SPP 2102 Light controlled reactivity of metal complexes

Symposium

Photochemistry of Metal Complexes: Theory Meets Experiment

29th to 31st of March 2023 in Rostock, Institut für Physik, Albert-Einstein-Str. 24





Contact

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The talks take place in the lecture hall "Hörsaal 1" (HS I) of the "Physik-Lehrgebäude" (Phy. Lehre).

Hansestadt Rostock - Übersichtskarte



SPP Workshop Photochemistry of Metal Complexes: Theory Meets Experiment

29.-31. March 2023, Rostock

Program

Wednesday, 29 th March	
9:00 - 14:00	Arrival and Registration
10:30 - 12:30	Workshop on Mental Health
12:30 - 14:00	Lunch in the Mensa
14:00 - 14:45	Tutorial on Theoretical Spectroscopy, Oliver Kühn
14:55 - 15:00	Opening Katja Heinze, Oliver Kühn, Stefan Lochbrunner
15:00 - 15:45	Mátyás Pápai (Wigner Research Centre for Physics – Budapest): Simulation of Ultrafast Singlet-Triplet-Quintet Dynamics in Photoswitchable Fe(II) Complexes
15:45 - 16:15	Coffee Break
16:15 - 16:45	Jakob Steube (Paderborn)/ Olga Bokareva (Kassel): Janus-type emission from cyclometalated iron(III) complexes
16:45 - 17:15	Patrick Zobel (Wien): Excited-State Dynamics Simulations of Transition-Metal Complexes
17:15 - 17:45	Dieter Sorsche (Ulm): Red Light Absorption in Coordination Complexes via MLCT Stabilization
17:45 - 19:15	Poster Session with coffee, drinks, and finger food
Thursday, 30 th March	

- 9:00 9:45 Michael Odelius (University of Stockholm): Photodissociation of ironpentacarbonyl - $Fe(CO)_5$ - from initial bursts of CO release to branching pathways in solution
- 9:45 10:15 Frederik Scherz (Darmstadt)/ Manuel Pech (Stuttgart): Experimental and computational investigation of photolytic dinitrogen release from 1,1'- diazdioferrocene and related systems
- 10:15 10:45 Shruthi Santosh Nair (Jena): *Excited state dynamics and photobasic properties of Ironcarbene complexes*
- 10:45 11:15 Coffee Break
- 11:15 11:45 Henrik Junge (LIKAT Rostock): Iron carbonyl complexes: Suitable catalysts for photochemical reduction reactions and source of various (active) species
- 11:45 12:15 Manuel Oelschlegel (Göttingen): Exploiting the Disulfide/Thiol Switch in a Photosensitizer-Acceptor Dyad: Implications for Artificial Photosynthesis and Photoredox Catalysis
- 12:15 12:45 Lukas Mai (Erlangen)/ Corinna Heusel (Münster): Evaluation of Cyclometalated Ir(III) Complexes as Energy Transfer Catalysts
- 12:45 14:00 Lunch in the Mensa
- 14:00 15:30 Lab Tour
- 15:30 16:00 Coffee Break

- 16:00 16:30 Nikos Doltsinis (Münster): Cyclometalated complexes of d⁸-configured metal ions as efficient triplet emitters
- 16:30 17:00 Andreas Steffen (Dortmund): Designing Circularly Polarized Triplet Emission in the Near-IR
- 17:00 18:30 Poster Session II with coffee, drinks, and brezen
- 19:30 22:00 Dinner at the "Ratskeller"

Friday, 31th March

9:00 - 9:45	Stefan Haacke (University of Strasbourg): Ultrafast spectroscopy of NHC-coordinated Fe(II) complexes: How to distinguish ³ MLCT and ³ MC states?
9:45 - 10:15	Markus Bauer (Bonn): Ultrafast Formation of a Platinum(II) Metallonitrene. Evidence for an Exceptional Azide Diradical Precursor
10:15 - 10:45	Linda Zedler (Jena): Photophysical and light-induced multi-photon and multi-electron charge-accumulation properties of covalent Ferrocene-POM dyads
10:45 - 11:15	Coffee Break
11:15 - 11:45	Michael Seitz (Tübingen): C-H Vibrational Quenching in Chromium(III) Spin-Flip Emitters
11:45 - 12:15	Rose Jordan (Köln): Heavy ancillary ligands for enhanced triplet emission: worth their weight in platinum?
12:15 - 12:45	Stephen Hashmi (Heidelberg): Elementary Steps in Gold Photocatalysis
12:45 - 12:50	Closing Remarks
12:50 - 14:00	Lunch in the Mensa / Departure

Simulation of Ultrafast Singlet-Triplet-Quintet Dynamics in Photoswitchable Fe(II) Complexes

<u>Mátyás Pápai</u>

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Low spin (LS) \leftrightarrow high-spin (HS) photoswitchable transition metal complexes have a great potential as molecular data storage devices, both in terms of data density and writing speed. In order to design and optimize the performance of advanced materials, it is vital to gain a profound mechanistic understanding of the LS \leftrightarrow HS photoswitching process. Pump-probe experiments utilizing femtosecond optical and X-ray pulses have delivered invaluable mechanistic insights, however, interpretations are often controversial and consistency is still lacking. Herein, we demonstrate for photoswitchable Fe(II) complexes how dynamical excited-state simulations can be exploited to guide and complement ultrafast experiments. For the $[Fe(NCH)_6]^{2+}$ model complex, we develop and apply a synergistic methodology taking advantage of the complementary power of quantum wavepacket dynamics and trajectory surface hopping (TSH) [1,2]. We utilize an efficient hybrid approach based on the combination of time-dependent density functional theory (TD-DFT) potential energy surfaces and multiconfigurational second-order perturbation theory (CASPT2) spin-orbit couplings; crucially, this enables access to the entire single-triplet-quintet dynamics. Utilizing this methodology, we offer decision to the decade-long debate on Fe(II) polypyridines: we show that the quintet HS state (⁵MC) is populated on a sub-ps timescale via a sequential mechanism involving the two ${}^{3}MC$ components ${}^{3}T_{1g}$ and ${}^{3}T_{2g}$, non-exponential dynamics, and coherent Fe-N breathing oscillations [3] (Figure 1).



Figure 1. Excited-state relaxation dynamics of Fe(II) polypyridines: left – $[Fe(bipy)_3]^{2+}$, as extracted from time-resolved experiments [4]; right – $[Fe(terpy)_2]^{2+}$ simulated dynamics (full-D TSH).

References

[1] M. Pápai: Photoinduced Low-Spin \rightarrow High-Spin Mechanism of an Octahedral Fe(II) Complex Revealed by Synergistic Spin-Vibronic Dynamics, Inorg. Chem. 60, (2021), 13950–13954.

[2] M. Pápai: Toward Simulation of Fe(II) Low-Spin \rightarrow High-Spin Photoswitching by Synergistic Spin-Vibronic Dynamics, J. Chem. Theory Comput. 18, (2022), 1329–1339.

[3] T. Rozgonyi, G. Vankó, M. Pápai: Branching Mechanism of Photoswitching in Fe(II) Polypyridyl Complexes Explained by Full Singlet-Triplet-Quintet Dynamics, Commun. Chem. 6, (2023), 7.

[4] K. S. Kjær et al.: Finding Intersections between Electronic Excited State Potential Energy Surfaces with Simultaneous Ultrafast X-ray Scattering and Spectroscopy, Chem. Sci. 10. (2019), 5749–5760.

SPP Workshop Photochemistry of Metal Complexes: Theory Meets Experiment

Janus-type emission from cyclometalated iron(III) complexes

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Iron is a dream candidate to substitute noble metals in photoactive complexes, but realization of photoactive iron compounds is demanding, due to the fast deactivation of their charge transfer states.¹ A typical approach to overcome these processes is to incorporate strong donor ligands like *N*-heterocyclic carbenes (NHC). This resulted in the first charge-transfer based luminescent iron-complexes in the +III oxidation state.² Recently we reported on the impact of another strong donor class, cyclometalated ligands, on the ground and excited states of an iron complex.³

Combining these two donors with four NHCs and two cyclometalating units led to the Fe(III) complex [Fe(ImP^H)₂][PF₆] (HImP^H = 1,1'-(1,3phenylene)bis(3-methyl-1-imidazol-2ylidene), showing an unprecedented Janus-type dual emission from both ligand-to-metal (LMCT) and metal-toligand charge transfer (MLCT) states (Figure 1).⁴

With a lifetime of 4.6 ns, the strongly reducing and oxidizing MLCT state can initiate electron transfer reactions.



Figure 1. Janus-emission present in the [Fe(ImP^X)]⁺ complexes.

Substitution in the ligand backbone with electron-donating and -withdrawing groups shows tunability of the excited states, while maintaining the dual emission. Theoretical considerations employing (TD)DFT calculations help to gain a better understanding of this unprecedented phenomenon.

¹Wenger, O. S. Is Iron the New Ruthenium? *Chem. Eur. J.* **2019**, *25* (24), 6043–6052. DOI: 10.1002/chem.201806148.

²Chábera, P.; Lindh, L.; Rosemann, N. W.; Prakash, O.; Uhlig, J.; Yartsev, A.; Wärnmark, K.; Sundström, V.; Persson, P. Photofunctionality of iron(III) N-heterocyclic carbenes and related d5 transition metal complexes. *Coordination Chemistry Reviews* **2021**, *426*, 213517. DOI: 10.1016/j.ccr.2020.213517.

³Steube, J.; Burkhardt, L.; Päpcke, A.; Moll, J.; Zimmer, P.; Schoch, R.; Wölper, C.; Heinze, K.; Lochbrunner, S.; Bauer, M. Excited-State Kinetics of an Air-Stable Cyclometalated Iron(II) Complex. Chem. Eur. J. **2019**, 25 (51), 11826–11830. DOI: 10.1002/chem.201902488.

⁴Steube, J.; Kruse, A.; Bokareva, O. S.; Reuter, T.; Demeshko, S.; Schoch, R.; Argüello Cordero, M. A.; Krishna, A.; Hohloch, S.; Meyer, F.; Heinze, K.; Kühn, O.; Lochbrunner, S.; Bauer, M. Janus-type emission from a cyclometalated iron(III) complex. *Nat. Chem.* **2023.** DOI: 10.1038/s41557-023-01137-w.

SPP Workshop Photochemistry of Metal Complexes: Theory Meets Experiment

Excited-State Dynamics Simulations of Transition-Metal Complexes

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Excited-state dynamical processes of transition-metal-complexes are difficult to study both in theory and experiment due to their large number of vibrational degrees of freedom and many close-lying electronic states. The combination of trajectory surface hopping (SH) approach on electronic potentials parametrized in a linear vibronic coupling (LVC) model now opens the avenue for full-dimensional theoretical simulations of the excited-state dynamics of transition-metal complexes on a picosecond timescale.¹ This is exemplified in this talk by two applications.

First, we report the photorelaxation dynamics of the molecular ruby $[Cr(dpd)_2]^{3+}$, a near-infraredemitter.² After excitation into the higher-lying metal-centered ${}^{4}T_1$ electronic states, we follow the decay into the emissive low-lying doublet states ${}^{2}T_1$ and ${}^{2}E$ (see Figure 1a).³ This decay is accompanied by an elongation of the Cr-ligand bonds as well as a twisting of the trans-coordinated pyridine units of the ddpd ligands.

Second, we simulated the reverse intersystem crossing (rISC) in the thermally activated delayed fluorescence (TADF) of carbene-copper-amide emitter used in OLEDs.⁴ We find highly efficient rISC that happens not around the global minimum in the lowest-lying triplet state T_1 , where the two ligands assume a co-planar coordination geometry, but around a higher-lying local T_1 minimum of perpendicular coordination geometry.⁵ This efficient rISC becomes possible due to coupling with a higher-lying triplet state. After rISC, the emitter can return to a co-planar coordination geometry in the lowest-lying singlet state S_1 , where fluorescence is very efficient (see Figure 1b).



Figure 1: Excited-state dynamics mechanisms

- ¹ J. P. Zobel, M. Heindl, F. Plasser, S. Mai, L. González, Acc. Chem. Res. 54, 3760-3771 (2021)
- ² S. Otto, M. Grabolle, C. Förster, C. Kreitner, U. Resch-Genger, K. Heinze, Angew. Chem. Int. Ed. 54, 11572-11576 (2015)
- ³ J. P. Zobel, H. Radatz, L. González, Molecules 28, 1668 (2023)
- ⁴ S. Shi, M. C. Jung, C. Coburn, A. Tadle, D. Sylvinson M. R., P. I. Djurovich, S. R. Forrest, M. E. Thompson, J. Am. Chem. Soc. 141, 3576-3588 (2019)
- ⁵ J. P. Zobel A. Wernbacher, L. González, Angew. Chem. Int. Ed. e202217620 (2023)

Red Light Absorption in Coordination Complexes via MLCT Stabilization

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Figure 1. Exceptional MLCT red-shift as a consequence of extending the π -system in Re(CO)₃(1,3,10,12-tape)Cl.

Stabilization of ligand-reduced states by extension of an electron-accepting π^* -system is one of the key strategies to obtain long-lived metal-to-ligand charge-transfer (MLCT) states that compete efficiently with metal-centered states in transition metal chromophores.¹ Expanding the heteroaromatic system of 4,4'-bipyrimidine (**bpm**) *via* 4,4'-biquinazoline (**bqz**) to 1,3,10,12-tetraazaperylene (**1,3,10,12-tape**) leads to a stepwise lowering of LUMO energies as characterized by a stepwise anodic shift of the reduction potentials. This is accompanied by a systematic bathochromic shift of the MLCT absorption in the respective series of rhenium(I)-based model chromophores including a record red-shift for the **1,3,10,12-tape** complex. Non-radiative decay to the ground-state occurs on a sub-ns time-scale in these complexes in accordance with the energy gap law.³ Ongoing investigations hence focus on the use of π -extended heteroaromatic ligands to access long-lived MLCT states in the lighter Mn(I) homologues of the reported systems.

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- ² Meitinger, N.; Mandal, S.; Sorsche, D.; Pannwitz, A.; Rau, S. Red Light Absorption of [Rel(CO)3(α -Diimine)Cl] Complexes through Extension of the 4,4'-Bipyrimidine Ligand's π-System. Molecules, 2023, 28, 1905.
- ³ Baiano, J. A.; Kessler, R. J.; Lumpkin, R. S.; Munley, M. J.; Murphy, W. R., Jr. Nonradiative Decay in Rhenium(I) Monometallic Complexes of 2,3-Di(2-Pyridyl)Pyrazine and 2,3-Di(2-Pyridyl)Quinoxaline. The Journal of Physical Chemistry, 1995, 99, 17680–17690.

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Photodissociation of ironpentacarbonyl - Fe (CO)₅ - from initial bursts of

CO release to branching pathways in solution

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Excited state molecular dynamics simulations of the initial non-adiabatic transitions after photoexcitation of ironpentacarbonyl reveal an intricate ultra-fast dissociation process¹. The ultrafast nuclear dynamics and non-adiabatic transitions are analyzed in terms of the shapes potential energy surfaces and crossings between manifolds of states with different character. We conclude that the coupled electron-nuclear dynamics involving metal-to-ligand charge-transfer excitations and dissociative metal-centered excited states results in a gradual transition from coherent bond oscillatory motion to reoccurring bursts of carbonmonoxide release.



Figure 1. Surface hopping from oscillations in bound states results in bursts of carbonmonoxide¹.

These initial events set the stage for the sequential CO release in gas phase and complex path-ways in ethanol solution as previously observed experimentally in X-ray photoelectron spectroscopy (XPS)² and iron L-edge resonant inelastic X-ray scattering (RIXS)³. Theoretical simulations of gas phase XPS and solution RIXS spectra based on multi-configurational quantum chemistry allow for kinetic modeling of the processes on different time-scales. The impact and challenges for explicit dynamical modelling of time-resolved X-ray spectra of these and related systems are discussed.

- ¹ A. Banerjee, M. R. Coates, M. Kowalewski, H. Wikmark, R. M. Jay, P. Wernet, M. Odelius, Nat. Commun. 13 1337 (2022).
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³ P. Wernet, K. Kunnus, I. Josefsson, I. Rajkovic, W. Quevedo, M. Beye, S. Schreck, S. Grübel, M. Scholz, D. Nordlund, W. Zhang, R. W. Hartsock, W. F. Schlotter, J. J. Turner, B. Kennedy, F. Hennies, F. M. F. de Groot, K. J. Gaffney, S. Techert, M. Odelius, A. Föhlisch, Nature 520 78–81 (2015).

Experimental and computational investigation of photolytic dinitrogen release from 1,1'diazdioferrocene and related systems

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Irradiation of 1,1'-diazidoferrocene (λ = 266 nm) leads to the release of dinitrogen from an azide moiety. While it is known that the related 1-azidoferrocene can undergo thermal decomposition to yield a ferrocenyl nitrene,¹ the photolytic process has only recently been studied with femtosecond ultraviolet-pump/mid-infrared-probe (UV/MIR) spectroscopy.² In combination with quantum chemical calculations, the photochemical processes leading to the generation of a 1-azido-1'-nitrenoferrocene species can be resolved.



Figure 1. Gibbs free energy profile in kJ/mol for the proposed photolytic N₂ dissociation pathway with DFT (D4-PBE0/def2-TZVP// D4-PBE/def2-TZVP) computed structures and spin densities.

Computations suggest that the decay of a spin-orbit coupled excited state leads to a triplet intermediate with a bent azide moiety, which is pre-organized for dinitrogen release. A transition state with a low activation barrier of $\Delta G_a = 15.1$ kJ/mol leads to release of dinitrogen to form the triplet 1-azido-1'-nitrenoferrocene photoproduct. As a continuation of this project, we have now synthesized a new ferrocene containing compound that has both an azido and a [Re(CO)₃] functionality. As both these components are photoactive and photolabile, we are currently investigating aspects such as selective bond activation, dependence of the photoactivation at one site on the other, and dependence of photoactivation wavelength on product formation through both experimental and computational methods.

¹ C. Steel, M. Rosenblum, and A. S. Geyh, *Int. J. Chem. Kinet.* 1994, **26**, 631-641.

² manuscript in preparation

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Excited state dynamics and photobasic properties of Iron-carbene complexes

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Proton transfer reactions represent one of the most fundamental processes in chemical reactions and living systems. Photo-induced proton transfer processes are unique and powerful in terms of their ability to manipulate reactions through efficient spatio-temporal control. One way to accomplish this is by using photoacids/photobases which in their excited states have a large variation of pKa when compared to their respective ground states.

Combining these photobasic systems with photoactive metal complexes enables to utilise the excellent optical properties of the latter expanding the potential of the whole system. Earlier studies have explored Ru and Ir based photobasic systems.^{1,2} In the last decade, both the photophysical properties of long-lived iron-NHC complexes³ as well as the photobasic properties of quinolines² have become the subject of many studies. Here we study the excited state and proton transfer properties of a novel photobasic quinoline substituted iron-carbene complex using steady-state and fs-transient absorption.

Understanding the dynamics of excited state proton transfer involves careful consideration of the electronic properties which are influenced by interaction between the donor and acceptor molecules and the surrounding solvent environment. We aim to characterize the influence of the iron center on the proton transfer properties of the quinoline in dependence of different solvents and in the presence of salt ions. We find that both the nature of the solvent as well as its microstructure surrounding the photobase have an influence on the excited state lifetimes of the complex as well as on its proton transfer abilities. In addition, we see indications of an energy transfer from the excited quinoline to the MLCT states.

- ¹ R. M. O'Donnell, R. N. Sampaio, G. Li, P. G. Johansson, C. L. Ward, G. J. Meyer, J. Am. Chem. Soc. 2016, 138, 11, 3891–3903
- ² I. Demianets, J. R. Hunt, J. M. Dawlaty, and T. J. Williams, Organometallics 2019, 38, 200-204
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Iron carbonyl complexes: Suitable catalysts for photochemical reduction reactions and source of various (active) species.

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Light might have a significant influence on the catalyst performance in chemical reactions. In this respect, photocatalytic proton and carbon dioxide reduction reactions are attractive due to its combination of renewable solar energy conversion and storage. Currently applied systems are either based on homogeneous or on heterogeneous materials, which possess a light harvesting and a catalytic subunit. In the presentation case studies of homogeneously catalysed proton¹ and CO_2^2 photoreduction with special emphasis on iron-based systems applying simple iron carbonyl sources will be discussed. Iridium as well as copper photosensitizers were applied, the latter resulting in a noble metal-free system.



Figure 1. Catalytic cycle for photocatalytic proton reduction applying an iridium photosensitizer and an iron carbonyl catalyst.¹

Investigating the reaction pathways by photoluminescence-, EPR-, Raman-, FTIR- and massspectroscopy, as well as time dependent DFT-calculations revealed the generation of a diversity of iron species possessing either activity for proton or carbon dioxide reduction or constituting deactivation pathways. Finally, it is demonstrated that iron carbonyl complexes can also be used for the synthesis of artificial metalloenzymes.³ Advantageously, appropriate enzymes combine CO₂ binding pockets and redox-active centres in close proximity. In the future this knowledge will set the basis to design photo(electro)chemical devices with tailored electron transfer cascades and without the need of sacrificial agents.

- ¹ H. Junge, N. Rockstroh, S. Fischer, A. Brückner, R. Ludwig, S. Lochbrunner, O. Kühn, M. Beller, *Inorganics* **2017**, *5*, 14.
- ² a) P. G. Alsabeh, A. Rosas-Hernández, E. Barsch, H. Junge, R. Ludwig, M. Beller, *Catal. Sci. Technol.* 2016, *6*, 3623 ; b) A. Rosas-Hernández, C. Steinlechner, H. Junge, M. Beller, *Green Chem.* 2017, *19*, 2356.
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Exploiting the Disulfide/Thiol Switch in a Photosensitizer-Acceptor Dyad: Implications for Artificial Photosynthesis and Photoredox Catalysis

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Since the sun is the primary source of energy on earth, the use of solar energy for the production of sustainable fuels is of pivotal importance for our society. Recently, light-driven proton-coupled electron-transfer (PCET) processes received great attention because they are key to innovative approaches for solar-to-fuel transformations, such as photocatalytic dihydrogen formation.¹

The ensemble of a transition-metal photosensitizer and a redox-active ligand is commonly used to combine light harvesting and charge accumulation in one molecular system. Most research in molecular systems is based on ruthenium bipyridine complexes with (di-)imine redox switches,² however, there is very little understanding of disulfide/dithiol-based redox switches attached to transition-metal photosensitizers as charge relay.³⁻⁵ Herein, we present a new rhenium photosensitizer decorated with a disulfide moiety, which is capable of storing two electrons and one proton in a light reaction, and release these in the form of H atom transfer (HAT) in a dark reaction. The complex is then employed as combined proof-of-concept photoredox- and HAT catalyst in the anti-Markovkinov-selective hydrofunctionalization of unactivated alkenes. The use of disulfides provides a promising alternative in molecular artificial photosynthetic systems, as the reduction step uses the provided driving force efficiently through potential inversion. Furthermore, efficient discharge is not only limited to HAT, but may also proceed via hydride transfer.



Figure 1. Reactivity scheme of the dyad based on a disulphide/thiol switch.

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² D. Polyansky, D. Cabelli, J. T. Muckerman, E. Fujita, T. Koizumi, T. Fukushima, T. Wada, K. Tanaka, *Angew. Chem.* **2007**, *46*, 4169–4172.

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5) J. Nomrowski, O. S. Wenger, J. Am. Chem. Soc. 2018, 140, 5343-5346.

Evaluation of Cyclometalated Ir(III) Complexes as Energy Transfer Catalysts

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Energy transfer catalysis is a powerful tool in organic synthesis, since it enables the use of mild and sustainable reaction conditions.^[1] To expand its applicability to further important substrate classes with triplet energies in the range of 70 kcal/mol, novel photosensitizers possessing higher triplet energies are highly desirable.

To evaluate the influence of ligands on the catalytic activity, triplet energy and solubility, a library of cyclometalated Ir-complexes with potential applications in energy transfer catalysis was created. The intramolecular dearomatization of benzothiophenes (challenging for energy transfer catalysis using visible light) and benzofurans (so far not possible using photocatalytic conditions) were chosen as model systems for the investigations.





Figure 1. Evaluation of three Ir-complex classes for the application in energy transfer processes such as the [2+2]-cycloaddition of benzothiophene or benzofurans.

Besides the well-established catalyst classes $[Ir(ppy)_2(bpy)]^{+[2]}$ and *fac*- $[Ir(ppy)_3]$,^[3] a third generation of the type *fac*- $[Ir(pmbi)_3]^{[4]}$ was evaluated for triplet energy transfer catalysis on the challenging model reactions. The last-mentioned complex class showed triplet energies of >75 kcal/mol and an increased catalytic activity in the model reactions. In contrast to the first two complex classes, even the benzofuran showed reactivity in this case.

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Cyclometalated complexes of d⁸-configured metal ions as efficient triplet emitters

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Two isoleptic bis-cyclometalated Pt(II) and Pd(II) complexes, namely [PtL] and [PdL] (see Fig. 1), bearing a tailored dianionic tetradentate ligand L²⁻ have been investigated¹. While [PtL] shows luminescence from metal-perturbed ligand-centered or from metal-metal-to-ligand charge-transfer triplet states in diluted solutions, in frozen glasses and in crystals, with high photoluminescence quantum yields and long lifetimes in the microsecond range even at RT, [PdL] surprisingly emits luminescence from aggregated species in concentrated fluid solutions, but decays predominantly nonradiatively in diluted solutions. We demonstrate that the radiationless deactivation can be suppressed in frozen glassy matrices at 77 K.



Figure 1. Emission spectra of [PtL] and [PdL] crystals.

A similar behaviour was observed for Pd(II) complexes with tridentate C^N^N aryl-pyridine-(benzo)thiazole ligands². High photoluminescence quantum yields of up to 0.79 were recorded in frozen glassy solvent matrices at 77 K along with emission bands showing pronounced vibrational progressions and peaking at about 520 nm. No photoluminescence was observed at 298 K in solution. Variation of the C^N^N ligand allowed to shift the experimental absorption energies from about 2.4 to 2.7 eV.

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SPP Workshop Photochemistry of Metal Complexes: Theory Meets Experiment

Designing Circularly Polarized Triplet Emission in the Near-IR

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Emitter materials that can exploit triplet excitons in the near-IR are of interest due to their potential application in bioimaging, device technologies and encryption schemes.¹ One of the biggest challenges for the design of suitable metal complexes for these purposes is the enhanced non-radiative decay of low energy states due to the energy gap law. In this presentation we will show our efforts in improving the relative radiative (k_r) and non-radiative (k_{nr}) rate constants to increase the quantum yields ϕ for emission beyond 600 nm. Specifically, we have invented paracyclophane based carbene ligands as π -chromophore ligands, which lead to k_r up to $2 \cdot 10^6$ s⁻¹ and $\phi = 0.8$ for deep red to near-IR emission due to efficient thermally activated delayed fluorescence (TADF) from copper(I) complexes (Fig. 1).² Another approach is the optimization of combining spin-orbit coupling (SOC) mediating metal centers and chromophore ligands. Currently, we are following a DFT guided strategy to investigate Pd(II) and Pt(II) compounds with carbene ligands as promising ultrafast near-IR emitters.³ Bearing in mind that many IT relevant applications require circularly polarized emission (CPL),⁴ the combination of this property with near-IR emission would be ideal. Thus, we are implementing chirality in the ligand scaffold of the Pd/Pt complexes by employing various paracyclophane motifs.⁵



Figure 1. Copper(I) complexes showing mechanochromic deep red to near-IR TADF properties.

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Ultrafast spectroscopy of NHC-coordinated Fe(II) complexes: How to distinguish ³MLCT and ³MC states ?

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Over the past ten years, the development of metalorganic photosensitizers based on earth-abundant first-raw transition metals has received increasing attention in the scientific community [1]. But, due to the inherently low ligand field splitting, as for instance in iron(II) complexes, low-lying metal-centered (MC) states lead to an ultrafast deactivation of the functionally important MLCT states. However, recent advances in the coordination chemistry of Fe(II) with N-heterocyclic carbene (NHC) ligands [2], made applications in solar energy conversion[3] or photocatalysis[4] possible, with relatively low conversion efficiencies though.

While the ligand field splitting explains the energetic order of MLCT and MC states for the ground state Fe-ligand geometry, many examples from ultrafast spectroscopy show that the excited state structural relaxation, e.g. lengthening of the Fe-L bond, changes this order leading to a preferential stabilization of MC states. Therefore, the structural rigidity of the complexes is a second parameter to be optimized for extended MLCT lifetimes [5]. In some cases, it was shown that both ³MC and ³MLCT states are populated on a sub-100 fs time scale directly from the ¹MLCT state, with the portion of ³MC states being a fundamental loss channel for any photo-sensitizer applications [6]. Ultrafast spectroscopy is facing here the challenge of spectroscopically differentiating the two kind of triplets states. We will show in this talk that ultrafast vibrational spectroscopy may do the job [7].

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Ultrafast Formation of a Platinum(II) Metallonitrene. Evidence for an Exceptional Azide Diradical Precursor.

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Transition metal nitrides/nitrenes are highly promising reagents for catalytic nitrogen atom transfer reactivity. They are typically prepared *in situ* upon optical irradiation of azido precursors. A full exploitation of their catalytic potential, however, requires an in-depth knowledge of the primary photo-induced processes and the structural/electronic factors that mediate the dinitrogen loss and the birth of the terminal metal-nitrogen core. Using femtosecond infrared-spectroscopy, we elucidated here the primary molecular-level mechanisms responsible for the formation of the unique platinum(II) nitrene, Pt(PNP)(N) with PNP = bis[2-(di-tbutylphosphino)ethyl]amide, having triplet ground state from the platinum(II) azide precursor, Pt(PNP)(N₃) (1), having a singlet ground-state. The spectroscopic data in combination with quantum-chemical calculations provide compelling evidence that product formation requires the initial occupation of an exceptional parent singlet excited state that features an azide diradical anion ligand coupled to a low-spin d⁸-configured Pt(II)-center. A subsequent azide-centered intersystem-crossing generates the Pt-bound triplet azide diradical which smoothly evolves into the triplet nitrene via N₂–loss in a near barrierless adiabatic dissociation.



Figure 1. Transient absorption spectra of complex 1 in liquid THF solution at room temperature

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Photophysical and light-induced multi-photon and multi-electron charge-accumulation properties of covalent Ferrocene-POM dyads

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Artificial systems for solar energy conversion often involve multi-photon and multi-electron steps, which require the accumulation of multiple reduction or oxidation species to promote the desired transformation. Developing polyoxometallate (POM)-based artificial systems for solar fuels generation is a promising approach since the molecular metal oxide clusters are characterized by unique electron storage and electron transfer properties.¹ POMs can be covalently functionalized with light-absorbing metal complexes like ferrocence as well as proton/electron donors, forming dyads and triads with tuneable (photo)redox-properties to control light-absorption and charge transfer properties to the POM (Figure 1). The research focuses on the investigation of this novel class of substances with respect to their light-induced multi-electron and multi-proton processes and to iteratively optimize them synthetically. To do so, we use spectroscopic tools such as time-resolved spectroscopy and spectroelectrochemistry to rationalize the light-induced formation and properties of charge separated states during multiple electron transfer from the peripheral groups to the POM.²



Figure 1. Schematic and molecular structure of Ferrocene-POM dyads and processes studied using spectroelectrochemical methods.

Time-resolved photophysical studies highlight that irradiation into the ferrocene absorption band (400 nm) results in a fast electron transfer from the ferrocene to the POM, resulting in an oxidized ferrocenium-cation as well as a reduced POM (featuring a characteristic intervalence charge-transfer (IVTC) transition of the tungsten cluster in the Vis-NIR range). To probe the individual charge-transfer steps of the POM the charge separated state was mimicked by electrochemical methods and its structure was probed by UV-Vis and rR spectroelectrochemistry.² The observed spectral changes upon reduction of the POM show that multiple charges are delocalized across multiple metal centres.

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C-H Vibrational Quenching in Chromium(III) Spin-Flip Emitters

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Chromium(III) luminescence has experienced a successful revival over the last years, especially with the development of spin-flip emitters such as $[Cr(ddpd)_2]^{3+}$ (Figure 1, left).¹ After its initial discovery² it could also be shown that the ${}^{2}E_{g}/{}^{2}T_{1g}$ emission efficiency could be substantially improved by perdeuteration of the ddpd ligand enabling quantum yields of up to 30% in deoxygenated solution at room temperature (Figure 1, right).³ While the aggregate effect of isotopic substitution of multiple C-D for C-H oscillators is quite straightforward to measure empirically, the intricacies of this vibrational quenching on the level of an individual oscillator is still not well understood.⁴ This talk will present a comprehensive experimental and theoretical analysis of this phenomenon, e.g. the measurement of vibrational properties of individual C-H oscillators in isotopomeric complexes [Cr(ddpd)₂]³⁺ as well as their effect on non-radiative deactivation of chromium-centered ${}^{2}E_{g}/{}^{2}T_{1g}$ states. In addition, the step-scan FTIR spectra of specific isotopomers also reveal interesting dynamics in the excited state landscape.



Figure 1. Left: Selectively deuterated complexes $[D_x]$ - $[Cr(ddpd)_2]^{3+}$; Right: Differences in vibrational quenching of chromium 2E_g emission by C-H vs. C-D oscillators.

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Heavy ancillary ligands for enhanced triplet emission: worth their weight in platinum?

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On our way towards efficient triplet emitters based on Ni(II), we are exploring the concept of introducing additional heavy elements into a complex to enhance its emission properties through the heavy atom effect.¹ Using the double cyclometalated Pt(II) complexes [Pt(C^N^C)PnPh₃] (C^N^C = 2,6-bis(2'-phenidyl)pyridine or dibenzoacridine, Pn = P, As, Sb) as a model system, we aim to understand in detail how the heavy ancillary ligands influence the complexes' photophysics. Steady-state absorption and emission spectroscopy, electrochemistry, DFT calculations and ultrafast transient absorption spectroscopy allowed for insight into the intricate interplay of the heavy atom effect, vibronic factors and electronic differences between both the C^N^C and PnPh₃ ligands contributing to the observed trends along the two series of complexes (Figure 1). The results of these in-depth studies suggest that while the mechanisms leading to the enhancement of triplet emission in the SbPh₃ containing compounds are more complex than initially postulated, our design principle has proven successful and can likely be applied for example to the Ni and Pd congeners of the herein studied complexes.²



Figure 1. Emission spectra of the complexes [Pt(dba)PnPh₃] (top), transient absorption spectra and decay associated spectra of [Pt(dba)SbPh₃] (bottom, λ_{exc} = 340 nm).

¹ S. C. Gangadharappa, I. Maisuls, D. A. Schwab, J. Kösters, N. L. Doltsinis, C. A. Strassert, J. Am. Chem. Soc. **2020**, 142, 21353–21367.

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Elementary Steps in Gold Photocatalysis

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Over the last decade gold-mediated photocatalysis has become a useful tool enabling unique transformations, while the dinuclear complex $[Au_2(\mu-dppm)_2]Cl_2$ and its derivatives have been thoroughly studied when exposed to UVA light,¹ mechanistic insights under irradiation with longer wavelengths remain yet elusive. From recent studies, three possible reaction paths can be formulated. In 2015, the Hashmi group reported a highly efficient alkynylation of tertiary amines using sunlight.² Therein, mechanistic experiments hinted at the formation of an "alkynyl radical" which was traced back to a single-electron transfer (SET; Path B) induced by the excited photocatalyst. In 2020, $[Au_2(\mu-dppm)_2]Cl_2$ was utilized in a direct synthesis of *gem*-diboronates from aryliodides under irradiation with blue LEDs.³ An Energy Transfer (EnT) mechanism was postulated to be responsible for the radical initiation (Path A). Our recent NMR as well as UV/VIS experiments point to the formation of a new gold complex in an oxidative addition (Path C). Irradiation of the observed intermediate with the addition of a nucleophile leads to the formation of the respective product and the recovery of the catalyst. Aiming at the formulation of a generally applicable theory for the three mechanisms, various computational as well as experimental studies were conducted including UV/Vis measurements, NMR spectroscopy and more.



Figure 1. Proposed theories for the gold-mediated activation mechanism of iodinated substrates with blue light based on experimental and computational methodologies.

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Poster

The posters should be displayed in the foyer during the whole symposium. Please be at your poster during the poster session on Wednesday (even numbers) or Thursday (odd numbers).

Optimally-tuned long-range corrected density functional for modeling excited states of photoactive iron complexes

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Iron complexes represent an attractive alternative to noble metal based photocatalysts as they are more abundant and economically feasible. However, the application of such complexes is rather limited due to the fast deactivation of metal-to-ligand charge-transfer (MLCT) states via metalcentered (MC) ones to the ground state. This relaxation destroys the initial charge separation in MLCT states desirable for further redox reactions. Thus, the search for novel complexes with longlived MLCT states and strategies concerning their rational design are highly warrant. To this end, the assistance of theory is required to rationalize the properties of excited states of transition-metal complexes.

In this work, we have applied optimally-tuned long-range corrected density functional theory for the modeling of ground- and excited state properties of various iron (III) complexes. The choice of the main theoretical approach in the current study is dictated by an objective to describe accurately metal-to-ligand charge-transfer (MLCT) states which are of crucial importance for creating long-living excited states involved in further photocatalytic reactions. Optimal tuning of range-separated functionals is a non-empirical way of modifying the exchange-correlation kernel such that the fundamental properties of exact functional are recovered. We discuss various tuning strategies based on the comparison with experimental spectra and multireference CASPT2 results [1, 2]. The character of singlet and triplet excited states and their energetic positions are shown to be very sensitive to the applied computational scheme. The elaborated computational protocol was used to assign absorption spectra, electrochemical measurements, including experiments with extended ligand systems, as well as the analysis of peculiarities of potential energy surfaces in excited electronic states.¹⁻⁵ Ongoing studies encompasses derivatives of a Janus-type complex⁴, as well as further compounds with chromophore ligands introduced to improve photocatalytic properties.^{1,3}

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NHC ligands represent very strong σ -donors, which can form metal complexes with unique properties. A lot of studies have focused on imidazole- and benzimidazole-based structures. There are, however, also naturally occurring NHC-type building blocks available, such as caffeine. The limited work performed on this natural product has been focused on monodentate complexes¹ and the remarkable antitumor and antibacterial properties of the complexes has mainly been ascribed to the health benefits of the organic ligand. We have applied the established route to prepare tridentate ligands to assemble a ligand framework featuring two caffeine moieties, as designated NCH-type binding sites. The ligand has been used to prepare Pt(II) and Pd(II) complexes.²



Figure 1. Absorption (left) and emission (right) spectra of the platinum complexes in acetonitrile.

While the Pd(II) complex is catalytically active in various cross-coupling reactions, the Pt(II) complexes with alkyne ligands possess photophysical properties similar to other known compounds. There is very little research regarding the caffeine as the NHC ligands for these types of complexes. Due to the bioavailability this approach might be beneficial as the educts are renewable and the decomposition products are harmless.

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Ultrafast UV-Vis Spectroscopy on the Reservoir-Effect of Fe^{II} Photosensitizers with Linked Organic Chromophores

<u>Miguel A. Argüello Cordero</u>,^a Ayla Kruse,^a Moritz Lang,^a Philipp Dierks,^b Olga Bokareva,^a Matthias Bauer,^b Katja Heinze,^c Oliver Kühn^a and Stefan Lochbrunner^a

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Transition metal complexes were investigated in the last years with respect to their light-harvesting properties and their possible application in chemical utilization of solar energy. Most of these photosensitizers (PS) are based on non-abundant metals like Ru and Ir, since they have long-lived triplet metal-to-ligand charge transfer (³MLCT) states that are essential for performing the intended chemical reactions. The substitution of the metal-centre by a more-abundant metal like Fe(II) was targeted in several investigations during the last years.^[1] The extension of the ³MLCT lifetime turned out to be the main challenge in the design of those alternative PSs. Some successes were achieved by designing a series of tridendate N-heterocyclic-carbene ligands that, bound to the Fe(II)-centre, exhibit combined σ -donor and π -acceptor properties.^[2] In these studies, ³MLCT lifetimes increasing from 0.15 to 528 ps were obtained. Another successful concept, that was observed for precious-metal-based PS, is the extension of the ligand(s) with a second chromophoric unit.^[3] This modification allows for a new feature in the excited-state relaxation of the PSs involving the local triplet state of the chromophoric unit (³Chrom). If the energies match, a population-equilibrium between the ³MLCT and the ³Chrom state can emerge in which most of the excited-state population is in the ³Chrom state. This so-called reservoir-effect yields clearly enlarged ³MLCT lifetimes for those PSs. In the current work we present the spectroscopic investigation of an Fe(II)-based PS that combines both introduced approaches for the first time and exhibits a resulting exited-state lifetime of 3.7 ns.



Figure 1. Molecular structure of the investigated Fe(II) PS with its linked chromophore (red) and the results of ultrafast transient absorption spectroscopy on the PS. For details see text.

Ultrafast transient-absorption spectroscopy was performed on the shown Fe(II)-based PS dissolved in acetonitrile (Fig. 1). A global lifetime analysis revealed three exponential decay components. Their amplitude spectra are given in the right panel of Fig. 1. The fastest component with a time constant of 2 ps reflects vibrational relaxation of excess-energy in the molecule. The decay time of 23 ps is assigned to the ³MLCT lifetime due to the strong amplitude in the bleach region. The time constant of 3.7 ns corresponds to the lifetime of the ³Chrom state on the chromophore unit. The latter is deactivated by repopulation of the ³MLCT state which decays then quickly into the ground state.

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Pressure dependent phosphorescence of [Cr(ddpd)2]³⁺ complexes

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Periodic density functional theory (DFT) calculations have been performed of crystalline $[Cr(ddpd)_2][BF_4]_3 \times 3CH_3CN$ (see Fig. 1) at different external pressures from 1.0 kbar to 84.0 kbar. While the monoclinic crystal system is essentially preserved, the lattice constants a, b, and c decrease by 7.5%, 9.5% and 10.9%, respectively, corresponding to a nearly isotropic compression. Experimentally, pronounced pressure-induced shifts of -7.7 and -14.1 cm⁻¹ kbar⁻¹ have been observed in the ${}^{2}E \rightarrow {}^{4}A_{2}$ and ${}^{2}T_{1} \rightarrow {}^{4}A_{2}$ spin-flip emission bands (octahedral symmetry notation)¹. DFT calculations of the isolated [Cr(ddpd)2]³⁺ complex extracted from the unit cell yield a shift of -10.2 cm⁻¹ kbar⁻¹ for the ${}^{2}T_{1} \rightarrow {}^{4}A_{2}$ emission. This is in fair agreement with experiment despite neglecting structural relaxation in the excited state.



Figure 1. DFT-optimized unit cell of [Cr(ddpd)₂][BF₄]₃×3CH₃CN at 1 kbar.

In addition, [Cr(ddpd)2]³⁺ has been studied in aqueous solution by performing classical MM simulations in the NPT ensemble to achieve the necessary configurational sampling. An accurate force field is being developed based on ab initio reference data using a recently proposed on-the-fly population swapping genetic algorithm technique^{2,3}.

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Multiconfigurational approaches to investigate electronic structure of open-shell transition metal complexes

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Transition metal complexes provide us with rich photochemistry that can be leveraged in different applications, such as catalysis, materials synthesis, solar energy conversion, and medicine. In this work, we theoretically investigate iron(III) and vanadium(II) complexes, see Fig.1. Iron(III) complexes with NHC donor groups feature long-lived charge transfer states with nanosecond lifetimes, making them good candidates as photosensitizers¹. Vanadium complexes are attractive as potential novel near-infrared (NIR) luminophores². However, their photoinduced processes have not been fully studied with atomistic detail due to their complicated electronic structure.



Figure 1. $[Fe(ImP)_2]^+$ and $[V(ddpd)_2]^{2+}$

Both complexes possess open-shell ground states: a spatially degenerate doublet ground state from a d⁵ configuration at the iron(III) center and a non-degenerate quartet ground state from a d³ configuration at the vanadium(II) center. Such open-shell states require a multiconfigurational treatment. To that aim, we are applying the complete active space self-consistent field (CASSCF) and restricted active space self-consistent field (RASSCF) methods, together with perturbation theory based on these CASSCF and RASSCF reference wavefunctions. We found that the choice of an active space able to describe the important electronic states while remaining computationally feasible is far from trivial.

We identified that a correct description of electronic excited states with ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT) character demands a fairly large active space, which includes orbitals with mainly 3d character, metal-ligand σ -bonding orbitals, 4d orbitals that account for the double shell effect of the 3d-shell and π , π^* orbitals of ligands. The most common low-lying excitations are metal-centered transitions for both compounds; in addition to them, we found LMCT transitions for Fe(III) complex and MLCT transitions for V(II). We investigated how the number of π , π^* ligand orbitals affects the energy of LMCT and MLCT states. Our findings showed the necessity of using large active spaces, so that RASSCF approaches can be a suitable alternative to obtain a qualitatively correct description of the excited states' characters.

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Do they talk? Cyclometalated Pt(II) complexes with light harvesting organic chromophores

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Our research group recently synthesized triplet emitting cyclometalated Pt(II) and Pd(II) complexes with *N*-deficient terpyridine derivatives.^[1] In view of the poor absorption of these complexes in the visible range, the idea of covalently attached strongly absorbing organic chromophores to form light harvesting systems evolved. The concept of integrating organic chromophores into the ligand backbone was previously introduced by *Castellano*,^[2] *Ziessel*^[3], and others but the attachment to cyclometalated *N*-deficient terpyridine derivatives is a complete novel research topic.



Herein C^N^N or C^N^C cyclometalated Pt(II) complexes carrying BODIPY or naphtalimide antennae are presented. The organic chromophore was connected to an ethynyl spacer and then either directly attached to the metal center as a coligand or integrated in the ligand backbone. The position of the chromophore in the complexes was studied by electrochemistry, absorption and photoluminescence spectroscopy.

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Amine Donors heavily influence lumincence properties of bis-NHC-pyridine-Ru^{II} complexes

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A current approach in excited state tuning is the is the use of N-heterocyclic carbenes (NHCs).¹ These very strong σ -donors lead to an increase of ligand field splitting. In addition, the combination with π -acceptors, such as pyridine, leads to stabilization of MLCT states. Thus, tridentate C^N^C type Ru^{II} complexes show pronounced r.t. luminescence with a ³MLCT lifetime of 820 ns as an example for Ref. 1.² However, functionalization of the pyridine backbone with donating amines bearing a free electron pair has not yet been investigated for this ligand motif in Ru complexes.



Amine functionalization leads to a pronounced destabilization of the frontier orbitals in C1-C3 in contrast to the references which can be attributed to the weakened π -acceptor capabilities of the pyridine ligand. Moreover, emission properties change drastically, as a dual emission (Fig. 1) as well as a heavily decreased fluorescence quantum yield at r.t. can be detected ($\Phi_{C1-3}\approx0.003$ %, $\Phi_{Ref.1,3}\approx0.94$ %). The low energy emission band shows lifetimes around a few hundred ps in all cases whereas the lifetime of the high energy band amounts to a few μ s under Ar. Using TD-DFT calculations, the latter one could clearly be assigned to a pyridine based ³MLCT emission. The comparison of the excited state absorption with spectroelectrochemical measurements also suggest an MLCT based emission for the high energy band emission. Similar observations from the literature together with the band assignment in the UV-vis could indicate an NHC based ³MLCT transition for the second emission line.



Fig. 2: Emission spectra of C1-C3 obtained in a degassed MeCN solution under argon (orange) and a non-degassed MeCN solution (turquoise) at r.t. with an excitation wavelength of 380 nm. Emission wavelength shown together with corresponding excited state lifetime under argon and spin density plot of the lowest triplet state.

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Tuning the excited state character of coordination compounds: Theory-guided design, synthesis and photophysics

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Evolving from the well-known *ppy* ligands for triplet emitters, tridentate *CNN*- and *NCN*-donor versions for Pt(II) complexes have been reported in great variety and detail over the past few years.^[1-5] The fact that *NCN*-type ligands tend to show much higher photoluminescence quantum yields at *rt* than their *NNC*-type isomers^[1-4] and their seemingly counterintuitive behaviour with different co-ligands quickly rose our interest and showed the need for a model to explain and predict their features. Thus, we designed a set of tetradentate ligands that formed a rigid basis for 'intramolecular coligands', altered the *ppy*-part of the molecule to obtain *NNCY*- and *NCNY*-isomers and studied their photophysical properties both at experimental and theoretical level.

Using Orca 5's fairly new ESD-module, we aimed to calculate phosphorescence rates using DFT and ended up benchmarking various DFT-methods as well as the impact of Herzberg-Teller-coupling.



Figure 1. General molecular structure (left) and logarithmic relative deviation of rates obtained theoretically (k_P) and experimentally (k_R) for one exemplary complex using several common DFT-functionals (right) to display the need for method-benchmarking.

We developed a model to explain the so-called '*NCN*-effect' and found satisfactory methods to compute vibronically-resolved phosphorescence spectra and also excited state dynamics. On our poster, we will present the newly found relations between structure and electronic properties in detail and give insights in how they can be used to design highly efficient triplet-emitters.

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SPP Workshop Photochemistry of Metal Complexes: Theory Meets Experiment

Poster – New Applications of Dinuclear Gold Catalysts in Photocatalysis

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Since the first application of the dinuclear gold complex $[Au_2(\mu-dppm)_2]Cl_2$ for the reductive cleavage of alkyl and aryl bromides,¹ the complex and its derivatives have been studied intensively, especially with respect to UVA induced reactions.² In this poster, we present the photocatalyzed synthesis of new molecular structures by utilizing known techniques as well as new methodologies for the preparation of dihydrobenzofurans and indolines starting from unactivated alkyl bromides. As recent studies have further shown the feasibility of $[Au_2(\mu-dppm)_2]Cl_2$ and its derivatives under irradiation with blue LEDs,³ we also present a set of transformations with aryl iodide precursors. These include C-P bond formation, C-C activation, and visible-light induced $C(sp^2)-C(sp^2)/C(sp)$ cross-coupling reactions.



Figure 1. New molecular structures and transformations synthesized by irradiation of dinuclear gold complexes by UVA and blue LEDs.

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Development of catalyst/semiconductor assemblies for efficient photocatalytic CO₂ reduction

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Reduction of CO_2 to C1 and C2 products has been a major challenge over the last decades. Both homogeneous and heterogeneous systems have been developed to achieve this goal.^[1] Nevertheless, dye sensitized semiconductors were scarcely used for photocatalytic CO_2 reduction, and noble metals such as ruthenium or iridium were often used for this purpose.^[2] Taking into consideration the potential applications of using a mixed system, it is possible to acquire advantages from both heterogeneous and known homogeneous systems.^[3]

Previously our group synthesized copper photosensitizer-TiO₂ composites and applied them on photocatalytic water reduction,^[4] showing that it is possible to combine both molecularly defined complexes with semiconductors, thus improving stability overall, being this the starting point of this work towards an improved system combining both stability of heterogeneous models and selectivity from molecularly defined non-noble metal systems.

Herein, we present the potential application of these heterogeneous materials as photosensitizers towards an efficient and selective CO₂ photoreduction to CO using only non-noble metals and BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzimidazole) as sacrificial reductant.



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Bulky Bis-Carbene Pd/Pt(0) Complexes as Potential NIR Emitters

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Near-infrared (NIR) emitters are attractive for biomedical and biosensing applications by exploiting the biological semitransparency window of tissue¹, but there are several other applications of such materials reported in the literature². Particularly, in combination with circulary polarized luminescence (CPL) technical limitations in the field of quantum computing can be overcome and the area of application can be expanded e.g. quantum cryptography.³

When designing novel NIR emitters, the primary challenge is to achieve sizeable radiative rate constants while avoiding rapid nonradiative deactivation of the excitation. The small energy gap between the electronic ground state and the lowest excited singlet and triplet states facilitates energy dissipation due to internal conversion or intersystem crossing. Therefore, ways to minimize the electronic-vibrational coupling have to be found. Bulky substituents that hinder the reorganisation of the nuclear framework appear to be beneficial for achieving high luminiscence efficiency of Cu(I) complexes.⁴

In this work, four Pt(0) and Pd(0) complexes with bulky carbene ligands have been investigated by combined density functional theory and multireference configuration interaction methods and associated property programs. The monoamido carbene MAC(dipp) features a buried volume of about 45%, the cyclic alkyl amino carbene CAAC^{Menthyl}(dipp) a buried volume of about 55%. The two-coordinate homoleptic complexes are found to be very rigid upon electronic excitation, resulting in remarkably small reorganization energies. Accordingly, the MLCT states of the bis-MAC(dipp)Pt(0) and bis-MAC(dipp)Pd(0) complexes are expected to have promising luminescence properties. For the bis-CAAC^{Menthyl}(dipp)Pt(0) complexes, theory predicts substantial MC contributions to the T₁ wavefunction which lead to strong spin–orbit coupling with the electronic ground state and rapid deactivation of the excitation.

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Low temperature emitting cobalt (III) complexes

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Photochemistry of transition metal complexes has become an active and challenging field in the recent years. A good number of iron-based photoactive complexes has been of interest recently shifting to a more sustainable and cheaper alternative than the heavier transition metals previously employed. Recently explored Janus emitting iron complexes further reiterates the importance of exploring further into the transition metal based photoactive complexes.¹ Cobalt also shows similar potential, with its higher oxidation state when compared to iron(II), enforces a stronger ligand field and coupling with intelligent ligand designs having low-lying π^* orbitals allow to overcome the deactivation of the CT excited state caused by low-lying metal centered states in transition metals. But only recently advances have been made to show that these complexes are capable of very long lifetimes originating from a triplet metal centered state and further two more examples from an LMCT state. Emissive MLCT states have not yet been observed for cobalt (III) complexes, but their long-lived excited states have already been utilized for photo-induced electron transfer reactions.²



Figure 1. Crystal structure of the cobalt (III) complexes (left). Experimental absorption spectra of complex in MeCN(right).

Following up on these strong foundations, we synthesized cobalt (iii) complexes coordinated by two C^C^C-ligands consisting of two methyl imidazole N-heterocyclic carbene (NHC) units attached to a coordinating phenylene. The complexes crystallize out in octahedral geometry. These complexes show MLCT absorption bands at 300 and 340nm as inferred from DFT calculations. These also exhibit high excited state lifetimes in the regimes of 1-2 ns. These complexes don't show any strong emission at room temperature but are capable of low temperature emission at 750nm when excited at wavlengths below 340nm. Similar behaviour has been previously observed in ruthenium *bis*(terpyridine) complexes and the non emissive behaviour at room temperature has been adjudged to be caused by thermal deactivation of the charge transfer state.

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SPP Workshop Photochemistry of Metal Complexes: Theory Meets Experiment

Mechanistic Understanding of De Mayo-type Ring Expansion Reactions Activated by Triplet-Triplet Energy Transfer

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Despite the fact that the conventional De Mayo reaction is unquestionable a very valuable synthesis method in organic chemistry, it has its limitations: the need for harsh UV-light and the predominance of the enol tautomer result in drawbacks such as poor functional group tolerance and limited starting reagents.^[1] Motivated by the aforementioned, we looked into a novel approach to the De Mayo ring expansion reaction, which is based on the direct sensitization of the enol tautomer *via* triplet-triplet energy transfer (TTEnT) using an Iridium photosensitizer.^[2,3] With this novel synthesis approach at hand, we generated a wide range of pharmaceutically important medium-sized rings under significantly milder conditions, excellent yields (up to 90%), and good functional group tolerance. Upon photoexcitation of the catalyst with near-visible light, a triplet-triplet energy transfer to the reagent molecules was confirmed, affording the needed 1,2-diradical intermediate. Still, also triplet-triplet energy back transfer to the catalyst took place. Several analytical, spectroscopical, and theoretical methods, revealed a complex photosensitization involving, on one hand, the substrate's keto-enol equilibrium and, on the other hand, the balance between forward and back energy transfer. Quantitative analyses afforded TTEnT rate constants of $k_{TTEnT} = 1.28 \times 10^{10}$ and $k_{bTTEnT} = 4.06 \times 10^9$ M·¹ s⁻¹.



Figure 1. Two-carbon ring expansion by dynamic kinetic sensitization

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Photophysical and photochemical investigations on a series of group IV carbonyl complexes with a meso-ionic carbene ligand

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Photo-catalysis is a well-explored field in contemporary research. It enables reactions under comparably mild conditions, that wouldn't otherwise take place. A drawback of most photo-catalysts is the requirement for rare metals as late transition metals or even rare earth metals. In order to make this field of research more sustainable and economical, it is of particular interest to develop photo-catalysts, that contain only earth-abundant metals. In this work we present a series of Cr(0), Mo(0) and W(0) carbonyl complexes that are able to stereo-selectively cleave a CO ligand under irradiation and recombine in the dark thereafter both in the solid phase and in solution. The photo-physical behavior regarding emission and excited state vibrations as well as the respective excited state lifetimes was investigated on using luminescence spestroscopy and step-scan spectroscopy. The results were compared to previously reported, isomeric complexes and backed up by DFT calculations.

Zinc(II) Carbene Complexes: Combining TADF with CPL

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E-mail: mousree.mitra@tu-dortmund.de, ondrej.mrozek@tu-dortmund.de Circularly Polarized Luminescence (CPL) emitters are an exciting class of photoluminescence compounds capable of generating circularly polarized light with unique optical properties useful for various applications in fields such as displays, bioimaging, optical communication or quantum computing. Recent considerable progress^[1,2] in the area of Zn(II) photoluminescent complexes with emission that includes triplet excited state motivated us to explore complexes bearing chiral cyclic (alkyl)(amino) carbenes (cAAC) for the preparation of novel CPL emitters based on cheap and abundant zinc metal. The reaction of menthyl-substituted cAAC and ZnCl₂ afforded rare lowcoordinated complex [Zn(^{Menthc}AAC)(Cl)₂], which were isolated and fully structurally characterized. Subsequent chlorido ligands exchange reaction for various bidentate benzene-1,2-dithiolates (bdt') led to a new series (Fig. 1) of zinc-based emitters of the type [Zn(^{Menthc}AAC)(bdt')].



Fig 1. Synthesis of new zinc(II) TADF/CPL emitters (left) and crystal structures of 2 and 3.

The combination of ^{Menth}cAAC as a strong acceptor of electron density in excited states and bdt ligand with strong donating properties resulted in a powerful push-pull electronic environment around zinc metal. As a result of this specific coordination sphere, complexes **2-4** feature a small singlet-triplet gap resulting in an efficient ISC/rISC and TADF process. In addition, the trigonal planar arrangement increased quantum yield by one order of magnitude (up to 0.28) compared to the previously reported dimeric structure.^[2] This, in combination with a relatively short lifetime of ~200 ns, resulted in very high values of radiative rate constants (up to 7.83 × 10⁵ s⁻¹). The chiral character of ^{Menthyl}cAAC ligand further allows to of generate CPL with high efficiency (g_{lum} up to ~1.2 × 10⁻²).

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Excited state dynamics and photobasic properties of Iron-carbene complexes

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Proton transfer reactions represent one of the most fundamental processes in chemical reactions and living systems. Photo-induced proton transfer processes are unique and powerful in terms of their ability to manipulate reactions through efficient spatio-temporal control. One way to accomplish this is by using photoacids/photobases which in their excited states have a large variation of pKa when compared to their respective ground states.

Combining these photobasic systems with photoactive metal complexes enables to utilise the excellent optical properties of the latter expanding the potential of the whole system. Earlier studies have explored Ru and Ir based photobasic systems.^{1,2} In the last decade, both the photophysical properties of long-lived iron-NHC complexes³ as well as the photobasic properties of quinolines² have become the subject of many studies. Here we study the excited state and proton transfer properties of a novel photobasic quinoline substituted iron-carbene complex using steady-state and fs-transient absorption.

Understanding the dynamics of excited state proton transfer involves careful consideration of the electronic properties which are influenced by interaction between the donor and acceptor molecules and the surrounding solvent environment. We aim to characterize the influence of the iron center on the proton transfer properties of the quinoline in dependence of different solvents and in the presence of salt ions. We find that both the nature of the solvent as well as its microstructure surrounding the photobase have an influence on the excited state lifetimes of the complex as well as on its proton transfer abilities. In addition, we see indications of an energy transfer from the excited quinoline to the MLCT states.

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SPP Workshop Photochemistry of Metal Complexes: Theory Meets Experiment

Towards a light-driven Heterobimetallic Hydrogen Evolution Catalyst

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Inspired by nature, artificial photosynthetic systems can be used to capture light and oxidize water coupled to the reduction of protons or other organic compounds to generate value-added chemicals or fuels. For the photo-driven synthesis of H₂, efficient proton reduction catalysts are needed.¹ Nature provides great inspiration in this regard, as hydrogenase enzymes are among the most efficient molecular catalysts for proton reduction.² In the NiFe hydrogenases, the active site reactivity is mostly centered at a thiolato-ligated Ni ion, and a proximal [4Fe4S] cluster serves as an electron reservoir.³

To generate H₂ photocatalytically, the experimental setup requires at a minimum an electron donor, a proton donor, a photosensitizer and a proton reducing catalyst.⁴ As a typical photosensitizer, Ru polypyridine or Ir phenylpyridine-type complexes are often chosen for the light-induced delivery of electrons following MLCT excitation. Previously, our group reported a new Ru-photosensitizer as well as a Ir-photosensitizer with a sulfurated bipyridine ligand, where peripheral disulfide/dithiol interconversions are used for redox control and charge storage.^{5,6}

These unique photosensitizers are now used as a dithiolato metalloligand towards a catalytically active 3d metal ion to combine the catalyst with the light harvesting component. Here we present the synthesis and comprehensive characterization of such new, heterobimetallic photosensitizer-catalyst dyads, including their spectroscopic and electrochemical signatures. Preliminary experiments towards photocatalytic H₂ evolution catalysis are described.

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Red light absorption in coordination complexes via MLCT stabilization

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Earth abundant Mn(I) based complexes with general composition $[Mn(CO)_3(L)(X)]$ (L: bidentate ligand, X: monodentate sought ligand) are to replace their Re(I) analogues as photosensitisers and catalysts.^{1,2} Typically, metal to ligand charge transfer (MLCT) excited state of Mn(I) complexes are quite reactive and prone to ultrafast ligand loss (CO or X) on femtosecond time scale.^{2, 3} By designing the ligand L with low-lying π^* orbital energy we can aim to stabilize the long-lived MLCT states over the shortlived ligand field states. Electronic levels can furthermore be influenced by exchanging the traditional solvents into supercritical CO₂ (scCO₂).¹ In order to establish our hypotheses and get sufficient understanding about the stability of the excited MLCT state of the complexes, studies on their photophysical properties by steady state and time resolved spectroscopy (nstransient absorption) are very important.

Here we will present photophysical characterizations of some newly synthesized $\text{Re}(\text{CO})_3[(\alpha-\text{diimine})\text{CI}]$ (α -diimine: 4,4'-biquinazoline, 1,3,10,12-tetraazaperylene, N-doped nanographene) complexes measured by spectroscopic techniques and discuss how the extension of the π -system in α -diimine (bidiazine) resulted in a strong bathochromic shift of the MLCT absorption in the complexes.⁴ Additionally, the decomposition pathways of model Mn(I) tricarbonyl complexes with 4,4'-disubstituted 2,2'-bipyridyl ligands (^Rbpy:= -^{*i*}Bu,-H, - CF₃) examined by transient absorption spectroscopy in CH₃CN and CH₂Cl₂ will be discussed.

Keywords: MLCT, 1,3,10,12-tetraazaperylene, N-doped nanographene, ns-transient absorption spectroscopy

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Computational Studies of TADF Emitting Zn(II)-CAAC Complexes

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Organic light-emitting diodes (OLEDs) gained outstanding attention as light sources in the past years. But there is still room for improvement regarding their efficiency and durability. Harvesting triplet as well as singlet states which appear in a ratio of 3:1 in OLEDs is crucial for high luminous efficiency. Thermally activated delayed fluorescence (TADF) is a mechanism that has the power to convert all excited states into emitted light. It is based on a reverse intersystem crossing (rISC) from the first triplet to the first excited singlet state with subsequent fluorescence. For powerful TADF high rISC and fluorescence, as well as low phosphorescence rates are required.

Molecules that can fulfill these requirements are transition metal complexes with d¹⁰ configuration. A small singlet-triplet energy gap (ΔE_{S-T}), sufficient spin—orbit coupling (SOC), and the lack of unproductive processes lead to high quantum yield TADF. Copper(I) complexes are well known in the field of TADF emitter materials due to their ability to induce the SOC required for rISC. In the less examined Zn(II) complexes the metal atom does not participate in the low-lying electronic excitation which results in tiny ΔE_{S-T} . MenthCAAC-Zn(II)-bdt (**1**) and MenthCAAC-Zn(II)-bdo (**2**) (Fig. 1) are both zinc complexes that qualify as TADF emitter molecules. Apart from the zinc(II) core, the molecules contain a CAAC on one side and a benzene-1,2-dithiol (bdt) or benzene-1,2-diol (bdo) ligand on the other.



Figure 1. Structures of the examined molecules.

Computational studies showed that both molecules have several energetically close conformers that only differ in the orientation of their ligands towards each other. However, these conformers show little differences in their photophysical properties. All conformers of (1) and (2) molecules have low-lying singlet and triplet ligand-to-ligand charge-transfer (LLCT) states with tiny ΔE_{S-T} that qualify as their emissive states. The spin—orbit couplings between these states are low, yet high (reverse) intersystem crossing rates are achieved in combination with the tiny energy gaps. The phosphorescence rates are so low that only emission from the singlet state is expected. The emission of (1) produces yellow light, while that of (2) is in the infrared region. Experimental results of (1) agreed well with the computational data. Both molecules are considered suitable as TADF-emitter materials.

Group 10 Metal Complexes for Near-IR Triplet Emission

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Near Infrared (NIR-) emission plays a crucial role in signal processing^{1a}, communication technologies, as well as bioimaging applications.^{1b,c} Designing necessary efficient molecular NIR emitters, however, is far from trivial and each substance class has its own challenges. Organic emitters suffer from statistically limited electroluminescence efficiencies, lanthanide complexes show poor radiative rate constants (k_r) and overall, the energy-gap-law sets a limit to the maximal quantum efficiency.^{1a,c} Our approach so far is the usage of coinage metal complexes, especially of copper complexes,^{2a} and recently also the group 12 metal zinc(II).^{2b} They benefit from photophysically inert d¹⁰ electron configurations, avoiding non-radiative transitions and the well established, high tunability of these compounds allow access to complexes exhibiting TADF resulting in high radiative rate constants.



Figure 1. Introducing unused chromophore ligands^{3a} to luminescent group 10 metal complexes.^{3b}

A new concept envisioned by us is the shift from well-known coinage metal d¹⁰ systems to the mostly overlooked zero valent complexes of palladium and platinum. Due to the low reduction potential of these metals, we envisage a high participation of the metal atom in charge transfer states resulting in an enhanced spin-orbit coupling. In addition, supposedly closely lying frontier orbital energies, equally due to the low reduction potential, allow deep red emission. These are favorable properties predicted from quantum chemical calculations on simple model systems. Our proclaimed goal is to introduce the trendsetting carbene ligands into the photophysics of group 10 metal complexes. This step will lead us to the proof-of-concept for this barely investigated class of emitters. In the future, this knowledge will be transferred to abundant nickel(0).

In summary, this project will allow new insights into and further understanding of the excited state properties of zero valent palladium and platinum complexes bearing carbene ligands and lead us to a promising new class of near infrared triplet emitters.

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Excited State Analysis of N2-Photoactivating Complexes

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Ammonia derived from atmospheric N_2 and fossil H_2 in the Haber-Bosch process represents the main source of nitrogen compounds as a base chemical for the synthesis of value-added products. In order to access a more diverse range of N-containing chemicals without relying on NH_3 as an intermediate, it is of high interest to develop tailored nitrogen-activating catalysts.

One way of achieving synthetic nitrogen fixation is selective light-driven N_2 cleavage. All known complexes for N_2 photoactivation have a linear core of the form M-N-N-M which undergoes geometric and electronic changes during the photochemical process. The mechanistic understanding of the underlying processes is still in its early stages and even the nature of the responsible excited state is insufficiently characterized.¹

For the rhenium^{2,3} pincer complexes of Schneider and coworkers, excitations within the M-N-N-M core are already identified on the time-dependent density functional theory level (see Figure 1).



Figure 1. The rhenium pincer complex of Schneider and coworkers and exemplary excitations within the Re-N-N-Re core.

However, relativistic effects to permit an appropriate treatment of spin-orbit coupling effects have not been included in those calculations yet. Here, we present an analysis of the electronic structure and excitation character based on spin-orbit coupled time-dependent density functional theory. In addition we will compare them with complete active space calculations with subsequent second-order perturbation theory as the complexity of the electronic structure should require multiconfigurational treatment.

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Experimental and computational investigation of photolytic dinitrogen release from 1,1'diazdioferrocene and related systems

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Irradiation of 1,1'-diazidoferrocene (λ = 266 nm) leads to the release of dinitrogen from an azide moiety. While it is known that the related 1-azidoferrocene can undergo thermal decomposition to yield a ferrocenyl nitrene,¹ the photolytic process has only recently been studied with femtosecond ultraviolet-pump/mid-infrared-probe (UV/MIR) spectroscopy.² In combination with quantum chemical calculations, the photochemical processes leading to the generation of a 1-azido-1'-nitrenoferrocene species can be resolved.



Figure 1. Gibbs free energy profile in kJ/mol for the proposed photolytic N₂ dissociation pathway with DFT (D4-PBE0/def2-TZVP// D4-PBE/def2-TZVP) computed structures and spin densities.

Computations suggest that the decay of a spin-orbit coupled excited state leads to a triplet intermediate with a bent azide moiety, which is pre-organized for dinitrogen release. A transition state with a low activation barrier of $\Delta G_a = 15.1$ kJ/mol leads to release of dinitrogen to form the triplet 1-azido-1'-nitrenoferrocene photoproduct. As a continuation of this project, we have now synthesized a new ferrocene containing compound that has both an azido and a [Re(CO)₃] functionality. As both these components are photoactive and photolabile, we are currently investigating aspects such as selective bond activation, dependence of the photoactivation at one site on the other, and dependence of photoactivation wavelength on product formation through both experimental and computational methods.

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C=C Bond Cleavage by a (PNP)Pt(II) Metallonitrene

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Aziridines are important and versatile synthons for the preparation of small molecules and drugs. A facile synthesis involves the reactivity between organic nitrenes and alkenes via metal-based catalysts.¹ Smith *et al.* observed the reaction of an Fe(IV) nitride complex with a range of styrenes, obtaining the corresponding aziridino complexes.² The free aziridine could easily be liberated by addition of TMS-Cl, closing a synthetic cycle.



Figure 1. Formation and reactivity of Pt(II) triplet metallonitrene with various substituted styrenes.

Our group recently examined the photolysis of Pd(II) and Pt(II) azide complex that lead to transient triplet metallonitrenes, capable of nucleophilic C-H insertion.^{3,4} We here demonstrate that the reaction between the transient Pt metallonitrene and styrene does not lead to the expected aziridino complex, but instead results in unsual C=C bond cleavage and the formation of Pt aldimido species (Figure 1). Spectroscopic (EPR, NMR, UV/Vis) and computational studies were performed to elucidate the mechanism.

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Light-induced electron transfer dynamics in dinuclear W(II) alkyne based complexes

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The photo-induced charge transfer dynamics of a dinuclear W(II)-Ir(III) **1** and a W(II)-Ru(II) **2** complex linked by a cyclometallating alkyne ligand [1] were investigated by femtosecond transient absorption spectroscopy in the UV-vis and in the region of the stretching frequency of the CO ligand at 1700-2100 cm⁻¹. Following 400 nm excitation both compounds exhibit instantaneous blue shift of the CO mode revealing reduced electron density at the tungsten and charge transfer to the other metal centre. The lifetime of the charge-separated state is about 10 ps. The IR transients show population in excited vibrational states of the CO stretching mode (up to v = 3) indicating highly non-statistical vibrational energy distributions for both the charge transfer and the ground state after back-electron transfer. In the ground state of **1**, intramolecular vibrational energy redistribution (IVR) from CO stretch to low frequency modes limits the overall cooling process of the molecule and extends it to more than 100 ps.



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The effect of phenyl substitution on Janus-emitting cyclometalated NHC-iron(III) complexes

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In the search for efficient photocatalysis with earth-abundant metals, Fe^{III} photosensitizers have gained popularity.¹⁻³ The recently developed [Fe(ImP)₂]⁺ shows an unprecedented Janus-type emission from both ²LMCT and ²MLCT states.⁴



Figure 1: Structure, absorption and emission spectra of the functionalized CCC-complexes.

To investigate whether this is a singular event or an inherent property of these complexes, a series of substituted cyclometalated NHC-iron(III) complexes was synthesized and characterized in its ground and excited states. The substituents include the electron-withdrawing nitrile, trifluoromethoxy trifluoromethyl and bromo groups, while electron-donating groups include the methyl, *tert*-butyl and methoxy groups. With the combination of cyclic voltammetry, UV-Vis and fluorescence spectroscopy, as well as time correlated single-photon counting, a picture of electronic influences on the dual emitting properties of this compound class was obtained.

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Merging Mechanochromic and Circularly Polarized Luminescence with Copper(I) Complexes

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Many photonic and optoelectronic applications, e.g., quantum computing, and display technologies, rely on the polarization of photons.^[1] While a joined setup of linear polarizers and quarter-wave plates can transform unpolarized light into circularly polarized light, these components suffer from losses in brightness and tend to be rather large.^[2] Developing emitter materials which can discriminate between the two helical orientations – i.e., yielding circularly polarized luminescence (CPL) – are paramount for efficient, lightweight and compact devices. Chiral lanthanide complexes are one well-studied emitter classes that achieve high luminescence dissymmetry but are of limited use in optical devices due to their small radiative rate constants.^[3]



 $\checkmark \text{NHC} - \text{chiral } R^1 \text{ and/or } R^2 \quad \checkmark \text{Anion} - \text{from chiral pool} \qquad \checkmark \text{Pyridine} - \text{camphor fused}$

Figure 1. Design scheme of Cu(I)-carbene complexes for mechanoresponsive CPL.

In contrast, complexes of copper(I) profit from the comparatively large spin-orbit coupling constant and beneficial d¹⁰ electron configuration of the metal centre, making them promising candidates for highly tuneable and efficient emitter materials. In the recent past, we investigated Cu(I)-carbene complexes as emitters for CPL^[4], on the one hand, and mechanoresponsive emission materials, on the other hand.^[5] In our current research, we aim at merging both properties within chiral cationic [Cu(NHC)(pyridine)] complexes to obtain switchable CPL emitters

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Femtosecond spectroscopy of new iron bi-dentate complexes with extended lifetimes

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Within the scope of photocatalytic water splitting for green hydrogen production, iron-based complexes have been massively studied and optimized over the last ten years in order to reach the yield of their more efficient ruthenium counterparts^{1,2}. If the amount of iron in Earth's crust represents an undeniable asset compared to the one of ruthenium – making the latter not suitable for large-scale applications² – the lifetime of its triplet metal-to-ligand charge transfer (³MLCT) state remains its weakest spot, mostly because of its fast deactivation via the lower lying Metal Centered (MC) states¹. Increasing the ³MLCT lifetime of such iron-based light harvesters is therefore a real challenge that can be overcome thanks to a rational design of ligands. In particular, Transient Absorption Spectroscopy (TAS) on newly developed Fe^{II} bi-dentate complexes with quinoline-based ligands revealed an interesting two-state parallel decay with an unprecedented lifetime of more than 100 ps. Yet, the assessment of the nature of this long-lived state still needs to be done.



Figure 1. (A) Chemical structure of complex **366**. (B) Transient absorption spectra of complex **366**. The long-lived exc. state absorption (375-430 nm) and ground state bleach (450-570 nm) reveals an excited state with ≈130ps lifetime.

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SPP Workshop Photochemistry of Metal Complexes: Theory Meets Experiment

Novel Luminescent Vanadium(II/III) Complexes

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At the present time the demand for technologies such as organic light-emitting diodes, photovoltaic systems, photocatalysis or optical sensors is increasing. For these applications photoactive complexes based on noble metals like ruthenium are typically employed. Since the earth-abundance of these metals is very low, it is desirable to replace them with more common metals such as vanadium. However, the usage of more abundant 3d metals is challenging due to the intrinsically small ligand field splitting. In such systems the lowest excited states are often highly distorted, non-emissive metal centered states.^[1]

Vanadium complexes have two potential luminescent oxidation states: V^{2+} , which has an electron configuration of d³ and a quartet ground state similiar to Chromium(III) complexes and V³⁺, which has a d² configuration and a triplet ground state. There are currently no known luminescent V²⁺ complexes. Low lying MLCT states will be generated due to facile oxidation of V²⁺ to V³⁺. When these MLCT states mix into the spin flip states, no emission will be observed.^[2,3]

Previous works by the Heinze Group used ddpd (N,N'-dimethyl-N,N'-dipyridine-2-yl-pyridine-2,6diamine), a strong σ -donating and weak π -accepting ligand, for the complexation of V^{2+/3+} complexes. The V²⁺ complex did not show any luminescence, whereas the V³⁺ complex was the first to display NIR-II-luminescence from a spin flip state at 293 K in solution.^[4,5]

Current research focuses on vanadium complexes with strong σ -donating and weak π -accepting ligands to prevent the previously mentioned mixed states and possibly enable luminescence. For this, the tripodal polypyridine ligand tpe (1,1,1-tris(pyrid-2-yl)ethane) and the anionic carbene ligand [phtmeimb]⁻ ([phenyl(tris(3-methylimidazolin-2-ylidene))borate]⁻) are used. (Fig. 1)



Figure 1. Planned Vanadium(II/III) complexes.

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Mononuclear iron(II/III) complexes with tripodal ligands

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The replacement of rare ruthenium with its lighter homologue iron in energy-transforming technologies e.g., OLEDs, PhOLEDS or in photocatalysis is targeted as a sustainable development. To achieve a similar luminescence and photoactivity like in ruthenium complexes, the intrinsically smaller ligand field splitting of the *3d*-element must be compensated by appropriately designed ligand systems. Based on the known complexes of the Bauer, Berkefeld and Wärnmark groups, complex systems are to be designed which exhibit luminescence while retaining the Fe^{II} center. ^[1-6]

Previously, the Heinze group was able to increase the ³MLCT lifetime in a rigid homoleptic Fe^{II} complex with high octahedricity to 9 ps employing tripodal ligands combining π -acceptor characteristics for the stabilization of the MLCT states and σ -donor properties in the form of NHCs for the destabilization of the MC states.^[7]

This combination of properties is to be further developed with heteroleptic Fe^{II} complexes of some literature-known tripodal ligands (see figure 1).^[2, 8, 9] Furthermore a novel tripodal ligand called [ptbm]⁻ (Di(2-pyridyl)(5-tert-butylbenzyl)methane) is introduced. In its cyclometallated state the now rigid ligand combines π -accepting and π - & σ -donating characteristics.



Figure 1: a) Novel ligand [ptbm]⁻, b) tpe, c) [phtmeimb]⁻, d) pdmi

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Controlling the Electronic Coupling in NIR Emitting Bis-CAArC-Pd/Pt(0) Complexes

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At the doorstep to the near infrared region (NIR), the energy gap law greets.¹ It states that the nonradiative decay rate k_{nr} increases exponentially with decreasing energy difference; unfortunately, the radiative rate shrinks cubically with the energy gap. Furthermore, the non-adiabatic coupling and the direct spin—orbit coupling (SOC) affect k_{nr} . Efficient luminescence requires thus a) weak coupling to the ground state S₀, and b) sizeable radiation rates.

This study examines the linear homoleptic Pd/Pt(0) complexes, employing the special cyclophane-CAArC depicted in fig. 1. Due to the chiral nature of the ligand, four stereoisomers with each various rotamers are possible. In contrast to standard carbenes, the cyclophane-CAArC possesses two low-lying acceptor π -orbitals, one located on the carbene, the other one in the backbone. They support a variety of low-lying excited states, including the low-lying states, that are typical for CAArC-complexes.

The electron rich metals induce metal to ligand charge transfer (MLCT) states with metal centred (MC) contributions. The prior one leads to luminescence rates in the order of 10^5 s^{-1} , the latter one to strong S₁-T_n SOC and nonradiative decay to the ground state S₀. Symmetry could forbid the coupling to the S₀, but the excitations localises onto one carbene.

In the Pt complexes, relativistic effects destabilise the MLCT and leave the triplet LE state in the CAArC backbone behind. It bears some MLCT admixture and phosphoresces with rates in the order of $10^3 \, \text{s}^{-1}$. First results attribute the large phosphorescence rate to the presence of the cyclophane moiety. The situation is less clear in the palladium complexes, where the MLCT states the LE state are all low-lying, but SOC is considerably smaller.



Figure 1: Complexes examined in this study.

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