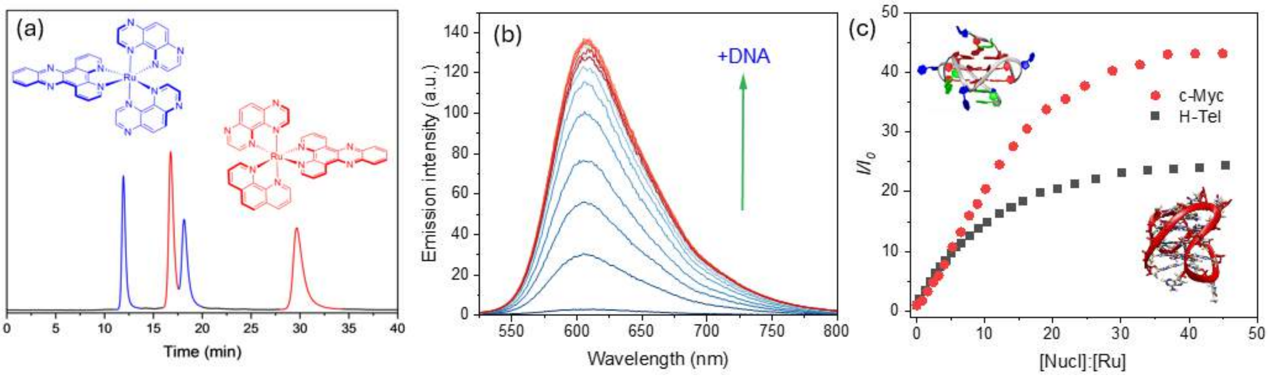

Figure 41: (a) Chromatogram of the resolution of a *tris*-heteroleptic complex containing a *bis*-heteroleptic complex as an impurity by chiral stationary phase-HPLC (CSP-HPLC). **(b)** luminescence titration of a *tris*-heteroleptic complex with B-DNA (stDNA). **(c)** luminescence response in the presence of different quadruplex structures.

Acknowlegments
Authors acknowledge Research Ireland for funding (SFI 21/FFP-P/10126 *PhotoGene*).

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Room-Temperature Phosphorescence of Cocrystals of Aromatic Bisimides and Triplet Sensitizer Pt(acac)$_2$

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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 Φ_{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]

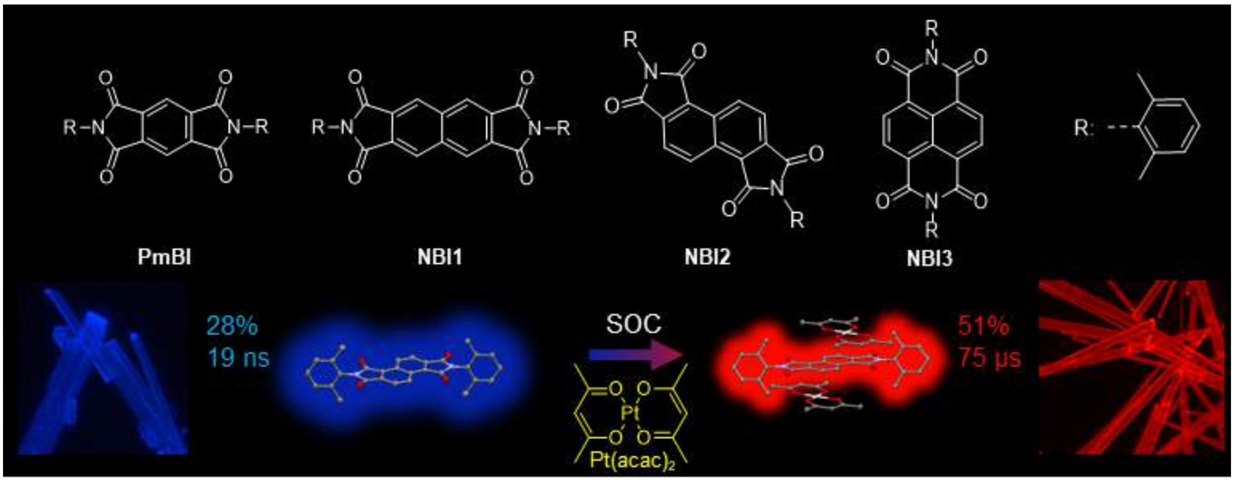

Figure 42. Chemical structures of the four investigated bisimides: **PmBI**, **NBI1**, **NBI2** and **NBI3**. **NBI2** shows by itself a blue fluorescence with Φ = 28% in the solid state, which is shifted to a bright red phosphorescence with up to 51% in its 1:1 cocrystal with the triplet sensitizer Pt(acac)$_2$.

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Photocatalytic CO_2 Reduction and H_2 Evolution in Aqueous Media with Water-soluble Complexes

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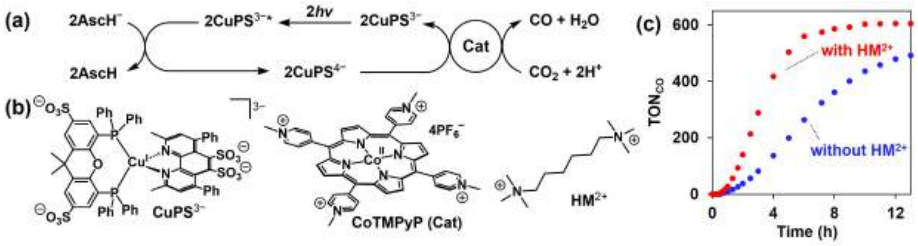

Figure 43. (a) Photocatalytic CO_2 reduction driven by **CuPS**$^{3-}$. (B) The structure of **CuPS**$^{3-}$, **CoTMPyP** and **HM**$^{2+}$. (C) Photocatalytic activities for CO formation in the presence (red) or absence (blue) of **HM**Cl_2 (50 mM). Photolysis was carried out in CO_2-saturated $NaHCO_3$ 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 ºC under Xe lamp irradiation (λ > 400 nm, 300 mW cm^{-2}).

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 CO_2-to-CO conversion by using a sulfonylated heteroleptic copper(I) photosensitizer (**CuPS**$^{3-}$) and a cobalt porphyrin CO_2 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 CO_2 reduction based on the enhanced efficiency of reductive quenching (Figure 1c).[2]

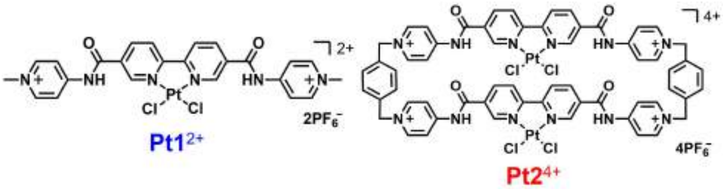

Figure 2. The structures of **Pt1**$^{2+}$ and **Pt2**$^{4+}$.

On the other hand, we have also explored Pt-based single-molecular photocatalysts for H_2 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**$^{4+}$, Figure 2) was investigated by photochemical and electrochemical technique.

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Photocatalytic degradation of nitrogen oxides (NO_x) in photoreactor with granulated regolith with TiO_2

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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 (TiO_2) 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 (TiO_2) 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 TiO_2 layers and designing an efficient bed for flow-through photoreactors.

A novel continuous flow photoreactor with TiO_2-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 TiO_2 photocatalytic layer. The decomposition of NO_x in the presence of granulated regolith with TiO_2 thin films was studied under various UV light intensities (10 W/m^2, 15 W/m^2, 20 W/m^2), humidities (30%, 50%, 70%), and gas flow rate (0.75 dm^3/min, 1.0 dm^3/min, 1.25 dm^3/min).

Aknowlegments

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Thermochromic circularly polarized luminescence for homochiral tetracopper(I) clusters

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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*)-[$Cu_4I_4(L)_4$], 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.

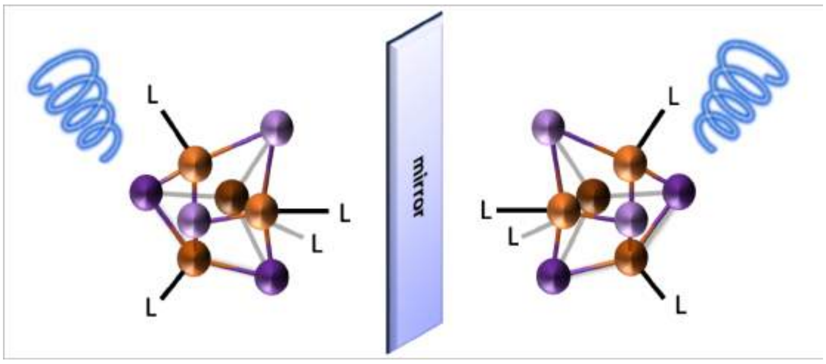

Figure 1. The expected molecular structures of enantiomer (*R,R,R,R*)- and (*S,S,S,S*)-[$Cu_4I_4(L)_4$] and the exhibition of circularly polarized luminescence (CPL).

Acknowledgements

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Ultrafast Photophysical and Photochemical Dynamics of Hexahalobismuthates(III)

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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, ~92 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 ~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.

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Photodriven charge accumulation on Cu(I) 4*H*-imidazolate complexes

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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.

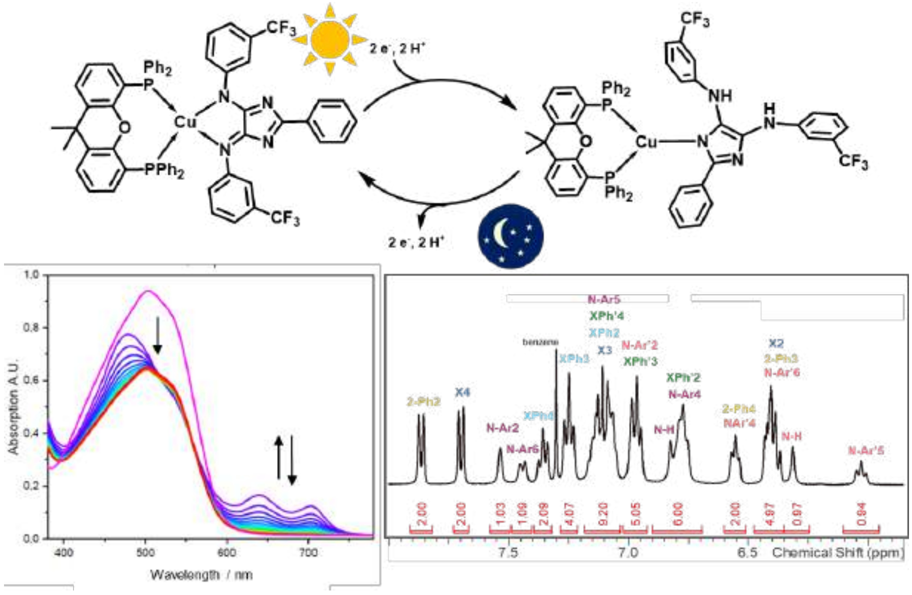

Figure 44. General scheme of the reaction system (top); UV-Vis absorption spectra recorded during the photoreduction of Cu(I)-4H-imidazolate complexes (bottom, left); 1H-NMR spectrum of the photoreduction product (bottom, right).

Aknowlegments

Thanks to the Transregional Collaborative Research Center TRR234 - CataLight

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Doublet charge transfer emission of Ce(III) complex with β-diketonate ligand

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Open-shell luminophores with character doublet-doublet transitions are attractive photofunctional materials for use in organic light-emitting diodes (OLED) and optical sensors[1]. Among them, luminescent trivalent cerium (Ce(III)) complexes, which have a single unpaired 4f-electron, become promising candidates as blue and green luminophores[2]. Previously, Ce(III) complex with strong-field ligands provides efficient doublet emission based on stabilized 4f-5d excited state[3]. 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 hexa-fluoroacetylacetonates (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.

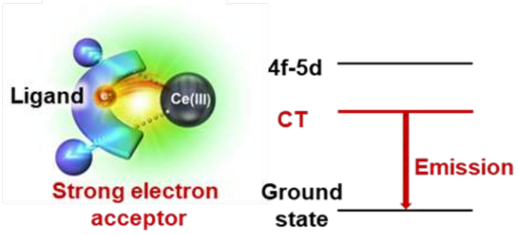
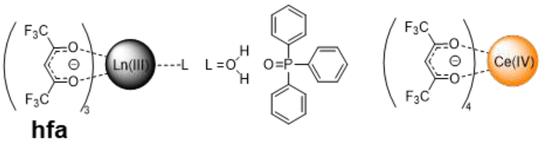


Figure 45. Conceptual illustration of charge transfer emission from π*- to 4f orbitals.



Ln(III)-hfa-L (Ln = Ce, Gd)

Ce(IV)-hfa

Figure 2. Molecular structures of **Ln(III)-hfa-L** and **Ce(IV)-hfa**.

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Synthesis, Characterization and Study of a novel Fe(II)-complex as potential photosensitizer

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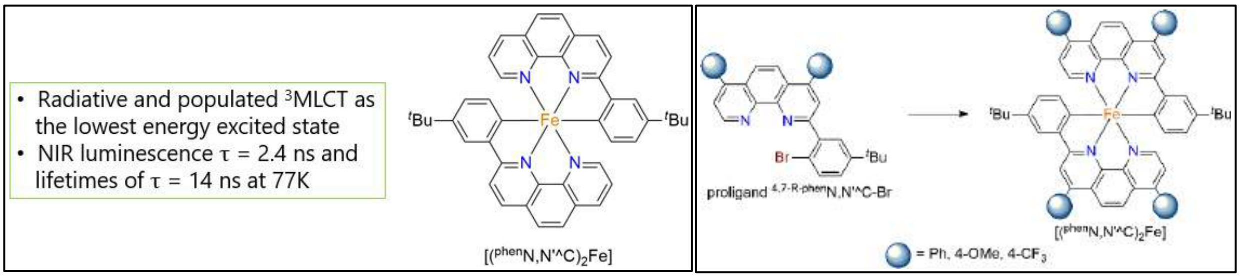
The search for alternatives replacing *Noble Metals* in the field of photochemistry has caught great attention in the last few years. Specifically, a lot of interest relies on Iron, since it is inexpensive and more ecologically benign. Indeed, many strategies has been evaluated to improve the lifetime 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 ^{3}MLCT excited state with a lifetime of τ = 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 3d^6 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.



- Radiative and populated ^{3}MLCT as the lowest energy excited state
- NIR luminescence τ = 2.4 ns and lifetimes of τ = 14 ns at 77K

Figure 1. (A) Photoreactive Fe(II)-complex reported by Leis *et. al.* **(B)** Fe(II)-complexes presented in this work.

Acknowledgments

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Three-Coordinate Cu(I) Complexes of Anionic N-Heterocyclic Carbenes

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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 μs). Their high excited-state energies (≈ 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.

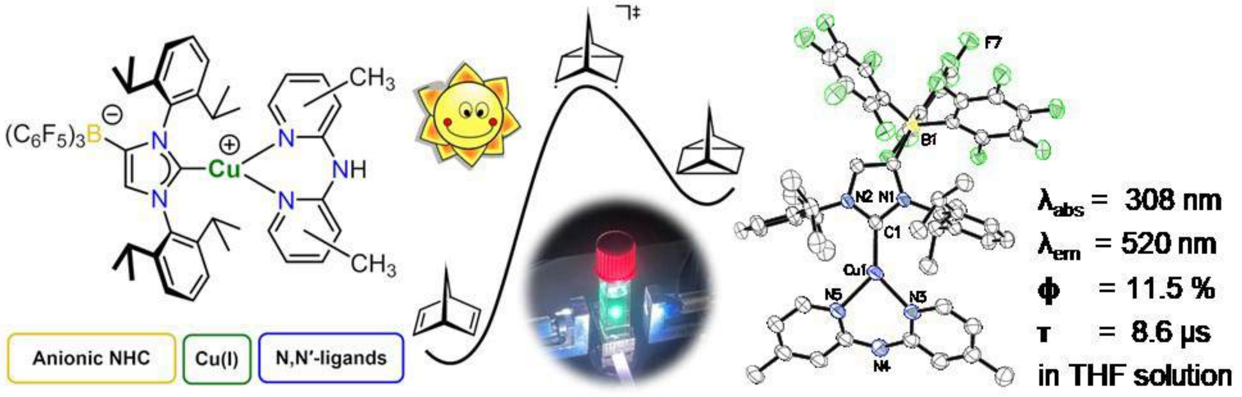

Figure 1. General structure of neutral [(WCA-NHC)Cu(N^N)] complexes (left) and a representative X-ray structure of complex C4 along with its main photophysical properties (right).

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Synthesis of highly luminescent, isomorphous Ag^I and Cu^I complexes; Effect of halogenido ligands on emission and relaxation

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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 $[Ag_2X_2(PPh_3)_2(R\text{-}pyz)]_n$ 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 $[Ag_2X_2(PPh_3)_2\text{-}(Me_2pyz)]_n$ (Me_2pyz: 2,5-dimethylpyrazine; X: I, Br, Cl) together with the Cu^I congeners $[Cu_2X_2(PPh_3)_2(Me_2pyz)]_n$ (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 S_1 and T_1 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 Me_2pyz complexes with isomorphous structures reveal that relaxation significantly affects the emission energy for Ag^I and Cu^I complexes.

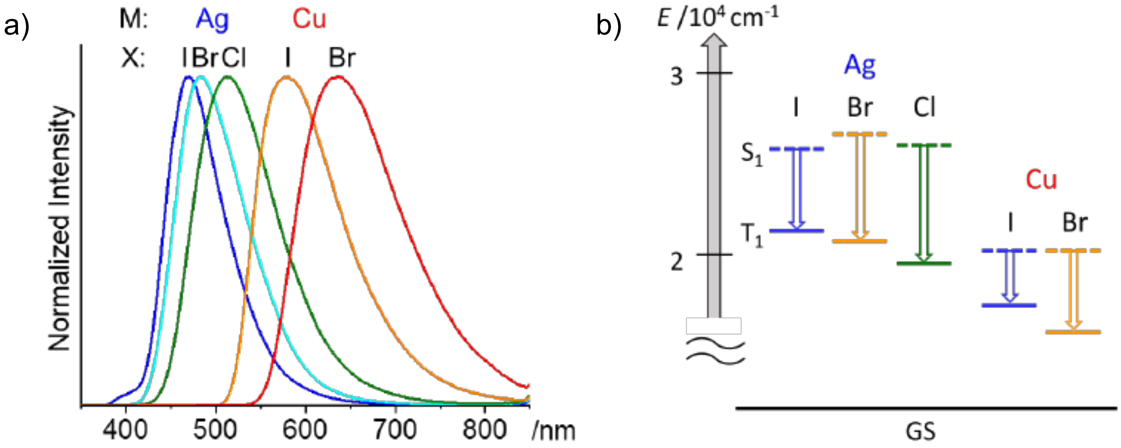

Figure 46. Emission spectra of $[Cu_2X_2(PPh_3)_2(Me_2pyz)]_n$ (a) and the energy diagram (b).

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Heteroleptic copper (I) complexes as suitable photosensitizers for new photo-induced organic transformations

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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 $[Cu(N^\wedge N)(P^\wedge P)]^+$ 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 $[Cu(N^\wedge N)(P^\wedge P)]^+$ 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 bond[5] using $[Cu(bcp)(DPEPhos)]PF_6$.

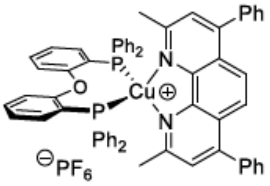

Figure 47. Structure of the $[Cu(bcp)(DPEPhos)]PF_6$ complex

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in cellulo investigation of the excited state dynamics of biologically relevant photoactive compounds

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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

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Identification of Metal-Centered Excited States Using Ultrafast Soft X- ray Spectroscopy

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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 → 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 $Cr(acac)_3$ 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]

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Key factors influencing cage escape in photoinduced electron transfer.

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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 1.5×10^{10} $M^{-1}s^{-1}$ 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.

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NHC-GOLD(I)-AMIDO COMPLEXES FOR PHOTOCATALYSIS

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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.

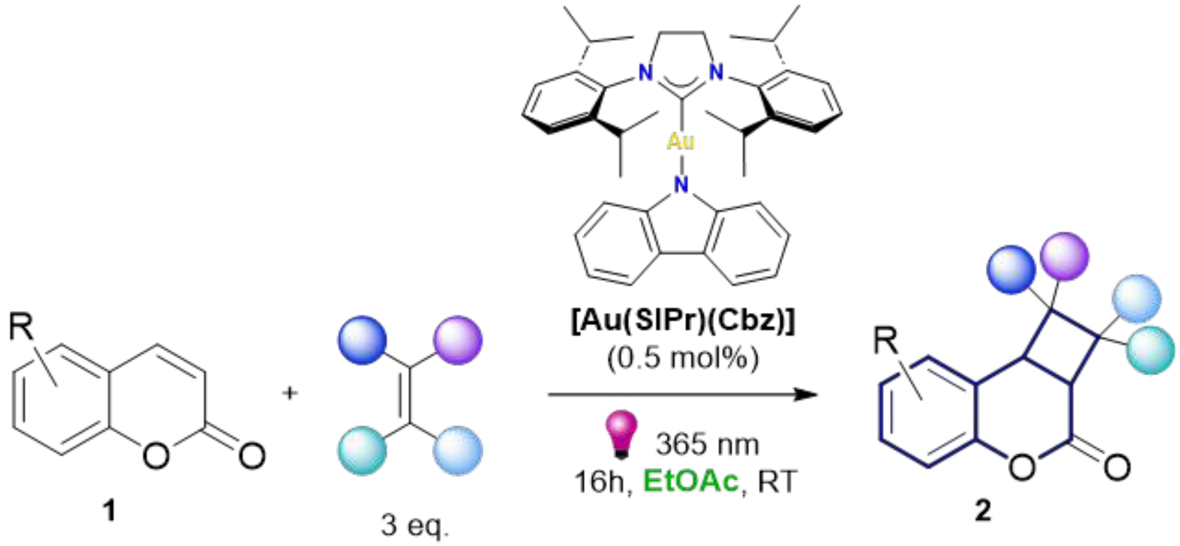

Figure 48. Scheme of the coumarin [2+2] cycloaddition sensitized by the NHC-Gold(I)-Amido complex

Acknowledgments

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Long-lived terphenyl radical anion super-reductant for photocatalysis formed *via* upconversion

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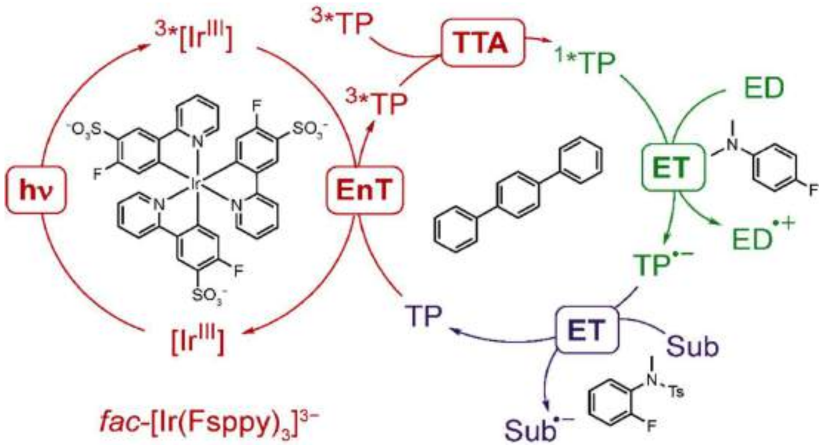
In biphontonic excitation, the energy of two photons with longer wavelengths is combined to yield higher energy intermediates. One approach using this concept is the conPET mechanism, where a photocatalytically generated radical anion is excited to form a highly reducing species. Typically, these excited 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 CO_2 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.



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Luminescent Cyclometalated Iridium(III) Polypyridine Complexes Modified with Dendritic Guanidinium Moieties as Molecular Glues for Combined Chemo-photodynamic Therapy

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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.

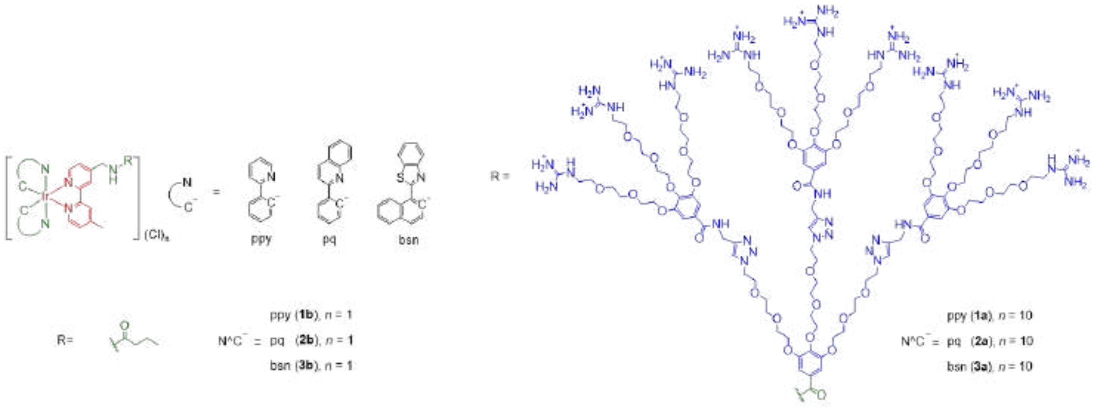

Figure 49. Structures of complexes **1a** – **3a** and **1b** – **3b**.

Aknowlegments

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Iron(III) Complexes with Luminescence Lifetimes of up to 100 Nanoseconds

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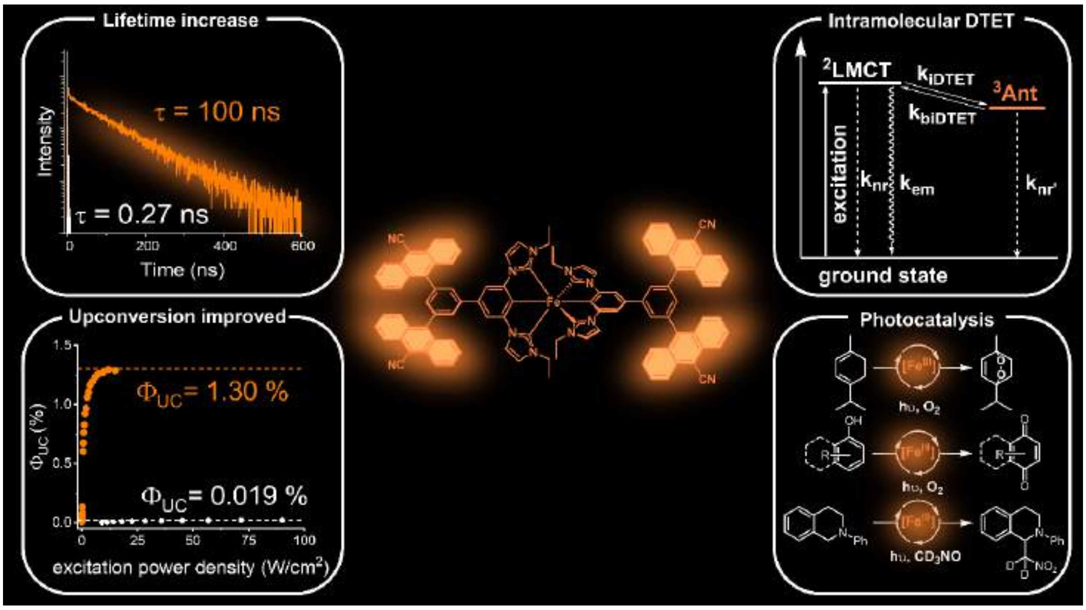
Although photophysical research has uncovered about a dozen luminescent iron(III) complexes so far, most display LMCT excited-state lifetimes limited to the subnanosecond range, usually too short lived to enable efficient bimolecular photochemical reactions.[1,2]

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 ^{2}LMCT 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.



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A novel cyclometalated Co^{III} triazolylidene photosensitiser complex displaying low-temperature emission and improved light harvesting

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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 ^{3}MLCT 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 ^{3}MC state photoactivity.[2] Furthermore, recent findings reveal how decay of Co^{III} ^{3}MC 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 ^{3}MC state lifetimes.[3] The recently reported complex [Co^{III}(ImP)$_2$]$^+$ (**1**) exhibits emission at 758 nm at 77 K which assigned to a ^{3}MC 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.

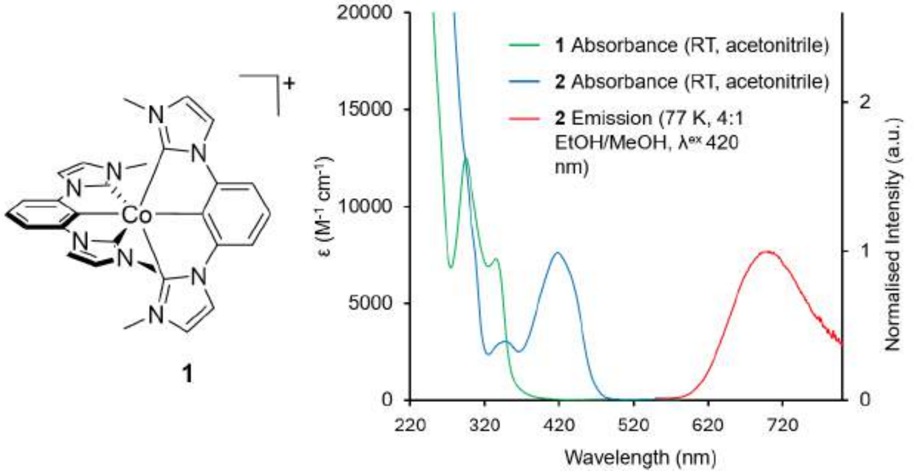

Figure 50. Chemical structure of [Co^{III}(ImP)$_2$]$^+$ (**1**, left); UV-Vis absorption spectra **1** and of the novel Co^{III} triazolylidene complex **2,** and normalised emission spectrum of **2** (right).

Aknowlegments

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Exploring the photophysical behaviours of imidazolylidene vs. triazolylidene Fe^{III} ‘abnormal’ carbene complexes

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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-radiatiative 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**, $[\mathrm{Fe^{III}(ImP)_2}]^+$, 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 ^{2}LMCT 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**.

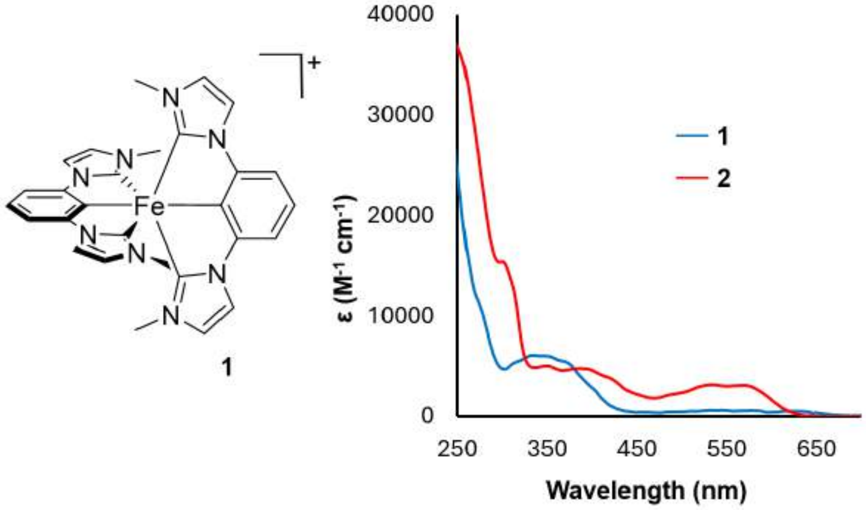

Figure 51. Chemical structure of $[\mathrm{Fe^{III}(ImP)_2}]^+$ (**1**, left), UV-Vis absorption spectra of **1** and of the novel Fe^{III} triazolylidene complex **2** (right).

Aknowlegments

Thanks to the Leverhulme Trust for funding this research (grant number RPG-2022-128).

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Selectively Targeting DNA Structure with Regio-pure Phthalocyanines: A Photophysical Study

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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 (τ = 200 μs) suitable for PDT but to form soluble aggregates in aqueous solution with rapid non-radiative decay (τ = 80 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.

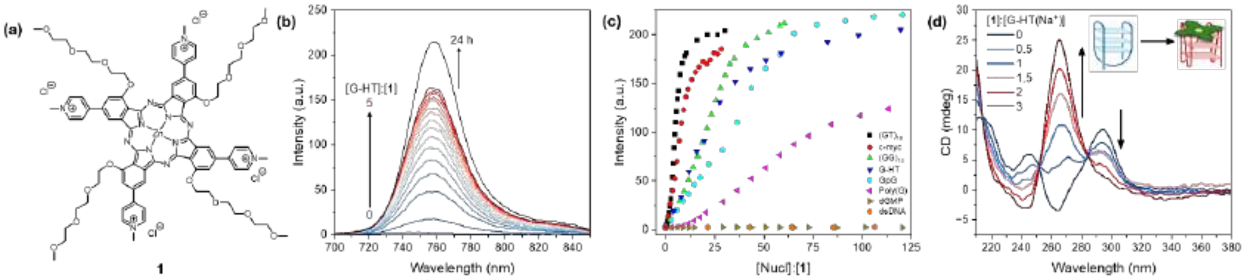

Figure 52. (a) Structure of **1**. (b) Emission spectra of **1** with addition of G-HT quadruplex. (c) Emission intensity of **1** with addition of nucleic acids. (d) Change in CD spectra of G-HT in the presence of **1**.

Acknowledgements

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Transparent WO_3 Films with Organized Mesopores and Oriented Crystallinity as a Robust Photoanode for Visible-Light-Driven Water Oxidation at Neutral pH

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Photoelectrochemical (PEC) water splitting is one of the most promising clean and sustainable energy-providing systems, in which green H_2 fuel is produced by utilizing abundant solar light. A critical requirement for PEC devices is a competent photoanode material for water oxidation. WO_3 photoanodes have attracted much attention owing to their visible light response (band gap, E_g = 2.6-2.8 eV). However, WO_3 photoanodes usually suffer from obstruction associated with separation, migration and reaction of the photon-generated holes during water oxidation. Herein, we present synthesis of efficent WO_3 photoanodes through nanstructure control, band gap engineering and crystal-facet design. First ever thermal crystalliztion in a small mesopore system (*ca*. 2-3 nm pores) of WO_3 photoanode has been acheived 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 N_2-intercalated pure monoclinic WO_3 has been obtained for improvement of visible light response, using hydrazine as N_2 source as well as a SDA.[2] Again, the transformation of WO_3 nanowires into active facets exposed hexagonal prisms has been demonstrated by simple tuning the synthesis temperature in presence of hydrazine. Single crystalline hexagonal prisms WO_3 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 WO_3 nanowires.[3] However, these photoanodes were prepared by squeeze of WO_3 paste over FTO substrates as a nontransparent thin layer. A highly transparent crystalline WO_3 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 WO_3 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 WO_3 layer without compromising the light absorption. The integrated system of WO_3 photoanode with a CoO_x co-catalyst gave high and stable photocurrent (98% photocurrent retained after 30 h, giving Faradaic efficiency O_2 evolution >90%) for PEC water oxidation under neutral pH conditions, which is rare for most of the reported WO_3 photoanodes.

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Dimensionally-Controlled Coordination Polymer Eu(III) Complexes

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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**).

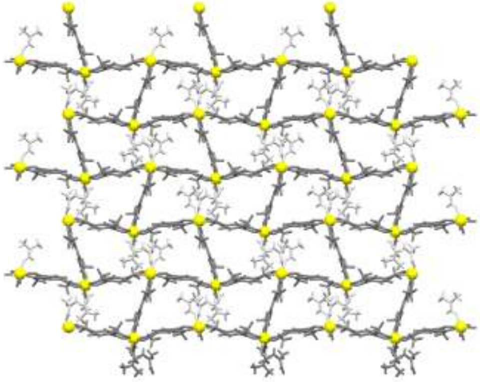

Figure 53. The packing structure of Eu(III) complex (yellow: Europium, gray: atoms including ligand, light gray: solvent (*N*, *N*-dimethylformamide))

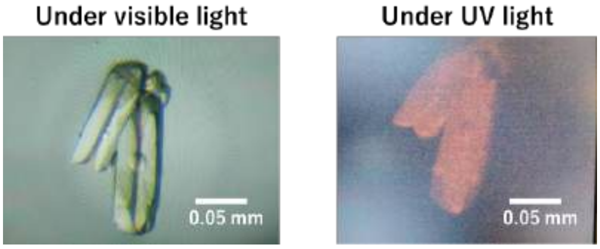

Figure 2. The picture of Eu(III) complex under visible(left) and UV (right) light.

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MCD and MCPL Studies on Octahedral $[Mo_6I_8Y_6]^{2-}$ Clusters in the Excited Triplet States

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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 phosphoresce 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 $[Mo_6I_8Y_6]^{2-}$ 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 $[Mo_6I_8Y_6]^{2-}$ 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.

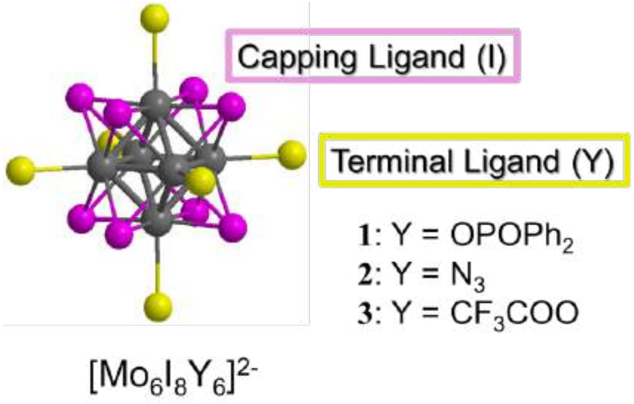

Figure 1. Molecular structures of $[Mo_6I_8Y_6]^{2-}$ clusters.

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Luminescent gold nanoparticles decorated with photoactive metal complexes for cellular imaging and photodynamic therapy

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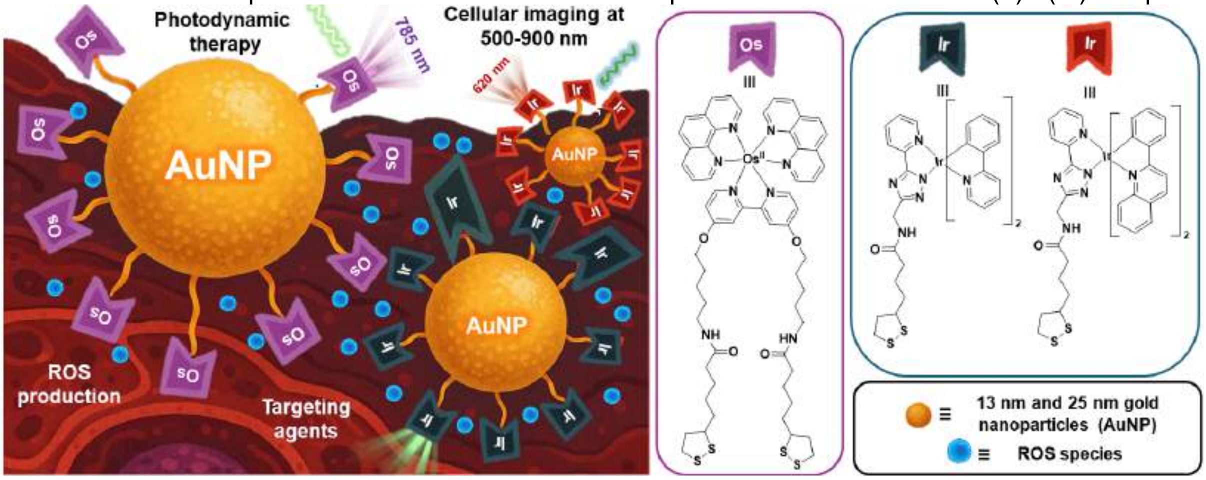
Gold nanoparticles, AuNP, are popular multimodal probes for cellular imaging and photothermal therapy. Surface functionalization of AuNP offers an innovative approach to deliver anticancer agents in cells and increase drug penetration and targeting[1]. We have been interested in the introduction of luminescent 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 nanoprobes for both imaging and cancer therapy.

Figure 54. Schematic representation of multifunctional nanoparticles decorated with Os(II)/Ir(III) complexes.



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Put a cage on it: Luminescent metal complexes in confined space

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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.

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

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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 ^{2}LMCT 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.

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The Characteristic of Photo-Induced ^{3}MLCT Emission Behavior for Ru-(Cyclometalated) Chromophores

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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]

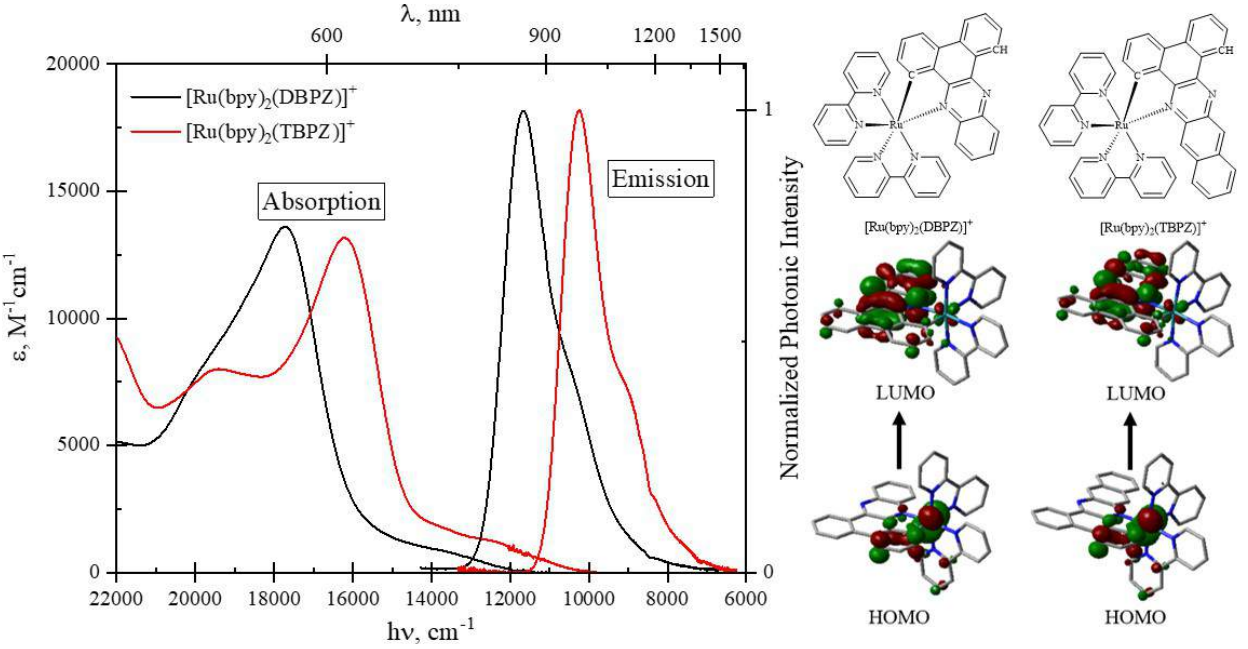

Figure 1. The 298K absorption spectra in CH$_3$CN and 77K emission spectra in butyronitrile glasses. (left panels), and structure of HOMO and LUMO (right panels) of Sn state for [Ru(bpy)$_2$(DBPZ)]$^+$ and [Ru(bpy)$_2$(TBPZ)]$^+$.

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Quantum Chemical Studies on a Heterodinuclear Rotaxane: Towards Biomimetic Photocatalysis

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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 curcurbit[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.

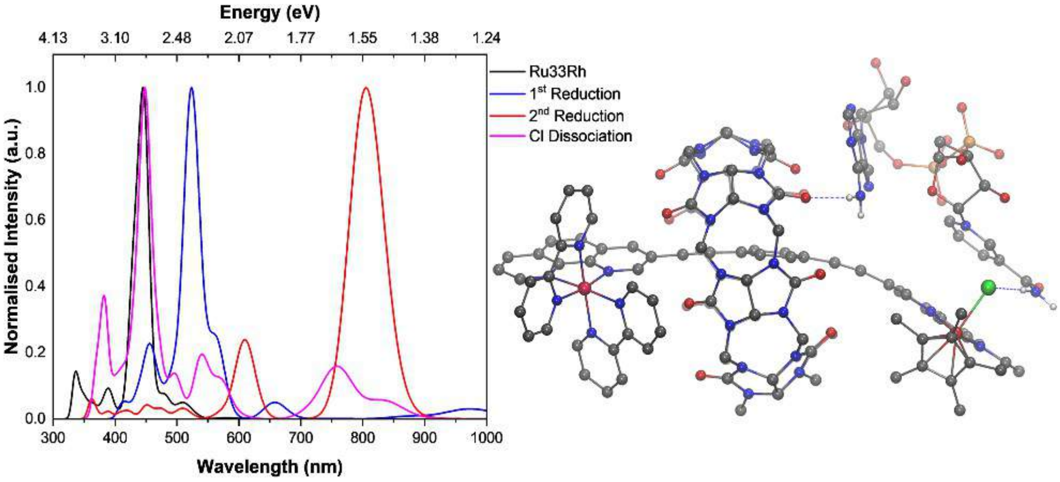

Figure 1. Computed UV-Vis spectra of the dimetallic dyad, for different oxidation states, along with a DFT-optimised geometry of the rotaxane molecule, during the catalytic cycle of NAD$^+$ reductive hydrogenation.

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