Swiss Chemical Society

# SCS Photochemistry Symposium 2022

June 17, 2022, 09.15 - 17.30
School of Engineering and Architecture Fribourg

Swiss Chemical Society
Photochemistry Section
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## Swiss Photochemistry Symposium 2022

The symposium is an initiative of the **Photochemistry Section** of the Swiss Chemical Society to promote the exchange within the photochemistry community in Switzerland and beyond.

The event comprises short contributions from **all areas of photochemistry** (please apply during the registration process) as well as three invited lectures.

Invited Lectures provided by:

- Prof. Julia Weinstein, Uni Sheffield, UK
- Prof. Pablo Rivera-Fuentes, EPFL Lausanne, University of Zurich as of Feb 2022
- Prof. Ferdinand Grozema, TU Delft, Netherlands

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The SCS and the meeting organizers gratefully acknowledge the generous support of its sponsors and exhibitors.

# Program

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|---|---|
| 09.15 | Registration, Coffee & Chat |
| 09.50 | Welcome Message |
| | Session 1 |
| 09.55 | ***Prof. Ferdinand Grozema***, TU Delft, Netherlands<br>«Towards hybrid 2D perovskites with functional organic components» |
| 10.25 | ***Dr. Malte Oppermann***, EPFL Lausanne<br>«Chiral control of spin-crossover dynamics in Fe(II) complexes» |
| 10.40 | ***Felix Glaser***, University of Basel<br>«New Pathways for Red Light Driven Photoredox Catalysis» |
| 10.55 | Short Break |
| | Session 2 |
| 11.00 | ***Prof. Pablo Rivera-Fuentes,*** University of Zurich, Switzerland<br>«Fluorescent probes for subcellular imaging» |
| 11.30 | ***Prof. Bernhard Spingler***, University of Zurich<br>«BODIPY-Based Photothermal Agents for Cancer Treatment» |
| 11.45 | ***Dr. Ricardo Fernández-Terán***, University of Sheffield, UK<br>«Ultrafast Two-Dimensional Infrared Spectroscopy of Transition Metal Hydrides: Couplings, Solvation and Proton-Coupled Electron» |
| 12.00 | Lunch Break |
| 12.50 | Photochemistry Section General Assembly |
| | Session 3 |
| 13.15 | ***Dr. Peter Stacko***, University of Zurich<br>«Renaissance of Cyanines: From Synthesis to NIR Photouncaging» |
| 13.35 | ***Dr. Jovana Milic***, Adolphe Merkle Institute, Fribourg<br>«Supramolecular Control in Hybrid Perovskite Photovoltaics» |
| 13.55 | ***10x 3min Elevator Talks*** |
| | ***Juraj Malincik***, University of Basel<br>«Emissive Properties of Helicene Carbon Nanohoops» |
| | ***Jihad Sissaoui***, University of Geneva<br>«Photoinduced Electron Transfer in Porphyrin-Fullerene Dyad at a liquid interface» |
| | ***Tobias Hendrik Bürgin***, University of Basel<br>«A Spin-Flip Excited Cr(III) Complex in Photoredox Catalysis» |
| | ***Dr. Cesare Berton***, EPFL Lausanne<br>«Performance boost of a merocyanine photoacid by supramolecular encapsulation» |
| | ***Anastasia Gitlina***, EPFL Lausanne<br>«Reversible switching of luminescence of Ir(III) complexes» |
| | ***Dr. Yinyin Bao***, ETH Zurich<br>«Machine Learning-Assisted Design of Full-Color Fluorescent Polymers» |

***Dr. Marina Russo***, University of Zurich
«Photouncaging of Carboxylic Acids from Cyanine Dyes with Near-Infrared Light»

***Dr. Momir Malis***, University of Zurich
«Nonadiabatic processes in condensed phase systems with ΔSCF»

***Subrata Patra***, University of Fribourg
«Visible Light-Mediated Regio-Selective De Novo Nitrative Difunctionalization of Alkenes Using Bench-Stable Organic Nitrating Reagent»

***Dr. Chandan Kumar***, University of Zurich
«Robust ΔSCF excited state calculations for molecules and materials»

14.30 Poster Session, Coffee & Networking

Session 4

15.45 ***Prof. Julia Weinstein,*** University of Sheffield, UK
«Towards IR-control of Ultrafast Charge Transfer in Donor-Bridge-Acceptor Complexes»

16.15 ***Priscila Cavassin***, University of Bern
«A spectroelectrochemical study of the doping in organic semiconductors»

16.30 ***Jimmy Maillard***, University of Geneva
«Super-Resolution Microscopy with Mechanosensitive Membrane Tension Probes»

16.45 ***Rahul Giri***, University of Fribourg
«Fluorinated Acyl Anhydrides in Switchable Divergent Photoredox Catalysis»

17.00 Poster Award Ceremony and Closing Remarks

# Tuning the properties of 2D halide perovskites through the organic component

Ferdinand Grozema

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Two-dimensional halide perovskites are analogues of 3D perovskites that are of strong interest for photovoltaics. These 2D-analogues have properties that are markedly different than those of the corresponding 3D perovskites, for instance a considerably larger band gap and much stronger interactions between electrons and hole in the inorganic part of the material, i.e. a much large exciton binding energy. We have shown in a recent study that also the exciton binding energy can be tuned over a large range by varying this thickness. Until recently, most of the large organic cations used in 2D or quasi-2D perovskite materials only act as a spacer, defining the dimensionality of the system. Their HOMO-LUMO gap is generally very large and the electronic properties of the resulting materials are fully determined by the properties of the inorganic layers.

In this work, we aim to introduce additional functionality in the organic part. This can be done using two approaches: an indirect one in which the organic component induces structural changes that in turn lead to changes in the electronic properties, and a direct one where the electronic states of the organic part of the material are directly involved. In this lecture I will discuss examples of both approaches. The first is the introduction of functional organic molecules in between the octahedral perovskite layers to induce charge separation. The second example involves the relation between the nature/structure of the organic component and the structural dynamics.

# Chiral control of spin-crossover dynamics in Fe(II) complexes

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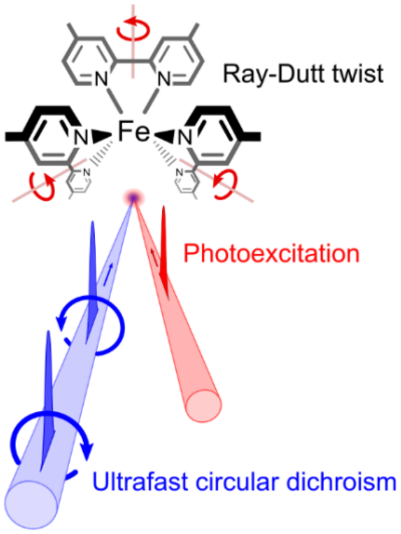

*Ultrafast circular dichroism uses circularly polarized laser pulses to probe the chiral properties of the photoexcited HS state*

Iron(II)-based spin-crossover (SCO) complexes hold tremendous promise as multifunctional switches in molecular devices due to a low-spin (LS) to high-spin (HS) state transition that can be triggered by light, pressure and temperature [1]. However, whilst ultrafast spectroscopy studies have achieved a detailed understanding of the photoinduced forward-SCO to the HS state, the back-SCO mechanism has remained unresolved – despite its crucial role in governing the technologically relevant lifetime of the HS state. Through ultrafast circular dichroism experiments on a prototypical chiral $\text{Fe}^{II}$ complex, we now show that the backward-SCO is governed by a symmetry-breaking torsional twist in addition to the well-known symmetric stretch mode of the metal-ligand bonds [2].

To this end, we characterize the back-SCO dynamics of the tris-chelate $\text{Fe}^{II}(\text{4,4'-dimethyl-2,2'-bipyridine})_3$ in solution, associated for stereocontrol with enantiopure Δ- or Λ-TRISPHAT anions [3]. Combining ultrafast circular dichroism [4] with transient absorption and anisotropy measurements, we find that the HS state decay is accompanied by ultrafast changes of its optical activity, reflecting the coupling to an asymmetric torsional twisting mode known as the Ray-Dutt twist. Quite remarkably, the diastereoselective ion-pairing suppresses the vibrational population of the newly identified reaction coordinate, thereby trapping the HS state in the potential of the Ray-Dutt twist and achieving a four-fold extension of the HS state's lifetime.

More generally, our results finally provide a complete reaction mechanism for the $\text{Fe}^{II}$ backward-SCO, which motivates the synthetic control of the involved torsional modes as a complementary route to manipulate the SCO dynamics of $\text{Fe}^{II}$ complexes.

[1] G. Molnár et al. *Adv. Mater.* **2018**, 30, 1703862
[2] M. Oppermann et al., *Nat. Chem. (accepted)*, preprint: https://doi.org/10.26434/chemrxiv-2021-v0pjv
[3] J. Lacour et al., *Angew. Chem. Int. Ed.* **1998**, 37, 2379
[4] M. Oppermann et al., *Optica* **2019**, 6, 56

# New Pathways for Red Light Driven Photoredox Catalysis

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Within the last decade the field of photoredox catalysis using multi-photonic mechanisms has grown rapidly and a variety of new systems have been investigated.[1–3] In contrast to well established methods that rely on one photoactive compound which absorbs two (or more) photons per catalytic turnover of substrate, combinations of two photoactive catalysts are underexplored.[4–6]

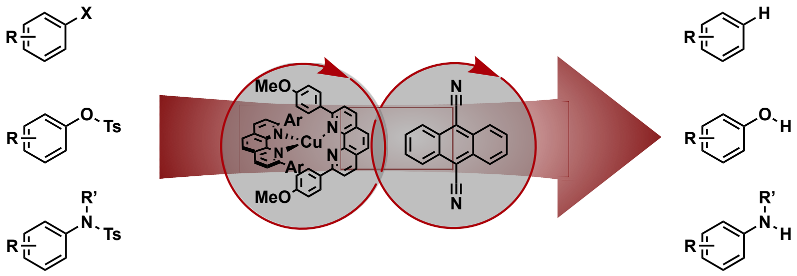

Figure 1: Schematic summary of the investigated catalytic system together with the investigated transformations.

Our approach adapts the concept of using two separate chromophores that is well-known from the Z-scheme of natural photosynthesis. The combination of two photoactive catalysts can perform challenging reductive transformations including dehalogenations of aryl halides as well as detosylations of protected phenols, amines and anilines (Figure 1). By the choice of a copper-based photosensitizer in combination with 9,10-dicyanoanthracene (DCA), red light instead of (typically used) blue or green irradiation sources can be used to achieve successful product formation.

Spectroscopic investigations of the reaction mechanism by time-resolved laser spectroscopy illustrate that a photoinduced electron transfer as well as a sensitization-initiated electron transfer pathway occur in solution. These findings indicate that both pathways can be relevant for the formation of the radical anion of DCA as key intermediate of the catalytic cycle.

The substrate scope - with over 40 substrates investigated - together with the mechanistic insights seem to offer new perspectives for red-light driven photoredox catalysis.

[1] F. Glaser, C. Kerzig, O. S. Wenger, *Angew. Chem. Int. Ed.* **2020**, *59*, 10266–10284.
[2] B. D. Ravetz, A. B. Pun, E. M. Churchill, D. N. Congreve, T. Rovis, L. M. Campos, *Nature* **2019**, *565*, 343–346.
[3] T. U. Connell, C. L. Fraser, M. L. Czyz, Z. M. Smith, D. J. Hayne, E. H. Doeven, J. Agugiaro, D. J. D. Wilson, J. L. Adcock, A. D. Scully, D. E. Gómez, N. W. Barnett, A. Polyzos, P. S. Francis, *J. Am. Chem. Soc.* **2019**, *141*, 17646–17658.
[4] C. Kerzig, M. Goez, *Chem. Sci.* **2016**, *7*, 3862–3868.
[5] M. Neumeier, D. Sampedro, M. Májek, V. A. de la Peña O'Shea, A. Jacobi von Wangelin, R. Pérez-Ruiz, *Chem. Eur. J.* **2018**, *24*, 105–108.
[6] A. Hu, Y. Chen, J.-J. Guo, N. Yu, Q. An, Z. Zuo, *J. Am. Chem. Soc.* **2018**, *140*, 13580–13585.

# Fluorescent probes for subcellular imaging

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Fluorescent probes are essential tools for imaging live cells and other biological specimens. Our lab has worked on the development of such probes, in particular for the observation and control of physiological events as they occur in live cells. One main avenue of this research has been the creation of photochemically active fluorescent sensors that can be activated on a molecule-by-molecule basis,[1,2,3] thus enabling super-resolution microscopy. These probes, however, are photoactivated with ultraviolet light, which induces significant toxicity. To overcome this limitation, we have developed fluorophores that combine photoactivation and thermal fluxionality to enable time-lapse, single-molecule imaging in live cells.[4,5] Finally, I will present recent advances in sensor design that enable truly universal subcellular targeting and ease of use by combining genetically encoded probes and fine-tuned small molecules.[6]

[1] E. A. Halabi, Z. Thiel, N. Trapp, D. Pinotsi, P. Rivera-Fuentes, *J. Am. Chem. Soc.* **2017**, *139*, 13200.
[2] Z. Thiel, P. Rivera-Fuentes, *Angew. Chem. Int. Ed.* **2019**, *58*, 11474.
[3] A. Eördögh, C. Paganini, D. Pinotsi, P. Arosio, P. Rivera-Fuentes, *ACS Chem. Biol.* **2020**, *9*, 2597.
[4] E. A. Halabi, D. Pinotsi, P. Rivera-Fuentes, *Nat. Commun.* **2019**, *10*, 1232.
[5] A. Eördögh, P. Rivera-Fuentes, unpublished results.
[6] S. Hübner, P. Rivera-Fuentes, unpublished results.

# BODIPY-Based Photothermal Agents for Cancer Treatment

Bernhard Spingler[1], Lukas Schneider[1], Martina Kalt[1], Samuel Koch[1], Shanmugi Sithamparanathan[1], Veronika Villiger[1], Johann Mattiat[1], Flavia Kradolfer[1], Ekaterina Slyshkina[1], Sandra Luber[1], Mathias Bonmarin[1], Caroline Maake[1]

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We will report about novel, easily accessible BODIPY photosensitizer for cancer treatment.[1] In contrast to established photodynamic therapy (PDT) agents [2, 3, 4], these BODIPY-based compounds show photothermal activity and their cytotoxicity is independent of reactive oxygen species (ROS). The agents show high toxicity upon light irradiation and low dark toxicity in different cancer cell lines in 2D culture as well as in 3D multicellular tumour spheroids (MCTSs). The ratio of dark to light toxicity (phototoxic index, PI [5, 6, 7, 8, 9, 10, 11]) of these agents exceeds 830’000 after irradiation with energetically low doses of light at 630 nm. Under hypoxic conditions (0.2% $O_2$), which are known to limit the efficiency of conventional photosensitizers (PSs) in solid tumours [12], an excellent phototoxic index of 360’000 was observed, indicating a photothermal mechanism of action (MOA). Both phototoxic values are the highest reported to date.

We thank the University of Zurich and the R'Equip programme of the Swiss National Science Foundation (project number 206021_164018) for financial support. L.S. was supported by a UZH Forschungskredit grant (Forschungskredit-Beitrag FK-085-19, co-financed together with the Colbianco Stiftung).

[1] L. Schneider, M. Kalt, S. Koch, S. Sithamparanathan, V. Villiger, J. Mattiat, F. Kradolfer, E. Slyshkina, S. Luber, M. Bonmarin, C. Maake, B. Spingler, manuscript submitted.

[2] R. L. Yanovsky, D. W. Bartenstein, G. S. Rogers, S. J. Isakoff, S. T. Chen, *Photodermatol. Photoimmunol. Photomed.*, **2019**, 35, 295-303.

[3] G. Gunaydin, M. E. Gedik, S. Ayan, *Front. Chem.*, **2021**, 9, 686303.

[4] S. Anand, T. A. Chan, T. Hasan, E. V. Maytin, *Pharmaceuticals*, **2021**, 14, 447.

[5] A. Naik, R. Rubbiani, G. Gasser, B. Spingler, *Angew. Chem. Int. Ed.*, **2014**, 53, 6938-6941.

[6] P. M. Antoni, A. Naik, I. Albert, R. Rubbiani, S. Gupta, P. Ruiz-Sanchez, P. Munikorn, J. M. Mateos, V. Luginbuehl, P. Thamyongkit, U. Ziegler, G. Gasser, G. Jeschke, B. Spingler, *Chem. Eur. J.*, **2015**, 21, 1179-1183.

[7] L. Schneider, M. Larocca, W. Wu, V. Babu, R. Padrutt, E. Slyshkina, C. König, S. Ferrari, B. Spingler, *Photochem. Photobiol. Sci.*, **2019**, 18, 2792-2803.

[8] R. Rubbiani, W. Wu, A. Naik, M. Larocca, L. Schneider, R. Padrutt, V. Babu, C. König, D. Hinger, C. Maake, S. Ferrari, G. Gasser, B. Spingler, *Chem. Commun.*, **2020**, 56, 14373-14376.

[9] N. A. Le, V. Babu, M. Kalt, L. Schneider, F. Schumer, B. Spingler, *J. Med. Chem.*, **2021**, 64, 6792–6801.

[10] R. Padrutt, V. Babu, S. Klingler, M. Kalt, F. Schumer, M. I. Anania, L. Schneider, B. Spingler, *ChemMedChem*, **2021**, 16, 694-701.

[11] L. Schneider, M. Kalt, M. Larocca, V. Babu, B. Spingler, *Inorg. Chem.*, **2021**, 60, 9416–9426.

[12] L. Hong, J. Li, Y. Luo, T. Guo, C. Zhang, S. Ou, Y. Long, Z. Hu, *Biomolecules*, **2022**, 12, 81.

# Ultrafast Two-Dimensional Infrared Spectroscopy of Transition Metal Hydrides: Couplings, Solvation and Proton-Coupled Electron Transfer

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Transition metal hydrides (TMH) are ubiquitous intermediates in many chemical and catalytic transformations, and can also be involved in proton-coupled electron transfer (PCET).[1,2] Despite their importance, their vibrational dynamics have been largely unexplored.

Using 2D-IR spectroscopy, we have recently shown that the M–H and M(C≡O) stretching modes become strongly coupled and delocalized—thus enhancing the weaker M-H mode—only when the hydride and CO ligands are in a trans configuration.[3] We exploited this enhancement to monitor the ultrafast solvation dynamics of the hydride ligand in aprotic solvents of varying polarities and viscosities. We observe a non-monotonic change in the amplitude of a long-lived inhomogeneous component vs. solvent basicity/acidity (**Fig. 1A**). We thus hypothesize that the hydride ligand acts as a molecular "*Dr. Jekyll and Mr. Hyde*"—manifesting a more hydridic or acidic character according to the nature of the solvent (**Fig. 1B**). When protic alcohols of differing acidity are added as co-solvents, we observe an increase in the amplitude of this long-lived solvation component, proportional to the amount of alcohol (**Fig. 1C**). Finally, using 2D-IR spectroelectrochemistry, we show that the protonation and oxidation state of the metal can be unambiguously determined, allowing us to monitor PCET reactions directly from the hydride perspective. In addition, we are able to monitor directly the differences in solvation of the cationic and neutral species, which play a crucial role in the transfer of the 2nd electron and subsequent PCET.

Altogether, these results illustrate—from a fundamental, microscopic and ultrafast perspective—how the nature of the solvent and solute–solvent interactions are intrinsically linked to the PCET reactivity of these complexes, opening future avenues towards its control.

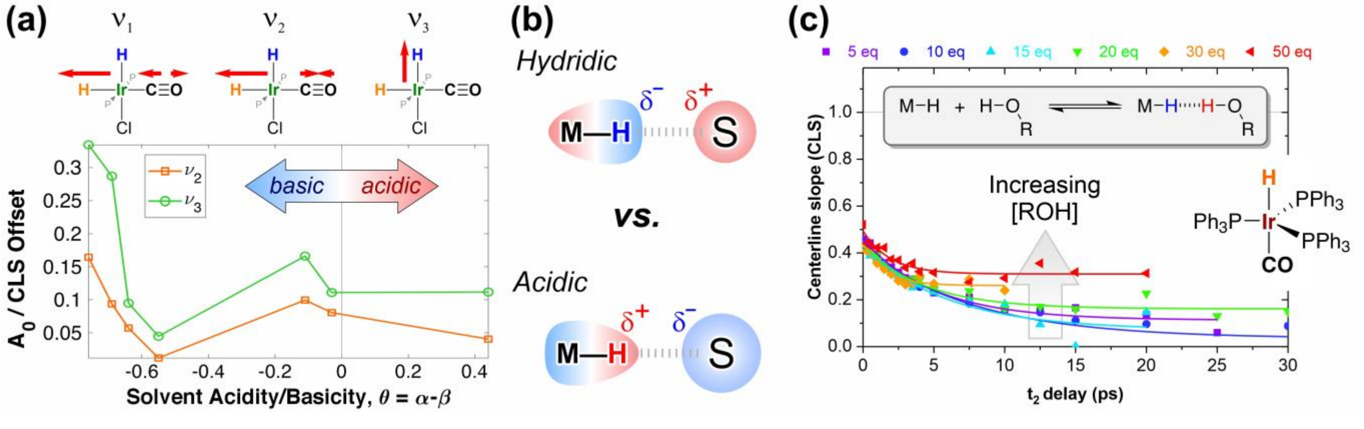

**Figure 1:** (***A***) Solvation dynamics of $[Ir(H)_2(CO)(PPh_3)_2Cl]$ in aprotic solvents; (***B***) Hydridic/acidic character of a TMH; (***C***) Solvation dynamics of $[HIr(CO)(PPh_3)_3]$ with fluorinated alcohols.

[1] T. Liu et al., *Nat. Chem.* **2018**, *10*, 81 87
[2] T. Liu et al., *J. Am. Chem. Soc.* **2019**, *141*, 17245–59
[3] R. Fernández-Terán et al., *Inorg. Chem.* **2020**, *59*, 7721–26.

# Renaissance of Cyanines: From Synthesis to NIR Photouncaging

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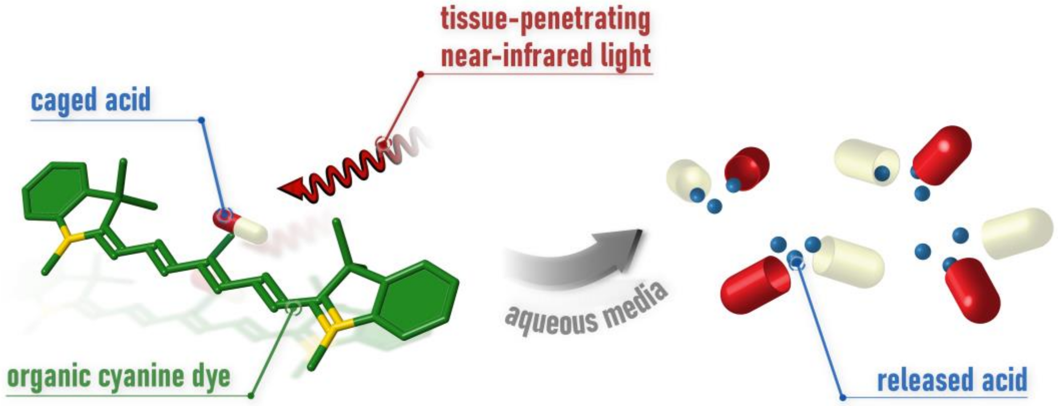
Cyanine dyes represent an indispensable class of chromophores in modern chemistry and biology. Especially heptamethine cyanines (Cy7) are appreciated for their absorption and emission in the tissue-penetrating near-infrared region (NIR; 650–850 nm). Herein, I will showcase that the development of a synthetic methodology for introduction of various substituents along the central cyanine chain enabled tailoring their photochemical and photophysical properties within three orders of magnitude.[1,2] Exercising this control over the structure–property relationship by a single substituent was subsequently harnessed in a number of distinct applications in various fields, including fluorescent probes, biosensors or dye-sensitized upconversion nanoparticles. Finally, I will demonstrate how our strategy fuelled the birth of a new class of cyanine-based photocages that are easily accessible on a multigram scale and efficiently release organic molecule cargo in live human cells upon irradiation with NIR light up to 820 nm with future therapeutic applications in mind.[3]



[1] L. Štacková, P. Štacko, P. Klán *J. Am. Chem. Soc.* **2019**, 141, 7155–7162.
[2] L. Štacková, E. Muchová, M. Russo, P. Slavíček, P. Štacko, P. Klán *J. Org. Chem.* **2020**, 85, 9776–9790.
[3] H. Janeková, M. Russo, U. Ziegler, P. Štacko *ChemRxiv*, **2022**, DOI: 10.26434/chemrxiv-2022-g16fd

# Supramolecular Control in Hybrid Perovskite Photovoltaics

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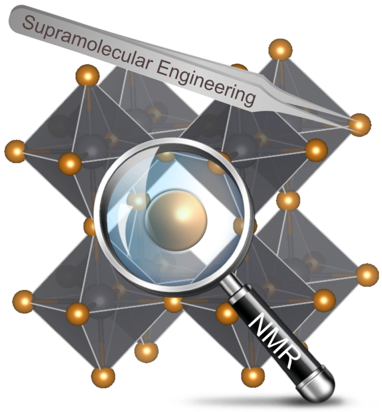
Hybrid organic-inorganic metal halide perovskites have become one of the leading semiconductors for solar-to-electric energy conversion in photovoltaics. However, they feature limited stabilities under operating conditions that hamper practical applications. To address this, we rely on templating hybrid perovskite materials by using supramolecular assemblies with organic components, such as through halogen bonding,[1,2] π-based interactions,[3] and host-guest complexation,[4,5] which has been uniquely assessed by solid-state NMR spectroscopy and NMR crystallography.[2,3] Moreover, we apply these strategies to form low-dimensional perovskite architectures with enhanced functionalities to further control the stabilities and performances of materials and devices.[3,6] As a result, we have achieved perovskite solar cells with superior operational stabilities without compromising photovoltaic performances,[3,4] providing a versatile strategy for advancing hybrid perovskite photovoltaics.



[1] M. L. Ball et al. *Chem. Mat*. **2022**, doi:10.1021/acs.chemmater.1c03117.
[2] M. A. Ruiz-Preciado et al. *J. Am. Chem. Soc*. **2020**, *142,* 1645.
[3] M. A. Hope et al. *J. Am. Chem. Soc*. **2021**, *143,* 1529.
[4] H. Zhang et al. *Nat. Commun.* **2021**, *12*, 3383.
[5] P. Ferdowsi et al. *J. Phys: Mater*. **2021**, *4*, 042011.
[6] J. V. Milić, *J. Mater. Chem. C* **2021**, *9*, 11428.

# A spectroelectrochemical study of the doping in organic semiconductors

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Organic mixed ionic-electronic conductors (OMIECs) are a class of organic materials that efficiently support both ionic and electronic transport. Due to this remarkable property, a broad range of emerging technologies, from energy storage to bioelectronics, rely on OMIECs. [1] A key property of these materials is their ability to be electrochemically doped, which is an efficient and reversible method to increase the materials electric conductivity. This process relies on the injection of carriers into the organic film, while the counterions from an electrolyte infiltrate the film and maintain charge neutrality. The electrochemical doping relies on a complex interplay between multiple factors, from electrolyte choice to molecule design and film morphology, and due to the increasing number of applications that rely on this process, there has been great interest in further understanding its properties and fundamental mechanisms. [2]

In this work, we explore the impact of the polymer film morphology on the electrochemical doping. We use time-resolved visible-near infrared (Vis-NIR) and in-situ Raman spectroscopy combined with electrochemical measurements to show that the ordered and disordered domains of poly(3-hexylthiophene) (P3HT) are doped through different mechanisms and kinetics. We demonstrate that for intermediate doping levels, polarons and bipolarons (singly and doubly charged species) coexist exclusively in the disordered domains. In the ordered domains, only polarons are observed until there are no more ordered undoped chains, and only at this point bipolarons start to be formed at these domains. We propose a kinetic model that described the reactions that take place and show that the ordered phase is doped faster than the disordered for all doping levels.

To confirm our propositions, we used in-situ electrochemical Raman spectroscopy, a technique very sensitive to local conformation. We obtained good agreement with the trends observed with Vis-NIR spectroscopy. Finally, we compared the doping of P3HT films with different degrees of morphology. We use regiorandom P3HT to investigate the doping in purely disordered films, and the results strongly correlate with our proposed kinetic model.

[1] J. Chung, A. Khot, B. M. Savoie, B. W. Boudouris, ACS Macro Letters, **2020**, 9, 646-655.
[2] E. M. Thomas, M. A. Brady, H. Nakayama, B. C. Popere, R. A. Segalman, M. L. Chabinyc, Advanced Functional Materials, **2018**, 28, 1803687.

# Towards IR-control of Ultrafast Charge Transfer in Donor-Bridge-Acceptor Complexes

**T. Cheng,[1] G. Wu,[1] C. Royle,[1] A. Auty,[1] M. V. Appleby,[1] R. Cowin,[1] I. Ivalo,[1]**
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One of the fascinating challenges in photochemistry is how to control reaction pathways, and direct reactivity "at will". Nuclear-electronic (vibronic) coupling is of particular interest in this regard since the Born-Oppenheimer approximation is not valid on the ultrafast timescales intrinsic to photo-processes. Perturbing vibronic coupling may thus offer a way to affect photochemical reactions.[1,2] Such perturbation can be achieved by introducing a narrow-band IR pulse after the initial population of an excited state to selectively affect vibration(s) that are coupled to electron transfer processes. To achieve this, we use a 3-pulse sequence {$UV_{pump}$-"narrow"$IR_{pump}$-$IR_{probe}$}, thereafter called "IR-control".

Our work on "IR-control" of electron transfer explores Pt(II) complexes as chromophores and/or bridges in the Donor-Bridge-Acceptor (DBA) systems. If the excited state relaxation occurs *via* a branching excited state, it becomes possible for a selective excitation of bridge vibrations to drastically change the yield of the product states, of up to 100%.[3,4] Further, rather intriguingly, we disocovered that the mechanism of IR-control might be different in a linear system (Fig 1, left) and a „molecular fork" system (Fig 1, right).

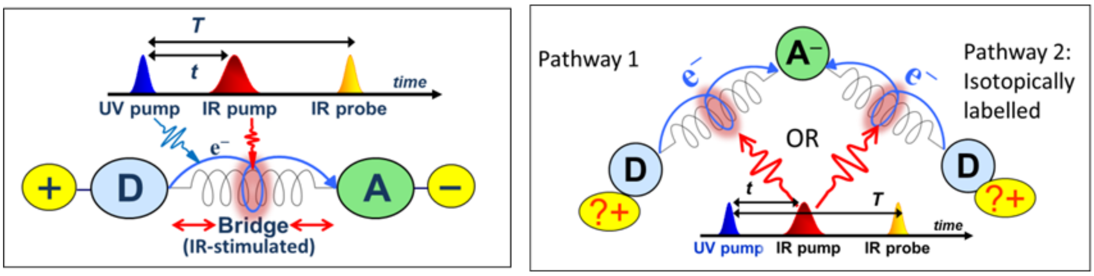

Fig 1. Modulation of electron transfer in a linear D-B-A system (Left), and in a "fork" system.

We now seek to understand the mechanism of the effect, what are the roles of high- and low-frequency modes? How does strong- vs. weak coupling regimes affect the outcome of IR-control?
To answer these questions, the dynamics of several new series of DBA-systems has been characterised by ultrafast transient absorption, time-resolved IR, 2DIR, and fluorescence upconversion[6] spectroscopies, and the IR-control studies undertaken. The results of these studies will be discussed.

Overall,"IR-control" potentially offers the means to direct charge flow along a selected reaction pathway, thus changing the outcome of light-driven reactions.

*We thank the EPSRC (research grants and funding for the Lord Porter Laser Laboratory at Sheffield), the STFC, the Newton Foundation, the UK XFEL hub, and the CSC for support.*

1. Crim, F. Fleming – Department of Chemistry – UW–Madison 2. Z. Ma *et al*, *Chem. Sci.* **2018**, 6395;
3. Delor, M. et al, *Science*, **2014**, *346*, 1492; 4. Delor, M. et al, *Nature Chem.*, **2015**, *7*, 689.
5. Delor, M. et al, *Nature Chem.*, **2017**, *9*, 1099. 6. Farrow, G. et al, *PCCP* **2021**, 21652.

# Super-Resolution Microscopy with Mechanosensitive Membrane Tension Probes

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The mechanical properties of cells are key parameters that regulate some of their functions and therefore, dysregulation in sensing their environment have implications in various diseases. Although it is generally accepted that membrane tension is a key parameter to many different cellular processes such as cell adhesion, endocytosis, exocytosis, phagocytosis, intracellular membrane trafficking and cell division, measuring in vivo forces like tension remains technically challenging. Newly designed oligothiophenes fluorescent probes displaying ground-state planarization at room temperature have led to the development of push-pull probes as mechanosensitive molecules, called "flippers"[1,2]. These probes insert easily into lipid membranes, where they display red-shifted absorption and a much stronger fluorescence emission in the liquid ordered ($L_o$) lipid phase than in the liquid disordered ($L_d$) phase due to the forces imposing a planarization of the chromophore already in its ground state. In this contribution, we evaluate different flipper derivatives for single-molecule localization microscopy imaging and report for the first time imaging below the diffraction limit with several mechanosensitive probes using the PAINT method (Point Accumulation for Imaging in Nanoscale Tomography)[3,4]. This work paves the way to the imaging of local forces with nanometric precision in cell biology.

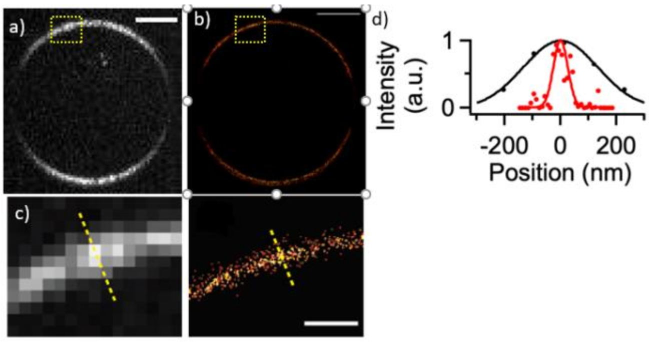

***Figure 1.*** *a) Diffraction limited image of a GUV made of lipids in the* $L_o$ *phase. b) PAINT super-resolution image of the same GUV. c) Magnified view of regions in boxes in b) and c). d) Cross-sections of the GUV membrane indicated by a line in d). Scale bars: a), b), c): 2 µm; d): 500 nm.*

(1) Soleimanpour, S.; Colom, A.; Derivery, E.; Gonzalez-Gaitan, M.; Roux, A.; Sakai, N.; Matile, S. Headgroup Engineering in Mechanosensitive Membrane Probes. *Chem. Commun.* **2016**, *52* (100), 14450–14453.

(2) Fin, A.; Vargas Jentzsch, A.; Sakai, N.; Matile, S. Oligothiophene Amphiphiles as Planarizable and Polarizable Fluorescent Membrane Probes. *Angew. Chem. Int. Ed Engl.* **2012**, *51* (51), 12736–12739.

(3) Garcia-Calvo, J.; Maillard, J.; Fureraj, I.; Strakova, K.; Colom, A.; Mercier, V.; Roux, A.; Vauthey, E.; Sakai, N.; Fürstenberg, A.; Matile, S. Fluorescent Membrane Tension Probes for Super-Resolution Microscopy: Combining Mechanosensitive Cascade Switching with Dynamic-Covalent Ketone Chemistry. *J. Am. Chem. Soc.* **2020,** *142* (28), 12034-12038.

(4) Maillard, J.; Drab, E.; Garcia, J.; Silaghi, M.; Matile, S.; Fürstenberg, A. *In preparation*.

# FLUORINATED ACYL ANHYDRIDES IN SWITCHABLE DIVERGENT PHOTOREDOX CATALYSIS

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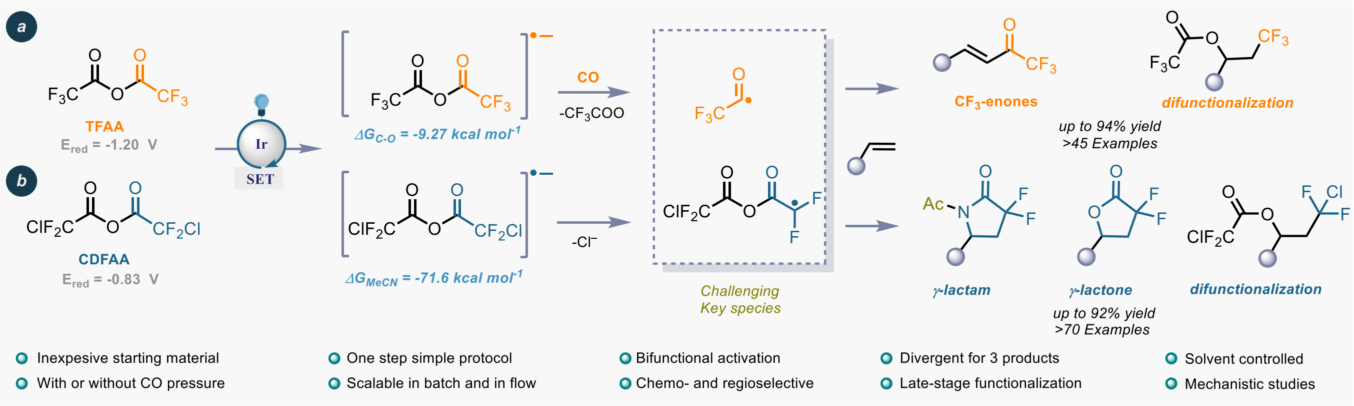
The outstanding impact of fluorine atom in drug discovery cannot be overestimated. Substantially, the incorporation of trifluoromethyl acyl ($CF_3CO$) and gem-difluoro ($CF_2$) moiety into the organic framework are highly sought due to the influence of these units on physicochemical and pharmacological properties of molecules. However, the introduction of these synthons requires the use of prefunctionalized starting materials or a surrogate at the beginning of the synthesis. To address this limitation, perfluorocarboxylic anhydrides can be selected as perfect precursors because they are abundant sources of fluorine building blocks and possess varied reactivity. Herein, we report a visible light-mediated photoredox activation of trifluoroacetic anhydride (TFAA) that occurs through a trifluoroacyl radical mechanism. Remarkably, this radical can be stabilized under a CO atmosphere, and in the presence of olefines, delivers the corresponding α,β-unsaturated trifluoromethyl ketone derivatives. This method can also be diversified into a trifluoromethylation protocol by simply changing the reaction parameters. Furthermore, we developed a mild and operationally simple strategy to access gem-difluoro compounds using chlorodifloroacetic anhydride (CDFAA) as a low-cost and readily available reagent. In this case photoredox activation selectively triggers pseudo-mesolytic cleavage of a C−Cl bond generating an α,α-difluorinated radical, that acts as an exceptional bifunctional intermediate in reaction with alkenes. The reactivity of this radical is further determined by the solvent effect, detailed mechanistic studies of which have shown to occur by three distinct pathways, delivering in a single chemical step α,α-difluoro-γ-lactams, γ-lactones, or difunctionalized compounds. These methodologies are flow and batch scalable, possess excellent chemo- and regioselectivity, as well as practical for late-stage diversification of biorelevant molecules.



[1] K. Zhang, Dr. D. Rombach, N. Y. Nötel, Prof. Dr. G. Jeschke. D. Katayev *Angew. Chem. Int. Ed.* **2021**, *60*, 22487 (*Highlighted in SYNFACTS,* **2021**).

[2] R. Giri, I. Mosiagin, I. Franzoni, N. Y. Nötel, S. Patra, D. Katayev *Manuscript in preparation* **2022**.

# Poster Presentation

[01] ***Dr. Yinyin Bao***, ETH Zurich
«Machine Learning-Assisted Design of Full-Color Fluorescent Polymers»

[02] ***Dr. Cesare Berton***, EPFL Lausanne
«Performance boost of a merocyanine photoacid by supramolecular encapsulation»

[03] ***Dario Bragagnolo***, University of Fribourg
«Evaluation of 4 photoremovable protecting groups for selective photolysis and chromatic orthogonality»

[04] ***Tobias Hendrik Bürgin***, University of Basel
«A Spin-Flip Excited Cr(III) Complex in Photoredox Catalysis»

[05] ***Adriano D'Addio***, University of Basel
«Geländer Molecules with orthogonal joints: Design and Synthesis of Macrocyclic Dimers»

[06] ***Anastasia Gitlina***, EPFL Lausanne
«Reversible switching of luminescence of Ir(III) complexes»

[07] ***Cedric Hoffmann***, University of Bern
«Spectroscopic investigation of charge dissociation and transport in organic solar cells»

[08] ***Isabelle Holzer***, University of Bern
«Using in-situ time-resolved Vis-NIR spectro-electrochemistry to study kinetics in IDTBT polymers»

[09] ***Jasmin Anastasia Kübler***, University of Basel
«Long-lived triplet states in isomeric Zn(II) complexes with charge transfer character used in energy-transfer photocatalysis, electron transfer and upconversion»

[10] ***Dr. Chandan Kumar***, University of Zurich
«Robust ΔSCF excited state calculations for molecules and materials»

[11] ***Subhradip Kundu***, University of Geneva
«Photoinduced Electron-Transfer Through the Mechanical Bond in a Supramolecular Dyad»

[12] ***Dr. Han Li***, University of Basel
«Photophysics of Perylene Diimide Dianions and Their Application in Photoredox Catalysis»

[13] ***Juraj Malincik***, University of Basel
«Emissive Properties of Helicene Carbon Nanohoops»

[14] ***Dr. Momir Malis***, University of Zurich
«Nonadiabatic processes in condensed phase systems with ΔSCF»

[15] ***Dr. Tomohiro Ogawa***, University of Basel
«Extending the 3MLCT excited-state lifetimes of Ni(II) complexes in solution»

[16] ***Subrata Patra***, University of Fribourg
«Visible Light-Mediated Regio-Selective De Novo Nitrative Difunctionalization of Alkenes Using Bench-Stable Organic Nitrating Reagent»

[17] ***Alexandre Rod***, University of Fribourg
«Photoinduced intramolecular cyclization via Norrish I reaction»

[18] ***Dr. Marina Russo***, University of Zurich
«Photouncaging of Carboxylic Acids from Cyanine Dyes with Near-Infrared Light»

[19] ***Dr. Narayan Sinha***, University of Basel
«Combination of strong pi- and sigma-donating ligand yields a cobalt(III) complex with a long-lived MLCT excited state»

[20] ***Jihad Sissaoui***, University of Geneva
«Photoinduced Electron Transfer in Porphyrin-Fullerene Dyad at a liquid interface»

[21] ***Estefania Sucre-Rosales***, Universite de Geneve
«Unraveling the Photoinduced Symmetry-Breaking Charge Separation (SB-CS) process in a PDI-based Cage»

# Machine Learning-Assisted Design of Full-Color Fluorescent Polymers

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Tuning the emission color of fluorescent materials in solid state is of great interest for both fundamental research and practical applications.[1] However, it is rather challenging to develop full-color polymers that have simple structure and are easy to synthesize. We recently discovered the possibility of manipulating excited states of single fluorophore-polymer conjugates via polymerization-mediated through-space charge transfer (TSCT).[2] Consequently, variation in solid-state emission color was observed. Here, directed by a machine learning model based on previously synthesized polymers, we report a versatile polymer platform with full-color emission tunability.[3] Using a single-fluorophore acceptor as the initiator, a series of electron-donor groups containing simple polycyclic aromatic moieties were introduced by facile copolymerization or post-functionalization. In line with the prediction results, the *de novo* designed TSCT polymers showed continuously tunable emission color (Figure 1). Theoretical investigations confirmed the structurally dependent charge transfer-induced emission redshifts. We further demonstrated this polymer platform can be used to design solid-state stimuli-responsive materials for light-controlled information encryption.

**Figure 1.** Photographs of TSCT polymers from various polycyclic aromatic monomers

[1] J. Hu, Q. Li, X. Wang, S. Shao, L. Wang, X. Jing, F. Wang, *Angew. Chem.* **2019**, 131, 8493–8497.
[2] S. Ye, T. Tian, A. J. Christofferson, S. Erikson, J. Jagielski, Z. Luo, S. Kumar, C. J. Shih, J. C. Leroux, Y. Bao, *Sci. Adv.* **2021**, 7, eabd1794.
[3] S. Ye, N. Meftahi, I. Lyskov, T. Tian, S. Kumar, A. J. Christofferson, D. A. Winkler, C. J. Shih, S. Russo, J. C. Leroux, Y. Bao, *ChemRxiv* **2022**, DOI: 10.26434/chemrxiv-2022-jf798.

# Performance boost of a merocyanine photoacid by supramolecular encapsulation

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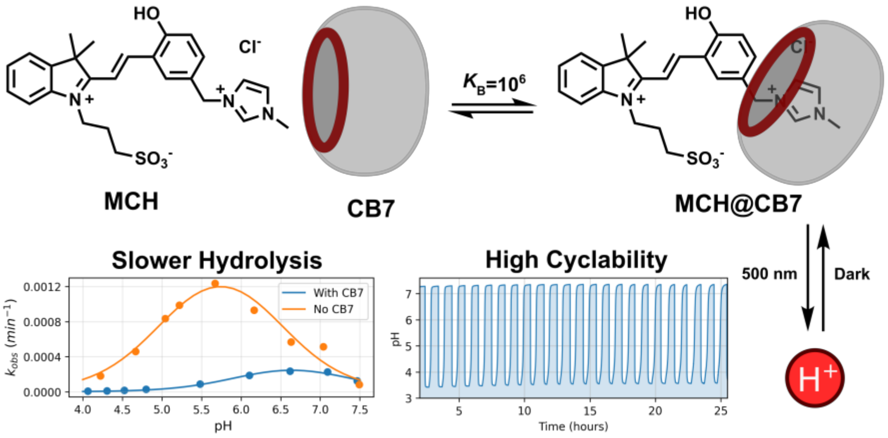
Merocyanine photoacids possess the ability to control the pH of their solutions by means of visible light irradiation. Their applications are remarkable and cover many fields including biochemistry[1], medicinal chemistry[2], material science and engineering[3], analytical chemistry [4], supramolecular chemistry[5] and synthetic organic chemistry[6]. However, the instability of merocyanines towards hydrolysis along with the poor solubility in water are important limiting factors in their application space. To circumvent these problems, we have synthesized and characterized an imidazolium merocyanine derivative displaying high water solubility and strong affinity towards cucurbit[7]uril. The host-guest complex becomes more stable towards hydrolysis and prolongs the timespan of operation.



In the presentation I will cover the main aspects of the aqueous (photo)chemistry of the merocyanine photoacids along with the supramolecular aspects that lead to a general increase of their performance in water.

[1] F. J. Rizzuto, C. M. Platnich, X. Luo, Y. Shen, M. D. Dore, C. Lachance-Brais, A. Guarné, G. Cosa, H. F. Sleiman, *Nature Chemistry* **2021**, *13*, 843–849.

[2] C. Wang, P. Zhao, G. Yang, X. Chen, Y. Jiang, X. Jiang, Y. Wu, Y. Liu, W. Zhang, W. Bu, *Materials Horizons* **2020**, *7*, 1180–1185.

[3] X.-M. Chen, X.-F. Hou, H. K. Bisoyi, W.-J. Feng, Q. Cao, S. Huang, H. Yang, D. Chen, Q. Li, *Nat Commun* **2021**, *12*, 4993.

[4] P. K. Patel, K. Y. Chumbimuni-Torres, *Analyst* **2016**, *141*, 85–89.

[5] S. M. Jansze, G. Cecot, K. Severin, *Chemical Science* **2018**, *9*, 4253–4257.

[6] B. Yang, K. Dong, X.-S. Li, L.-Z. Wu, Q. Liu, *Organic Letters* **2022**, *24*, 2040–2044.

# Evaluation of 4 photoremovable protecting groups for selective photolysis and chromatic orthogonality

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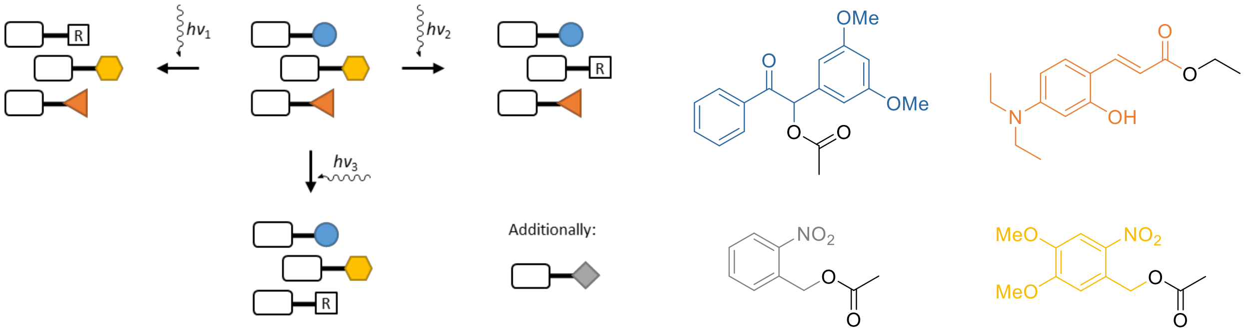
The principle of selectively addressing several photolabile moieties in presence of each other by applying light of different wavelengths is called chromatic orthogonality and it found use in different research areas including solid state chemistry and chemical biology. In this work the known chromatical orthogonal dimethoxybenzoin/nitroveratryl pair in combination with *o*-hydroxycinnamic and *o*-nitrobenzyl groups were used to investigate the feasibility and limitations of higher level chromatic orthogonal systems in solution.



In this study unlinked derivatives of these photolabile protecting groups (PGGs) were synthesised and irradiated in different mixtures, what facilitated the investigation of the properties of the single moieties and study of the interactions between the different PGGs. Thereby, we showed that by irradiating at λ = 265 nm the dimethoxybenzoin PGG and at λ = 405 and 800 nm the *o*-hydroxycinnamic PGG could be selectively addressed in the presence of other PGG derivatives. Furthermore it was possible to identify several sequences, which could be used to remove the moieties one after the other by irradiating at λ = 265, 300, 405 and 800 nm.

[1] Bochet, C. G.*, Angew. Chem. Int. Ed.* **2001**, *40 (11)*, 2071–2073
[2] Goguen, B. N.; Aemissegger, A.; Imperiali, B., *J. Am. Chem. Soc.* **2011**, *133* (29), 11038–11041
[3] del Campo, A.; Boos, D.; Spiess, H. W.; Jonas, U., *Angew. Chem. Int. Ed.* **2005**, *44* (30), 4707–4712

# A Spin-Flip Excited $Cr^{III}$ Complex in Photoredox Catalysis

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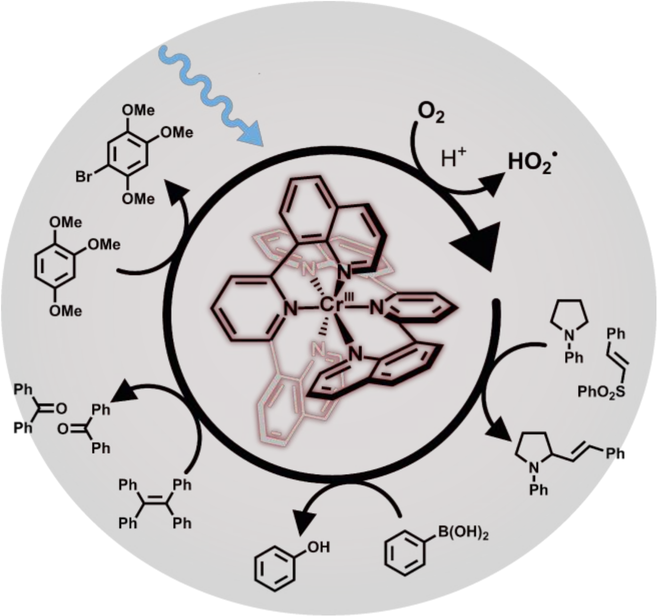
$Ru^{II}$ polypyridines are commonly employed as catalysts in photoredox transformations, whereas $Cr^{III}$ analogues are only little explored in comparison and have been mainly investigated for their luminescence properties.[1] Owing to the spin-flip nature of the lowest electronically excited state of $d^3$ metal luminophores, which stands in contrast to the metal-to-ligand charge transfer (MLCT) excited state of their $d^6$ counterparts, it is not self-evident that $Cr^{III}$ complexes would have to show similar photoredox activity.



$[Cr(dqp)_2]^{3+}$ (dqp=2,6-bis(8′-quinolinyl)pyridine) is part of a novel series of $Cr^{III}$ complexes with tridendate polypyridyl ligands ensuring nearly perfect octahedral and rigid coordination geometries.[2] We found that the driving-force dependence for photoinduced electron transfer from 10 different donors to $[Cr(dqp)_2]^{3+}$ is very similar to that of a $Ru^{II}$ polypyridine reference. We conclude that electron transfer to the spin-flip excited state of $[Cr(dqp)_2]^{3+}$ is facilitated to the same extent as in the case of MLCT-excited $Ru^{II}$ complexes. Consequently, $[Cr(dqp)_2]^{3+}$ was employed as catalyst in photoredox reactions that have not previously been explored for this compound class. This includes aerobic bromination of methoxyaryls, oxygenation of 1,1,2,2-tetraphenylethylene, aerobic hydroxylation of arylboronic acids, and vinylation of *N*-phenyl pyrrolidine.

[1] W. R. Kitzmann, J. Moll, K. Heinze, *Photochem. Photobiol. Sci.* **2022**, doi.org/10.1007/s43630-022-00186-3.

[2] J. R. Jiménez, B. Doistau, C. M. Cruz, C. Besnard, J. M. Cuerva, A. G. Campaña, C. Piguet, *J. Am. Chem. Soc.* **2019**, *141*, 13244–13252.

# Geländer Molecules with orthogonal joints: Design andSynthesis of Macrocyclic Dimers

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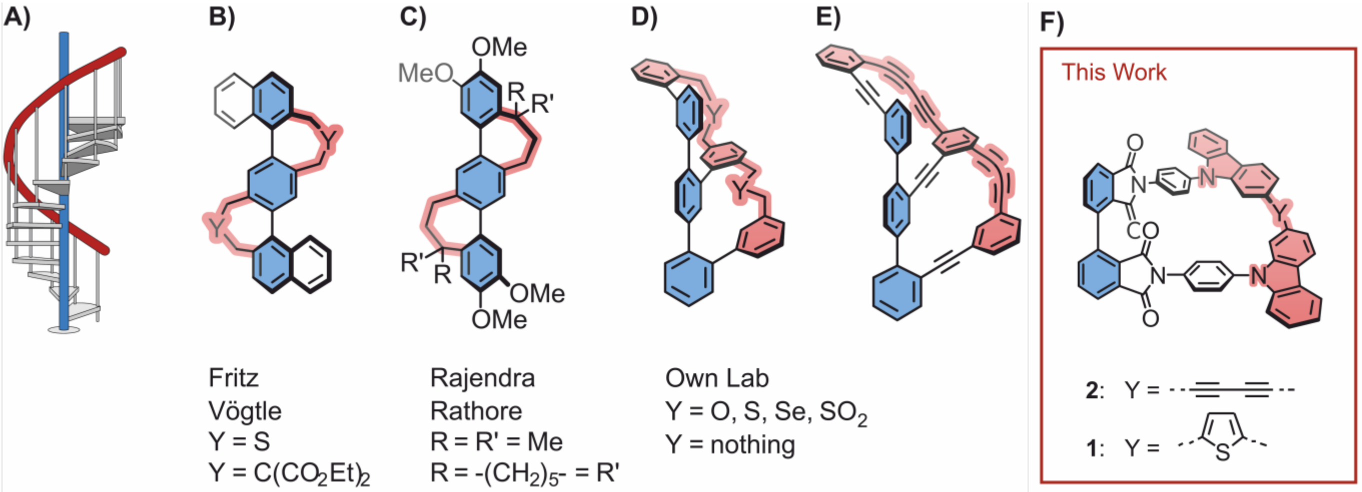
Linking a molecular rod (backbone) with long linkers (banister) forces the latter to wrap around the former, inducing helical chirality (Scheme 1). The wrapping of the linker is reminiscent of the banister of a spiral staircase (Scheme 1A), thus prompting Vögtle and co-workers to coin the German term "Geländer"-oligomers for these architectures (Scheme 1B).[1] In their early investigation, they linked adjacent phenylenes in terphenylene with short linkers yielding beside the chiral (*M,M*) and (*P,P*) isomers the achiral (*M,P*) meso-form in a statistical distribution.[2] Our group introduced the concept of length mismatch in ladder-oligomers, reporting the first "Geländer"-oligomer with the banister wrapping continuously around the backbone in 2014 (Scheme 1D). If a single strand in a ladder-oligomer is elongated, the longer strand (banister) wraps around, the shorter strand (backbone).[3] These structures only contain one helical axis, and therefore, only chiral (*M*) and (*P*) isomers are found. Due to the asymmetry of the junction connecting backbone and banister, regioisomers are eventually formed in a late divergent step by the rotation of the junctions.[4] By symmetrizing the molecular design, the divergent step is circumvented. The helical structure can be formed in two subsequent robust homo-coupling steps and, together with the symmetrical design, eventually allows to synthesize longer oligomers efficiently.



Scheme 1: Figure 1: **A)** Sketch of a spiral staircase as inspiration of "Geländer" molecules with an axle (blue) and a helical banister (red). "Geländer" helices of **B)** Vögtle, **C)** Rathore, and **D)** and **E)** from our own lab. **F)** New "Geländer" macrocycles **1** and **2** with rectangular arrangements between axle and rung, as well as between rung and banister.

The macrocycles herein described are the first symmetric "Geländer" dimer (Scheme 1F). We report their synthesis, their chiral resolution, and their chiroptical activity.

References

[1] B. Kiupel *et al.*, *Angew. Chem. Int. Ed.* 37 (**1998**) 3031.
[2] M. Rickhaus *et al.*, *Chem. Soc. Rev.* 45 (**2016**) 1542.
[3] M. Rickhaus *et al., Angew. Chem. Int. Ed.* 53 (**2014**) 14587.
[4] R. Mannancherry *et al.*, *Chem. Sci.* 9 (**2018**) 5758.

# Reversible switching of luminescence of Ir(III) complexes

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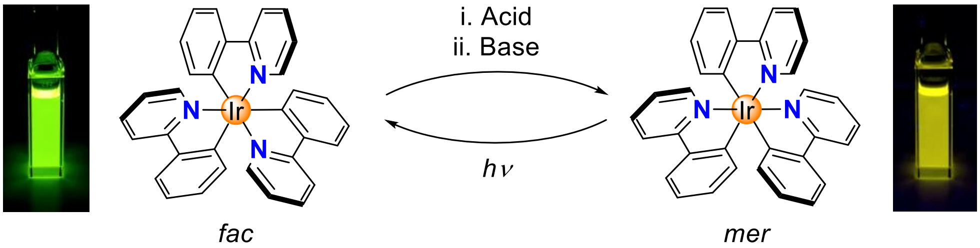
Chromism is a reversible change of color induced by external stimuli (e.g. light, heat, chemical reaction). Chromic compounds provide a solid basis for smart materials that are the most commonly applied nowadays in high-technology, such as electronics, optics, thermometry, biomedicine, textile fabrication etc.[1] Recently, chromic metal complexes are of growing interest because of their diverse structures and functions. Recent achievements have been reached in the metal complexes featured by well-known photochromic switches like azobenzenes, merocyanines, diarylethenes.[2] However, the chromic metal complexes based on their intrinsic stimuli-induced behavior, which could open a new field of switches, are rare because of limited methodologies of designing of such compounds.

Hereby we introduce a new class of chromic molecular switches based on luminescent arylpyridyl Ir(III) complexes widely known due to their unique chemical and photophysical properties.[3] Luminescence chromism of the complexes is achieved by a reversible switching between two geometric isomers (*fac* and *mer*) having distinct emission properties (Scheme 1).



Scheme 1. Switching between *fac*-$Ir(ppy)_3$ and *mer*-$Ir(ppy)_3$.

The switching procedure combines a well-studied photo-induced *mer*→*fac* isomerization[4] and a novel acid-base-induced *fac*→*mer* isomerization developed first in our group. The chemically induced isomerization is fast, clean, quantitative, tolerant to different substituents, and stereoselective. It also opens up a new synthetic possibility to access the *mer* isomers, which are difficult to prepare otherwise.

The luminescence chromism of Ir(III) switches was found reversible for at least ten cycles. As a proof-of-concept, a luminescent display was prepared as a demonstration of possibility to use this complexes for such type of smart materials as rewritable data storage devices.

The authors greatly appreciate a financial support from Swiss National Science Foundation (SNSF) and EPFL as well as facility/equipment available within EPFL.

[1] W. Chen, Y. Pan, J. Chen., *Chin. Chem. Let.*, **2018**, *29*, 1429-1435.
[2] C.-C. Ko, V. Wing-Wah Yam, *J. Mater. Chem*., **2010**, *20*, 2063-2070.
[3] E. Zysman-Colman, Iridium(III) in Optoelectronic and Photonics Application, *John Wiley & Sons*, Chichester, West Sussex, **2017**.
[4] A. McDonald, M. Lutz, L. von Chrzanowski, *Inorg. Chem*., **2008**, *47*, 6681-6691.

# Spectroscopic investigation of charge dissociation and transport in organic solar cells

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We present here results from electro-modulated differential absorption (EDA) spectroscopy on organic photovoltaic (OPV) materials. OPVs show advantages such as transparency, flexibility, low cost and light weight over inorganic solar cells.[1] However, they are still lagging behind when it comes to power conversion efficiencies (PCEs). A lot of work has been done in the last decades to optimize materials and their morphology and to understand the mechanism of charge generation. This has allowed to increase the PCE from 5% to even more than 17%[2] in blended OPVs with an electron donor (D) and a non-fullerene acceptor (NFA) as electron accepting (A) material. Either the D or A material of the blend can absorb a photon at their respective absorption wavelength to generate an exciton which then can diffuse to a D-A interface, creating a charge transfer (CT) state and eventually separate into unbound charges. To increase the efficiency of OPVs, charge transport is an important process which needs to be further investigated and optimized. Time-resolved EDA spectroscopy can be used to determine charge mobility. On an ultra-short timescale, the changes in electro-absorption (EA), which occur due to transport and extraction of photogenerated unbound charges, can be tracked with a resolution of 100 femtoseconds. We present here EDA results of NFA-based blends excited at different wavelengths. Whether CT states remain bound or dissociate into unbound charges is a matter of their local environment.[3] But unlike unbound charges, CT states cannot be tracked by conventional EDA. Therefore, we show here a new technique to record also their local environment: A third low-energy, high-wavelength beam can be included to re-excide CT states to increase their chance to separate. With this 'push'-EDA, it should be possible to get an idea about the local mobility of push-separated CT states and why they rather stayed bound than dissociate by themselves. Combining both spectroscopic techniques will lead to a better understanding of the mechanism of charge separation and will help to design more efficient NFA OPVs in the future.

References:

[1] L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H. L. Yip, Y. Cao, Y. Chen, *Science* **2018**, *361*, 1094-1098.

[2] Y. Cui, H. Yao, J. Zhang, T. Zhang, Y. Wang, L. Hong, K. Xian, B. Xu, S. Zhang, J. Peng, Z. Wei, F. Gao, J. Hou, *Nat Commun* **2019**, *10*, 2515.

[3] M. Causa, J. De Jonghe-Risse, M. Scarongella, J. C. Brauer, E. Buchaca-Domingo, J. E. Moser, N. Stingelin, N. Banerji, *Nat Commun* **2016**, *7*, 12556.

# Using *in-situ* time-resolved Vis-NIR spectro-electrochemistry to study kinetics in IDTBT polymers

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Organic bioelectronics deals with the study of organic electronic devices which are working at the interface of biology and electronics, encompassing wearable to implantable devices, which e.g., can work as sensitive biomedical sensors. Organic semiconducting materials combine advantageous properties such as their soft and flexible nature, versatile processing and synthetic tunability making it possible to span such a high range of applications.[1] In the recent years, much focus was so far on electrical characterization of the devices, in order to improve fabrication methods and to find better material options. Hence there is still a need for a more in-depth understanding on the fundamental effects happening during the functioning of bioelectronic devices.[2] A semiconducting material which recently sparked large interest due to its outstanding charge carrier mobility of up to 1 $cm^2V^{-1}s^{-1}$ in organic field effect transistors (OFET) is IDTBT, a donor-acceptor copolymer with a planar and near-torsion-free backbone allowing for such high mobility.[3] Four IDTBT polymer with different amount of alkyl versus glycol side chains were chosen here to control the conformation, local morphology and ion-affinity of IDTBT. We used *in-situ* time-resolved Vis-NIR spectro-electrochemistry and Multivariate Curve Resolution (MCR) analysis to assign different bands in the absorption spectrum to the different kins of species present during the doping process (neutral segments, polarons, bipolarons). Furthermore, the evolution of the species as a function of time could be determined and an overview of IDTBT redox kinetics was established.

[1] J. Rivnay, R. M. Owens, G. G. Malliaras, *Chem. Mater.*, 2014, **26**, 679-685.

[2] J. Chung, A. Khot, B. M. Savoie and B. W. Boudouris, *ACS Macro Letters*, 2020, **9** (5), 646-655.

[3] X. Zhang, H. Bronstein, A. J. Kronemeijer, J. Smith, Y. Kim, R. J. Kline, L. J. Richter, T. D. Anthopoulos, H. Sirringhaus, K. Song, M. Heeney, W. Zhang, I. McCulloch, D. M. DeLongchamp, *Nat. Commun.*, 2013, **4**, 2238.

# Long-lived triplet states in isomeric Zn(II) complexes with charge transfer character used in energy-transfer photocatalysis, electron transfer and upconversion

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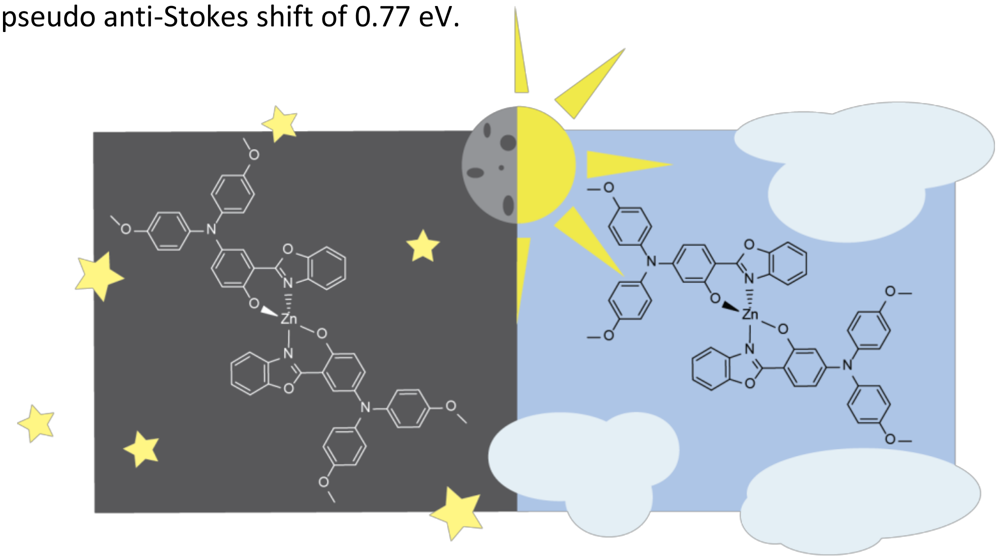
Developing photoactive complexes based on first-row transition metals represents an important challenge in modern photochemistry. The completely filled valence orbitals in $3d^{10}$ metals renders metal-centred nonradiative deactivation pathways inefficient and can therefore lead to long-lived metal-to-ligand charge transfer (MLCT) excited states, as often observed in Cu(I) complexes.[1,2] Zn(II) complexes in contrast have a higher oxidation state and the MLCT states are therefore shifted to higher energies.[3] Thus, their photophysical and -chemical properties more typically rely on ligand-based excited states.

Two structural isomers of homoleptic, tetrahedral zinc(II) complexes with photoactive intraligand charge-transfer (ILCT) excited states are presented. Despite their structural similarity, they differ in photophysical properties: [Zn(*m*-L)$_2$], the "night complex", absorbs in the visible range and has more efficient intersystem crossing to its dark triplet state. The second complex, [Zn(*p*-L)$_2$] or the "night complex", in contrast has a higher fluorescence quantum yield and absorbs mainly in the UV region. DFT calculations suggest that [Zn(*m*-L)$_2$] exhibits stronger charge-transfer character, which causes the observable differences in absorption and furthermore leads to different triplet energies and intersystem crossing efficiencies. Both complexes can be used in triplet-triplet energy transfer (TTET) photocatalysis, and laser flash photolysis experiments provided direct evidence for photoinduced electron transfer reactivity. Furthermore, the absorption properties of [Zn(*m*-L)$_2$] qualify it as a sensitizer for the triplet-triplet annihilation upconversion from blue to UV with 1,4-bis((SiMe$_3$)ethynyl)naphthalene as annihilator, resulting in a pseudo anti-Stokes shift of 0.77 eV.



[1] M. Ruthkosky, C. A. Kelly, F. N. Castellano, G. J. Meyer, *Coord. Chem. Rev.* **1998**, *171*, 309–322.

[2] S. Garakyaraghi, C. E. McCusker, S. Khan, P. Koutnik, A. T. Bui, F. N. Castellano, *Inorg. Chem.* **2018**, *57*, 2296–2307.

[3] O. S. Wenger, *J. Am. Chem. Soc.* **2018**, *140*, 13522–13533.

# Robust ΔSCF excited state calculations for molecules and materials

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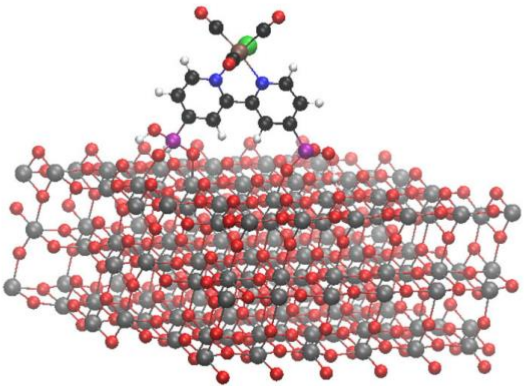
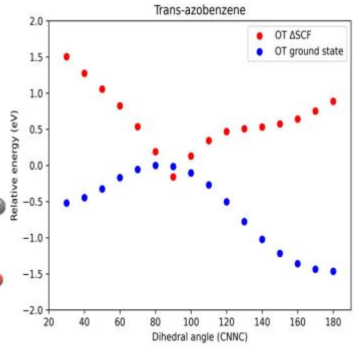
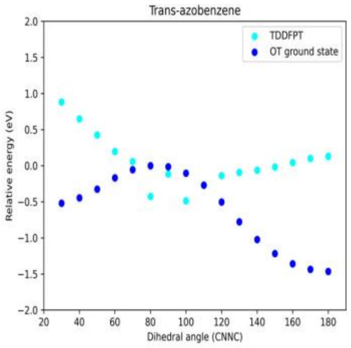
The direct energy functional minimization method using the orbital transformation (OT) scheme [1] in the program package CP2K has been explored for Δ self-consistent field (ΔSCF) calculations with fractional occupations. This allows to exploit the ΔSCF method for various kinds of molecules and periodic systems [2]. Vertical excitation energies of molecular heteroaromatic systems and condensed phase systems, such as solvated ethylene and solvated uracil obeying periodic boundary conditions, are reported using the ΔSCF method. The first singlet excitation energy profile of trans-azobenzene is investigated along the C-N-N-C dihedral angle to show the robustness for excitation energy calculation near conical interaction region. Additionally, we have implemented a recently proposed State-Targeted Energy Projection (STEP) algorithm [3] for diagonalization based SCF in CP2K. It is found that the OT scheme for fractional-occupation ΔSCF provides a smooth and robust SCF convergence for all investigated excitation energies and (non-)periodic systems.





(a)



(b)

[1] J. VandeVondele, J. Hutter, *J. Chem. Phys.*, **2003**, 4365
[2] C. Kumar, S. Luber, *J. Chem. Phys.*, **2022**, *156*, 154104
[3] K. Carter-Fenk, J. Herbert, *J. Chem. Theory. Comput.*, ***2020****, 5067-5082*

# Photoinduced Electron-Transfer Through the Mechanical Bond in a Supramolecular Dyad

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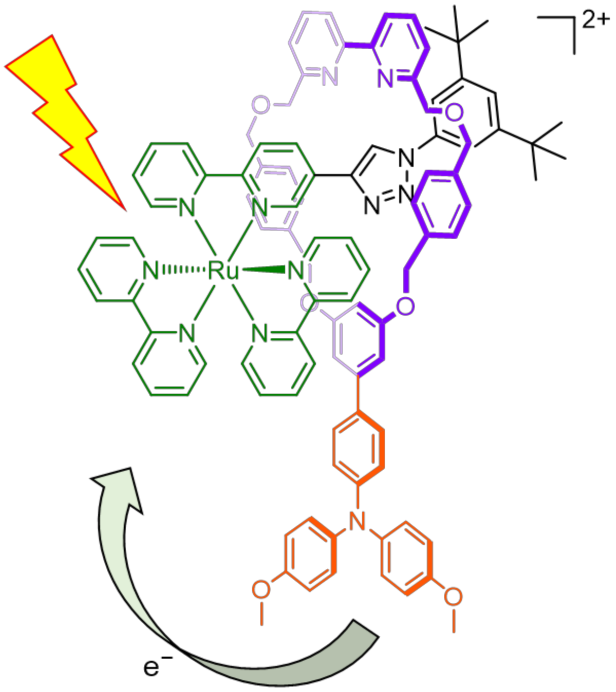
Photoinduced Electron transfer (PET) has been widely explored in covalently connected molecular motifs, mostly focusing on how various bridging motifs facilitate PET.[1] Although research has predominantly focused on PET through covalent bridges, an emerging field is through-space PET.[2] Within this framework, mechanically-interlocked molecules such as catenanes and rotaxanes represent a particularly interesting scaffold for PET, due to their unique three-dimensional topology and dynamic nature.[3]

Despite interest in PET in rotaxanes dating back to Sauvage's original work in the field,[4] fundamental insight into PET in mechanically-interlocked systems remains underdeveloped. To address this, herein is presented a systematic spectroscopic investigation on PET through the mechanical bond, using a supramolecular dyad comprised of a $[Ru(bpy)_3]^{2+}$ photosensitizer and a triarylamine (TAA) donor, situated on different components of a [2]rotaxane.



[1] B. Albinsson, J. Mårtensson, *J. Photochem. Photobiol. C Photochem. Rev.*, **2008**, *9*, 138-155.
[2] B. M. Graff, D. N. Lamont, M. F. L. Parker, B. P. Bloom, C. E. Schafmeister, D. H. Waldeck, *J. Phys. Chem. A*, **2016**, *120* (30), 6004–6013.
[3] A. S. D. Sandanayaka, H. Sasabe, T. Takata, O. Ito, *J. Photochem. Photobiol. C Photochem. Rev.*, **2010**, *11*, 73-92.
[4] J.-C. Chambron, S. Chardon-Noblat, A. Harriman, V. Heitz, J.-P. Sauvage, *Pure Appl. Chem.*, **1993**, *65* (11), 2343–2349.

# Photophysics of Perylene Diimide Dianions and Their Application in Photoredox Catalysis

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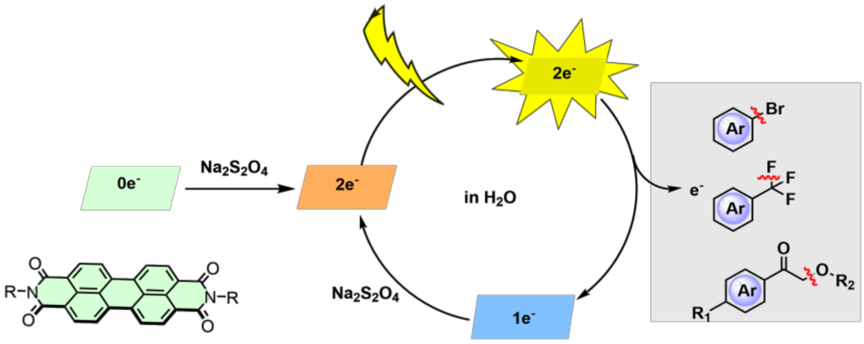
The two-electron reduced forms of perylene diimides (PDIs) are luminescent closed-shell species whose photochemical properties seem underexplored. We report here an in-depth optical spectroscopic study of several $PDI^{2-}$ derivatives in both organic solvent and water. Furthermore, we disclose the usage of a $PDI^{2-}$ for the photocatalysis of organic reactions, both in neat water and in water-acetonitrile mixtures using a phase transfer reagent as co-catalyst.



Our proof-of-concept study demonstrates that straightforward (single) excitation of PDI dianions with green photons provides an excited state that is similarly or more reducing than the much shorter-lived excited states of PDI radical monoanions ($PDI^{\bullet-}$), which are typically accessible after biphotonic excitation with blue photons. Thermodynamically demanding photocatalytic reductive dehalogenations and reductive C−O bond cleavage reactions of lignin model compounds have been performed using sodium dithionite ($Na_2S_2O_4$) acts as a reductant, either in aqueous solution or in biphasic water−acetonitrile mixtures in the presence of a phase transfer reagent. Our work illustrates the concept of multi-electron reduction of a photocatalyst by a sacrificial reagent prior to irradiation with low-energy photons as a means of generating very reactive excited states.

[1] F. Würthner, C. R. Saha-Moller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, *Chem. Rev.* **2016**, *116*, 962-1052
[2] M. R. Wasielewski, *Acc. Chem. Res.* **2009**, *42*, 1910-1921.
[3] S. Neumann, O. S. Wenger, *Inorg. Chem.* **2019**, *58*, 855-860.
[4] I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science* **2014**, *346*, 725-728.
[5] E. Shirman, A. Ustinov, N. Ben-Shitrit, H. Weissman, M. A. Iron, R. Cohen, B. Rybtchinski, *J. Phys. Chem. B* **2008**, *112*, 8855-8858.

# Emissive Properties of Helicene Carbon Nanohoops

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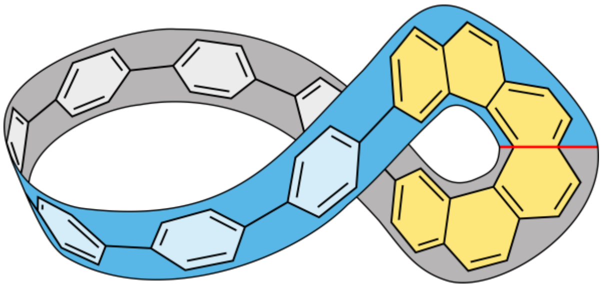
Helicenes are polyaromatic hydrocarbons consisting of *ortho*-fused benzene rings which adopt a helical screw-like shape.[1] They display strong chiroptical properties and circularly polarized luminescence although with a low quantum yield. Substantial synthetic modification of the helicene backbone is required in order to improve their emissive properties.[2]

On the other hand, cyclo-paraphenylenes ([*n*]CPPs) have been proven to have favorable luminescence properties, such as visible-light fluorescence with a high quantum yield, which is often preserved even in solid state.[3,4] However, the absence of chirality in CPPs prevent them to display circularly polarized luminescence. This could be circumvented by introducing a chiral unit to the structure of CPPs.[5]

In this contribution, the design and synthesis of helicene carbon nanohoops as chiral emitters that combine helicene scaffolds and [*n*]CPPs will be discussed.[6] The structure of the nanohoops was studied by single crystal X-ray diffraction, 1D and 2D nuclear magnetic resonance, and mass spectrometry and the photophysical properties investigated by absorption and emission spectroscopies. Helicene carbon nanohoops possess emission properties similar to symmetry-broken [*n*]CPPs. We have managed to obtain an enantiomerically pure sample of a helicene carbon nanohoop and study circularly polarized luminescence. Lastly, we discovered that helicene carbon nanohoops adopt Möbius topology in the solid state and in solution.



[1] M. Rickhaus, M. Mayor, M. Juríček *Chem. Soc. Rev.*, **2016**, *45*, 1542–1556
[2] C.-F. Chen *et al., Chem. Commun.* 55 (**2019**) 13793.
[3] K. Itami *et al., Org. Biomol. Chem.* 10 (**2012**) 5979.
[4] R. Jasti *et al., Chem. Sci.* 10 (**2019**) 3786.
[5] Y. Mazaki *et al., Chem. Eur. J.* 26 (**2020**) 1323.
[6] T. Šolomek *et al., ChemRxiv* (**2021**) DOI: 10.26434/chemrxiv.13817498.v1

# Nonadiabatic processes in condensed phase systems with ΔSCF

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The variational delta self-consistent field (ΔSCF) density functional theory (DFT) based method enables full atomistic simulations of nonadiabatic processes in condensed phase systems by balancing computational costs and accuracy of the description of excited electronic state properties. This avoids the bottleneck of computing all the excited electronic states in the usually dense excited electronic state manifolds encountered during the nonadiabatic molecular dynamics in the condensed phase, for example with time-dependent DFT methods, but instead only the excited electronic states of interest are directly determined. We will discuss novel Ansätze in order to incorporate spin-orbit coupling and certain multi-reference characters into ΔSCF calculations. We applied our methodology for the investigation of nonradiative deactivation mechanisms in a number of solvated systems, emphasizing the details of chromophore-environment interactions and their influence on photochemical processes in condensed phase systems.

[1] M. Mališ, S. Luber, *J. Chem. Theory Comput.*, **2020**, 16, 4071-4086.
[2] M. Mališ, S. Luber, *J. Chem. Theory Comput.*, **2021**, 17, 1653-1661.
[3] E. Vandaele, M. Mališ, S. Luber, *Phys. Chem. Chem. Phys.,* **2022**, 24, 5669-5679.
[4] E. Vandaele, M. Mališ, S. Luber, *J. Chem. Phys.*, **2022**, 156, 130901.
[5] M. Mališ, E. Vandaele, S. Luber, in revision.

# Extending the $^3$MLCT excited-state lifetimes of Ni(II) complexes in solution

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Square planar Ni$^{II}$ complexes have received growing interest in the field of photoredox catalysis.[1] Although excited states of Ni$^{II}$ complexes seem to play important roles in photoredox catalytic reactions, investigations of electronically excited states and their relaxation pathways in Ni$^{II}$ complexes are yet scarce. In most of the so far reported square-planar Ni$^{II}$ complexes, initially formed metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) states decay very rapidly to energetically lower-lying metal-centered (MC) states.[2] Here, we present our attempts to extend the MLCT excited state lifetimes in solution at room temperature. Toward this goal, we employed a tridentate chelate ligand providing a rigid coordination geometry and a strong ligand field. To complete the square planar coordination geometry, sterically demanding (monodentate) isocyanides were used to further enhance structural rigidity and to protect Ni$^{II}$ from solvent coordination (Figure 1A inset).

Figure 1A presents the UV-Vis absorption spectra of the three synthesized Ni$^{II}$ complexes, showing relatively intense MLCT bands around 400 nm. After excitation into these MLCT bands, ground-state bleaching (GSB) of that band was observed and a characteristic excited-state absorption (ESA) feature appeared around 450-500 nm (Figure 1B). The decays of the ESA were substantially faster than the GSB recoveries, suggesting that the initially populated MLCT state with its diagnostic ESA signal between 450 and 500 nm decays to an energetically lower-lying MC state. The MLCT decays showed extended lifetimes upon increasing the steric demand of the monodentate isocyanide ligand.

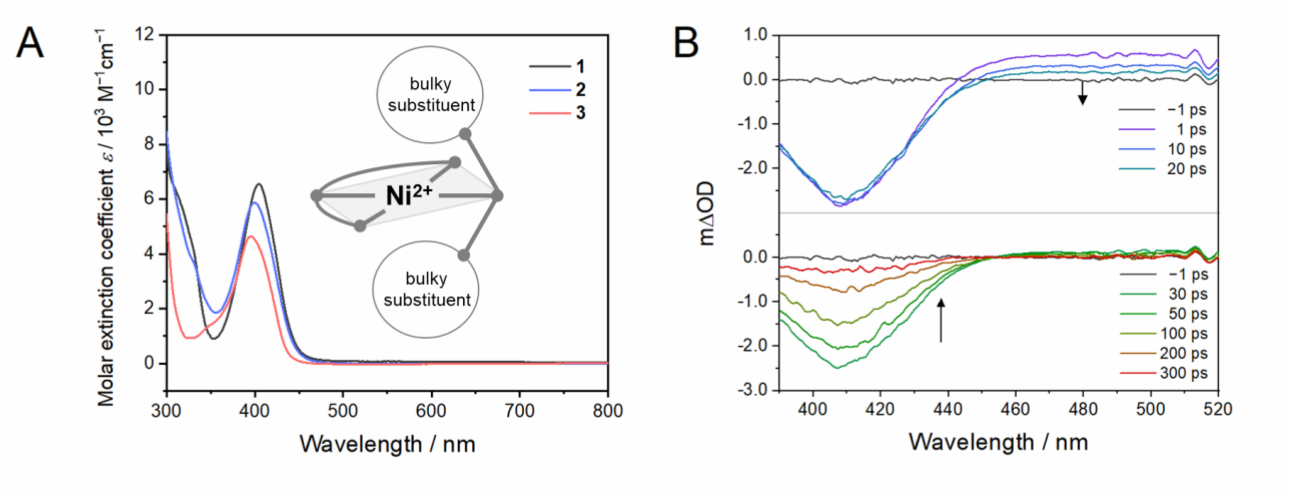

Figure 1. A) UV-Vis absorption spectra of Ni complexes in CH$_3$CN at RT. B) Transient UV-vis absorption spectra

[1] Welin, E. R.; Le, C.; Arias-Rotondo, D. M.; McCusker, J. K.; MacMillan, D. W., *Science* **2017**, *355*, 380.

[2] Ting, S. I.; Garakyaraghi, S.; Taliaferro, C. M.; Shields, B. J.; Scholes, G. D.; Castellano, F. N.; Doyle, A. G., *J. Am. Chem. Soc.* **2020**, *142*, 5800. Hong, J.; Fauvell, T. J.; Helweh, W.; Zhang, X.; Chen, L. X., *J. Photochem. Photobiol., A* **2019**, *372*, 270

# Visible Light-Mediated Regio-Selective De Novo Nitrative Difunctionalization of Alkenes Using Bench-Stable Organic Nitrating Reagent

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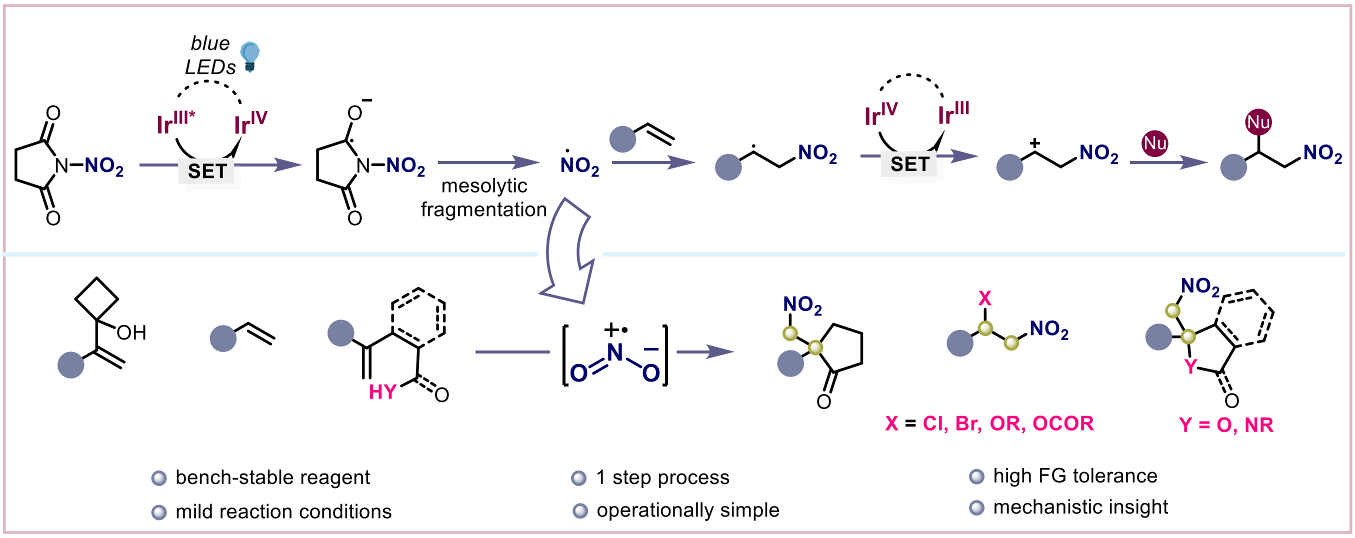
Alkenes are readily accessible feedstocks in organic synthesis. Difunctionalization of alkenes is a compelling strategy to construct complex molecules rapidly through chemo- and regioselective installation of two critical functional groups. Despite a significant progress, nitrative difunctionalization is still challenging from both the synthetic and practical perspective.[1] Methods for direct carbonitration of organic molecules rely on the formation of nitronium ($NO_2^+$) ion in highly caustic nitric acid mixtures, which limits the scope, especially for the acid-sensitive functional groups.

We herein report a visible light-mediated slow liberation of nitryl radicals ($\bullet NO_2$) from a bench stable, inexpensive N-nitrosuccinimide reagent allowing highly selective nitrative difunctionalization of unsaturated compounds. This reagent provides access to β-nitro cyclopentanones *via* semipinacol rearrangement, an eco-friendly route to construct all-carbon quaternary stereocenters. Alkenes in the presence of nucleophiles such as alcohols, amines and acids, yield the corresponding 1,2-disubstituted products. In addition, this process makes it possible to synthesize nitro-derived lactams/lactones in good to excellent yields by an intramolecular reaction. Of note, the presence of halogen source in the reaction mixture allows to access structurally important vicinal 1,2-halonitro compounds, which can be further converted into vital small building blocks. Due to the mildness and robustness of this methodology, a large variety of functional groups are well tolerated using standard reaction conditions. Detailed mechanistic studies strongly suggested that a mesolytic N–N bond fragmentation originates liberation of a nitryl radical.[2] The practicability of this strategy is demonstrated in late-stage functionalization of complex structures and biorelevant molecules.



- bench-stable reagent
- mild reaction conditions
- 1 step process
- operationally simple
- high FG tolerance
- mechanistic insight

[1] S. Patra, I. Mosiagin, R. Giri, D. Katayev *Synthesis* **2022**, DOI: 10.1055/s-0040-1719905.
[2] K. Zhang, B. Jelier, A. Passera, G. Jeschke, D. Katayev *Chem. Eur. J.* **2019**, *25*, 12929–12939.

# Photoinduced intramolecular cyclization via Norrish I reaction

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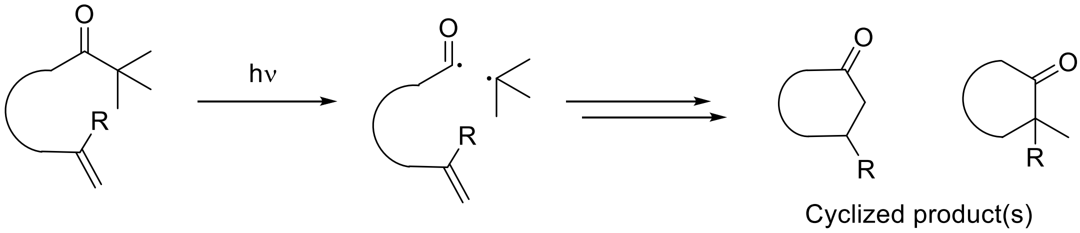
In the last decades, photochemistry has become more important in synthesis, with the wish to develop greener and more sustainable chemistry. Applying this chemistry to the synthesis of natural products leads to new possibilities in terms of transformations and bond formation. In this project, the idea is to use a photochemical reaction, the Norrish type I, to afford cores bearing multiple rings via an intramolecular cascade reaction. Norrish reactions were described for the first time by Norrish in 1932[1] and were widely studied, and as well applied in the synthesis of natural products.[2] Nevertheless, it was, to the best of our knowledge, never used to form multi-ring systems via an intramolecular cascade reaction. In this work, the focus stands in the study of short chain irradiations. By performing several modifications on the substrates, as well as screening different conditions, the change in the ratio between desired products and Paternó-Büchi products could be observed, leading toward the desired cycles.



Looking at those promising results, achieving the desired cyclization on longer chains could lead to the formation of cores using a simple irradiation. Those could further be used in the synthesis of natural products.

[1] Norrish, R. G. W.; Kirkbride, F. W., *J. Chem. Soc.* **1932**, 1518
[2] Albini, A., *Photochem Photobiol Sci* **2021**, *20* (1), 161–181

# Photouncaging of Carboxylic Acids from Cyanine Dyes with Near-Infrared Light

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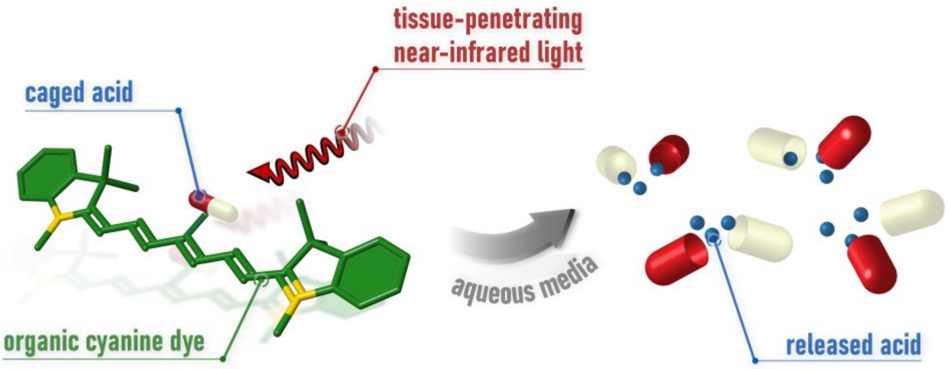
Photocages are light-sensitive groups that take advantage of biorthogonality as well as unparalleled spatial and temporal resolution of light as a stimulus to unmask and restore activity of a substrate.[1] However, extending their application towards therapeutic utility requires shifting their absorption into the near-infrared (NIR) phototherapeutic window (650–900 nm), a region of wavelengths applicable in the body.

Although, NIR light offers unparalleled advantages as a biocompatible stimulus, the lack of molecules operating in such a region limits its use. The development of photocages that operate in this region represents a fundamental challenge due to the low energy of the excitation light.[2] Herein, we repurpose cyanine dyes into photocages that are available on a multigram scale in three steps and efficiently release carboxylic acids in aqueous media upon irradiation with NIR light up to 820 nm. The photouncaging process is examined using several techniques, providing evidence that it proceeds via photooxidative pathway. We demonstrate the practical utility in live HeLa cells by delivery and release of the carboxylic acid cargo, that was otherwise not uptaken by cells in its free form. In combination with modularity of the cyanine scaffold, the realization of these accessible photocages will fully unleash the potential of the emerging field of NIR-photoactivation and facilitate its widespread adoption outside the photochemistry community.



[1] P. Klán, T. Šolomek, C. G. Bochet, A. Blanc, R. Givens, M. Rubina, V. Popik, A. Kostikov, J. Wirz, *Chem. Rev.* **2013**, *113*, 119–191.

[2] R. Weissleder, *Nat. Biotechnol*. **2001**, *19*, 316–317.

# Combination of strong $\pi$- and $\sigma$-donating ligand yields a cobalt(III) complex with a long-lived MLCT excited state

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Rare and expensive $4d^6$ and $5d^6$ transition metal complexes with long-lived metal-to-ligand charge transfer (MLCT) excited states are widely used in various important applications of photophysics and photochemistry such as solar energy conversion, photodynamic therapy, photo(redox)catalysis and light emitting diodes. In this regard, cyclometalated $Ir^{III}$ complexes with long-lived MLCT excited states are important class of compounds,[1] and often strong $\sigma$-donors and strong $\pi$-acceptors ligands are used to obtain such compounds. We are interested to obtain an isoelectronic $Co^{III}$ complex with a MLCT excited state as both Ir and Co belong to the same group in the periodic table of elements. Our work aligns with the currently growing interest in photoactive first-row transition metal complexes.[2] When strong $\sigma$-donating ligands are used to obtain $Co^{III}$ complexes, mainly ligand-to-metal charge transfer (LMCT) or metal-center (MC) excited states are usually obtained.[3,4] To achieve an elusive $Co^{III}$ complex with substantial MLCT excited state character, we use an alternative ligand design strategy where a tridentate ligand is used, in which a strong $\pi$-donating amido donor and two strong $\sigma$-donating (weakly $\pi$-accepting) N-heterocyclic carbene (NHC) donors are combined (Figure 1). The newly developed $Co^{III}$ complex has been characterized by NMR spectroscopy, mass spectrometry and X-ray crystallography, and its photophysical properties have been studied by cyclic voltammetry, UV-Vis spectroscopy, spectro-electrochemistry, ps-and fs-transient absorption spectroscopy in addition to DFT calculations. The present complex has a 1.2 ns MLCT excited state lifetime and can transfer an electron to methyl viologen dication upon blue light excitation.

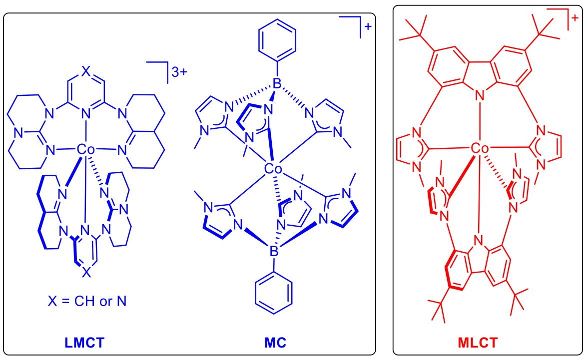

**Figure 1**. Previously studied (in blue) and present (in red) cobalt (III) complexes with different types of photoactive excited states.

[1] I. N. Mills, J. A. Porras, S. Bernhard, *Acc. Chem. Res.* **2018**, *51*, 352–364.
[2] O. S. Wenger, *J. Am. Chem. Soc.* **2018**, *140*, 13522–13533.
[3] A. K. Pal, C. Li, G. S. Hanan, E. Zysman-Colman, *Angew. Chem. Int. Ed.* **2018**, *57*, 8027–8031.
[4] S. Kaufhold, N. W. Rosemann, P. Chábera, L. Lindh, I. Bolano Losada, J. Uhlig, T. Pascher, D. Strand, K. Wärnmark, A. Yartsev, P. Persson, *J. Am. Chem. Soc.* **2021**, *143*, 1307–1312.

# Photoinduced Electron Transfer in Porphyrin-Fullerene Dyad at a liquid interface

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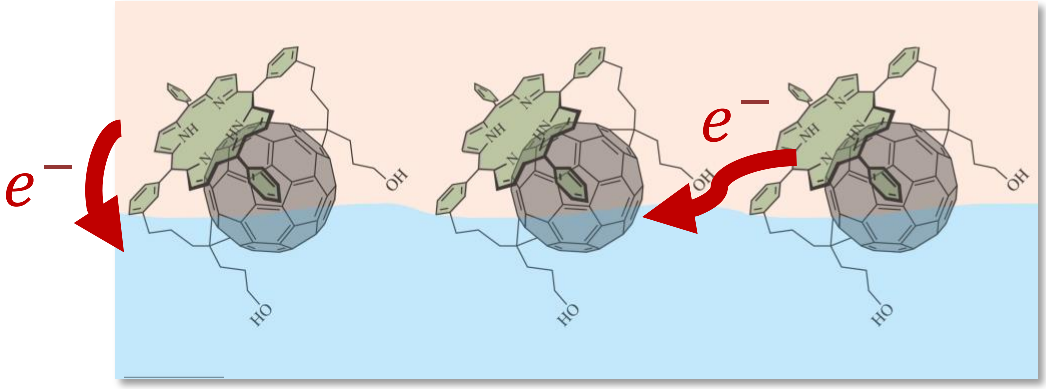
Organic Photovoltaics (OPVs) have gained increasing attention during the past decades as an alternative energy source. These devices rely on absorption of photons by small organic molecules followed by charge transfer at the interface in the donor and acceptor materials. Therefore, understanding the charge-separation process at interface of two materials with different dielectric properties is of paramount importance for the future development of superior devices.

We approach this problem using the excited-state properties of an amphiphilic porphyrin-fullerene dyad and of its porphyrin analogue adsorbed at water/dodecane interface using second harmonic generation (SHG). The Polarized SHG experiments confirm the results of MD simulations. The interfacial orientation of the porphyrin subunit is different for the dyad and the porphyrin analogue. Time-resolved SHG measurements reveal a concentration dependence of the excited state dynamics of both compounds upon Q-band excitation implying the occurrence of intermolecular quenching processes. A significantly slower ground-state recovery of the dyad compared to the porphyrin analogue is observed, in agreement with the population of a longer-lived state, most probably a charge separated state.



# Unraveling the Photoinduced Symmetry-Breaking Charge Separation (SB-CS) process in a PDI-based Cage

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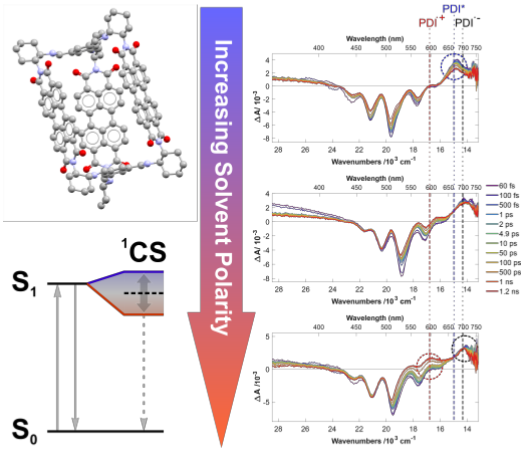
In a photoinduced symmetry-breaking charge-separation (SB-CS) process, an electron transfer occurs between two identical chromophores, which can be used for applications in harvesting of solar energy. We have previously reported the first example of a rylene cage with delayed fluorescence [1], presumably by a reverse SB-CS process. As a follow-up work, herein we present the transient electronic spectra of the PDI-Cage in increasing polarity toluene/benzonitrile solvent mixtures. As the polarity of the solvent increases, two transient bands centered around 650 and 700 nm can be observed, the last one being overlapped with the excited state absorption (ESA). These bands can be attributed respectively to the radical cation and radical anion of PDI, constituting clear evidence of the SB-CS process.



The TA spectra in pure toluene and 80:20 Tol/BzCN mixture showed no evidence of the presence of the radical species, which appear only at increased polarity mixtures. This is in agreement with a higher stabilization of the $^1$CS state in polar environments, that prompts the population of this state after photoexcitation to $S_1$ in an equilibrium. The backward reaction of this equilibrium re-populates the $S_1$ state and is then responsible for the previously reported delayed fluorescence of these compounds. Further studies in the NIR-region are being carried out to extend the observable wavelength and collect further evidence of the radical anion spectral signature, preventing its overlap with the ESA transient band.

[1] Huang, Song, Prescimone, Aster, Cohen, Mannancherry, Vauthey, Coskun and Solomek, *Chem. Sci.*, 2021, 12, 5275.

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