

Research Training Group 2482

ModISC

“Modulation of Intersystem Crossing”



Symposium

22. – 23.09.2022

Heinrich Heine University Düsseldorf

Graduiertenkolleg 2482

Modulation of Intersystem Crossing

Electronic excitation of molecules impacts diverse areas ranging from photobiology to molecular electronics, from basic science to applications, such as organic light emitting diodes (OLED). Intersystem crossing (ISC), the non-radiative interconversion of electronic states with different spin multiplicities, is a key process in photochemistry and photophysics. The efficiency and kinetics of ISC can render electronically excited molecules photo-labile or -stable, emissive or dark. This Research Training Group proposes to study and modulate ISC in molecules by chemical substitution and by varying the molecular environment. It promotes and fosters interdisciplinary research seeking for a deeper understanding of emission enhancement by controlling ISC from singlet to triplet and its reverse. Closely related to this highly topical research, a cross-curricular PhD training program was established, taking into special consideration diverse scientific backgrounds of the candidates. The doctoral researchers are strategically mentored by co-supervision teams of PIs holding complementary expertise. In addition, workshops with international speakers, RTG symposia, and the RTG training will enhance the educational and subject-specific didactical skills of the young researchers as an optimal preparation for future work in academia or industry.

Research Training Group 2482 (GRK 2482) is funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation).

Program

Thursday, September 22, 2022

12:45 pm Registration

01:00 pm Welcome, Thomas J. J. Müller

Session 1

Chair: Tobias Böhmer

01:15 pm Novel star-shaped conjugated macromolecules with fused cores for photonic and electronic applications

[Peter Skabara](#)

Ramsay Chair of Chemistry, University of Glasgow, UK

02:00 pm Synthesis and characterisation of conformationally twisted triphenylamine dyes as potential TADF emitters

[Julia Wiefermann](#), Thomas J. J. Müller

Institute of Organic Chemistry and Macromolecular Chemistry, Heinrich Heine University Düsseldorf

02:30 pm From Curricular Innovation to Science Communication

[Lena Halbrügge](#)

Institute of Chemistry, University of Potsdam

03:00 pm Coffee Break

Session 2

Chair: Jeremy Kaminski

03:30 pm NFDI4Chem: Shaping digital and cultural change in chemistry

[John D. Jolliffe](#)

NFDI4Chem Task Area 5: Community and Training, Johannes Gutenberg-University Mainz, Germany

04:00 pm Large area flexible OLED lighting – Manufacturing technologies and applications

[Christian May](#)

Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP, Dresden, Germany

04:45 pm Short Break

05:00 pm Synthesis of porphene, an antiaromatic analog of graphene

Thomas F. Magnera ^[a], Paul I. Dron ^[a], Jared P. Bozzone ^[a], Milena Jovanović ^[a], Igor Rončević ^[b], Wei Bu ^[c], Elisa M. Miller ^[d], [Josef Michl](#) ^[a,b]

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06:00 pm Dinner

Friday, September 23, 2022

Session 3

Chair: Lena Halbrügge

10:00 am Welcome

10:15 am Triplet states of organic emitter molecules: problem for electroluminescence, opportunity for photonics

[Sebastian Reineke](#)

Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP) and Institute for Applied Physics, Technische Universität Dresden

11:00 am Cr/Photoredox dual-catalyzed synthesis of α -benzylic alcohols, isochromanones, 1,2-diols and 1,2-thio-alcohols

[Johannes Erchinger](#)

Westfälische Wilhelms-Universität Münster

11:30 am A TADF emitter studied by Time Resolved Near Infrared spectroscopy

[Wiebke Haselbach](#) ^[a], [Jeremy M. Kaminski](#) ^[b], [Laura N. Kloeters](#) ^[c], [Thomas J.J. Müller](#) ^[c], [Oliver Weingart](#) ^[b], [Christel M. Marian](#) ^[b], [Peter Gilch](#) ^[a], [Bárbara E.N. de Faria](#) ^[a]

^[a] Heinrich Heine University Düsseldorf, Institute of Physical Chemistry, Femtosecond Spectroscopy, ^[b] Heinrich Heine University Düsseldorf, Institute of Theoretical and Computational Chemistry, ^[c] Heinrich Heine University Düsseldorf, Institute of Organic Chemistry and Macromolecular Chemistry

12:00 am Vibronic contributions to through-bond and through-space charge transfer transitions in donor-acceptor type TADF emitters

[Jeremy M. Kaminski](#), [Tobias Böhmer](#), [Luka M. Duben](#), [Christel M. Marian](#); Heinrich Heine University Düsseldorf, Institute of Theoretical and Computational Chemistry

12:30 pm Lunch

Session 4

Chair: Tobias Böhmer

01:30 pm **Simulating and screening photophysics of transition-metal complexes**

[Patrick Zobel](#)

University of Vienna, Institute of Theoretical Chemistry, Austria

02:15 pm **Postersession & Coffee break**

04:15 pm **Strategies for enhancing thermally activated delayed fluorescence**

[Anna Köhler](#)

University of Bayreuth, Germany

05:15 pm **Closing remarks**

Abstracts of Talks

Novel star-shaped conjugated macromolecules with fused cores for photonic and electronic applications

Peter Skabara, Ramsay Chair of Chemistry, University of Glasgow, UK

Star-shaped oligofluorene-truxene materials are excellent materials for frequency downconversion and application in organic lasers and visible light communications. To open up the potential of star-shaped structures for applications such as OLEDs and OLETs, we designed novel core systems to improve aggregation in the solid state whilst retaining respectable levels of emission. In this talk, I present the synthesis and characterisation of some new materials, including TriR and Ind3HBC, which are based on soluble fused cores of graphene fragments.

Synthesis and characterisation of conformationally twisted triphenylamine dyes as potential TADF emitters

Julia Wiefemann, Thomas J. J. Müller, Institute of Organic Chemistry and Macromolecular Chemistry, Heinrich Heine University Düsseldorf

The development of functional organic chromophores is a topic of high relevance and interest. Triphenylamine derivatives are particularly interesting due to their high thermal and photochemical stability.^[1] In addition, they are often employed in thermally activated delayed fluorescence (TADF) dyes. By distortion, the HOMO-LUMO frontier molecular orbital overlap is minimized and thus a small $\Delta E(S_1-T_1)$ is expected.^[2] This enables TADF to occur. TADF chromophores make it possible to design OLEDs more efficiently, as they significantly increase the internal quantum yield of the emission.^[3] Four novel conformationally twisted triphenylamine dyes were readily synthesized by bromine-lithium exchange borylation-Suzuki sequence (BLEBS) in moderate to good yields.

Their electronic properties were studied by absorption and emission spectroscopy revealing blue to green yellowish emission in solution as well as in the solid state and upon embedding into a PMMA (polymethylmethacrylate) matrix. Moreover, the substances show a positive emission solvatochromism exposing large Stokes shifts from toluene to dichloromethane. By low temperature measurements small $\Delta E(S_1-T_1)$ values were estimated in solution and in the PMMA matrix. First time-resolved measurements indicate TADF properties.

References:

^[1] S. Thayumanavan, S. Barlow, S. R. Marder, *Che. Mater.* 1997, 9, 3231.

^[2] H. Kaji, H. Suzuki, T. Fukushima, K. Shizu, K. Suzuki, S. Kubo, T. Kumino, H. Oiwa, F. Suzuki, A. Wakamiya, Y. Murata, C. Adachi, *Nat. Commun.* 2015, 6, 8476.

^[3] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* 2012, 492, 234.

Printed Electronics as a Hands-on Experiment for Science Teaching

Lena Halbrügge, Institute of Chemistry, University of Potsdam

Printed electronics are electronic devices that are completely or partially made by printing processes [1]. These devices are getting more and more established in our daily life. There are already RFID-chips or touch-screens that can be printed [1,2]. Conductible layers can be printed one over another to either transfer data or make devices emit light. Devices that are developed this way can be very thin and also flexible [2].

The technical printing procedure of an EL-foil was transferred into a “Hands-on-experiment” for Science Teaching by our workgroup. Step by step the different layers are applied on a conductive substrate. The core element of the EL-foil is a color, based on doped zinc sulfide, which functions as a semiconductor. Furthermore, a dielectric and a counter electrode are used to complete the device. In the end conductive silver ink is applied to connect a voltage source. The manufactured EL-foil is flexible and shines brightly at a voltage of around 100 V (AC). The functional principle of the device is based on the piezoelectric excitation of electrons in the semiconducting material followed by their relaxation under light emission [3].

In the talk the different steps will be experimentally conducted to show in which way the didactics transforms current research and development into experiments for science teaching purpose.

[1] M. Schewe, H. Rost, *Kunststoffe*, 2012, 101(10), 38-42.

[2] S. I. Verstraelen, K. Hecker, 2019, <https://www.chemanageronline.com/themen/chemikalien-distribution/gedruckte-elektronik-ist-im-alltag-angekommen>.

[3] M. Dür, S. M. Goodnick, S. S. Pennathur, J. F. Wagner, M. Reigrotzki, R. Redmer, *Journal of Applied Physics*, 1998, 83, 3176-3185.

NFDI4Chem: Shaping digital and cultural change in chemistry

John D. Jolliffe, NFDI4Chem Task Area 5: Community and Training Johannes Gutenberg-Universität Mainz, Department Chemie; jdjolliffe@uni-mainz.de; <https://nfdi4chem.de/>

More and more digital research data is being generated in science. Concepts for research data management (RDM) are therefore being searched for: Which file formats should be used in the long term? How and where should the research data be stored? What information about experiments or calculations should be stored in the metadata? How can people from your own group as well as external people access the data? How can the research data be easily found by people and computer systems? All these questions are included in the implementation of the FAIR Data principles (findable, accessible, interoperable and re-usable).

NFDI4Chem was formed as a consortium for chemistry within the national research data infrastructure (Nationale Forschungsdateninfrastruktur NFDI). In addition to university and non-university research institutions, infrastructure institutions and the German Chemical Society (GDCh), the Bunsen Society (DBG), and the German Pharmaceutical Society (DPhG) are also represented here.

In this talk, the consortium briefly introduces itself and sets out its central goals and most important contributions for RDM in chemistry, as well as the practical challenges. The vision of NFDI4Chem is to seamlessly digitalize the entire workflow in chemical research. Starting at the bench with the provision of Open-Source electronic lab notebooks (ELNs), through developing standards, interfaces, and tools, NFDI4Chem strives to remove the analogue gaps from the digital data lifecycle. Publishers and funding bodies are also already beginning to make requirements for FAIR research – find out more how you can make the most of our free offers and services to support you in digitalizing your labs and making your research data FAIR.

Large area flexible OLED lighting – Manufacturing technologies and applications

Christian May, Fraunhofer Institut für Organische Elektronik, Elektronenstrahl- und Plasmatechnik FEP

OLED lighting technology offers huge possibilities for novel lighting products, especially for automotive applications. OLED design starts where LED lighting tiles are at the design limits. OLED modules exhibit unique characteristics like bendability, segmentation, transparency, color tunability, ultra-low thickness and a nearly unlimited range of shapes. The strength of the OLED technology are the amazing design possibilities. Pilot manufacturing facilities have existed in Europe and Asia for several years. The introduction of OLED taillights in 2016 marked its entry into automotive applications.

Large volume commercial success can only be achieved if unique design possibilities are consequently employed in novel application scenarios and cost-effective roll-to-roll production technology. Flexible substrates made primarily of barrier-coated polymer film, but also metal foils or ultra-thin glass have been investigated for use in OLED manufacturing. Each has advantages and disadvantages. OLED prototypes on polymer substrates as well as ultrathin glass have been realized at Fraunhofer FEP. Major development topics are the improvement of device stability and brightness. This includes intensive work on encapsulation as well as the development of stacked OLED architectures on flexible substrates. Fraunhofer FEP has shown OLED processing along the entire value chain for the fabrication of flexible OLEDs in both sheet-to-sheet and roll-to-roll processes.

Furthermore, the talk gives insights to enhance the transfer from basic research to industrialization using attractive funding opportunities for industry and scientist as realized in projects like ACTPHAST4R and PhotonHub Europe.

Synthesis of porphene, an antiaromatic analog of graphene

Thomas F. Magnera ^[a], Paul I. Dron ^[a], Jared P. Bozzone ^[a], Milena Jovanović ^[a], Igor Rončević ^[b], Wei Bu ^[c], Elisa M. Miller ^[d], **Josef Michl** ^[a,b]

^[a] Department of Chemistry, University of Colorado, Boulder, CO 80309-0215, U.S.A., ^[b] Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences; Prague, Czech Republic, ^[c] ChemMatCARS, University of Chicago; Lemont, IL 60439, U.S.A., ^[d] Chemistry and Nanoscience Center, National Renewable Energy Laboratory; Golden, CO 80401, U.S.A.

Two-dimensional organic materials offer atomic precision for optoelectronics and energy-efficient nanoelectronics, but most are not easily patterned and tuned. The fully conjugated Zn-porphene, $(C_{20}N_4Zn)_4$ has now been prepared from Zn porphyrin by oxidative polymerization on aqueous surface and transferred to solid substrates. Its structure was established by imaging as well as in-situ and ex-situ spectroscopy. Reversible insertion of other metal ions is possible and promises an atomic canvas for painting with thousands of distinct metal ions and ligands without taking any δ centers out of conjugation. Unlike earlier computational results, which predicted a $P4mm$ (D_{4h}) square unit cell and metallic conductivity, ours resemble those for antiaromatic molecules and predict Zn-porphene to be a two-dimensional antiaromatic semiconductor with a pair of $P2mm$ (D_{2h}) rectangular unit cells, rapidly interconverting via a $P4mm$ (D_{4h}) square structure by tunneling and/or thermal excitation. This result is supported by measurements of electrical conductivity and of N(1s) chemical shift in X-ray photoelectron spectra.

Triplet states of organic emitter molecules: problem for electroluminescence, opportunity for photonics

Sebastian Reineke, Dresden Integrated Center for Applied Physics and Photonic Materials (IAPP) and Institute for Applied Physics, Technische Universität Dresden, Nöthnitzer Str. 61, 01187 Dresden, Germany, sebastian.reineke@tu-dresden.de

Organic light-emitting diodes (OLEDs) have come a long way since they have been introduced in 1987. What has been realized very early on is the fact that excitonic triplet states strongly limit the electroluminescence efficiency, calling for strategies to harvest such spin-1 configurations radiatively. Here, both phosphorescence from organometallic complexes and thermally activated delayed fluorescence (TADF) from organic donor-acceptor molecules are widely studied molecular concepts. For OLEDs, the corresponding excited state lifetime should be as short as possible to comply with the switching time and intensity requirements of displays and similar applications. Stepping away from electroluminescence, the long excited-state lifetime of triplet states, which can be as long as few seconds, offers an additional dimension for functional photonic systems. Here, fluorescence and phosphorescence easily span 7 to 8 orders of magnitude in lifetime. In this presentation, I will discuss some recent OLED results that make use of high efficiency emitter concepts at the beginning and then turn to some photonic applications that specifically make use of long-lived triplet excited states.

Cr/Photoredox dual-catalyzed synthesis of α -benzylic alcohols, isochromanones, 1,2-diols and 1,2-thio-alcohols

Johannes Erchinger, Westfälische Wilhelms-Universität Münster

Alkylation of aldehydes offers an attractive C-C bond forming protocol, wherein the design of the alkylating agent could render attractive and decorated alcohol motifs. Instigated by the classical organometallic chemistry which rather has certain limitations, we pondered of applying a dual Cr/photocatalytic strategy of generating structurally diverse alcohols in a mild and efficient manner. Herein, we disclose the synthetic generality of our catalytic approach to access α -benzylic alcohols, isochromanones, 1,2-diols and 1,2-thio-alcohols with aldehydes as electrophilic partner. Chromium was chosen for this purpose owing to its low basicity and thus high chemoselective nature of reactivity. The dual catalytic set-up features a broad substrate scope with good functional group tolerance and displays facile scale-up. The direct access towards biologically relevant scaffolds contributes to the synthetic utility of the method. A detailed mechanistic study supports a catalytic photoredox pathway being operative.

A TADF emitter studied by Time Resolved Near Infrared spectroscopy

Wiebke Haselbach, Jeremy M. Kaminski, Laura N. Kloeters, Thomas J.J. Müller, Oliver Weingart, Christel M. Marian, Peter Gilch, Bárbara E.N. de Faria, Heinrich-Heine-Universität Düsseldorf

Dyes exhibiting thermally activated delayed fluorescence (TADF) can convert singlet (25%) and triplet (75%) excitons into light. This enables their utilization as emitters in OLED. ^[1-3] The generated triplet excitons are converted into the emissive singlet ones via reverse intersystem crossing (rISC).

In metal-free organic TADF emitters, the energetically lowest singlet and triplet excitations are charge transfer (CT) ones. This ensures a small singlet-triplet energy gap of the order of $k_B \cdot T$ (~ 25 meV) — a requirement for TADF. In addition, adequately large rISC rate constants are mandatory. Due to the CT character, direct spin-orbit coupling mediating rISC is small. Therefore, rISC has to be promoted by vibronic mixing involving locally excited (LE) states ^[3]. For a better comprehension of the mechanism, the LE states were energetically localized relative to the CT ones by time resolved near infrared spectroscopy. For a prototypical TADF emitter the experimental results are in excellent agreement with quantum-chemical ones ^[4,5]. Furthermore, the effect of the energy gap between the CT and LE states on the rISC kinetics was investigated, mainly using the strong solvent dependence of the CT energies.

References:

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- ^[2] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature*, 2012, 492(7428), 234–238.
- ^[3] T.J. Penfold, E. Gindensperger, C. Daniel, C.M. Marian, *Chem. Rev*, 2018, 118(15), 6975-7025.
- ^[4] G.A. Sommer, L.N. Mataranga-Popa, R. Czerwieńiec, T. Hofbeck, H.H. Homeier, T.J.J. Müller, H. Yersin, *J. Phys. Chem. Lett.*, 2018, 9(13), 3692-3697.
- ^[5] W. Haselbach, J.M. Kaminski, L.N. Kloeters, T.J.J. Müller, O. Weingart, C.M. Marian, P. Gilch, B.E.N. de Faria, manuscript in preparation.

Vibronic contributions to through-bond and through-space charge transfer transitions in donor-acceptor type TADF emitters

Jeremy M. Kaminski, Tobias Böhmer, Luka M. Duben, Christel M. Marian; Heinrich-Heine-Universität Düsseldorf, Institute for Theoretical Chemistry and Computational Chemistry

Thermally activated delayed fluorescence (TADF) is a promising strategy to improve the efficiency of organic light emitting diodes (OLED). Typical organic emitters consist of a donating and an accepting moiety. Depending on the arrangement of donor and acceptor, two types of charge transfer (CT) processes can be distinguished.

A connection via a single bond enables so-called through-bond CT. Alternatively, donor and acceptor can be arranged via a suitable bridge such that charge can be transferred through space (through-space CT). Both molecular design principles provide a wide range of possibilities to modulate excited-state energies and non-radiative rate constants.

To design efficient TADF emitters, an extensive understanding of excited-state characters and processes such as intersystem crossing (ISC), reverse intersystem crossing (rISC) and internal conversion (IC) is crucial. Especially symmetry-forbidden transitions require the incorporation of vibronic interactions for a meaningful comparison with experimental data.

In collaboration with the group of A. P. Monkman (University Durham, UK), we investigated the through-bond CT emitter DMAC-TRZ and the through-space CT emitter TpAT-tFFO ^[1] by quantum chemical methods and discuss why the incorporation of vibronic interactions is inevitable. Additionally, we show that a locally excited triplet state in energetic proximity of the respective CT state can mediate and accelerate ISC and rISC.

References:

^[1] Chem. Sci., 2022, 13, 7057-7066

Simulating and screening photophysics of transition-metal complexes

Patrick Zobel, University of Vienna, Institute of Theoretical Chemistry, Austria

The study of excited-state dynamics of transition-metal complexes is challenging due to their large number of vibrational degrees of freedom and many close-lying electronic states.^[1] When quantum dynamics is used to simulate transition-metal complexes, this imposes the use of truncated models with typically only few degrees of freedom and electronic states, where the electronic potentials are often described in parameterized vibronic-coupling models. An alternative to quantum dynamics that can include all degrees of freedom and large number of electronic states is given by on-the-fly surface hopping (SH) methods. However, the repeating cost of the underlying electronic structure calculations restricts the range of possible simulation times for molecules the size of transition metal complexes severely.

By using SH on vibronic-coupling potentials, we can now lift the simulation-time restriction in SH and enable full-dimensional nonadiabatic dynamics simulations of transition-metal complexes on picosecond time scales.^[2,3] This is first demonstrated for a near-infrared emitting vanadium(III) complex with an open-shell triplet ground state. Using multi-reference CASSCF-derived linear vibronic-coupling (LVC) potentials, we can unravel the relaxation mechanism populating the phosphorescent singlet state.^[4] Based on the mechanistic insights, several derivatives of the complex are proposed to improve luminescence and their excited-state dynamics are simulated as well, an effort only possible due to the efficiency of the SH/LVC approach.

References:

^[1] Zobel and González, JACS Au, 1, 1116-1140 (2021)

^[2] Plasser et al., Phys. Chem. Chem. Phys. 21, 57-69 (2019)

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Strategies for enhancing thermally activated delayed fluorescence

Anna Köhler, University of Bayreuth, Germany, anna.koehler@uni-bayreuth.de

Organic light-emitting diodes (OLEDs) can make full use towards light emission of both, spin-singlet and spin-triplet excited states, when the usually non-emissive triplet state converts to an emissive, yet higher energy singlet states through thermal activation. Such thermally activated delayed fluorescence (TADF) requires high reverse intersystem crossing rates. In my presentation, I shall give examples for several chemical design strategies on how this may be achieved. In particular, I will focus on the role of meta-versus-para-connection between donor and acceptor constituents, and on the role of donor and acceptor strength. The role of triplet-triplet annihilation in the spectra may also be commented on.

Poster Abstracts

P01 Designing flavins with desired optical properties - A crystal engineering approach

Takin Haj Hassni Sohi, Heinrich Heine University, Institute of Inorganic Chemistry and Structure Chemistry 1, Crystal Engineering

Recent advances on organic solid-state chromophores have led to several potential applications in diverse fields promising great interest from a broad range of research. Moreover, tunability, flexibility and low cost characterize and add to a great advantage for potential usability of organic chromophores. A substance group of interest is alloxazine including its isomer isoalloxazine, the latter being the basis for flavins. With the majority of flavin research being focused mainly in solution, the solid-state characteristics, especially structural characterization of this chromophore, remain almost unstudied. Here, co-crystallization is proposed as an alternative route for tailoring flavins optical properties in the solid state. With the isoalloxazine derivative roseolumiflavin we were able to successfully design three robust binary co-crystals with hydrogen and halogen bonding motives. In acidic environment, ternary co-crystals are formed. The co-crystals exhibit altered optical properties in the solid state confirming easily accessible luminescence modification via a crystal engineering approach. Structural characterization of roseolumiflavin and its multicomponent crystals display differences in crystal packing with rearranged hydrogen bonded and π - π stacking motifs being noticeable as a result of the co-crystal formation. Our findings thus render new possibilities to investigate on flavins in the aspect of crystal engineering for controlled tuning of optical properties of organic chromophores.

P02 MIA chromophore in solid state environment

Simon Hédé, Heinrich Heine University, Institute of Theoretical and Computational Chemistry

Flavins are luminescent chromophores that play an important role in biological photoreception. ^[1] Their luminescence properties strongly depend on their environment. 10-methyl-isoalloxazine (MIA) shows only weak fluorescence in the crystalline state, while it turns into a potent fluorescence emitter when embedded into various metal organic frameworks (MOFs). In this study, we investigate the fluorescence emission of MIA in its crystal structure, in MIL-53(Al) and in MOF-5 with plane-wave methods ^[2] and with combined quantum mechanics/molecular mechanics (QM/MM) strategies. ^[3] Our calculations show that the mechanism of fluorescence quenching involves multiple π -interacting MIA molecules. The MOF can restore MIA fluorescence to its intensity in aqueous solution ^[4] with only little influence on absorption and emission wavelengths, thus providing a solid environment for technical applications.

References:

^[1] The evolution of flavin-binding photoreceptors: an ancient chromophore serving trendy blue-light sensors, A. Losi et al., *Annu. Rev. Plant. Biol.*, 2012, 63, 49.

^[2] QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials, P. Giannozzi et al., *J. Phys. Condens. Matter.*, 2009, 21, 395502.

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P03 Fluorinated Flavins for Modulation of Intersystem Crossing

Mira Kubitz, Heinrich Heine University, Institute of Organic Chemistry and Macromolecular Chemistry

Flavins, a class of yellow redox-active chromophores, are ubiquitous in nature and are an essential moiety of many photoreceptor proteins as well as important cofactors in enzyme catalysis. Two characteristics make them so special. First, induction of photochemical processes following absorption of blue light and second, their redox-activity with participation in both one- and two-electron transfer processes. By modifying the structural motif of the isoalloxazine core system, their photophysical properties can be altered to qualify them for different applications. For example, an increased fluorescence quantum yield could open new applications like optical imaging while increased triplet quantum yields could be interesting for singlet oxygen production (photodynamic therapy). For this purpose, fluorine substituents are highly suitable due to their strong electronic bias and their small size with little sterical impact on biological activity. In comparison to previously reported mono-fluorinated derivatives of 10-methyl-isoalloxazine (MIA), one additional mono-fluorinated MIA and one multiply fluorinated MIA were synthesized. Fluorination in 9 and 7,8-position, respectively, were motivated by previously reported quantumchemical calculations. The good agreement with experimental results was verified for the 9F-MIA whose photophysical properties have not been reported by now. The predicted additivity of multiple fluorinations was supported by the 7,8F-MIA derivative, whose fluorescence quantum yield was predicted to be comparatively high. Experimental results of spectroscopy in aqueous solution were in agreement with quantumchemical calculations as well. For 7,8F-MIA a fluorescence quantum yield of 42 % was obtained (MIA 22 %), which is a big step towards possible fluorescence applications.

P04 Benzylic C-H acylation by cooperative NHC and photoredox catalysis

Lena Lezius, Organic Chemical Institute, Westfälische Wilhelms University Münster

Methods that enable site selective acylation of sp^3 C-H bonds in complex organic molecules are not well explored, particularly if compared with analogous transformations of aromatic and vinylic sp^2 C-H bonds. We report herein a direct acylation of benzylic C-H bonds by merging N-heterocyclic carbene (NHC) and photoredox catalysis. By using the combination of these two catalytic modes a reductive radical NHC catalysis is possible which works via a ketyl radical as the key intermediate. The method allows the preparation of a diverse range of benzylic ketones with good functional group tolerance in moderate to excellent yields under mild conditions. The reaction can be used to install acyl groups on highly functionalized natural product derived compounds and the C-H functionalization works with excellent site selectivity. The combination of NHC and photoredox catalysis offers new options for the preparation of benzyl aryl ketones.

P05 Charge-transfer terms in short-range excitation energy transfer calculations

Simon Metz, Christel M. Marian, Institute of Theoretical and Computational Chemistry, HHU Düsseldorf, Germany

Organic light-emitting diodes (OLEDs) established themselves as a light-source technology for displays of any kind. The newest (4th) generation of OLED devices utilize an energy transfer process, a so-called hyperfluorescence mechanism. The emissive layer consists of two active molecules, an auxiliary dopant with thermally activated delayed fluorescence (TADF) properties which harvests singlet and triplet excitons and transfers the excitation to a fluorescent molecule, through a singlet excitation energy transfer (SEET) mechanism. Hyperfluorescent OLEDs combine the 100 % internal quantum efficiency of the TADF molecule with the narrow and intense emission of the fluorescence emitter. For the understanding and improvement of such a donor-acceptor system it is not only important to describe the SEET processes but also unwanted transitions. Triplet excitation energy transfer (TEET) from the TADF dopant to the triplet states of the fluorescent molecule, for example leads to a loss of efficiency due to a lack of emission pathways from these triplet states. At short distances between donor and acceptor this mechanism is dominated by charge-transfer states (bridging ionic configurations). Such contributions are currently not well described in our existing energy transfer program. With the help of Dyson orbitals, the overlap between wavefunctions differing in the number of one electron, the charge-transfer terms are included beyond the typical single configuration treatment and a more accurate determination of the short-range energy transfer is possible.

P06 Phenazine-based dyes and linkers for metal organic frameworks (MOFs)

Dietrich Püschel, Heinrich Heine University Düsseldorf, Institute of Inorganic Chemistry I

A number of prominent (dihydro)phenazine derived dyes are known (e.g. safranines), including the interesting case of N,N'-bis-(4-cyanophenyl)phenazine, featuring Thermally Activated Delayed Fluorescence properties, relatively rare for a planar, symmetric and compact molecule. The easily N-functionalizable dihydrophenazine core grants access to linear building blocks for porous polymers, both covalent- (COFs) and coordination bonded- (MOFs) ones. The luminescent- and redox properties of the derived compounds offers advanced potential for applications, including tuneable light emission, photocatalysis, and sensorics. Our work is focussed on the investigation of different cyano(bi)phenylphenazines as well as porous coordination polymers based on the derived carboxylates as luminescent materials.

P07 Avoiding Switching of Dithienylethenes via Cationic State in Solution Processed Light-Emitting Organic Memory Diodes

Elisabeth Pankert, University of Cologne, Department of Chemistry, Institute of Physical Chemistry

In the course of digitalization and the associated ever-increasing volume of data, the need for efficient high-density data storage is constantly rising. Organic memory devices (OMEMs) can be fabricated cost-efficiently by solution-processing, even on flexible substrates. One approach is the use of organic photochromic compounds, so called molecular switches, such as dithienylethenes (DTEs), which exhibit high fatigue resistance and can undergo a photoinduced ring-closing and opening reaction. The frontier molecular orbitals of ring-closed and ring-open DTE isomers have a large energetic difference, enabling the utilization of the compound as switchable hole injection barrier and thus controlling the electrical current and the brightness of a light-emitting diode. This enables access to a multitude of intermediate states and accordingly offers potential for multi-level memory applications. We use a DTE derivative with oxetane functionalized side chains (XDTE) enabling a fully solution processed device by crosslinking via cationic ring-opening polymerization (CROP). While the non-crosslinked, closed isomer exhibits excellent thermal stability, pronounced thermally activated ring-opening of the DTE core is observed for the derivative crosslinked via CROP. We investigated the thermally activated ring-opening in dependence of the amount of added photoacid generator (PAG) acting as CROP initiator and found an impressive correlation between the PAG concentration and the thermal opening. This can be attributed to a cationic opening mechanism caused by a charge doping of the DTE core during proton generation via PAG. The p-doped closed DTE core is in difference to the uncharged DTE no longer stable regarding thermally activated ring-opening. We also analyzed how underlying hole transport layers with varying HOMO energy levels affect the tendency for thermally activated DTE ring-opening. By adding post-treatment steps and reducing the number of charges after layer processing the thermally activated ring-opening could be significantly reduced. To avoid charge doping and undesirable ring-opening via cationic species of the DTE core during crosslinking we developed a novel compound with methacrylate side chains (MA-DTE) and investigated free radical polymerization (FRP) as an alternative crosslinking method. We found suitable conditions for solution processing and subsequent crosslinking of MA-DTE. The derivative showed excellent thermal stability in the crosslinked state and the resulting memory device has comparable electrical characteristics to the one based on XDTE.

P08 Incorporation of TADF dyes into MOF MIL-68

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TADF dyes are an interesting research topic due to their ability to access both singlet and triplet energy states for fluorescence. MOFs on the other hand offer a defined pore network that can be filled by a fitting dye molecule. Different TADF dyes have been incorporated into variants of the MOF MIL-68. Stability, loading capacity and influence on fluorescence have been measured.

P09 Computational Search for Pd/Pt(0) Complexes Emitting Circularly Polarized NIR Radiation

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In our SPP application, we envisioned Ni/Pd/Pt(0) complexes displaying NIR-luminescence. As further challenge, these complexes should emit circularly polarized light, preferably via phosphorescence, with high luminescence quantum yield and large dissymmetry factor g_{lum} . A first step towards this goal is the identification of reliable, effective motives for NIR emitters, to subsequently inject chirality and describe guidelines for the circularly polarized phosphorescence. All should culminate in effective circular polarized phosphorescence.

Upon wandering towards the NIR-region, the energy gap law poses a main challenge. According to this relation, the probability of intersystem crossing (ISC) increases exponentially with decreasing energy difference ΔE between interacting states. Large direct spin-orbit coupling (SOC) with the ground state and pronounced geometric displacements enhance the ISC probability. On the one hand, the T_1 state needs to be protected from nonradiative decay, on the other hand strong radiative rates require a large electric transition dipole moment, which, in case of the phosphorescence, is achieved either through large first-order SOC with the ground state or second-order intensity borrowing of brighter upper states. Moreover, the radiative rate constant shrinks with increasing wave lengths.

In the here reported first approach, we scanned several Pd(0) and Pt(0) complexes from the class of trigonal carbene-metal-phosphine complexes and homoleptic dicarbene complexes. In the trigonal phosphine complexes, the lowest excited states are of MLCT-character, with electron density being transferred from a metal-ligand bond to an antibonding π -orbital on the phosphine or carbene. As a consequence of the d^9 configuration, a large Jahn-Teller distortion (JTD) takes place in the S_1 and T_1 excited states. Strong vibronic coupling combined with large direct SOC between S_0 and T_1 facilitates fast non-radiative deactivation. Substantial JTD might be lessened by steric congestion of the ligands, but no potential case of favorable intensity borrowing has been found yet. The results for the linear complexes are more promising. Large structural distortion upon entering the T_1 was not observed and the strong π -acceptor character of the employed CAAC ligands causes low-lying MLCT states in the NIR. Spatial separation of hole and electron orbitals causes a small $\Delta E(S-T)$ and even suggests TADF instead of phosphorescence, with good fluorescence rates in the μs regime. Hence, this class appears to satisfy our requirements for efficient NIR-emitters and will be investigated further.

P10 Direct Access to Unnatural Cyclobutane α -Amino Acids through Visible Light Catalyzed [2+2]-Cycloaddition

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Cyclobutane amino acids ^[1] have evolved as an interesting class of derivatives for the development of new classes of strained, conformational restricted peptide mimetics for medical applications, as well as diverse uses as synthetic building blocks or catalysts. ^[2-5] In this work, we report the first, selective, photocatalyzed [2+2]-cycloaddition of dehydroamino acids with styrene-type olefins. This simple, mild and scalable approach relies on the use of the triplet energy transfer catalyst [Ir(dFCF3ppy)₂dtbpy]PF₆ under visible light irradiation and provides fast access to value-added substituted strained cyclobutane α -amino acid derivatives.

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P11 Luminescent Copper(I)-Complexes bearing an anionic N-Heterocyclic Carbene: Towards new TADF emitters

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The anionic diamido-NHC 1,3-bis(2,6-diisopropylphenyl)-5-methyl-4,6-dioxo 3,4,5,6-tetrahydro-pyrimidin-5-ylidene-2-ylidene is used to prepare a series of luminescent, linear as well as trigonal, heteroleptic copper(I)-complexes, some of which showing TADF behavior due to a very small $\Delta E(S-T)$ value. Apart from the NHC, either pyridine derivatives, triphenylphosphine or halides are employed as ligands. A key role lies in the versatile precursor for these complexes, a water and air-stable 1D coordination polymer composed of only the NHC and Cu(I), such that the copper is linearly coordinated by the carbene carbon atom and one oxygen atom of the carbenes' backbone. This polymer can easily be broken down to the monomeric emitter molecules by simply adding the desired ligand to its dispersions in dichloromethane. In solution though, the molecules are in equilibrium with this highly insoluble compound and dissociated ligand, which forced us to limit our spectroscopic investigations to the emitters' well-defined crystalline state, determined by single crystal x-ray diffraction. However, non-classical hydrogen bonding in the crystal lattices of all emitters is observed, which results from their very high dipole moments calculated to be in the range of 15 to 20 D in the gas phase, introducing further complications for theoretical investigations and spectroscopic data analysis.

P12 Characterization of conformationally constrained fluorophores with delayed fluorescence

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Chromophores exhibiting thermally activated delayed fluorescence (TADF) are valuable candidates for new generations of OLED-devices. The main characteristic of the TADF mechanism is that thermal energy promotes reverse intersystem crossing (rISC) from the triplet to the singlet state due to a small $\Delta E(S-T)$, from where the molecule emits delayed fluorescence. In this way, harvesting both singlet and triplet states through prompt and delayed fluorescence is possible such that TADF emitters can achieve the limit of 100% internal quantum efficiency. Various bi(hetero)aryl donor-acceptor systems are characterized within this work. The methyl-substituted derivative was already proven to be a TADF emitter [1]. In this work, we show how different substituents on the linker between donor and acceptor and the presence of oxygen affect the photophysical properties of the molecules.

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P13 Synthesis of Chiral Ag(I)-Bisimine Complexes and Quinazolinone Blue Light Emitters

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The use of chiral complexes for asymmetric catalysis and transformations is well established in organic synthesis. In contrast, the combination of a C₂-symmetric backbone for metal bonding and fixation of a substrate via hydrogen bonding in the same ligand is not investigated in detail so far.

Herein, we report the synthesis of 1,1'-binaphthalene-2,2'-diamine (BINAM)- and diaminocyclohexane (DACH)-I bisimine ligands with different urea groups for the formation of silver(I) complexes, which may be used in asymmetrical catalysis of carbonyl compounds. Variation of the urea group and substitution pattern of the aromatic ring leads to ligands with different bite angles. Complex formation with silver(I) salts was investigated by ¹H-NMR-spectroscopy.

One of the intermediate products in ligand synthesis, ortho-urea-benzaldehyde, shows intramolecular cyclization in slightly acidic media resulting in the formation of N substituted quinazolinonium compounds. These cations show a strong light blue emission by irradiation with UV light in various solvents and the solid state. The addition of nucleophiles, such as alcohols, lead to quenching of the fluorescence.

P14 Search of a promising TADF emitter: Computational investigation of 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 a 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 d^{10} 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 Zinc(II) complexes the metal atom does not participate in the low lying electronic excitation which results in tiny ΔE_{S-T} . Two promising molecules are MenthCAAC-Zn(II)-bdt and MenthCAAC-Zn(II)-bdo. Apart from the Zinc(II) core, the molecule contains a chiral CAAC ligand with a L-menthyl residue on one side and a benzene-1,2-dithiol (bdt) or benzene-1,2-diol (bdo) ligand on the other.

Minima of the molecules were obtained via density functional theory. Energetically close conformers with different ligand twists were found and their excited state energies investigated with DFT/MRCI. Subsequently SOC's were calculated with the SPOCK program and the (r)ISC rate constants were calculated according to the Fermi golden rule.

Surprisingly, the exchange of sulfur with oxygen led to a red shift of the vertical emission from red for 1 to NIR for 2. Apart from that, both complexes show similar photophysical properties. A very low ΔE_{S-T} of $< 300 \text{ cm}^{-1}$ together with sufficiently large SOC matrix elements lead to quick $S_1 - T_1$ equilibration and delayed fluorescence on the μs timescale. Importantly, the rapid rISC persists even at low temperatures and the good TADF emitter properties appear to be nearly conformer independent. First experiments support the theoretical predictions.

P15 The implementation and application of the vertical Hessian method for the calculation of Franck-Condon Spectra

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In order to design efficient emitting materials for practical devices such as organic light emitting diodes (OLED) an extensive understanding of excited-state characters and processes is crucial. An important photophysical property to predict is the emission spectrum that can be calculated using the Franck-Condon principle in the harmonic approximation.

Many highly emissive emitters undergo strong geometrical changes after an electronic excitation. In particular, strong displacements can be observed in charge transfer states (CT) that are desired for so-called thermally activated delayed fluorescence (TADF) emitters. Typical methods using adiabatic geometries and normal modes in the Cartesian coordinate system fail to yield reliable results for a meaningful comparison with experimental data.

The Vertical Hessian Method (VH)^[1] was implemented into the VIBES^[2,3] code to bring remedy. While the application of this method to small systems in the implicit solvent model shows significant improvement it yet has to be tested in the explicit solvent environment.

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P16 Synthesis and Characterisation of Conformationally Twisted Triphenylamine Dyes as Potential TADF Emitters

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The development of functional organic chromophores is a topic of high relevance and interest. Triphenylamine derivatives are particularly interesting due to their high thermal and photochemical stability.^[1] In addition, they are often employed in thermally activated delayed fluorescence (TADF) dyes. By distortion, the HOMO-LUMO frontier molecular orbital overlap is minimized and thus a small $\Delta E(S_1-T_1)$ is expected.^[2] This enables TADF to occur. TADF chromophores make it possible to design OLEDs more efficiently, as they significantly increase the internal quantum yield of the emission.^[3] Four novel conformationally twisted triphenylamine dyes were readily synthesized by bromine-lithium exchange borylation-Suzuki sequence (BLEBS) in moderate to good yields.

Their electronic properties were studied by absorption and emission spectroscopy revealing blue to green yellowish emission in solution as well as in the solid state and upon embedding into a PMMA (polymethylmethacrylate) matrix. Moreover, the substances show a positive emission solvatochromism exposing large Stokes shifts from toluene to dichloromethane. By low temperature measurements small $\Delta E(S_1-T_1)$ values were estimated in solution and in the PMMA matrix. First time-resolved measurements indicate TADF properties.

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P17 From Curricular Innovation to Science Communication

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Science Communication is getting more and more important to society and thereby also to the scientific system. It also became a criterion for the support of research associations [1]. Therefore, it is crucial to encourage doctoral students in communicating research to society. To support the science communication skills of the doctoral students of ModISC we offer different possibilities. This way on the one hand the students get the option to practice talking about science and research to a non-scientific audience and on the other hand we get data to improve the different offers.

This year the doctoral students of ModISC supported the girls at the Girls`Day of the HHU. We developed a "Hands-on Experiment" for science teaching with regard to curricular innovation in schools which the girls performed with the help of the students. Before they did a training to familiarize themselves with the experiment and any problems that may arise. The poster shows the Girls`Day itself, the training and also the self-assessment of the doctoral students with regards to manage the supervision.

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P18 Time Resolved Near Infrared Spectroscopy – why and how

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Emitters for organic light emitting diodes (OLEDs) ought to efficiently convert singlet and triplet excitons into light. A promising concept in this respect is thermally activated delayed fluorescence (TADF). In TADF emitters, triplet excitons are converted into emissive singlet ones. The respective emitters are commonly of charge transfer (CT) character which ensures small energy gaps between singlet and triplet excitons. Such small gaps are a prerequisite for TADF. However, the CT character diminishes the direct spin-orbit coupling between the singlet and triplet states and thereby hampers their equilibration. As shown theoretically, spin-vibronic coupling can mitigate this. [1] The energy denominators in the respective expressions contain $S_1 \rightarrow S_n$ ($n = 2, 3, 4, \dots$) and $T_1 \rightarrow T_n$ ($n = 2, 3, 4, \dots$) excitation energies.

We here report on progress in determining these excitation energies spectroscopically. The respective transitions are located in near infrared (NIR) region. A brief overview on approaches of time resolved spectroscopy in the NIR is given. First result on a TADF emitter containing a triarylamine donor and 1,4-dicyanobenzene acceptor moiety [2] are presented and discussed in relation to spin-vibronic coupling.

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