Revisiting charge-carrier dynamics in gold nanoclusters: ultrafast intersystem crossing drives excited-state dynamics

Tristan Blandenier[1], Subhradip Kundu[2], Thomas Bürgi[2], Malte Oppermann[1]

[1]Department of Chemistry, University of Basel, Klingelbergstr. 80, 4056 Basel, CH
[2]Department of Physical Chemistry, University of Geneva, Quai Ernest-Ansermet 30, 1205 Geneva, CH
t.blandenier@unibas.ch

Thiolate-protected gold nanoclusters (Au-NCs) are small nanoparticles comprising only a few tens of gold atoms and exhibit single-electron photoexcitations with UV-Vis absorption cross-sections higher than many organic dyes. These molecular-like transitions differ from the plasmonic response commonly observed in larger gold nanoparticles and are thus particularly attractive for light-energy conversion processes [1]. However, despite much progress in the synthesis of Au-NCs with bespoke properties, the understanding of the excited-state dynamics that govern their photophysical functions remains incomplete. In this respect, there is mounting evidence that the formation and relaxation of triplet states play a much more important role in their photophysics than previously assumed [2]. Nevertheless, the underlying intersystem crossing dynamics have not yet been resolved conclusively on the relevant ultrafast time scale [3].

To address this challenge, we conducted a photophysical investigation of the prototypical Au-NC $Au_{38}(2\text{-}PET)_{24}$, using ultra-broadband transient absorption (TA) with sub-50 fs resolution in combination with photoluminescence spectroscopy. We find that the excited-state dynamics are dominated by a sub-picosecond intersystem crossing from the lowest excited singlet state, while internal conversion from higher singlet states unexpectedly proceeds on a slower picosecond time scale. On this basis, we are able to provide a complete picture of the formation and relaxation dynamics of triplet states in $Au_{38}(2\text{-}PET)_{24}$, thereby explaining its photoluminescence properties. More generally, our results may thus contribute to ongoing efforts in tailoring the charge-carrier dynamics of AuNCs, with a view to realizing their potential for light-energy conversion processes [4].

[1] M. Zhou, R. Jin, *Annu. Rev. Phys. Chem.* **2021**, *72*, 121-142.
[2] H. Sakai, S. Hiramatsu, A. Akiyama, Y. Negishi, T.Hasobe, *Chem. Comm.* **2025**, *61*, 913-916.
[3] G. He, S. Chen, R. Jin, *J. Phys. Chem. Lett.* **2025**, *16*, 13118-13131.
[4] M. Zhou, T. Higaki, G. Hu, M.Y. Sfeir, Y. Chen, D. Jiang, R. Jin, *Science*, **2019**, *364*, 279-282.

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

J. T. Casanova,[1] S. Giannini,[2] G. Prampolini,[2] A. Monari,[3] A. Cannizzo[1]

[1] *Institute of Applied Physics, University of Bern, Bern, Switzerland.* [2] *Istituto di Chimica dei Composti Organometallici (ICCOM-CNR), Area della Ricerca del CNR, Via Moruzzi 1, I-56124 Pisa, Italy* [3] *Université Paris Cité and CNRS, ITODYS, Paris, France;*
jakob.casanova@unibe.ch

It was recently reported that Pt quinoxdt dithiolene complexes have a photochemical response, which markedly depends on the excitation wavelength leading to an anti-Kasha (AK) behavior. AK originates from a competition between the functional process in the upper photo-excited state and internal conversion towards the lowest excited state. Experimental evidence shows that internal conversion, which is typically a few femtoseconds, is in these systems astonishingly slowed down to 1-2 ps.[1-2]
In addition, the excitation into higher excited states seems to allow the systems 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 using time-dependent density functional theory aimed at clarifying the unanswered questions: low efficiency of the internal conversion, photocycle, intermediated states and structure of the long-lived configuration. Thus, fully understanding the AK behavior in these systems and in perspective, optimize their performance.
In this contribution, we will explore the excited state dynamics using two complementary approaches: Surface Hopping including Arbitrary Couplings (SHARC)[3-4] and quantum-derived force field Joyce[5-7]. We will also show the two approaches unique advantages while showing Joyce's preliminary results For SHARC, we will give a first approach to unraveling the AK dynamics, starting from a simple picture (Figure 1).

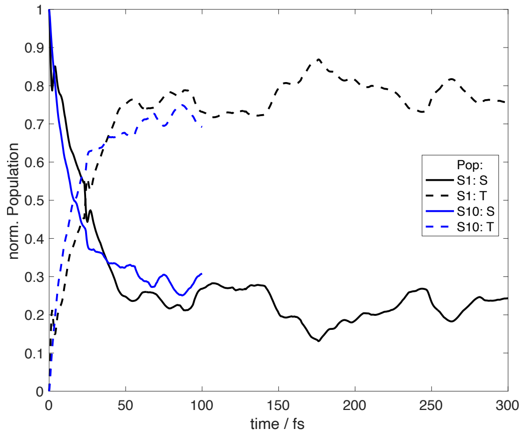


Figure 1: Dynamics of S1 and S10 only seperated by Singlets and Triplets, calculated by SHARC.

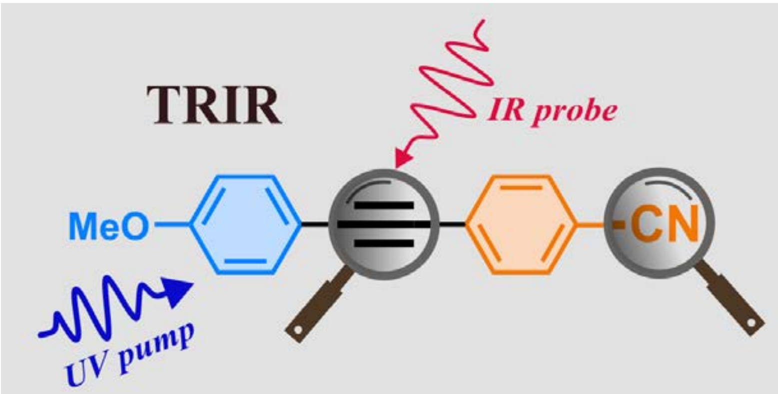
[1] M. Gazzetta, F. Artizzu, S. S. Attar, L. Marchio, L. Pilia, E. J. Rohwer, T. Feurer, P. Deplano, A. Cannizzo, *The journal of physical chemistry. A* **2020**, *124*, 10687-10693;
[2] S. Attar, D. Espa, F. Artizzu, L. Pilia, A. Serpe, M. Pizzotti, G. Di Carlo, L. Marchio, P. Deplano, *Inorg Chem* **2017**, *56*, 6763-6767.
[3] S. Mai, P. Marquetand and L. González, WIREs Comput. Mol. Sci., 2018, e1370;
[4] Mai, S.; D. Avagliano, M. Heindl, P. Marquetand, M.F.S.J. Menger, M. Oppel, F. Plasser, S. Polonius, M. Ruckenbauer, Y. Shu, D.G. Truhlar, L. Zhang, P. Zobel, L. González. *SHARC3.0: Surface Hopping Including Arbitrary Couplings: Program Package for Non-Adiabatic Dynamics*, 2023; https://sharc-md.org/.
[5] I. Cacelli and G. Prampolini, J. Chem. Theory Comput., 3, 1803 (2007).
[6] V. Barone, I. Cacelli, N. De Mitri, D. Licari, S. Monti, and G. Prampolini, Phys. Chem. Chem. Phys., 15, 3736 (2013).
[7] Cerezo, J., Prampolini, G. and Cacelli, I. Theoretical Chemistry Accounts, 137, 80 (2018).

Two Markers Are Better than One: Understanding TRICT with an Additional Vibrational Sensor on the Acceptor Moiety

Alena Chernikova, Joseph Kölbel, Ricardo J. Fernández-Terán*

Department of Physical Chemistry, University of Geneva. CH-1205 Geneva, Switzerland
alena.chernikova@etu.unige.ch

Donor–Bridge–Acceptor (DBA) dyads are versatile chromophores which can access an intramolecular charge-transfer (ICT) state upon excitation. Their tuneable excited-state properties render them useful across fields such as solar energy conversion and molecular electronics, where controlled charge transfer is important.[1] Tailoring a candidate to a specific application requires precise understanding of its excited state character, an indicator for the efficiency of the subsequent charge separation.[2] Thus, elucidating the corresponding photophysics is necessary for uncovering the involved relaxation mechanisms and pathways. In certain DBA dyads, twisted and rehybridized intramolecular charge transfer (TRICT) has been proposed as a possible excited state deactivation pathway, whose formation is facilitated in polar, low viscosity environments.[3] However, neither the universality of this phenomenon, nor the electronic structure of the TRICT state are fully understood.



Transient infrared spectroscopy (TRIR) is uniquely suited to pinpoint structural changes in excited states. We used this advantage to investigate a donor-bridge-acceptor diphenylacetylene-based dyad, featuring a distinctly vibrationally active triple bond and cyano group. Introducing the cyano group as a secondary vibrational sensor allowed us to understand the electronic configuration on the acceptor moiety in the charge separated state. As a result, the molecule was found to exhibit excited-state relaxation consistent with a TRICT pathway. Scanning both the polarity as well as viscosity coordinates, we shed light on the strong environment-dependence of charge separation strength. Our findings were further supported with transient electronic absorption spectroscopy (TA), from fs to µs, elucidating the potential of back-hybridisation from the TRICT state into a planar triplet state.

[1] B. Albinsson, M. P. Eng, K. Pettersson, M. U. Winters, *Phys. Chem. Chem. Phys.* **2007**, *9* (44), 5847–5864.
[2] Z. Wei, A. M. Philip, W. F. Jager, F. C. Grozema, *J Phys Chem C Nanomater Interfaces* **2022**, *126* (45), 19250–19261.
[3] B. Dereka, D. Svechkarev, A. Rosspeintner, M. Tromayer, R. Liska, A. M. Mohs, E. Vauthey, *JACS* **2017**, *139*, 16885-16893.

Pump-Pump-Probe Spectroscopy to Investigate the Consecutive Photoinduced Electron Transfer Mechanism with Perylene Diimide

Daniel H. Cruz Neto, Estefanía Sucre-Rosales, Eric Vauthey

Department of Physical Chemistry, University of Geneva, Quai Ernest-Ansermet 30, 1211 Geneva, Switzerland
daniel.cruzneto@unige.ch

The use of excited organic radical ions as photocatalysts for thermodynamically challenging synthetic reactions has been a topic of intense research in the past few years. Since the first report on the use of the excited radical anion of a perylene diimide derivative ($^{2}PDI^{\bullet-}*$) as a photocatalyst for the reduction of aryl halides in what came to be known as consecutive photoinduced electron transfer (conPET) mechanism,[1] many questions have been raised as the mechanism is constantly under scrutiny. This process is based on the excitation of PDI in the presence of a sacrificial electron donor, reductively quenching $^{1}PDI*$ to generate its radical anion form. From there, a second photon excites $^{2}PDI^{\bullet-}$ and produces the species that is claimed to be the photocatalyst in the synthetic reaction. One of the main points of scrutiny in this mechanism is the very short lifetime of the D_1 excited state of $^{2}PDI^{\bullet-}*$ (145 ps),[2] making it highly unlikely for this species to engage in any diffusion-driven electron transfer process with a substrate. Previous studies have attributed the observed photocatalytic activity to photoproducts of the decomposition of $^{2}PDI^{\bullet-}*$,[2] or even considered a pre-association between the excited radical anion and the substrate,[3] but a full description of the mechanism involving this elusive species is still missing. Our photophysical approach to this problem consists in photochemically generating the radical ion species and later probing its excited state properties via ultrafast optical absorption spectroscopy by using a pump-pump excitation strategy. We show that direct quenching of $^{1}PDI*$, as originally proposed in the mechanism, is an inefficient strategy due to an ultrafast geminate charge recombination that prevents the radical anion to be accumulated in solution. We circumvent this shortcoming upon directly populating the excited triplet state ($^{3}PDI*$) by using a halogenated electron donor, and then we quench it with a second donor to yield the freely diffusing $^{2}PDI^{\bullet-}$ species. From there, a second actinic pump can be used to selectively populate the excited state of the photogenerated $^{2}PDI^{\bullet-}$, probing its ultrafast dynamics in the presence and absence of aryl halide substrates.

[1] I. Ghosh, T. Ghosh, J.I. Bardagi, B. Konig. *Science* **2014**, *346*, 725-728.
[2] M. Marchini, A. Gualandi, L. Mengozzi, P. Franchi, M. Lucarini, P.G. Cozzi, V. Balzani, P. Ceroni. *Phys. Chem. Chem. Phys.* **2018**, *20*, 8071-8076.
[3] B. Pfund, D. Gejsnaes-Schaad, B. Lazarevski, O.S. Wenger. *Nat Commun.* **2024**, *15*, 4738.

Photo-induced dynamics in liquid crystal chromophores investigated by UV-Vis femtosecond spectroscopy

Prantic Debnath[1*], M. Murillo-Sanchez[2], Laura Cattaneo[2], Andrea Cannizzo[1]
[1]University of Bern Sidlerstrasse 5, CH 3012 Bern, Switzerland, [2]Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany;
[*]e-mail: Prantic.debnath@unibe.ch

Photo-induced molecular reconfiguration in liquid crystal chromophores is a key factor influencing their excited-state behavior and electronic properties. Femtoscond UV-Vis transient absorption spectroscopy provide access to the controlled formation and concentration-dependent emergence of excimers in nCB liquid crystalline systems. This offer significant opportunities and allow in achieving a deep knowledge of the electronic processes guiding such molecular reconfiguration. This in turn will reveal new emergent electronic properties that such LC do not present in the ground state. for fundamental understanding and technological developments.In this work, we systematically investigate the ultrafast photophysical dynamics of cyanobiphenyl-based liquid crystals (5CB,8CB & 8OCB), focusing specifically on the early-time molecular responses leading to structural changes and critical to excimer formation. Utilizing femtosecond transient absorption spectroscopy, we distinguish monomeric behavior from the onset of excimer formation, providing detailed insights into the underlying mechanisms and kinetics on the picosecond timescale. Our initial results emphasize the rapid isomerization and planarization processes occurring within the first tens to hundreds of picoseconds, forming a foundational understanding of how these structural changes facilitate subsequent excimer formation observed at longer timescales. Additionally, we examine the effect of increased concentration, which significantly enhances excimer formation, as evidenced by characteristic spectral shifts indicative of intermole-

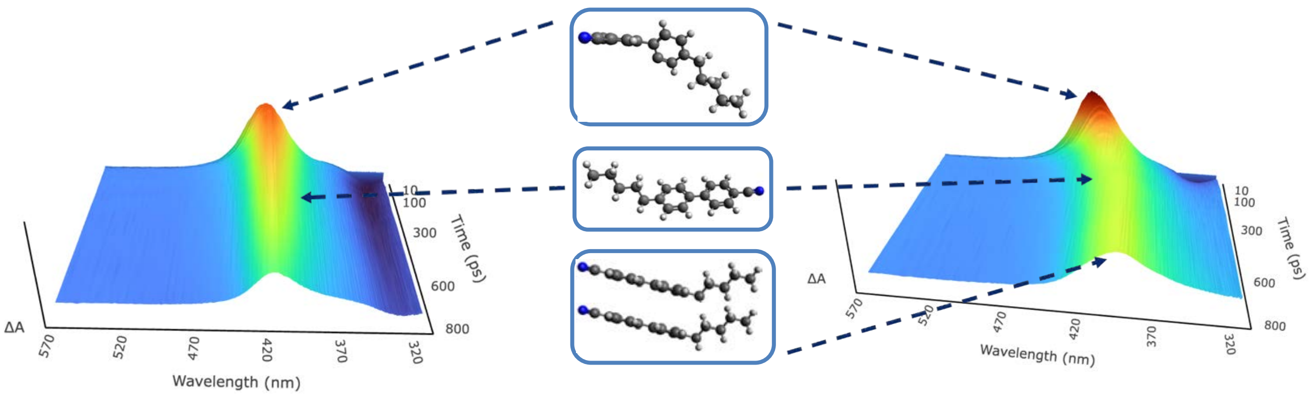


Fig: 3D transient absorption spectra of 5CB showing early-time isomerization in dilute solution (left) and concentration-dependent excimer formation at longer times (right), relevant for liquid-crystal photonics.

cular interactions. This ongoing research aims to elucidate the relationship between molecular configuration, dynamics, and emergent photophysical properties in liquid crystals ultimately advancing liquid crystal-based photonic technologies.

[1] Ikeda, T.; Kurihara, S.; Tazuke, S. *J. Phys. Chem.* **1990**, *94*, 6550-6555.

[2] Klock, A. M.; Rettig, W.; Hofkens, J.; van Damme, M.; De Schryver, F. C. *J. Photochem. Photobiol. A: Chem.* **1995**, *85*, 11-21.

Room-Temperature Luminescence of Air-Stable Nickel(0) Complexes

Henri Eggenweiler, Oliver S. Wenger

Department of Chemistry, University of Basel, St. Johanns-Ring 19, 4056 Basel, Switzerland
E-Mail: timhenri.eggenweiler@unibas.ch

In photochemistry and physics copper(I) complexes emerged as a suitable alternative for noble metals, like ruthenium or iridium.[1, 2] Their isoelectronic analogue, nickel(0), remained largely unexplored, although previous studies suggest that nickel(0) complexes could display favorable photophysical properties.[3, 4] Nevertheless, significant challenges persist, including the absence of photoluminescence in solution at room temperature and limited air stability.[5] To overcome these key limitations, strong-field ligands with sterically demanding substituents, resulting in rigid coordination environments, are required. Chelating isocyanide ligands fulfill these requirements, and our work aims to establish photoluminescent, bench-stable nickel(0) complexes and to study their properties in greater depth.

Herein, we report two new air-stable homoleptic nickel(0) isocyanide complexes, both exhibiting photoluminescence in solution at room temperature. The origin of the emission, attributed to a metal-to-ligand charge-transfer (MLCT) excited state, is investigated with time-resolved laser spectroscopy and DFT calculations. Our results illustrate part of the untapped innovation potential still existing in first-row transition metal photophysics and photochemistry.

[1] F. N. Castellano, M. C. Rosko, *Acc. Chem. Res.* **2024**, *57*, 2872–2886.
[2] F. Doettinger, C. Kleeberg, C. Queffélec, S. Tschierlei, Y. Pellegrin, M. Karnahl, *Catal. Sci. Technol.* **2023**, *13*, 4092.
[3] T.-N. Streit, M. Sellin, B. Lazarevski, O. S. Wenger, M. Malischewski, *Inorg. Chem.* **2026**, *65*, 5374–5386.
[4] H. Kunkely, A. Vogler, *J. Organomet. Chem.* **2003**, *684*, 113–116.
[5] L. A. Büldt, C. B. Larsen, O. S. Wenger, *Chem. Eur. J.* **2017**, *23*, 8577–8580.

Controlling Photoactive Excited States in Co(III) and Ni(II) Complexes Through Ligand

Ilse Friedländer[a], Polina Yaltseva[a,b], Alessandro Prescimone[c], Oliver S. Wenger[a]

[a]Department of Chemistry, University of Basel, St. Johanns-Ring 19, 4056 Basel, Switzerland
[b]Current address: Paul Scherrer Institut PSI, Forschungsstrasse 111, 5232 Villigen, Switzerland
[c]Department of Chemistry, University of Basel, Mattenstr. 22, 4058 Basel, Switzerland
E-Mail: ilseeva.friedlaender@unibas.ch

In photochemistry changing from well-established 4d and 5d metals to their more abundant 3d analogues comes with the challenge of an intrinsically lower ligand field splitting. This facilitates deactivation of metal-to-ligand charge-transfer (MLCT) states through lower lying metal-centered (MC) states yielding lower excited state energies, shorter excited state lifetimes and lower photoluminescence quantum yields. Therefore, understanding how to influence the ligand field splitting for 3d metals is needed to optimize their application potential. For this, a series of ligands with tuned electronics based on 2,6-di(quinoline-8-yl)pyridine (**dqp**) was synthesized and their influence on Co(III) and Ni(II) investigated.

The **dqp** ligand forms complexes with optimized bite-angles and a nearly ideal octahedral coordination geometry.[1-3] The substitution of the 4'-position of quinoline and the 4-position of pyridine with nitrogen yields the ligands 2,6-di(quinoxalin-5-yl)pyridine and 2,6-di(quinoxalin-5-yl)pyrazine with increasing π-acceptor and decreasing σ-donor abilities.[4]

The key finding is that the electronic structure of the chelate affects the ligand field in the case of the more positively charged Co(III) fundamentally differently than in Ni(II). The underlying reason for this finding appears to be that our bite angle-optimized ligands act as π-donors towards Co(III), whereas they act as π-acceptor ligands towards Ni(II). This effect had been suspected to occur previously in Fe(II) complexes, but in those cases was more difficult to probe due to overlapping MLCT absorptions.[5] The Ni(II) complexes investigated here provide clearer comparative insight in this regard.[6] These results contribute to an improved understanding of how ligand electronics can be tailored to achieve favorable photophysical properties in first-row metal complexes.

[1] 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.
[2] P. Yaltseva, T. Maisuradze, A. Prescimone, S. Kupfer, O. S. Wenger, *J. Am. Chem. Soc.* **2025**, *147*, 29444–29456.
[3] C. Zahn, M. Pastore, J. L. P. Lustres, P. C. Gros, S. Haacke, K. Heyne, *J. Am. Chem. Soc.* **2024**, *146*, 9347–9355.
[4] G. A. Parada, L. A. Fredin, M.-P. Santoni, M. Jäger, R. Lomoth, L. Hammarström, O. Johansson, P. Persson, S. Ott, *Inorg. Chem.* **2013**, *52*, 5128–5137.
[5] A. Ghosh, J. T. Yarranton, J. K. McCusker, *Nature Chemistry* **2024**, *16*, 1665–1672.
[6] N. R. East, C. Dab, C. Förster, K. Heinze, C. Reber, *Inorg. Chem.* **2023**, *62*, 9025–9034.

Simulating nonadiabatic dynamics in photodissociation using MASH

Daniele Furlanetto, Jeremy O. Richardson

ETH Zürich Inst. Mol. Phys. Wiss. Zürich Switzerland
daniele.furlanetto@phys.chem.ethz.ch

The photodissociation of molecules can be simulated through nonadiabatic molecular dynamics methods. Semiclassical methods allow the on-the-fly simulations of molecules in full dimensionality, and they need to be benchmarked to assess their robustness. The mapping approach to surface hopping (MASH) is a novel deterministic method that ensures consistency and time-reversibility.

MASH and standard fewest-switches surface hopping (FSSH) are compared to full quantum-mechanical results on model systems and on-the-fly photodissociation of ammonia. The mapping approach to surface hopping (MASH) solves the inconsistency between the active state and the electronic coefficients, showing improvements in all the systems studied. The electronic populations after dissociation are calculated to compare the different methods. The standard surface hopping can fail to describe the long-time limit distribution of active state, while MASH describes the correct limit thanks to internal consistency and detailed balance at the same computational cost. In this way, MASH appears to be an excellent simulation approach that describes without further corrections the electronic populations after photodissociation.

Capturing ortho, meta and para substituent effects on excited-state symmetry breaking

Chinju Govind[1] , Lysander Presser[2], Thomas Müller[2] Eric Vauthey[1]*

[1]Department of Physical Chemistry, University of Geneva, CH-1211 Geneva, Switzerland
[2]Institut für Organische Chemie und Makromolekulare Chemie Heinrich-Heine-Universität Düsseldorf Universitätsstrasse 1, 40225 Düsseldorf, Germany

E-mail: chinju.maniyeriveettil@unige.ch

The localization of exciton in acceptor-donor-acceptor (A–D–A) type molecules, which leads to excited-state symmetry breaking (ES-SB)[1], depends on many parameters such as the solvent polarity, the electron-donating and accepting strength of the D-A units and their separation distance.[2] Here, we investigate how the ortho, meta and para substituents of a symmetric double-branched A-D-A (*m*-CN, *o*-CN and *p*-CN, Fig.1) molecule with a phenothiazine central core affect the nature and dynamics of its lowest singlet excited state by ultrafast electronic and vibrational absorption spectroscopies. Time-resolved infrared (TRIR) absorption spectra were obtained by probing the stretching frequency of the -C≡N groups in solvents of varying polarity. In nonpolar cyclohexane (CHX), the TRIR spectra display a single -C≡N band for all molecules, attributed to an even distribution of excitation over the whole molecule. In polar solvent (dimethyl sulfoxide(DMSO)), the less conjugated *m*-CN doesn't show any signature of ES-SB. By contrast, the spectra of the *o*-CN and *p*-CN exhibit a pronounced band splitting, which is comparatively larger for *o*-CN, indicating higher asymmetry. These results demonstrate that, along with solvent polarity, the orientation, position and the degree of conjugation of the electron-accepting substituent play a major role for ES-SB in A-D-A systems. Additionally, the effect of ortho and meta substituted CN groups on the same benzene group will also be discussed.

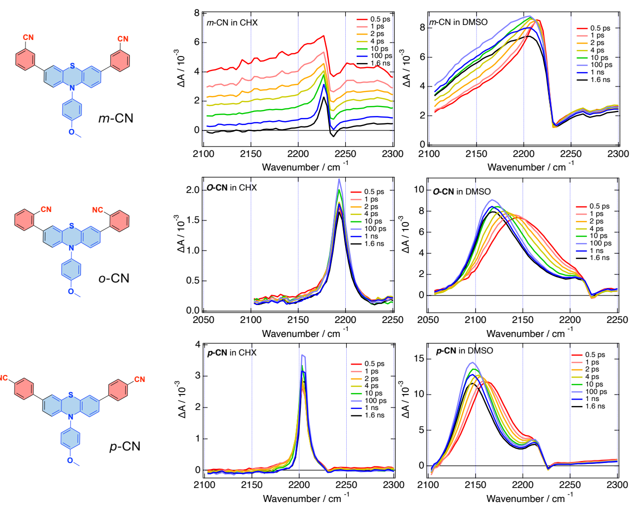


Figure 1. Chemical structure of the phenothazine derivatives with meta, ortho and para substituted CN groups and time-resolved infrared spectra in CHX (left) and DMSO (right). A single −C≡N band in CHX suggests a quadrupolar excited state and the appearance of broad and new −C≡N bands around 2140 cm^{-1} in more polar solvents indicates an increased localisation of the excitation on one branch.

[1] B. Dereka, A. Rosspeintner, Z. Li, R. Liska, E. Vauthey, *J. Am. Chem. Soc.* **2016**, *138*, 4643-4649.

[2] C. Govind, E. Balanikas, G. Sanil, D. T. Gryko and E. Vauthey, *Chem. Sci.*, **2024**, 15, 17362–17371.

Excited trisaminocyclopropenium radical dication initiates photoredox catalysis through ultrafast intermolecular electron transfer

Ronny Hardegger[1], Ajeet Kumar[2], Björn Pfund[1], Jürgen Hauer[2*], Oliver S. Wenger[1*]

[1]Department of Chemistry, University of Basel, St. Johanns-Ring 19, 4056 Basel, Switzerland
[2]Technische Universität München, Fakultät für Chemie, 85748 Garching b. München, Germany
ronny.hardegger@unibas.ch

Excited radical ions have emerged as attractive but debated organic photocatalysts, as their picosecond excited state lifetimes are generally considered too short for diffusion-controlled photoinduced electron transfer (PET).[1] Here, we provide direct spectroscopic evidence that the excited trisaminocyclopropenium radical dication ($^{*}TAC^{\bullet 2+}$) acts as the catalytically active species. Mechanistic studies reveal that preassociation between $TAC^{\bullet 2+}$ and arene substrate in the ground state enables productive PET beyond the diffusion limit.[2] Furthermore, we developed a biphotonic excitation strategy to generate $^{*}TAC^{\bullet 2+}$ photochemically. This strategy complements photoelectrochemical methods and enables aerobic oxidative functionalization of arenes such as mesitylene and benzene.[3] These results support the role of excited radical ions as viable photocatalysts and expand the conceptual scope of multiphoton photoredox strategies.

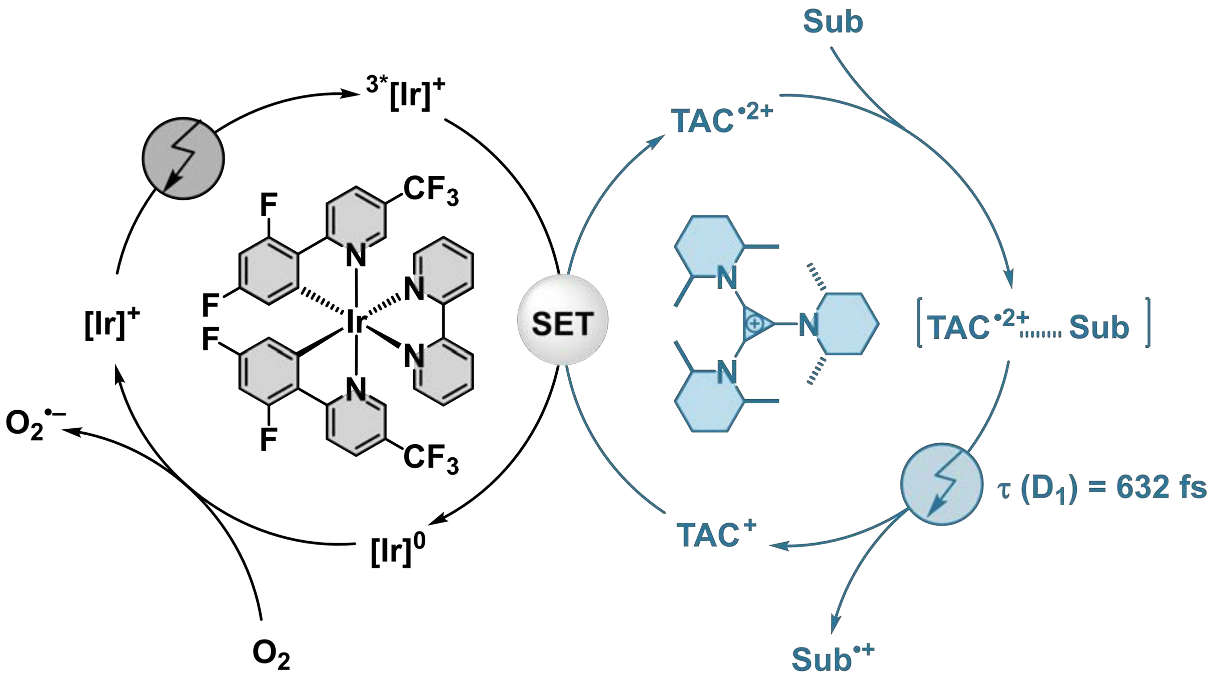


Figure 1. Biphotonic excitation strategy for arene functionalization mediated by TAC^+ and $[Ir]^+$ photocatalysts.

[1] Pfund, B.; Wenger, O. S. JACS Au **2025**, 5, 426–447.
[2] Pfund, B.; Gejsnaes-Schaad, D.; Lazarevski, B.; Wenger, O. S. Nat. Commun. **2024**, 15, 4738.
[3] Wu, S.; Zurauskas, J.; Domanski, M.; Hitzfeld, P. S.; Butera, V.; Scott, D. J.; Rehbein, J.; Kumar, A.; Thyrhaug, E.; Hauer, J.; Barham, J. P. Org. Chem. Front. **2021**, 8, 1132–1142.

Spin-flip time-dependent density functional theory within the Sternheimer formalism

Luis I Hernandez Segura, Sandra Luber

University of Zürich
luisignacio.hernandezsegura@uzh.ch

In this work we present the state-of-the-art on low-scaling methods for spin-flip time dependent density functional theory (SF TDDFT) calculations. To this aim, the Sternheimer formalism is employed to allow SF TDDFT calculations without the explicit need of unoccupied molecular orbitals, we name the resulting method SF TDDFPT. We implemented this method into the CP2K package to take advantage of its highly efficient methodologies, in particular, the Gaussian and plane-wave method and the auxiliary density matrix method. The former is used to lower the computational scaling of the electron-electron repulsion and exchange-correlation contributions in the spin-flip kernel and the later is used for the calculation of the Fock exchange contribution with a reduced computational scaling. The resulting excitation energies are obtained within 0.3 eV with respect to highly accurate excitation energies. The optimized bond lengths, using PBE and PBE0, were found to be within 1 pm from the CCSD reference.

[1] R. Sternheimer, Physical Review, 1951, 84, 244–253.
[2] G. Lippert, J. Hutter, M. Parrinello, Molecular Physics, 1997, 92, 477-488.
[3] J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, Computer Physics Communications, 2005, 167, 103–128.
[4] M. Guidon, J. Hutter, J. VandeVondele, Journal of Chemical Theory and Computation, 2010, 6, 2348–2364.
[5] P.-F. Loos, A. Scemama, M. Boggio-Pasqua, D. Jacquemin, Journal of Chemical Theory and Computation, 2020, 16, 3720–3736.
[6] Y. A. Bernard, Y. Shao, A. I. Krylov, The Journal of Chemical Physics 2012, 136, 204103.

Fluorescence imaging of liquid–liquid phase-separated protein condensates

Gladys Jaccard[1,2], Dominik Gendreizig[1], Enrica Bordignon[1], Alexandre Fürstenberg[1,2]

[1] Department of Physical Chemistry and [2] Department of Inorganic and Analytical Chemistry, University of Geneva, 1205 Geneva, Switzerland.
Email: gladys.jaccard@unige.ch

Liquid–liquid phase separation (LLPS) creates biomolecular condensates with physicochemical properties distinct from the surrounding dilute phase [1]. Yet, their internal hydration, viscosity, and molecular mobility remain difficult to quantify. To address this challenge, we investigate the nanoscale physicochemical environment within protein condensates using a combined fluorescence approach based on Fluorescence Lifetime Imaging Microscopy (FLIM), Time-Correlated Single Photon Counting (TCSPC), and Fluorescence Correlation Spectroscopy (FCS).

As an initial model system, γD-crystallin was used to establish a robust methodology for probing local microenvironments using hydration-sensitive fluorophores such as ATTO655. Condensates formed in the presence of PEG 6000 exhibit markedly decreased molecular mobility, up to 30-fold slower diffusion in the dense phase, and significantly increased fluorescence lifetimes, consistent with reduced water accessibility and a compact, partially dehydrated internal environment [2]. These observations agree with recent reports on γD-crystallin LLPS and its dense-phase properties [3]. Together, they demonstrate that lifetime-based sensing provides a sensitive and non-invasive readout of local hydration within protein condensates.

Building on this methodology, we are now extending the approach to BSA condensates to evaluate the generality of these microenvironmental signatures across distinct protein-based LLPS systems.

[1] Alberti, S.; Gladfelter, A.; Mittag, T. Cell **2019**, *176 (3)*, 419–434.
[2] Maillard, J.; Rumble, C. A.; Fürstenberg, A. J. Phys. Chem. B **2021**, *125 (34)*, 9727–9737.
[3] Gendreizig, D. et al. J. Phys. Chem. B **2025**, *129 (4)*, 1185–1196.

From hours to seconds of processing: Exploiting surface restructuring as a mechanism for core/shell doping of Rh,La:$SrTiO_3$ photocatalysts

Melanie Johanning[1], Mara Blöchlinger[1], Oliveira Wanderson da Silva[2], Coral Felipe[3], Hannah Johnson[3], Mathieu Soutrenon[2], Kevin Sivula[1]

[1] Laboratory for Molecular Engineering of Optoelectronic Nanomaterials (LIMNO), EPFL, Lausanne, Switzerland
[2] Institute of Systems Engineering, HES-SO Valais- Wallis, Sion, Switzerland
[3] Advanced Materials Engineering, Toyota Motor Europe, Zaventem, Belgium

email: melanie.johanning@epfl.ch

Rh,La-doped strontium titanate (Rh,La:$SrTiO_3$) is a promising photocatalyst material for solar-driven H_2 production. The state-of-the-art Rh,La:$SrTiO_3$ formed from a 2-step solid state reaction features an undoped core/doped shell structure. To systematically understand the effect of the spatial dopant distribution, advances in the synthesis procedures to control the dopant distribution are needed.

In this presentation, we compare techniques for synthesizing Rh,La:$SrTiO_3$ nanoparticles with different dopant distributions based on comprehensive characterization including photocatalytic performance tests as well as STEM-EDX, XPS, and ICP-MS to analyze the dopant distribution. Our findings show that concentration gradient-driven diffusion into $SrTiO_3$ contributes negligibly to doping at 1100 °C. In contrast, two factors are critical for controlled, rapid doping: A readily-available, homogeneously distributed dopant source, and a surface restructuring of the precursor. These allow core/shell doping of $SrTiO_3$ in only 10 min of thermal annealing.

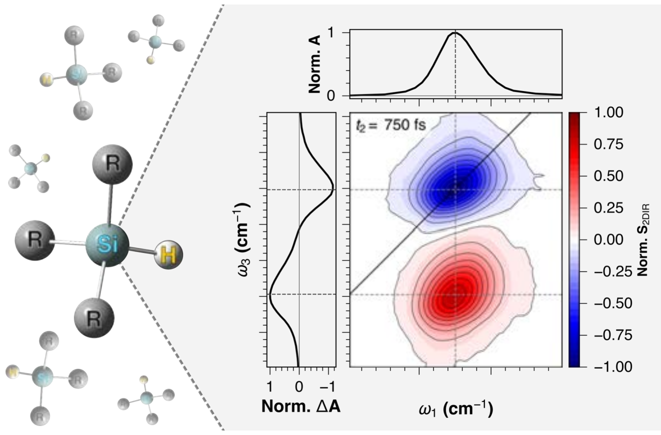
We applied these findings for the synthesis of particles with thinner shells, novel features, and better performance. Flash photothermal doping was realized within 10 s, and rapid thermal doping allows to control the kinetics of Rh incorporation vs. oxidation. We report insights on the doping mechanism and effect of the dopant distribution in Rh,La:$SrTiO_3$ along with novel synthesis approaches for the fast synthesis of core/shell structures.

Vibrations Resolve Dissociations: A 2D-IR-Based Method to Determine Bond Dissociation Free Energies in Solution

Joseph Kölbel,[a] Laurent Sévery,[b] Ricardo J. Fernández-Terán[a*]

[a] Department of Physical Chemistry, University of Geneva. CH-1205, Geneva, Switzerland.
[b] Université Grenoble Alpes, CNRS, CEA, IRIG, Laboratoire de Chimie et Biologie des Métaux. Grenoble, 38000 France.
joseph.koelbel@unige.ch

Accurate determination of bond dissociation free energies (BDFEs) is essential for the quantitative description of proton-coupled electron transfer (PCET) processes,[1] or the determination of hydricity.[2] Despite their fundamental significance, the direct determination of BDFEs remains experimentally and conceptually challenging. Conventional methodologies often rely either on equilibrium measurements employing reference compounds with established BDFEs, or on the construction of thermodynamic cycles.[3,4] An alternative strategy is to derive the BDFE from the corresponding bond dissociation enthalpy (BDE), however experimentally determined BDEs are typically obtained from gas-phase studies and therefore neglect solvation effects, whilst quantum-chemical predictions often show appreciable discrepancies relative to experimental benchmarks.[1]



Our contribution to this field is a purely spectroscopic approach to the precise and easy estimation of BDEs in the solvents of interest. By employing two-dimensional infrared (2D-IR) spectroscopy, we successfully reproduced the BDEs of a range of silanes and subsequently extended the available library by determining BDE values across multiple solvent environments. In addition, we report, for the first time, experimental BDEs for an additional derivative, showcasing the ability of our method to systematically investigate solvent and substitution effects on BDEs within an entire class of compounds. Given that specific solute–solvent interactions frequently limit the accuracy of purely computational methods or gas-phase measurements, this novel approach not only facilitates the identification of such interactions but also enables their direct characterisation on picosecond timescales without the need for additional modifications.

[1] R. G. Agarwal, S. C. Coste, B. D. Groff, A. M. Heuer, H. Noh, G. A. Parada, C. F. Wise, E. M. Nichols, J. J. Warren, J. M. Mayer, *Chem. Rev.*, **2022**, *122*, 1–49.
[2] L. Sévery, N. Emmanuel, M. Alexis, C. Thibault, *Inorg. Chem.*, **2025**, *64*, 12927–12931.
[3] G. W. Margulieux, S. Kim, P. J. Chirik, *Inorg. Chem.*, **2020**, *59*, 15394–15401.
[4] M. Lucarini, P. Pedrielli, G. F. Pedulli, S. Cabiddu, C. Fattuoni, *J. Org. Chem.*, **1996**, *61*, 9259–9263.

Visualization of bond scission events in polymeric materials with a coumarin-based mechanophore using confocal microscopy

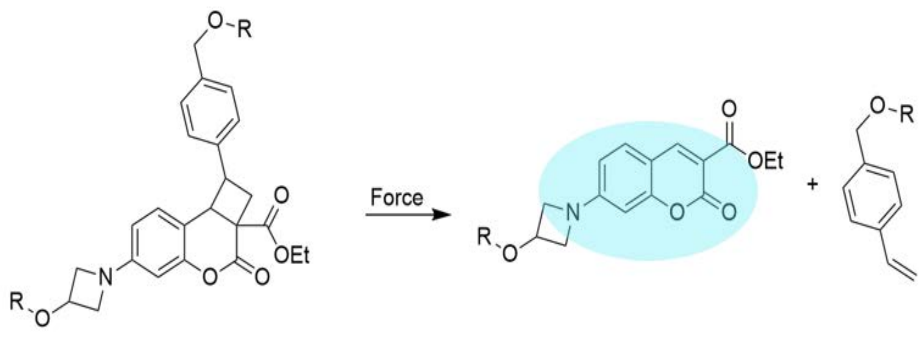
Juliette Lavainne[1, 2], Yang Li[2], Jessica M. Clough[2*]

[1]*University of Bordeaux, Bordeaux, France*

[2]*Adolphe Merkle Institute, University of Fribourg, Fribourg, Switzerland*

juliette.lavainne@unifr.ch

Failure in polymeric materials is often caused by the application of mechanical forces,[1] making it important to understand how stress and strain distribute in these materials. One of the ways to achieve this is by visualizing local stress using confocal laser scanning microscopy, which provides spatially resolved, three-dimensional imaging of fluorescence signals from within the material on microscopic length scales.[2] However, this requires the development of mechanophores with absorption and emission in the visible region of the spectrum. In this work, an azetidin coumarin-based mechanophore with absorption and emission in the visible range was successfully developed. The mechanophore contains a cyclobutane motif that, under mechanical force, undergoes retro- [2+2] cycloaddition, leading to activation of the coumarin. Mechanophore activation was studied in solution by ultrasound sonication, in polymer glasses by scratching, and in elastomeric networks by uniaxial tensile testing. The chemical and optical changes were characterized by ^{1}H NMR, UV-Vis absorption, fluorescence and SEC. Finally, mechanophore activation was visualized using confocal laser scanning microscopy. In addition to its activation signal in the visible region, this coumarin-based mechanophore offers several advantages: it can be synthesized in 2 steps, is stable under heat and light irradiation, and upon mechanoactivation generates a coumarin fluorophore with a high quantum yield.[3]



References:

[1] Caruso, M. M.; Davis, D. A.; Shen, Q.; Odom, S. A.; Sottos, N. R.; White, S. R.; Moore, J. S., *Chem. Rev.* **2009**, *109* (11).

[2] Stratigaki, M.; Göstl, R, *ChemPlusChem* **2020**, *85* (6), 1095–1103.

[3] Patawanich, P.; Bedding, M.; Ryder, W.; Payne, R.; New, E.; Adair, L, *ChemRxiv* **2025** (0925).

Bio-functionalizing optically active HfO_2 nanoparticles with bisphosphonates

Evelina Liari[1,2,3*], David E Salazar Marcano[2], Nicolas Hofer[2], Elizaveta Maksimova[2], Celestino Padeste[1], Adrian A. Wanner[1], Jonathan De Roo[2]

[1] *Department of Biology and Chemistry, Paul Scherrer Institut, Forschungstrasse 111, Villigen*
[2] *Department of Chemistry, University of Basel, Mattenstrasse 22, Basel*
[3] *Swiss Nanoscience Institute, Klingelbergstrasse 82, 4056 Basel*

HfO_2 nanoparticles (NPs) have emerged as alternative to fluorides and chemically stable host matrices for optically active Ln^{3+}, which can be utilized in a plethora of bio-applications (1,2). However, maintaining their colloidal stability in physiological conditions, while preserving their optical properties, is remaining a challenge that limits their widespread exploitation in in vivo studies (3). Herein, we compare PEG-functionalized phosphonates and bisphosphonates as potential ligands for optically active HfO_2 NPs. Nuclear Magnetic Resonance (NMR) and Dynamic Light Scattering (DLS) showed the capability of bisphosphonates to provide colloidal stability of the NPs in physiological conditions (4). In addition, the chemical stability and the influence of the ligand on the optical properties of the NPs were characterized. Finally, we showed the versatility of bisphosphonates, since they also offer colloidal stability to fluorides, an additional host matrix for Ln^{3+}. Overall, we conclude that optically active HfO_2 NPs capped with bisphosphonates are promising tools in nanomedicine, overcoming some of the current limitations.

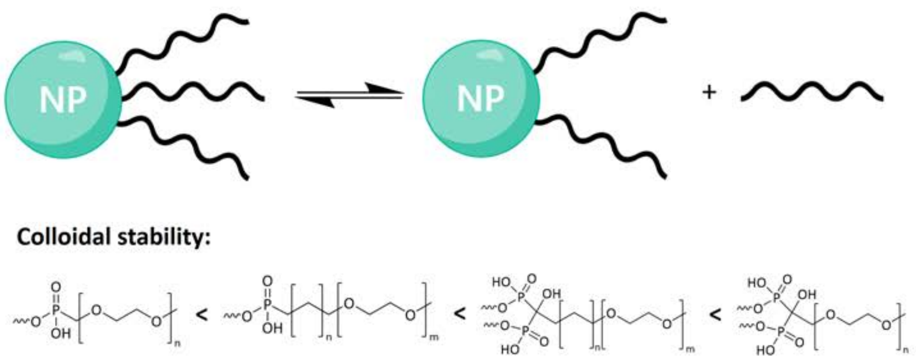


Fig. 1: Ligand desorption of HfO_2 NPs with different phosphonate based ligands and their colloidal stability in aqueous and phosphate buffered saline (PBS).

[1] Seno, C.; Reichholf, N.; Salutari, F.; Spadaro, M. C.; Ivanov, Y. P.; Divitini, G.; Gogos, A.; Herrmann, I. K.; Arbiol, J.; Smet, P. F.; De Roo, J. *J. Am. Chem. Soc*. **2024,** *146*, 20550-20555

[2] Gerken, L. R. H.; Keevend, K.; Zhang, Y.; Starsich, F. H. L.; Eberhardt, C.; Panzarasa, G.; Matter, M. T.; Wichser, A.; Boss, A.; Neels, A.; Herrmann, I. K. *ACS Appl. Mater. Interfaces* **2019,** *11*, 437−448

[3] Labrador-Paez, L.; Kostiv, U.; Widengren, J.; Liu, H. *Adv. Optical Mater*. **2023**, *11*, 2200513

[4] Deblock, L.; Goossens, E.; Prokatath, R.; De Buysser, K.; De Roo, J. *JACS Au* **2022**, *2*, 711–722

Unusual excited-state dynamics in the $[Au_{25}(PET)_{18}]^0$ nanocluster

Luis E. Llanes-Montesino[1], Gonzalo Angulo[2], Thomas Bürgi[1] and Arnulf Rosspeintner[1]

[1] Physical-Chemistry Department, University of Geneva, Ernest-A 30, Geneva, Switzerland.
Luis.LlanesMontesino@unige.ch
[2] Institute of Physical-Chemistry, PAS, Kasprzaka 44/52, 01-224 Warsaw, Poland.

Among the more than 100 structurally resolved metal nanoclusters (NCs) with ultra-small cores (<2 nm), $Au_{25}(SR)_{18}$ (SR = PET, 2-phenylethanethiol) is the most studied, typically existing in three oxidation states (−1, 0, +1). However, systematic photophysical investigations remain scarce, largely due to incomplete spectral coverage, insufficient NIR sensitivity in commercial fluorometers, and the lack of accurate measurements [1]. Using a custom home-built setup capable of measurements beyond the reach of standard instrumentation, our results reveal a low-energy absorption band at 9 kK (fig. 1), not reported in the literature [2], and a strong excitation-energy dependence of both emission profile and peak position (fig. 2), representing the first observation of such behavior in gold nanoclusters. Time-resolved emission data show distinct temporal evolution for each excitation energy. Compared with the closed-shell anion, the neutral cluster displays clear deviations from Kasha's and Vavilov's rules and highly distributed, strongly non-monoexponential photoluminescence decays. These observations support a working hypothesis involving dark states and delayed fluorescence to explain the unconventional emission pathways of the neutral species.

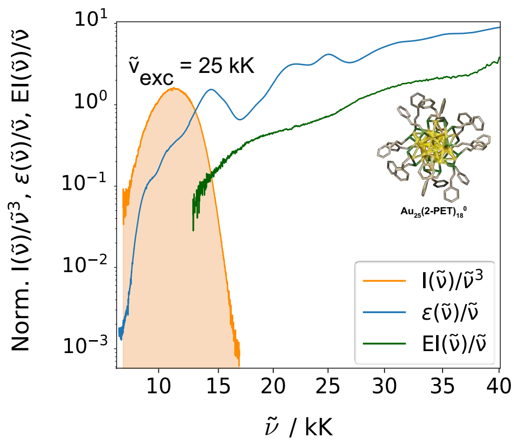


Figure 1. Normalized lineshapes of absorption, excitation and emission of $[Au_{25}(PET)_{18}]^0$ in dichloromethane.

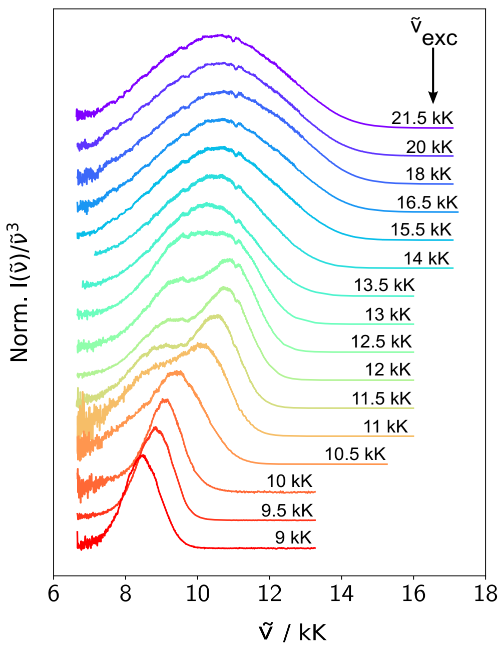


Figure 2. Normalized excitation-dependent emission spectra of $[Au_{25}(PET)_{18}]^0$ in dichloromethane.

[1] Chakraborty, I., Pradeep, T. *Chem. Rev.*, **2017**, 117 (12), 8208–8271.
[2] Green, T.; Jin, R.; Knappenberger, K. L., Jr. et. al. *J. Phys. Chem. A* **2014**, *118*, 10611–10621.

Lanthanide-Doped Zirconia Nanoparticles (ZrO_2 NPs) for Color-Tuning and NIR-Driven Upconversion Photocatalysis

Giacomo Morselli, Nico Reichholf, Anju Bindu Modan, Jonathan De Roo

Department of Chemistry, University of Basel, Mattenstrasse 22, 4058 Basel, Switzerland
giacomo.morselli@unibas.ch

Zirconia (ZrO_2) represents a promising alternative to conventional hosts such as $NaYF_4$ for lanthanide-doped nanoparticles due to its high chemical stability, biocompatibility, and photophysical inertness. Despite these advantages, its use has been relatively limited because of its higher phonon energy, which reduces lanthanide emission brightness and synthetic challenges. In our laboratories, we adopted a surfactant-free synthetic strategy that enables excellent lanthanide incorporation within ZrO_2 nanoparticles.[1] Time-resolved emission spectroscopy allowed us to identify distinct emission contributions from lanthanide ions located in different regions of the nanoparticles, either near the surface or within the core. Guided by these insights, the rational design of core-shell architectures significantly improved the photophysical properties of these materials[1,2] and enabled the exploration of co-doped systems. In particular, we investigated downconversion processes such as Tb^{3+}→Eu^{3+} energy transfer, demonstrating that the transfer efficiency strongly depends on the spatial separation of the dopants within core–shell structures.

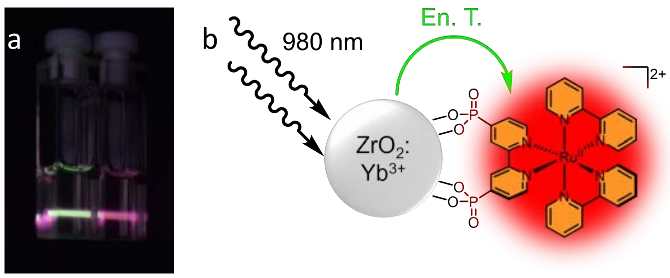


Figure 1 (a) Digital picture of suspensions of ZrO_2:Yb^{3+} NPs co-doped with green emissive Tb^{3+} and red emissive Eu^{3+} upon 980-nm excitation. (b) Scheme representing the working principle of ZrO_2:Yb^{3+} NPs functionalized with $[Ru(bpy)_3]^{2+}$ showing the upconversion process upon excitation at 980 nm and the subsequent population of the metal complex excited state.

Building on this understanding, we extended our studies to upconversion systems. We report for the first time the synthesis of ZrO_2 NPs solely doped with Yb^{3+} capable of converting NIR light into visible emission. Upon excitation at 980 nm, in absence of activators, cooperative emission from Yb^{3+} occurs at 502 nm with long lifetimes (~ 1 ms). This emission can sensitize various lanthanide emitters (Er^{3+}, Tb^{3+}, Eu^{3+}), enabling color tuning (Fig. 1a), or be exploited to excite photocatalysts tethered to the nanoparticle surface. Surface functionalization with $[Ru(bpy)_3]^{2+}$ results in the population of its ^{3}MLCT excited state under 980 nm irradiation, leading to emission at 636 nm (Fig. 1b) and enabling NIR-driven photoredox catalysis. This approach provides a platform for performing photocatalytic transformations under NIR light while avoiding direct excitation of visible-absorbing substrates.

[1] C. Seno, N. Reichholf, F. Salutari, M. C. Spadaro, Y. P. Ivanov, G. Divitini, A. Gogos, I. K. Herrmann, J. Arbiol, P. F. Smet and J. De Roo, *J. Am. Chem. Soc.* **2024**, *146*, 20550–20555.

[2] N. Reichholf, S. Horta, D. Van der Heggen, C. Seno, J. Pulparayil Mathew, M. Ibáñez, P. F. Smet and J. De Roo, *ACS Nano* **2025**, *19*, 30371–30382.

Chiral excited-state dynamics drive circularly polarized luminescence in a europium complex

Livia Müller[1], Michele Puppin[2], Gennaro Pescitelli[3], Francesco Zinna[3], Malte Oppermann[1]

[1] Department of Chemistry, University of Basel, Switzerland
[2] Lausanne Centre for Ultrafast Science, École Fédérale Polytechnique de Lausanne, Switzerland
[3] Department of Chemistry and Industrial Chemistry, University of Pisa, Italy
li.mueller@unibas.ch

Chiral molecules and materials with circularly polarized luminescence (CPL) promise applications in display technology, optical sensing, and quantum information science. [1] However, achieving a high degree of circular polarization is an open challenge, partly because the chirality of electronic excited states remains difficult to characterize during their evolution.

Here, we employ ultrafast circular dichroism spectroscopy (TR-ECD) [2] combined with ultrafast absorption spectroscopy to map out the complete electronic and chiral structural evolution of a prototypical CPL emitter, CsEu((+,-)-hfbc)\textsubscript{4} (hfbc = 3-heptafluorobutyryl camphorate). [3] In this system, the helically arranged chiral ligands act as sensitizers: they harvest light and transfer energy to the Eu(III) ion, whose parity-forbidden transitions prevent direct excitation. The coupling of these metal-centered transitions to the chiral ligand environment gives rise to the exceptionally high degree of circular polarization. [4]

The transient absorption data reveal that energy transfer proceeds via a ligand-localized triplet state in approximately 150 ps. Additionally, we identify a previously unreported quenching channel via the direct decay of ligand-localized singlet states to the ground state that competes with the energy transfer channel and reduces the sensitization efficiency by approximately 30%.

Most importantly, upon energy transfer, the TR-ECD measurements display an increase in optical activity of the ligand system. We assign this to an ultrafast structural rearrangement from a slightly distorted toward a near-perfect square-antiprismatic (SAPR) geometry, corresponding to an increase in twist angle of $\Delta\alpha = 3.0° \pm 1.4°$. This brings the complex within experimental uncertainty of the ideal SAPR ($\Delta\alpha = 45°$) known to maximise CPL, and thereby provides, for the first time, the molecular structure adopted in the functionally relevant excited state. [5] More generally, our approach enables the direct determination of the stereochemical configuration of CPL-active excited states on ultrafast time scales, thereby elucidating the underlying structure-function relationship. This paves the way to unraveling the mechanisms of more complex CPL materials, with a view to further improving their designs.

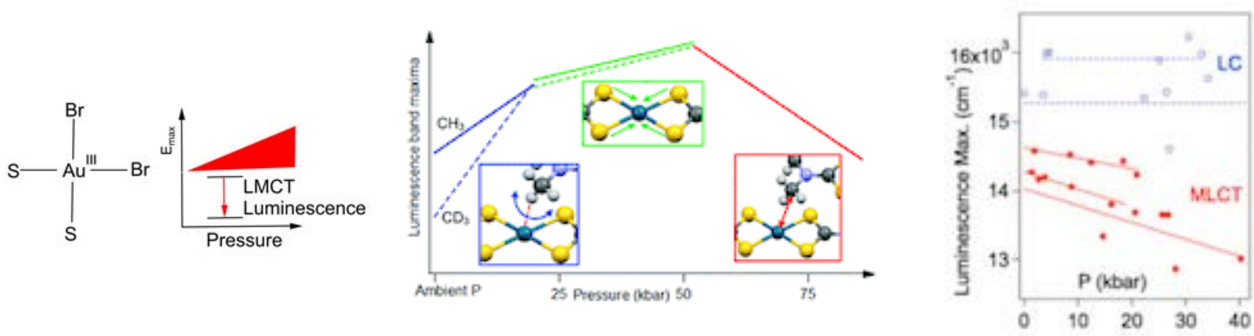
[1] J. Crassous, M. Fuchter, D. Freedman, N. Kotov, J. Moon, M. Beard, S. Feldmann, *Nat. Rev. Mat.,* **2023**.
[2] M. Oppermann, B. Bauer, T. Rossi, F. Zinna, J. Helbing, J. Lacour, M. Chergui, *Optica*, **2019**, *6*, 56-60.
[3] J. L. Lunkley, D. Shirotani, K. Yamanari, S. Kaizaki, G. Muller, *J. Am. Chem. Soc.,* **2008**, *130*, 13814-13815.
[4] S. Di Pietro, L. Di Bari, *Inorg. Chem.,* **2012**, *51*, 12007-12014.
[5] L. Müller, M. Puppin, G. Pescitelli, F. Zinna, M. Oppermann, *ChemRxiv*, **2026**.

Luminescence spectroscopy of square-planar d^8 complexes at variable pressure: a rich variety of properties to explore

Christian Reber

Département de chimie, Université de Montréal, Montréal, Canada
Research Fellow, DFG 5781 Stimulus-responsive luminescent coordination compounds
christian.reber@umontreal.ca

Square-planar transition metal complexes with the d^8 configuration and nickel(II), palladium(II), platinum(II) and gold(III) metal centers[1-3] often show luminescence. Numerous applications from imaging to photocatalysis have been documented. Variable-pressure experiments on solids provide insight on excited-state characteristics for metal-centred (d-d), MLCT, LMCT and ligand-centred (LC) transitions, an unusually rich variety of emitting states. Bandshapes, intensities and lifetimes can all be tuned by external pressures in the ambient pressure to approximately 5 GPa (50 kbar) range, as can the energy order of the excited states. Both intramolecular[1-3] and intermolecular[4] structure variations distinctly influence luminescence properties.



[1] Bélanger-Desmarais, N.; Connelly, E.; Reber, C.
Canadian Journal of Chemistry, **2026**, doi: 10.1139/cjc-2025-0225
[2] Reber, C.; Grey, J. K.; Lanthier, E.; Frantzen, K. A.
Comments on Inorganic Chemistry, **2005**, 26, 233-254.
[3] Poirier, S.; Lynn, H.; Reber, C.; Tailleur, E.; Marchivie, M.; Guionneau, P.; Probert, M. R.
Inorganic Chemistry, **2018**, 57, 7713-7723.
[4] Levasseur-Thériault, G.; Reber, C.; Aronica, C.; Luneau, D. *Inorganic Chemistry,* **2006**, 45, 2379-2381.

In situ photochemical studies by NMR using an integrated light probe

Sophie Renou

QUAD Systems AG, Industriestrasse 31, 8305 Dietlikon, Switzerland
sophie.renou@quadsystems.tech

Understanding light-driven chemical processes requires tools that can study reaction pathways under controlled irradiation conditions. We present a high-performance liquid-state NMR probe equipped with an integrated light system, allowing in situ photochemical experiments directly inside the NMR spectrometer.

The probe is available for 300 to 600 MHz NMR systems and behaves as a standard NMR probe when no illumination is needed, ensuring full experimental flexibility. Light irradiation is provided by LEDs arranged outside around the NMR coils and sample, ensuring uniform and high light density illumination and precise control of irradiation conditions. The system is fully compatible with sample changers and routine software, while maintaining uncompromised NMR performance.

This approach enables real-time monitoring of photochemical reactions, facilitating the study of kinetics, intermediates, and reaction mechanisms without the need for external irradiation setups, which are sometimes heavy and cumbersome. The ability to combine controlled light activation with high-resolution NMR detection opens up new perspectives for the study of a wide range of photochemical systems and experiments, enabling more advanced and automated applications.

Solvent and Isotope Effects on Photoinduced Proton Transfer in 1,1′-Bi-2-naphthol (BINOL)

Diana Rüesch[1], Lidia Zaharieva[1,2], Jan Helbing[1]

[1]Department of Chemistry, University of Zurich, CH-8057 Zurich, Switzerland
[2]Institute of Electronics, Bulgarian Academy of Sciences, BG-1784 Sofia, Bulgaria
jan.helbing@chem.uzh.ch

Under prolonged UV-irradiation, 1,1′-Bi-2-naphthol (BINOL) is known to undergo photoinduced reactions involving intramolecular proton transfer processes that have been associated with solvent-mediated mechanisms [1,2]. We have used transient vibrational spectroscopy supported by density functional calculations to better understand the underlying reaction steps and their solvent-dependence.

Measurements were performed in acetonitrile, methanol, and methanol-d_1, as well as in mixtures with controlled additions of H_2O and D_2O. Following the decay of the fluorescent excited state, we observe a long-lived intermediate for approximately one third of the initially excited molecules, with a full recovery of the ground state after 100 ns in methanol. Under identical conditions in methanol-d_1, on the other hand, a new bleach signal, most prominent in the OH bending region, can be seen after the decay of the intermediate state. The signal persists up to microsecond delays, and we attribute it to OD→OH exchange, with the proton originating from the naphthol ring.

Previous studies have suggested that proton or deuteron transfer in BINOL systems is strongly dependent on the presence of water, believed to facilitate the process through hydrogen-bonded networks [1]. In contrast, our results indicate that proton/deuteron transfer can already occur in neat methanol, while it is indeed enhanced at very high water concentrations (>1M).

These findings provide new insight into solvent-assisted H/D transfer in BINOL and highlight the importance of isotopic substitution in revealing underlying reaction pathways.

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[1] M. Flegel, M. Lukeman, P. Wan, *Can. J. Chem.*, **2008**, 86.2, 161–169.
[2] M. Cavazza, M. Zandomeneghi, A. Ouchi, Y. Koga, *J. Am. Chem. Soc.*, **1996**, 118.41, 9990–9991.

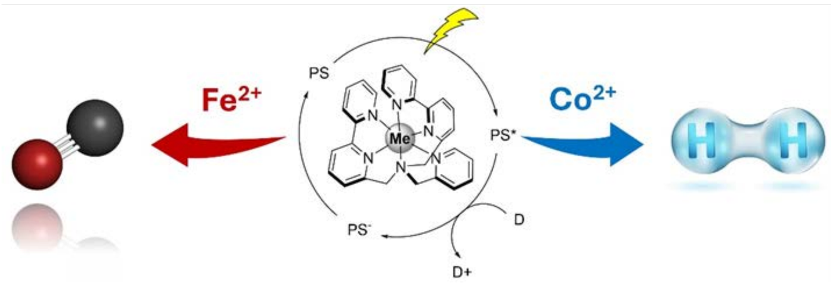
A Tale of Two Metals: Switching Selectivity Towards CO_2 Reduction in Heptacoordinate Complexes

Albert Ruggi,[1] Federico Droghetti,[2] Florian Lemken,[3] Mirco Natali,[2] Lubomír Rulíšek,[3]

[1]Département de Chimie, Université de Fribourg, Ch. du Musée 9, 1700 Fribourg, Switzerland
[2]Dipartimento di Scienze Chimiche, Farmaceutiche ed Agrarie, Università di Ferrara, 46, Via L. Borsari, Ferrara,Italy.
[3]Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo náměstí 2, Praha, Czech Republic.

albert.ruggi@unifr.ch

CO_2 reduction reaction (CO_2RR) is a crucial process for converting a well-known greenhouse gas into valuable fuels and chemicals, offering a sustainable approach to energy production and carbon utilization.[1] The photo- or electrochemical transformation of CO_2 into a singular carbon-based product still constitutes a significant challenge. In particular, protons and efficient catalysts are necessary to respectively decrease the thermodynamic and kinetic barrier, and these conditions often also trigger the competitive process of proton reduction to hydrogen.[2] We have recently found that a heptacoordinate Co(II) complex (known to efficiently produce hydrogen)[3] is also a competent catalyst for CO_2 reduction, albeit with low selectivity, since hydrogen remains the predominant product. Remarkably, we have observed that replacement of the Co(II) centre with Fe(II) induces a switch in selectivity towards CO_2 reduction (Scheme 1). The catalytic efficiency of this process can be further optimized upon variation of different parameters (i.e. strength of proton source, irradiation power, and nature of the sensitizer).[4] We have achieved unprecedent efficiencies (Φ_{CO} up to 36 %, TON_{CO} >1000) and selectivity (> 99%) in CO production by using a photochemical system sensitized by an organic dye in the presence of trifluoroethanol as proton donor.[5] In this presentation, we will detail our findings on parameter optimization and mechanistic insights that elucidate how these factors govern catalytic performance, offering a pathway to highly efficient and selective CO_2 conversion systems.



[1] S. C. Peter, *ACS Energy Lett.*, **2018**, *3*, 1557.
[2] E. Boutin, L. Merakeb, B. Ma, B. Boudy, M. Wang, J. Bonin, E. Anxolabéhère-Mallart, M. Robert, *Chem. Soc. Rev.* **2020**, *49*, 5772.
[3] F. Lucarini, M. Pastore, S. Vasylevskyi, M. Varisco, E. Solari, A. Crochet, K. M. Fromm, F. Zobi, A. Ruggi, *Chem. Eur. J.* **2017**, *23*, 6768.
[4] (a) F. Droghetti, A. Amati, F. Pascale, A. Crochet, M. Pastore, A. Ruggi, M. Natali, *ChemSusChem* **2023**, e202300737 (b) F. Droghetti, F. Lemken, L. Rulíšek, A. Ruggi, M. Natali, *ACS Catal.* **2024**, *14*, 16920.
[5] F. Droghetti, L. Villa, A. Sartorel, L. Dell'Amico, A. Ruggi, M. Natali, *ChemSusChem* **2025**, e202402627.

Understanding the photoinduced electron-transfer quenching of PDI radical anion

Estefania Sucre-Rosales[1], Daniel H. Cruz-Neto[1], Eric Vauthey[1]

Department of Physical Chemistry, University of Geneva, CH-1211 Geneva, Switzerland
estefania.sucrerosales@unige.ch

Due to its very high reducing potential, the lowest electronic excited state of the radical anion of the perylene diimide chromophore ($^{2}PDI^{\cdot -}$) has recently been proposed as an organic photocatalyst in the reduction of aryl halides such as 4-bromoacetophenone (4BAP). These reactions are reported to follow the so-called consecutive-photoinduced electron transfer mechanism (conPET), in which the successive absorption of two photons allows first the generation of the $^{2}PDI^{\cdot -}$ using a sacrificial electron donor, and second the population of the electronic excited state of $^{2}PDI^{\cdot -}$. However, this mechanism has been questioned by Ceroni1, who pointed out that, first, the very short excited state lifetime of $^{2}PDI^{\cdot -}$ (145 ps) precludes its diffusion-controlled quenching by the reaction substrate, and, second, the absorption of this radical anion at the wavelength used in the original report (425 nm) is negligible. These authors attributed the photocatalytic activity to an unidentified radical species resulting from the photodegradation of $^{2}PDI^{\cdot -}$. More recently, Schanze et al. studied the quenching of $^{2}PDI^{\cdot -}$ by aryl halides using transient absorption spectroscopy, and conclude that the quenching was entirely dynamic and diffusion-controlled. We will present our reinvestigation of the quenching dynamics of $^{2}PDI^{\cdot -}$ using transient electronic absorption spectroscopy in the visible and near IR regions. Our results show that, contrary to previous conclusions, static quenching is indeed operative, and becomes very efficient at high quencher concentration. However, the recombination of the ensuing quenching product is so fast that the proposed conPET mechanism is highly inefficient.

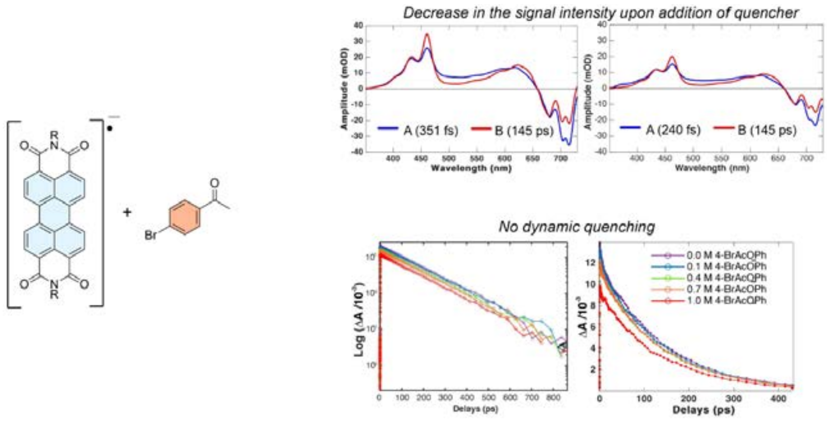


Figure. Left: PDI radical anion and 4-bromoacetophenone (4-BAP). Upper right: Evolution-associated difference spectra (EADS) of PDI with and without 4-BAP. Bottom right: Kinetic traces

[1] Marianna Marchini, Andrea Gualandi, Luca Mengozzi, Paola Franchi, Marco Lucarini, Pier Giorgio Cozzi, Vincenzo Balzani and Paola Ceroni, Phys. Chem. Chem. Phys., **2018**, 20, 8071-8076

From Excitons to long lived charges: Ultrafast charge carrier dynamics in PCE10:ITIC Bulk heterojunction Nanoparticles for photocatalysis.

Gopika Suresh[1], Maximillian M. Horn[1], Arthur E. Bouchez[2], Kevin Sivula[2], Natalie Banerji*[1]

[1]Department of chemistry, Biochemistry and Pharmacy, University of Bern, Bern CH-3012, Switzerland
[2]Laboratory for Molecular Engineering of Optoelectronic Nanomaterials, Institute of Chemical Sciences and Engineering, E cole Polytechnique Fédérale de Lausanne (EPFL), Lausanne CH-1015, Switzerland

gopika.suresh.unibe.ch

Photocatalytic hydrogen generation using donor–acceptor (D:A) bulk heterojunction(BHJ) nanoparticles has made significant progress in recent years. Here, In this work investigate the charge carrier dynamics of a high performing 3:7 blend of PCE10:ITIC nanoparticle[1,2] using a newly developed transient absorption spectroscopy setup that synchronizes two ultrafast laser sources to generate electronically controlled delays extending up to 100 µs, overcoming the limitations of conventional mechanical delay stages[3]. We observe efficient exciton-to-charge conversion in this nanoparticle dispersion and spin coated BHJ film and the presence of long-lived charge carriers in nanoparticle dispersion without a cocatalyst. Both dry films and nanoparticle dispersion exhibit comparable initial charge decay kinetics, but film dispersed in water shows initial rise component in the kinetics, which we attribute to confinement-induced recombination and influence of dielectric environment. These findings highlight the critical role of morphology and the dielectric environment in governing charge carrier dynamics and provide insights for optimizing BHJ photocatalysts.

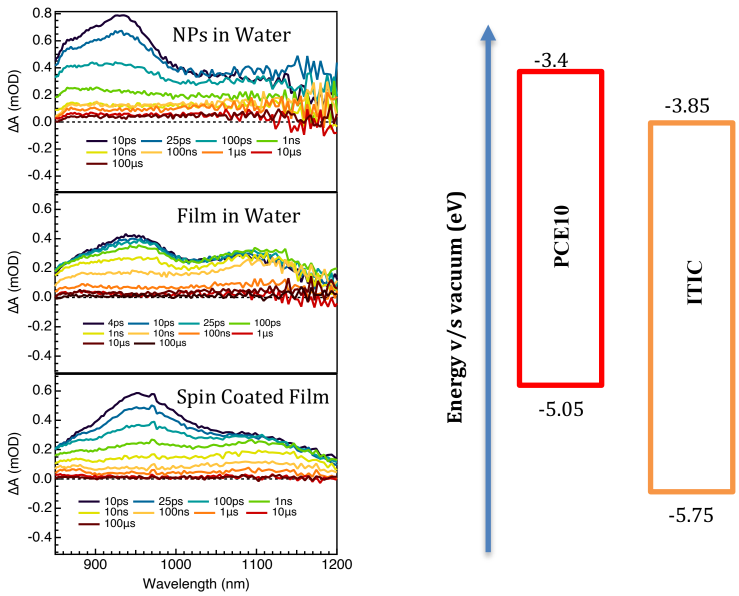


Fig : Transient absorption decay dynamics and Right: energy level alignment of PCE10 and ITIC.

1) Bouchez, Arthur E., et al. "Unexpected Pathway in Organic Semiconductor Nanoparticle Formation." *ACS nano* 19.31 (2025): 28469-28477

2)Firth, Connor R., et al. "A Halted Photodeposition Technique Controls Co-Catalyst Loading and Morphology on Organic Semiconductor Nanoparticles for Solar H2 Production." *Advanced Energy Materials* 15.38 (2025): 2403372

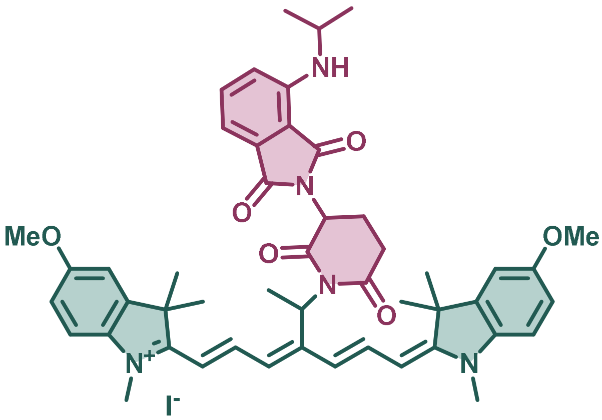
3)Antonucci, Laura, et al. "Asynchronous optical sampling with arbitrary detuning between laser repetition rates." *Optics Express* 20.16 (2012): 17928-17937.

Merging near-infrared photocages and PROTACs into molecular chameleons

Juliette Swit, Katarzyna Hanc, Lisa Jobst, Peter Štacko

Department of Chemistry, University, CH-8057 Zurich, Switzerland

Proteolysis-targeting Chimeras (PROTACs) are promising therapies for disabling disease-causing proteins. Their structure consists of two functionally different ligands and a linker.[1] The PROTAC acts as bridge between an E3-ligase and a target protein causing the protein to be tagged and subsequently recognized by the cellular proteasome to be degraded. Despite their many advantages such as high effectiveness against "undruggable proteins", they suffer from poor pharmacokinetic properties and off-target effects.[2] Recent studies revealed that PROTACs, depending on their combination of ligands and linker, can behave as molecular chameleons partially minimizing the poor pharmacokinetics.[3] In this project, we are developing a platform to control the behaviour and activity of PROTACS by photocages that respond to tissue-penetrating light.



[1] Cromm, P. M.; Crews, C. M. *Cell Chemical Biology* **2017**, *24* (9), 1181–1190.
[2] Cecchini, C.; Pannilunghi, S.; Tardy, S.; Scapozza, L. *Front. Chem.* **2021**, *9*, 672267.
[3] Garcia Jimenez, D.; Rossi Sebastiano, M.; Vallaro, M.; Ermondi, G.; Caron, G. *J. Med. Chem.* **2024**, *67* (13), 11421–11434.
[4] Russo, M.; Zielinska, D.; Hanc, K.; Ramundo, A.; Meier, D.; Szabo, A.; Štacko, P. *JACS Au* **2025**, *5* (6), 2632–2640.
[5] Russo, M.; Janeková, H.; Meier, D.; Generali, M.; Štacko, P. *J. Am. Chem. Soc.* **2024**, *146* (12), 8417–8424.

Light-Triggered Substrate Coordination as a New Mode of Photochemical Reactivity in First-Row Transition Metal Complexes

Simon Trippmacher, Oliver S. Wenger

University of Basel, Department of Chemistry, St. Johanns-Ring 19, 4056, Basel, Switzerland
simon.trippmacher@unibas.ch

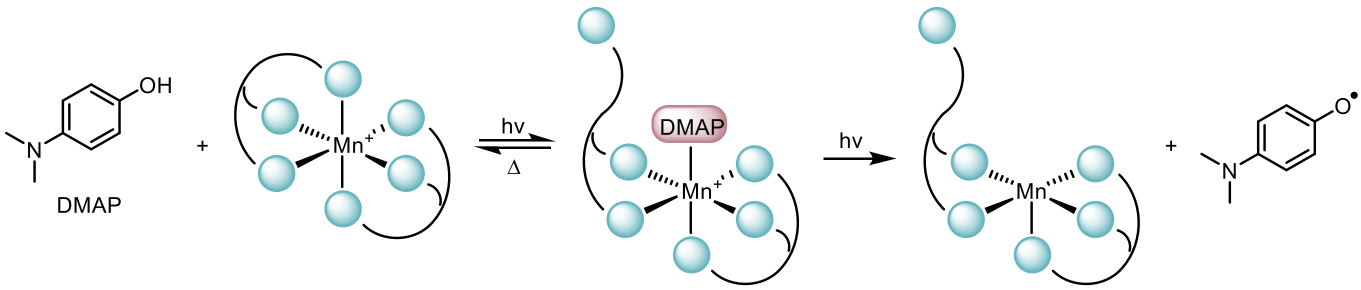


Figure 1 Mechanism of the reversible photoinduced ligand substitution and substrate activation. Light excitation leads to the substitution of one of the chelate arms by a substrate molecule (red). Upon reexcitation, the coordination bond to the substrate is homolytically cleaved, liberating the activated substrate in the form of an organic radical.

Light-induced bond homolysis is a common mode of substrate activation in which a coordination bond is cleaved upon photoexcitation. This reactivity is typically observed for highly oxidizing metal complexes such as Cu(II), Ni(III), Fe(III), Ce(IV), and Co(III).[1,2]

We present a manganese(I) complex that undergoes reversible light-triggered ligand substitution, as recently observed for a chromium(0) complex.[3] In our new manganese(I) complex, we further extend this concept to enable inner-sphere photoreactivity: Upon irradiation, one arm of the chelating ligand dissociates and *N,N*-4-dimethylaminophenol (DMAP) occupies the free coordination site. This newly formed species can be excited upon which the Mn-DMAP bond is homolytically cleaved, releasing an organic radical.

This proof-of-concept study demonstrates that a formally inert Mn(I) complex can be photoactivated to transiently generate an open coordination site, enabling substrate binding and subsequent light-induced substrate activation and radical formation.

Acknowledgements. This work has been supported by the Swiss National Science Foundation, project number 207329.

[1] F. Juliá, *ACS Catal.,* **2025**, *15*, 4665–4680.
[2] A. Marie May, J. L. Dempsey, *Chem. Sci.,* **2024**, *15*, 6661–6678.
[3] N. Sinha, J. Wellauer, T. Maisuradze, A. Prescimone, S. Kupfer, O. S. Wenger, *J. Am. Chem. Soc.,* **2024**, *146*, 10418–10431.

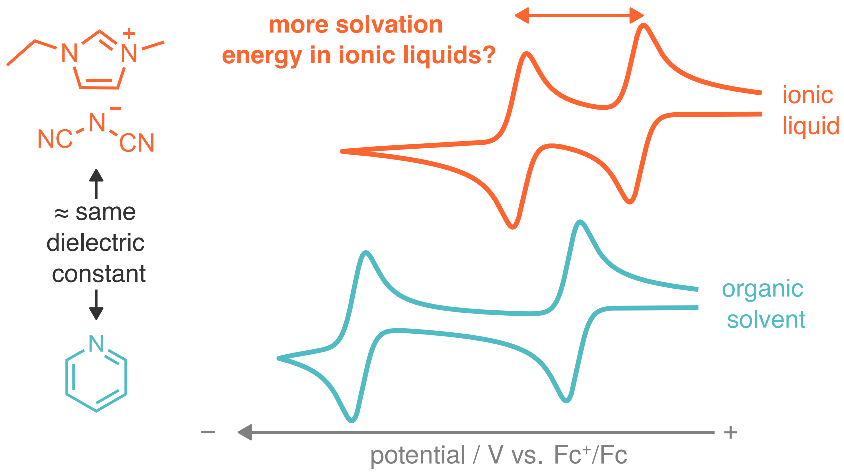
When Dielectric Constants Deceive: Interrogating Solvation in Ionic Liquids with Cyclic Voltammetry

Johannes Wega, Franck Guignard, Eric Vauthey

Department of Physical Chemistry, University of Geneva, Quai Ernest Ansermet 30, 1205 Geneva, Switzerland
Johannes.wega@unige.ch

Ionic liquids have emerged as an interesting alternative to conventional organic solvents in applications based on photoinduced electron transfer, such as photoredox catalysis or organic photovoltaics due to their unique physicochemical properties.[1,2] Based on their moderate static dielectric constants[3] on the order of ε_r = 8–15, one would expect ionic liquids to behave similarly to moderately polar solvents such as dichloromethane in photoinduced electron transfer.

Herein[4], we develop a framework to infer solvation energies from relative shifts of cyclic voltammetric waves of organic solute reduction measured in different media. Our results reveal that ionic liquids offer significantly increased ionic solvation energies compared to conventional solvents with the same static dielectric constant and effectively behave as highly polar solvents in electron transfer reactions. To explain the observed trends, we derive a modified Born equation that takes into account the effect of ionic strength. We show that the ionic solvation energy in low-polarity media can be increased to reach that of highly polar solvents at high ionic strengths because of charge-screening effects, thereby explaining the high solvation power of ionic liquids, since they are molten salts with molar ionic strengths. The results presented offer a framework to understand salt effects in photoinduced electron transfer reactions and pave the way for investigating salt-induced ion separation in moderately polar media.



[1] F. Endres, *Z. Phys. Chem.* **2004**, 218, 225-284.
[2] P. A. Forero-Cortés, M. Marx, N. G. Moustakas, F. Brunner, C. E. Housecroft, E. C. Constable, H. Junge, M. Beller, J. Strunk, *Green Chem*. **2020**, *22*, 4541-4549.
[3] H. Weingärtner, *Z. Phys. Chem.* **2006**, 220, 1395-1404.
[4] J. Wega, F. Guignard, E. Vauthey, *J. Phys. Chem. B* **2026**, 130, 2897-2907.

Proton Cranes: Switching Mechanism of Photoinduced Long-Range Intramolecular Proton Transfer

Lidia Zaharieva[1,2], Diana Rüesch[1], Søren W. Svenningsen[3], Fadhil Kamounah[3], Michael Pittelkow[3], Liudmil Antonov[2], Jan Helbing[1]

[1]Department of Chemistry, University of Zürich, CH-8057 Zürich, Switzerland
[2]Institute of Electronics, Bulgarian Academy of Sciences, BG-1784 Sofia, Bulgaria
[3]Department of Chemistry, University of Copenhagen, DK-2100 Copenhagen, Denmark
jan.helbing@chem.uzh.ch

Proton cranes are molecular systems in which intramolecular proton transfer (IPT) can occur over long distances upon photoexcitation [1,2]. Here, we investigate the switching mechanism of 8-(benzo[d]thiazol-2-yl)quinolin-7-ol (HQBT) using time-resolved vibrational spectroscopy supported by density functional theory calculations.

Upon photoexcitation of the enol tautomer (off-state), HQBT undergoes an ultrafast excited-state proton transfer from the stator unit to the rotor segment, forming a short-lived intermediate. Rotation of the side arm in the excited state then enables proton relocation across a larger molecular distance. Following relaxation to the ground state, the system adopts its keto form (on-state), thereby completing the switching cycle (Figure 1).

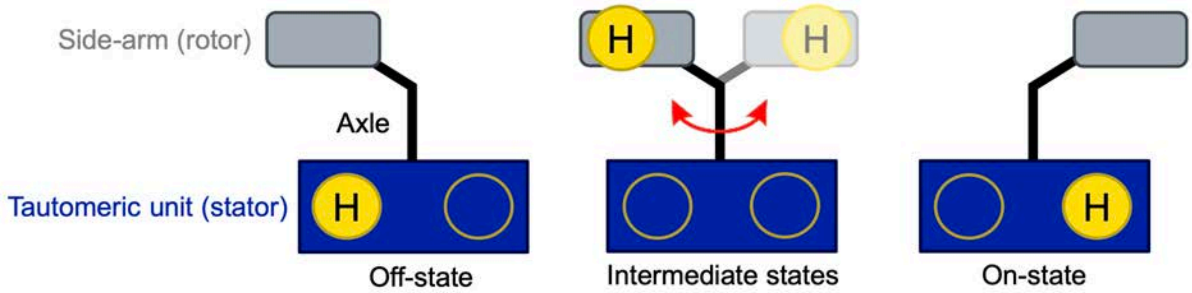


Figure 1: A sketch of the action of a molecular switch (proton crane), operating through IPT mechanism.

Spectroscopic observations and calculations indicate that the switched state consists of two interconverting keto forms. This metastable state gradually returns to the initial enol structure over several seconds at ambient conditions.

These findings provide insight into the design of conjugated proton cranes and strategies for tuning their energy landscape and dynamic response.

This research is carried out and financed within the framework of the second Swiss Contribution SCIEX.

[1] D. Nedeltcheva-Antonova, L. Antonov, *Wiley-VCH, Weinheim, Germany*, **2016**, 273–294.
[2] C. Rehhagen, M. A. Argüello Cordero, F. S. Kamounah, V. Deneva, I. Angelov, M. Krupp, S. W. Svenningsen, M. Pittelkow, S. Lochbrunner, L. Antonov, *J. Am. Chem. Soc.*, **2024**, 146(3), 2043–2053.