Julius-Maximilians-
UNIVERSITÄT
WÜRZBURG

Molecular biradicals: structure, properties and reactivity

September 28-29, 2016

Niederstetten

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Preface

Dear Participants,

Welcome to the first workshop of our research training school GRK 2112 on "Molecular Biradicals" in Niederstetten. It is now almost one year since the GRK started with a start-up workshop that saw presentations on the scientific background by selected principal investigators. Since then a number of graduate students has started a thesis and first results on the properties of biradicals have been reported. It is thus time to discuss the scientific progress. To my mind this workshop serves a number of purposes that I want to summarize:

- First, graduate students are supposed to present their project either in talks or as posters. While preliminary results will certainly constitute a part of several contributions, the focus will be on the description of the scientific background. What is the goal of the project? What methods do you choose and why? Which difficulties do you encounter? Make sure that you present you project in a way that everybody can understand the central ideas. And don't hesitate to ask if you don't understand something in the presentations of others.
- Furthermore we want to promote interactions between graduate students. Can another student provide you with support, suggestions for alternative approaches or even ideas for future joint projects? Maybe a synthetic chemist has an interesting molecule for the spectroscopist or the theoretician can suggest a good approach to address an experimental difficulty. Beer, wine and soft drinks at the poster session will facilitate communication and might help to achieve this goal.
- The workshop gives you also a chance to talk to your co-supervisor or maybe even to find a co-supervisor, if you don't have one yet. Often enough he/she will provide you with good (or sometimes not so good) ideas for your project.
- In addition you are invited to give feedback on the GRK. Do you have suggestions for the next workshop, for the lecture series or for the GRK in general?
- At the end of the workshop you will hopefully understand better why "Molecular Biradicals" are an attractive research field and return to Würzburg with fresh ideas for your own project and new contacts to the other research groups

Before concluding this preface I want to thank the organizing team, Eileen Welz, Hansi Schmitt and in particular Uschi Rüppel for all the work they put into making this event happen.

I am looking forward to a stimulating and productive workshop,

Ingo Fischer

Location information

Niederstetten

The little town (around 5000 inhabitants) is located about 50 km southern of Würzburg in the valley of the little river Vorbach, which is a subsidiary stream of the Tauber. It is close to the Bavarian border but already situated in Baden-Württemberg. The front cover shows the town square with the town hall and the *"Schimmelturm"*, which is 15.5 m high and was used for protection of the town in former times. The fountain in front of the town hall illustrates the *"Steidemer Männle"* (find out more about this saga on a board on the town hall wall).

Did you know? Over 100 years the biggest piglet market in Germany took place in Niederstetten! No wonder, as the local farmers specialized in cultivating pigs since the 1950s. Over 500 piglets were sold there every week. But unfortunately structural transformation made the market close in 2013.

Schloss Haltenbergstetten

This castle complex was built around 1200 and converted into a palace in the 16th century. After the secularization the "Fürsten zu Hohenlohe-Jagstberg" acquired the castle from the prince-bishopric of Würzburg in 1803 and they are still living there today. You can find a hunting and natural history museum in the building.

Personalities

A famous son of Niederstetten is *Albert Sammt*, who was born in 1889 as the son of a ropemaker. 23 years old, he started to work with the Zeppelin airship building company. He was the navigator of the zeppelin which first crossed the Atlantic Ocean (1924) and as an Officer he survived the accident of the Hindenburg in Lakehurst (1937). He became commander of the last German zeppelin "Graf Zeppelin" and died at the age of 93 years in Niederstetten, where he is buried.

Program

Wednesday, September 28

08:45	**Bus ride** to Niederstetten (Parking Area “Physikalische Chemie”)	
10:30	**Bernd Engels**	Opening remarks and organization details
Session I	Chair: E. Welz	
10:45	**Engelbert Reusch** AK Fischer	Photoelectron Spectroscopy of *ortho*-benzyne
11:15	**Hans-Christian Schmitt** AK Fischer	A fs time-resolved study of *ortho*-benzyne and its precursor
11:45	**Charlotte Brückner** AK Engels	Calculating Singlet-Triplet Gaps to Screen for Singlet-Fission Candidates: The Role of HF Exchange and DFT Correlation
12:15	*Lunch*	
Session II	Chair: H.-C. Schmitt	
14:00	**Klaus Eckstein** AK Hertel	Developing a Flow Cell Design for Time-resolved Spectroelectrochemistry
14:30	**Michael Auth** AK Dyakonov	Doping of (6,5)-Single-Wall Carbon Nanotubes determined by quantitative Electron Paramagnetic Resonance
15:00	**Markus Gernert** AK Steffen	A Cyclic Alkyl(Amino)Carbene as π-Chromophore for phosphorescent Cu(I)-Complexes
15:30	*Coffee Break*	

Session III Chair: B. Hupp

16:00	**Heiko Hildenbrand** AK Brixner	Time-resolved Circular Dichroism Spectroscopy of Hemoglobin
16:30	**Andrea Deißenberger** AK Braunschweig	Neutral Captodative Biradicals Stabilized by Cyclic (Alkyl)(Amino)Carbenes
17:00	**Ulrich Müller** AK Pflaum	Studies on single para-xylylene bridged perylene bisimide macrocycles at strong photo-excitation
18:00	*Dinner*	
19:30	**Postersession**	

Thursday, September 29

Session IV Chair: D. Schmidt

09:00	**Julia Merz** AK Marder	Pyrene MO Shuffle: Adjusting the HOMO-LUMO gap by changing the frontier MO ordering
09:30	**Michael Wenzel** AK Mitrić	Nonadiabatic dynamics of the pyrene dimer and excimer
10:00	**Julian Böhnke** AK Braunschweig	Reacivity of BoronBoron Multiple Bonds
10:30	**Postersession**	*With Coffee*
12:30	*Lunch*	*With Coffee afterwards*

Session V Chair: U. Müller

14:00	**Rodger Rausch** AK Würthner	Isoindigoradicals and –biradicals: Synthesis and characterization
14:30	**Kilian Hader** AK Engel	Identification of effective exciton–exciton annihilation
15:00	**Benjamin Hupp** AK Steffen	Highly Efficient Mechanochromic Luminescence of Structurally Simple Cu(I) NHC Complexes
15:30	**Meeting of PhDs**	
15:50	**Ingo Fischer**	Concluding Remarks
16:00	**Bus ride** to Würzburg	

Postersession

Name	Group	Poster
Auth, Michael	Dyakonov	Doping of (6,5)-Single-Wall Carbon Nanotubes determined by quantitative Electron Paramagnetic Resonance
Brückner, Charlotte	Engels	Calculating Singlet-Triplet Gaps to Screen for Singlet-Fission Candidates: The Role of HF Exchange and DFT Correlation
Bunzmann, Nikolai	Dyakonov	Spin-sensitive Investigation of Organic Light Emitting Diodes based on Thermally Activated Delayed Fluorescence
Buschmann, Rachel	Krüger	Synthesis of precursors for extended π-systems with a tribenzotriquinacene core
Eckstein, Klaus	Hertel	Transient Absorption Spectroelectrochemistry of a (6,5) Carbon Nanotube Thin Film
Flock, Marco	Fischer	A fs time-resolved UV/IR Study of Benzocylcobutene-1,2-dione
Hammer, Sebastian	Pflaum	Exciton Transport and Dissociation at Organic Single Crystal Surfaces
Hirsch, Florian	Fischer	Study of the self-reaction products of o-benzyne radicals via IR/UV ion-dip-spectroscopy
Hupp, Benjamin	Steffen	Highly Efficient Mechanochromic Luminescence of Structurally Simple Cu(I) NHC Complexes
Lindner, Joachim	Mitrić	Theoretical Studies On The Water Oxidation Mechanism in Ruthenium Macrocyclic Systems
Meier, Michael	Braunschweig	Synthesis of new borole compounds based on thiophene deriatives
Mims, David	Lambert	Synthesis of a novel Donor – Sensitizer – Acceptor Triad for the Investigation of Magnetic Field Effects
Schmidt, David	Würthner	Perylene Bisimide Radicals and Biradicals: Synthesis and Molecular Properties

Seifert, Sabine	Würthner	Defined Electron-Poor Nanographenes: One-Pot Synthesis and Single Crystal Structure Analysis
Turkin, Arthur	Lambert	Synthesis and Characterization of Squaraine-Squaraine Copolymers
Wehner, Johannes	Engel	Two-Dimensional Spectroscopy of Homo- and Hetero-Dimers
Welz, Eileen	Engels	Theoretical investigations of o-benzyne and the benzyne cation radical

Talks

I-1: Wednesday , September 28th – 10:45-11:15

Photoelectron Spectroscopy of *ortho*-benzyne

Engelbert Reusch, Philipp Constantinidis, Patrick Hemberger, and Ingo Fischer

Ortho-Benzyne (o-C_6H_4), which occurs as an unstable intermediate in chemical reactions, is a key-intermediate for soot formation. It has been investigated by various techniques like matrix isolated IR and NMR spectroscopy. Even though conventional Photoelectron Spectra (PES) of this biradical already exist, the correct ionization energies and the assignment of bands to o-Benzyne are still discussed.

To obtain new insights this study applies Photoelectron Photoion Coincidence Spectroscopy (PEPICO), which yields mass selected PES.

Benzocyclobutene-1,2-dione, synthesized by the procedure of South and Liebeskind [1], has been chosen as a precursor generating o-Benzyne. Hence, the biradical was produced by flash pyrolysis, stabilized in the gas phase and photoionized by tunable vacuum ultraviolet synchrotron radiation.

This presentation gives an overview of photoionization experiment and results of o-Benzyne, executed at the Swiss Light Source (SLS) using synchrotron radiation (Villingen, Switzerland). Planed future experiments on other biradicals will be discussed.

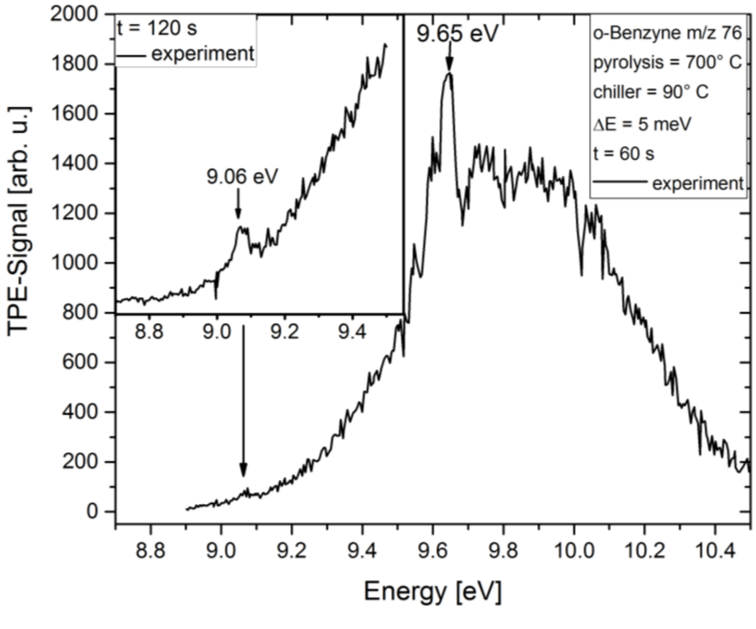


Figure: *Mass selective Threshold Photoelectron Spectrum of o-Benzyne.*

[1] South, M. S., Liebeskind, L.S., *J. Org. Chem.,* **47**, 3815 (1982).

I-2: Wednesday , September 28th – 11:15-11:45

A fs time-resolved study of *ortho*-benzyne and its precursor

Hans-Christian Schmitt, Marco Flock, Anja Röder, Lionel Poisson, Ingo Fischer, Xianon Ma and Tobias Brixner

The history of the biradical *ortho*-benzyne from its early beginnings as an unobservable intermediate until its present status as theoretically challenging molecule with important applications in synthesis is still in progress [1]. Despite some spectroscopic studies the intrinsic properties of o-benzyne are still not well understood.

In order to get a deeper insight in the excited state dynamics of the isolated molecule we performed a fs gas phase experiment. The pyrolysis technique allowed us to generate the biradical and by the use of a pump(266 nm)-probe(800 nm) spectroscopy we could measure the ultrafast dynamics.

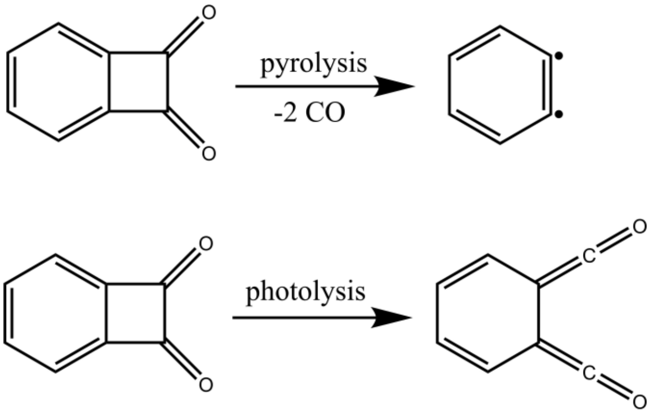


Figure: *upper trace: generation of o-benzyne by pyrolysis in the gas phase.*
lower trace: photolysis in the liquid phase reveals bond cleavage in 4-ring..

Furthermore, we performed a fs UV-pump-IR-probe experiment in the liquid phase. We could nicely resolve that excitation of the precursor at 300 nm leads to a fast bond cleavage in the 4-ring and the formation of a bisketene.

[1] C. Wentrup C, *Aust. J. Chem,* **63**, 979–986 (2010).

I-3: Wednesday , September 28th – 11:45-12:15

Calculating Singlet-Triplet Gaps to Screen For Singlet-Fission Candidates: Understanding The Role of HF Exchange and DFT Correlation

Charlotte Brückner and Bernd Engels

Vertical and adiabatic singlet and triplet excitation energies of molecular p-type semiconductors calculated with various DFT functionals and wave-function based approaches are benchmarked against MS-CASPT2/cc-pVTZ reference values. A special focus lies on the singlet-triplet gaps that are very important in the process of singlet fission. Singlet fission has the potential to boost device efficiencies of organic solar cells, but the scope of existing singlet-fission compounds is still limited. A computational prescreening of candidate molecules could enlarge it; yet it requires efficient methods accurately predicting singlet and triplet excitation energies. Different DFT formulations (Tamm-Dancoff approximation, linear response time-dependent DFT, Δ-SCF) and different spin scaling schemes along with several ab initio methods (spin-component scaling, spin-opposite scaling; CC2, ADC(2)/MP2, CIS(D), CIS) are evaluated with respect to their accuracy. While wave-function based methods yield rather reliable singlet-triplet gaps, many DFT functionals are shown to systematically underestimate triplet excitation energies. To gain insight, the impact of exact exchange and correlation is addressed. The influence of the amount of exact exchange on triplet excitation energies is analyzed by means of non-empirical IP-tuning and functional variation, and it is shown to vary as a function of the molecular structure. The local differential correlation between the ground and the triplet excited state is identified as a key parameter decisive for triplet state energies. Upscaling the scaling coefficients of local correlation in different DFT functionals is shown to result in more accurate triplet energies.

II-1: Wednesday , September 28th – 14:00-14:30

Developing a Flow Cell Design for Time-resolved Spectroelectrochemistry

Klaus Eckstein and Tobias Hertel

Electrochemistry is a widely used tool to measure the rate and determine the thermodynamics of an electrochemical reaction. However, the species formed in the reaction cannot be determined by electrochemistry alone and good chemical intuition or an additional species-selective method is needed [1]. Therefore, electrochemistry has been coupled to spectroscopic methods like absorption spectroscopy in the UV-VIS-NIR [2] and infrared region [3], Raman spectroscopy [4], luminescence spectroscopy [5] and magnetic resonance techniques (NMR or ESR) [6,7]. However, the combination of advanced time-resolved spectroscopy and electrochemistry remains scarce.

The aim of the GRK project presented in this presentation is the development of a suitable cell design for spectroelectrochemical experiments using short laser pulses in the VIS and NIR spectral region to measure the dynamics of *in situ* generated radicals. Since the products of the electrochemical reaction may not be stable under intense photoexcitation a continuous exchange of sample material is intended.

Furthermore, a short insight into a study using time-resolved spectroelectrochemistry at a carbon nanotube film fixed at the working electrode surface is given. The underlying physical principles regarding this experiment and the results are discussed in more detail at the poster presentation.

[1] W. Kaim and J. Fiedler,*Chem. Soc. Rev.,* **38**, 3373 (2009).

[2] R. Holze, *J. Solid State Electrochem.* **8**, 982 (2004).

[3] K. Ashley and S. Pons, *Chem. Rev.* **88**, 673 (1988).

[4] M. Kalbac *et al.*, *Nano Lett.* **11**, 1957 (2011).

[5] S. Chatterjee *et al.*, *J, Phys. Chem. A*, **117**, 12749 (2013).

[6] R. Boisseau *et al.*, *Anal. Chem.,* **87**, 372 (2015).

[7] S. Klod and L. Dunsch, *Magn. Reson. Chem.***,** **49**, 725 (2011).

II-2: Wednesday , September 28th – 14:30-15:00

Doping of (6,5)-Single-Wall Carbon Nanotubes determined by quantitative Electron Paramagnetic Resonance

Michael Auth[1], Andreas Sperlich[1], Florian Späth[2], Tobias Hertel[2] and Vladimir Dyakonov[1,3]

[1] Experimental Physics VI, Julius Maximilian University of Würzburg, D-97074 Würzburg, Germany

[2] Institute of Physical and Theoretical Chemistry, Julius Maximilian University of Würzburg, D-97074 Würzburg, Germany

[3] Bavarian Centre for Applied Energy Research (ZAE Bayern), D-97074 Würzburg, Germany

Doping is generally known as a viable and widely spread method to alter the electrical abilities of semiconductor materials. Hereby the knowledge about the distinct dopant concentrations inside the materials is of crucial importance, but is also difficult to determine. Electron Paramagnetic Resonance (EPR) may sensitively probe localized charge carriers, e.g. defects, dopants or local charges opening up a way to estimate their concentration. Here, we discuss the basic principles behind EPR and especially quantitative EPR measurements, including all the parameters one needs to keep in mind for reliable quantitative estimations. As material system, we investigated (6,5)-Single-Wall Carbon Nanotubes (SWNTs), as their exceptional electrical conductivity makes them potentially interesting to improve charge transport in organic optoelectronics. The knowledge about doping concentrations is essential to use p- and n-doped SWNTs for p-n-junctions in future electronic devices.

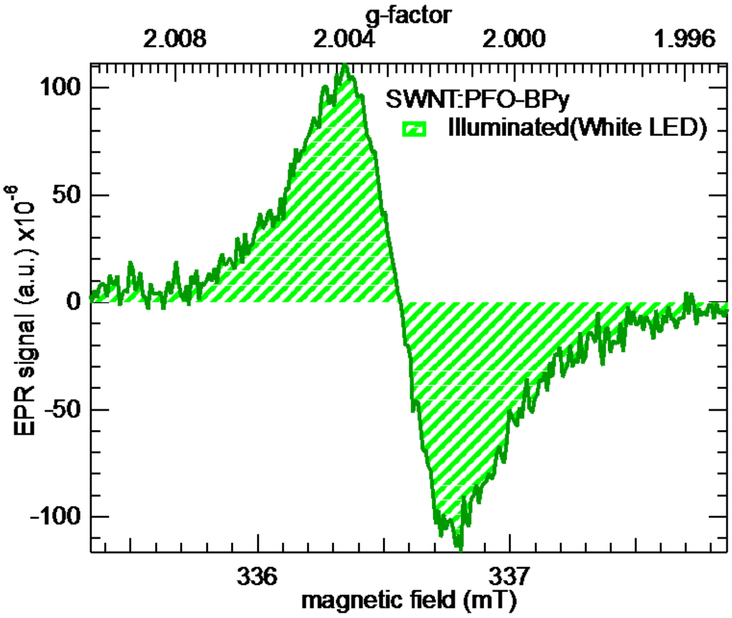


Figure: *(6,5)-SWNT EPR signal under illumination with a white LED.*

II-3: Wednesday , September 28th – 15:00-15:30

A Cyclic Alkyl(Amino)Carbene as π-Chromophore for phosphorescent Cu(I)-Complexes

Markus Gernert and Andreas Steffen

Since the beginning of the 21st century, copper(I) complexes have been established as highly interesting emitter materials due to the low cost of Cu in comparison to Ir or Pt and the absence of non-radiative metal centred d-d* transitions [1]. Four coordinate cationic homo- and heteroleptic compounds with diimine and phosphine ligands are the most extensively studied family of luminescent Cu^{I} complexes. Stabilization of the three-coordinate geometry is possible through a judicious choice of ligands, in particular bulky amides, phosphines, and *N*-heterocyclic carbenes (NHCs) [2]. Among those, NHCs have been shown to serve as very strong σ-donors and even as π-chromophores in one recent report [3].

Bearing in mind the stronger σ-donation and π-acceptor properties of cyclic alkyl(amino)carbenes in comparison to NHCs, we have set out to investigate the luminescence properties of a series of linear and trigonal Cu^{I}-CAAC^{Me} complexes, which show photophysical behavior vastly different from their NHC congeners. Linear Cu^{I}-CAAC^{Me} complexes are brightly phosphorescent in the blue to green region, leading to the fastest Cu^{I}-based T$_1$ emitter to date, whereas linear Cu^{I}-NHC compounds do not emit. Trigonal [Cu^{I}(CAAC^{Me})(diimine)]PF$_6$ complexes emit in the near-IR region, the luminescence is significantly red shifted in comparison to their NHC analogues [4].

blue:	[Cu^{I}(CAAC^{Me})$_2$]PF$_6$
green:	[Cu^{I}(CAAC^{Me})Cl]
yellow:	[Cu$_2$(μ-SPh)$_2$(CAACMe)$_2$]
red:	[Cu^{I}(CAAC^{Me})(phen)]PF$_6$

Figure 1: *The CAAC^{Me} ligand (left) and different Cu^{I}-CAAC^{Me} complexes under UV-radiation (right)*

[1] A. Barbieri, G. Accorsi, N. Armaroli, *Chem. Commun.*, 2185 (2008)

[2] Valentina Krylova, Peter Djurovich, Jacob Aronson, Ralf Haiges, Matthew Whited, Mark Thompson, *Organometallics*, **31**, 7983 (2012)

[3] Valentina Krylova, Peter Djurovich, Brian Conley, Ralf Haiges, Matthew Whited, Travis Williams, Mark Thompson, *Chem. Commun.*, **50**, 7176 (2014)

[4] M. Gernert, U. Müller, M. Haehnel, J. Pflaum, A. Steffen, *Chem. Sci. (*2016), in revision.

III-1: Wednesday , September 28th – 16:00-16:30

Time-resolved Circular Dichroism Spectroscopy of Hemoglobin

Heiko Hildenbrand, Andreas Steinbacher, Federico Koch, Marco Schmid and Tobias Brixner

Circular dichroism (CD) is a common technique to analyze chiral samples. by their difference in absorption of left and right circularly polarized light. However, chiral signals are small and the typically utilized long optical path lengths, high concentrations, and long integration times in steady-state measurements are not suitable for ultrafast spectroscopy. Hence, only few chirality-sensitive spectroscopic approaches in the liquid phase are known in the literature [1,2].

Here, we present broadband time-resolved CD spectroscopy which is based on a setup capable of mirroring an arbitrary polarization state of an ultrashort laser pulse. Hence, by passing a broadband probe pulse through this setup we can switch between opposite handedness on a shot-to-shot basis to detect pump-induced CD changes. To demonstrate the capabilities of this approach we investigated the early photochemistry of oxygenated hemoglobin and myoglobin by time-resolved circular dichroism and transient absorption spectroscopy in the visible spectral region, since the spectrometer is capable of acquiring both signals simultaneously.

As the polarization-mirroring setup is in principle able to mirror an arbitrary polarization state, it is not limited to time-resolved CD spectroscopy but also ellipsometry or anisotropy experiments can be performed.

[1] Julia Meyer-Ilse, Denis Akimov, and Benjamin Dietzek, *Laser Photon. Rev.* **7**, 495 (2013).

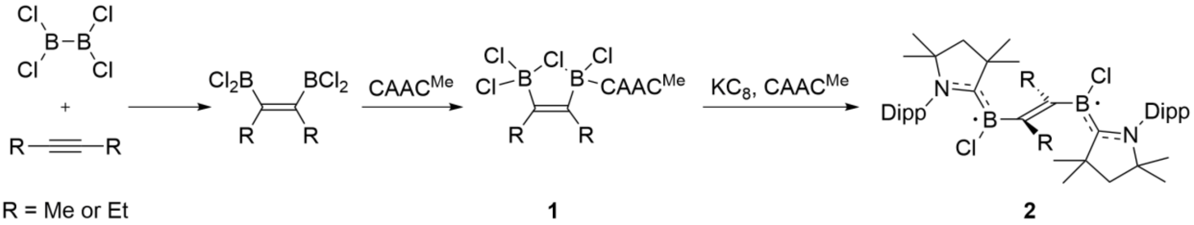
[2] Kotaro Hiramatsu, and Takashi Nagata, *J. Chem. Phys.* **143**, 121102 (2015).

III-2: Wednesday , September 28th – 16:30-17:00

Neutral Captodative Biradicals Stabilized by Cyclic (Alkyl)(Amino)Carbenes

Andrea Deißenberger, Regina Drescher, and Holger Braunschweig*

The first neutral boron-containing radicals stabilized by cyclic (alkyl)(amino)carbenes (CAAC) were synthesized and fully characterized by our group.[1] These radicals showed an extraordinary stability to high temperatures as well as a larger spin density on boron, compared to known boryl radicals.[2] In this work, we show the first synthesis of a neutral boron-containing biradical stabilized by cyclic (alkyl)(amino)carbenes. The synthesis starts with the addition of B_2Cl_4 to an alkyne, followed by the stabilization of this diborylated species with one equivalent of the CAAC forming the intramolecular stabilized compound **1**. Reduction using potassium graphite in the presence of another equivalent of CAAC leads to the deep blue colored biradical **2**. Structural characterization by X-ray analysis shows comparable bonding parameters to the previously published CAAC-stabilized radicals of our group. EPR studies show a large hyperfine coupling of each unpaired electron with both the nitrogen and the boron atom, indicating isolated radical sites.



Scheme: *Synthesis of captodative stabilized biradicals.*

[1] P. Bissinger, H. Braunschweig, A. Damme, I. Krummenacher, A.K. Phukan, K. Radacki, S. Sugawara, *Angew. Chem. Int. Ed.* **53**, 7360 (2014).

[2] e.g. C.-W. Chiu, F.P. Gabbaï, *Angew. Chem. Int. Ed.* **46**, 1723 (2007).

III-3: Wednesday , September 28th – 17:00-17:30

Studies on single para-xylylene bridged perylene bisimide macrocycles at strong photo-excitation

Ulrich Müller, Peter Spenst, Matthias Stolte, Frank Würthner and Jens Pflaum

Quantum emitters like single organic molecules can serve as non-classical light sources in quantum communication and quantum metrology applications. Single Perylene Bisimides (PBIs) are ideal candidates for single photon emitters due to their chemically tunability, strong fluorescence and high photostability [1].

By means of a confocal-microscopy set-up we analyze the changes in the single molecules' emission spectra over several minutes and characterize single quantum emission by correlating photon arrival times. We will highlight the rich excitation dynamics of para-xylylene bridged PBI-macrocycles in the limit of low and high laser excitation powers and compare them to single chromophores: At low excitation intensities PBI-macrocycles act as bright and stable single photon emitters due to a fast excitation energy transfer between the different chromophores of a cycle. By increasing the excitation intensity the co-existence of mulit-excitonic states on the macrocycles becomes more likely and the process of exciton-exciton-annihilation controls the molecules' emission.

We provide a continuous-time stochastic Markov model to explain our observations and to advance the understanding of excitation and relaxation processes in multi-chromophoric systems.

[1] F. Schlosser et al., *Chem. Sci.* **3**, 2778 (2012).

IV-1: Thursday , September 29th – 09:00-09:30

Pyrene MO Shuffle

Adjusting the HOMO-LUMO gap by changing the frontier MO ordering

Julia Merz, Julian Fink, Hamad Al Mamari, Ivo Krummenacher, Alexandra Friedrich,
Martin Hähnel, Antonius Eichhorn, Todd B. Marder

Pyrene is a polycyclic aromatic hydrocarbon (PAH) that has very interesting photophysical properties which makes it suitable for a broad range of applications [1]. The 2,7-positions of pyrene are situated on nodal planes in both the HOMO and LUMO. Hence, electrophilic reactions take place at the 1-, 3-, 6-, and 8-positions. We developed a selective method to substitute directly the 2,7-position by an iridium-catalyzed C-H borylation [2]. We report a series of new donor-acceptor and donor-donor pyrene systems with remarkable properties. Donors can raise HOMO-1 above the pyrene HOMO whereas acceptors can lower LUMO+1 below the pyrene LUMO which facilitates strong communication through the pyrene bridge. Further we could demonstrate the effectiveness of our pyrene bridge in comparison with biphenyl by photophysical and electrochemical measurements that are supported by DFT calculations and contrast with previous reports.

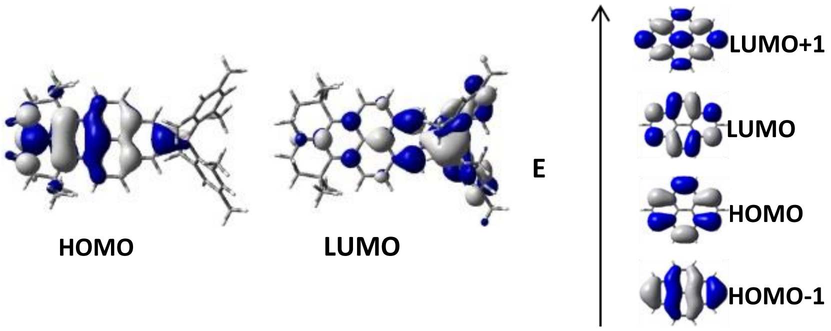


Figure: *Frontier orbitals of our synthesized D-π-A compound (left) and of pyrene (right).*

[1] T. M. Figueira-Duarte and K. Mullen, *Chem. Rev.*, **2011**, 111, 7260.

[2] A. G. Crawford, Z. Liu, I. A. I. Mkhalid, M.-H. Thibault, N. Schwarz, G. Alcaraz, A. Steffen, J. C. Collings, A. S. Batsanov, J. A. K. Howard, T. B. Marder, *Chem. Eur. J.* **2012**, 18, 5022.

IV-2: Thursday , September 29th – 09:30-10:00

Nonadiabatic dynamics of the pyrene dimer and excimer

M. Wenzel, J. Hoche, and R. Mitrić

Nonadiabatic dynamics are necessary to describe situations where the coupling of nuclear and electronic motion is strong as is the case at conical intersections. Inclusion of nonadiabatic effects are essential for the description of non-radiative relaxation processes and the time evolution of systems that undergo vertical excitation.

One way to include these effects is a semi-classical description of the system in combination with surface hopping. The semi-classical picture uses an ensemble of trajectories to represent the nuclear wavepacket, where each trajectory is propagated on an electronic potential energy surface. Non adiabatic effects are then incorporated by the surface hopping scheme. For each trajectory is a probability calculated to switch the electronic state respectively the electronic potential energy surface, dependent on the coupling of electronic and nuclear motion at every timestep. [1]

This is demonstrated by investigation of the pyrene dimer, which forms an excimer after an vertical excitation of the ground state. The nonadiabatic dynamics show which of the different possible pathways are followed by the system. In this case the vertical excitation of the pyrene dimer leads to a structural change from the parallel displaced structure to the fully stacked geometry in the excited state, while the dynamics simulation allows to follow this process step by step.

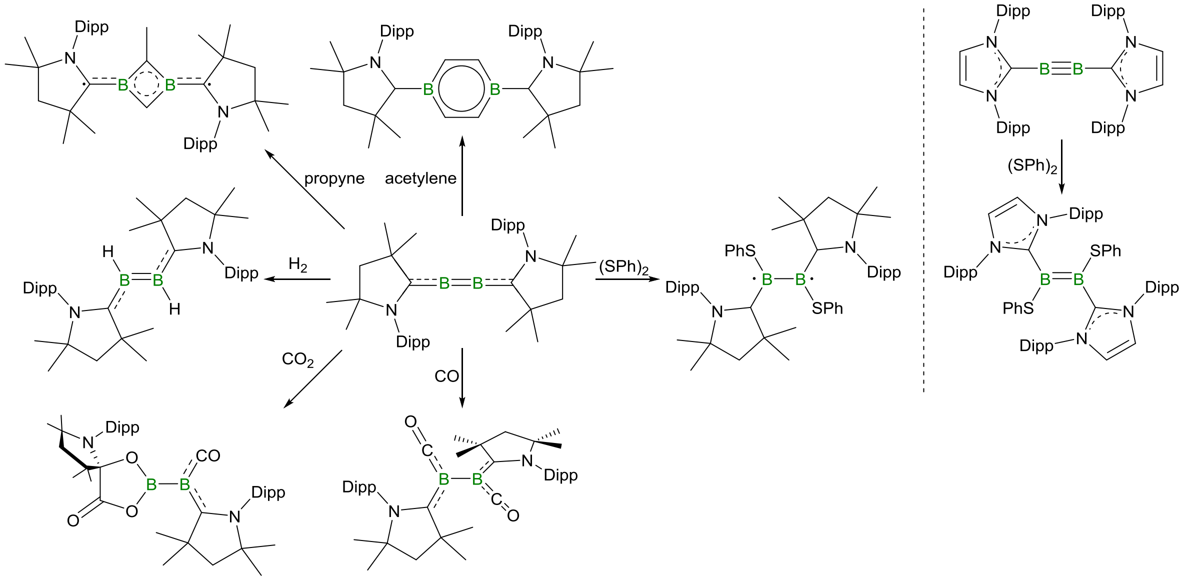
[1] P. G. Lisinetskaya, and R. Mitrić, *Phys. Rev. A*, **83**, 033408 (2011).

IV-3: Thursday , September 29th – 10:00-10:30

Reacivity of BoronBoron Multiple Bonds

Julian Böhnke, Theresa Dellermann, Kai Hammond, Holger Braunschweig

The utilization of cyclic (alkyl)(amino)carbenes (CAACs) to stabilize the highly reactive B2 unit led to the formation of a diboracumulene (C=B=B=C), in contrast to the discrete B–B triple bond observed with NHC donors (C-B≡B-C).[1,2] The capacity of the CAAC ligands to withdraw π-electron density from the B–B bond has provided access to a range of unique bonding situations, which in turn provide information about the influence of the carbene. Reactivity studies on this system led to base adducts (isonitriles, NHCs),[3] activation of small molecules (CO, CO2, H2) [4] and cycloadditons with formation of archetypal aromatic species (acetylene, propyne) [5], illustrating the synthetic potential of multiple bonds featuring boron. Furthermore, the 1,2-addition of a dichalcogen reagent to the (NHC-stabilized) diboryne led to a diborene, whereas the reaction with the (CAAC-stabilized) diboracumulene forms an isolable and room-temperature stable 1,2-diradical.



[1] H. Braunschweig, R. D. Dewhurst, K. Hammond, J. Mies, K. Radacki, A. Vargas, Science, **2012**, 336, 1420–1422.

[2] J. Böhnke, H. Braunschweig, W. C. Ewing, C. Hörl, T. Kramer, I. Krummenacher, J. Mies, A. Vargas, Angew. Chem. Int. Ed. **2014**, 53, 9082–9085.

[3] J. Böhnke, H. Braunschweig, T. Dellermann, W. C. Ewing, T. Kramer, I. Krummenacher, A. Vargas, Angew. Chem. Int. Ed. **2015**, 54, 4469–4473.

[4] J. Böhnke, H. Braunschweig, T. Dellermann, W. C. Ewing, K. Hammond, T. Kramer, J. O. C. Jimenez-Halla, J. Mies, Angew. Chem. Int. Ed. **2015**, 54, 13801–13805.

[5] M. Arrowsmith, J. Böhnke, H. Braunschweig, M. A. Celik, C. Claes, W. C. Ewing, I. Krummenacher, K. Lubitz, C. Schneider, Angew.Chem.Int.Ed. **2016**, 55, 11271–11275.

V-1: Thursday , September 29th – 14:00-14:30

Isoindigoradicals and –biradicals: Synthesis and characterization

Rodger Rausch, David Schmidt, and Frank Würthner

Open shell organic molecules are of fundamental interest for numerous applications like organic magnetism, non-linear optics, organic spintronics, and singlet-fission or energy storage devices. Although a brought variety of different biradicaloid systems has already been prepared and successfully been implemented in organic (opto)electronic devices, the inherent instability of such compounds often leads to oxidative degradation.[1] In this contribution, we report the synthesis of isoindigo radicals and –biradicals that exhibit a remarkable stability, facilitating their unambiguous characterization. According to our detailed experimental and computational study, **OS-1**$^{\cdot\cdot}$ exhibits an singlet-open shell biradicaloid ground state, with a small singlet triplett energy gap of 5.4-6.3 kJ mol^{-1} [Fig. 1].

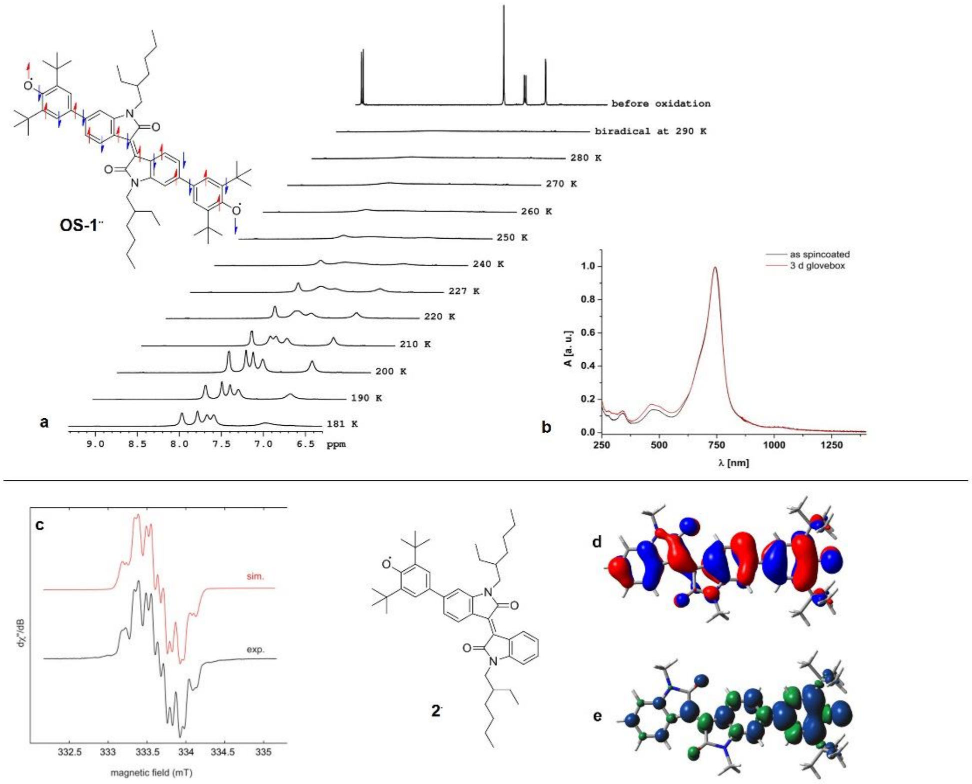


Figure 1: *(a) temp. dependent* ^{1}*H-NMR and (b) solid state UV/Vis absorption spectra of* **OS-1**$^{\cdot\cdot}$. *(c) ESR-spectrum (exp. black; sim. red), (d) SOMO and (e) electron density distribution of* **2**$^{\cdot}$**.**

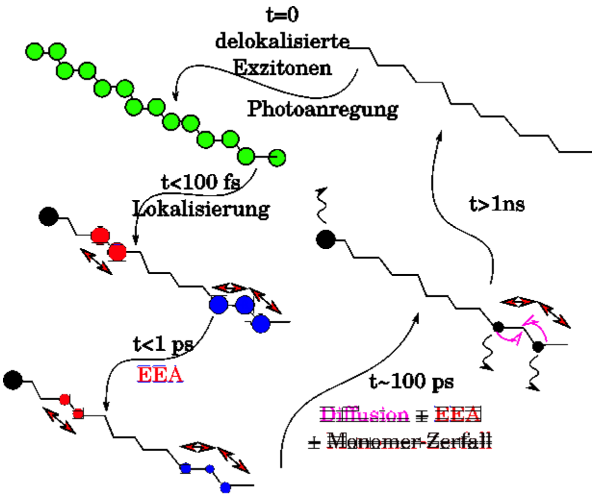
[1] a) Abe, M., *Chem. Rev.* **113**, 7011–7088 (2013). b) Canesi, V. E. , Fazzi, D., Collela, L., Bertarelli, C., Castiglioni, C., *J. Am. Chem. Soc.* **134**, 19070-19083 (2012). c) Qiao, Y., Guo, Y., Yu, C., Zhang, F., Xu, W., Liu, Y., Zhu, D., *J. Am. Chem. Soc.* **134**, 4084-4087 (2012).

V-2: Thursday , September 29th – 14:30-15:00

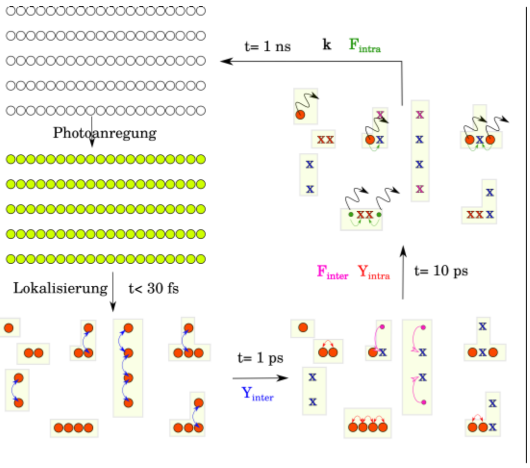
Identification of effective exciton–exciton annihilation

K. Hader and Volker Engel

Ultrafast time-resolved transient absorption spectroscopy is able to monitor the fate of the excited state population in molecular aggregates or polymers. Here we use a microscopic model model derived by V.May [1] to describe exciton–exciton annihilation (EEA) processes in squaraine–squaraine copolymers and MEH-PPV. Transient absorption time traces measured at different laser powers could be reproduced. The analysis for both systems is similar: Immediately after laser-excitation a localization of excitons takes place within the femtosecond time-regime. This is followed by exciton–exciton annihilation which is responsible for a fast decay of the exciton population. At later times, excitations being localized on units which are not directly connected remain so that diffusion dominates the dynamics and leads to a slower decay. We thus provide evidence for EEA tracked by time-resolved spectroscopy [2].



Left Figure: *schematic representation of the relevant processes in the squaraine-squaraine-copolymere.*



Right Figure: *schematic representation of the relevant processes in MEH-PPV*

[1] V. May, *J. Chem. Phys.* **140**, 54103 (2014).

[2] K. Hader, V. May, C. Lambert, und V. Engel, *Phys. Chem. Chem. Phys.* **18**, 13368 (2016).

V-3: Thursday , September 29th – 15:00-15:30

Highly Efficient Mechanochromic Luminescence of Structurally Simple Cu(I) NHC Complexes

Benjamin Hupp, Jörn Nitsch, and Andreas Steffen*

Despite the simple structure of linearly coordinated dinuclear Cu(I) NHC complexes, the full potential of these compounds has yet to be discovered. They could show great promise as luminophores, as their high efficiencies and complex photophysics have already been hinted at[1]. To investigate the properties of such compounds, we synthesized a series of new dinuclear Cu(I) complexes. They show a strong, dual emission from blue to yellow, of which the relative intensities change upon mechanical stimulation; a phenomenon known as mechanochromic luminescence [2].

Our photophysical and theoretical studies suggest that in some cases, intermolecular Cu-Cu interactions are responsible for the low energy emission band. Most recent studies, however, indicate that in other cases, the F-substituted anion might have a significant influence on the emission of the compound. The untreated dinuclear Cu(I) complex **1**, for example, shows blue emission in the solid state, whereas after grinding, the solid exhibits 10-fold increased yellow luminescence; luminescence in solution is negligible. The BF_4^- compound, on the other hand, exhibits a quantum yield of over 20 % in solution.

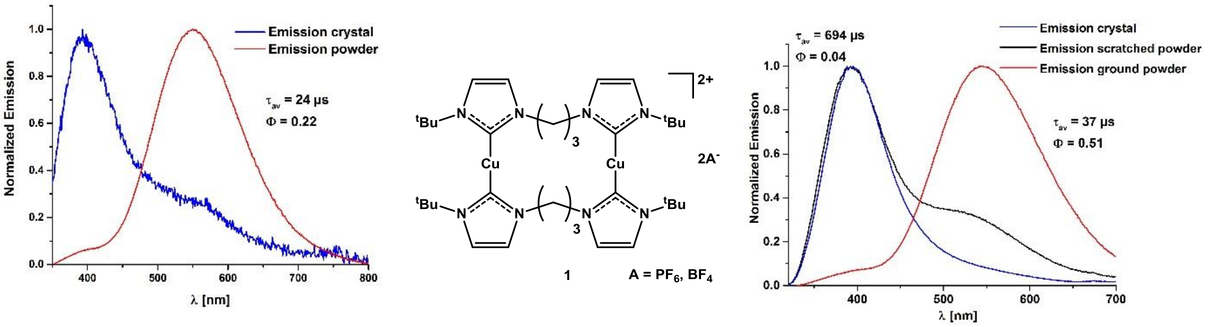


Figure1: *C3-bridged dinuclear Cu(I) NHC complex* **1** *(middle) and the emission spectra of the* BF_4 *salt (left) and the* PF_6 *salt (right) in the solid state.*

[1] T. Tsubomura et al., *Dalton Trans.*, 6795 (2009).

[2] A. Steffen et al., *in preparation* (2016).

Postersession

Doping of (6,5)-Single-Wall Carbon Nanotubes determined by quantitative Electron Paramagnetic Resonance

Michael Auth[1], Andreas Sperlich[1], Florian Späth[2], Tobias Hertel[2] and Vladimir Dyakonov[1,3]

[1] Experimental Physics VI, Julius Maximilian University of Würzburg, D-97074 Würzburg, Germany

[2] Institute of Physical and Theoretical Chemistry, Julius Maximilian University of Würzburg, D-97074 Würzburg, Germany

[3] Bavarian Centre for Applied Energy Research (ZAE Bayern), D-97074 Würzburg, Germany

Doping is generally known as a viable and widely spread method to alter the electrical abilities of semiconductor materials. Hereby the knowledge about the distinct dopant concentrations inside the materials is of crucial importance, but is also difficult to determine. Electron Paramagnetic Resonance (EPR) may sensitively probe localized charge carriers, e.g. defects, dopants or local charges opening up a way to estimate their concentration. Here, we discuss the basic principles behind EPR and especially quantitative EPR measurements, including all the parameters one needs to keep in mind for reliable quantitative estimations. As material system, we investigated (6,5)-Single-Wall Carbon Nanotubes (SWNTs), as their exceptional electrical conductivity makes them potentially interesting to improve charge transport in organic optoelectronics. The knowledge about doping concentrations is essential to use p- and n-doped SWNTs for p-n-junctions in future electronic devices.

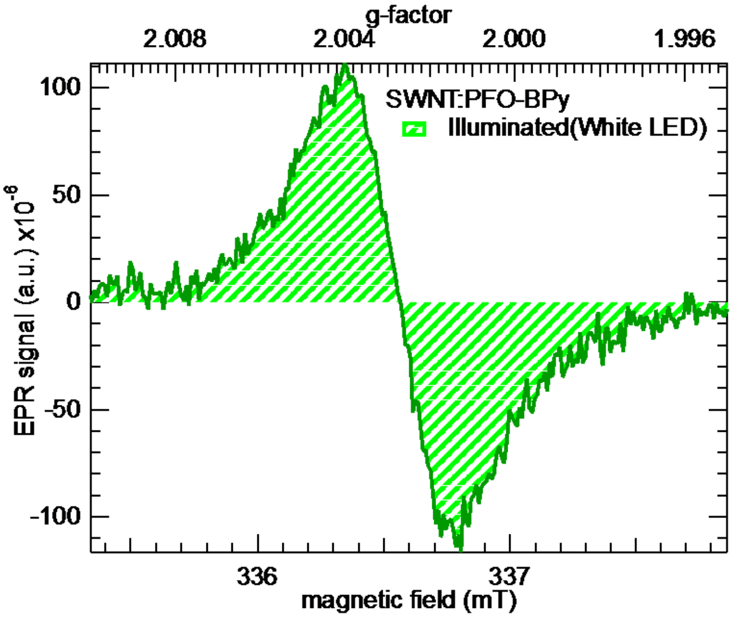


Figure: *(6,5)-SWNT EPR signal under illumination with a white LED.*

Calculating Singlet-Triplet Gaps to Screen For Singlet-Fission Candidates: Understanding The Role of HF Exchange and DFT Correlation

Charlotte Brückner and Bernd Engels

Vertical and adiabatic singlet and triplet excitation energies of molecular p-type semiconductors calculated with various DFT functionals and wave-function based approaches are benchmarked against MS-CASPT2/cc-pVTZ reference values. A special focus lies on the singlet-triplet gaps that are very important in the process of singlet fission. Singlet fission has the potential to boost device efficiencies of organic solar cells, but the scope of existing singlet-fission compounds is still limited. A computational prescreening of candidate molecules could enlarge it; yet it requires efficient methods accurately predicting singlet and triplet excitation energies. Different DFT formulations (Tamm-Dancoff approximation, linear response time-dependent DFT, Δ-SCF) and different spin scaling schemes along with several ab initio methods (spin-component scaling, spin-opposite scaling; CC2, ADC(2)/MP2, CIS(D), CIS) are evaluated with respect to their accuracy. While wave-function based methods yield rather reliable singlet-triplet gaps, many DFT functionals are shown to systematically underestimate triplet excitation energies. To gain insight, the impact of exact exchange and correlation is addressed. The influence of the amount of exact exchange on triplet excitation energies is analyzed by means of non-empirical IP-tuning and functional variation, and it is shown to vary as a function of the molecular structure. The local differential correlation between the ground and the triplet excited state is identified as a key parameter decisive for triplet state energies. Upscaling the scaling coefficients of local correlation in different DFT functionals is shown to result in more accurate triplet energies.

Spin-sensitive Investigation of Organic Light Emitting Diodes based on Thermally Activated Delayed Fluorescence

Nikolai Bunzmann[1], Sebastian Weißenseel[1], Michael Auth[1], Stefan Väth[1],
Andreas Sperlich[1] and Vladimir Dyakonov[1,2]

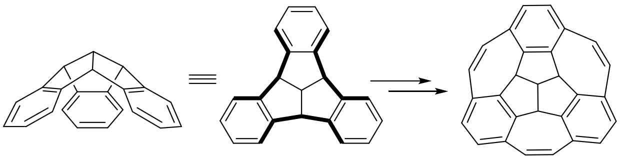
[1]Experimental Physics VI, Julius Maximilian University of Würzburg, 97047 Würzburg, Germany
[2]Bavarian Centre for Applied Energy Research (ZAE Bayern), 97074 Würzburg, Germany

The major drawback of conventional fluorescent light emitting diodes (OLEDs) is the fact that only 25% of injected electrons and holes form emissive singlet excitons, whereas 75% form longlived triplets, which decay non-radiatively. However, if the used materials are designed to exhibit an energy splitting ΔE_{ST} between singlet and triplet state in the order of thermal energy k_BT, reverse intersystem crossing (RISC) from triplets to singlets is strongly enhanced. Thereby, so-called thermally activated delayed fluorescence (TADF) is induced, allowing for a dramatic increase of efficiency. That is why TADF OLEDs provide high potential for economical and sustainable light sources. However, the process of RISC, which is in principal spin forbidden, is not fully understood yet. Therefore we investigate the role of spins in the TADF mechanism by applying spin-sensitive techniques, which are suitable to elucidate processes, in which triplet states are involved. We use electrically and electroluminescence detected magnetic resonance (EDMR, ELDMR) techniques, where transitions between spin substates, which are split in an external magnetic field, are driven by a tunable microwave source, realized by a non-resonant stripline. By evaluating the dependence of multi-frequency ELDMR and EDMR spectra on experimental conditions such as microwave frequency, microwave intensity, temperature, current, etc, detailed information of the investigated spin system can be obtained.

Synthesis of precursors for extended π-systems with a tribenzotriquinacene core

Rachel Buschmann and Anke Krueger

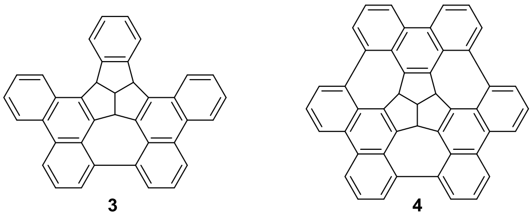
Tribenzotriquinacene (TBTQ, 1) is a bowl-shaped aromatic hydrocarbon, whose curved structure derives from the three fused five-membered rings at its centre. Investigations into the singlet and triplet states of the triquinacene core would provide a valuable insight into the properties of these molecules and the synthesis of a TBTQ bisanion has already been reported.[1,2] Theoretical studies have indicated that TBTQ can be considered as a defect centre in a distorted nanographene.[3] The aim is to functionalise 1 by bridging the bay regions (indicated in bold below) and thereby extend the carbon network to give PAH 1.



1 **2**

Figure 1: *Curved structure of TBTQ 1 and extended derivative 2.*

The first strategy for TBTQ synthesis was developed by Kuck and coworkers, [4] but the triple cyclisation method from Hopf et al. [5] is an improvement as it allows access to ortho-functionalised derivatives, by using suitably substituted starting materials. Examples of ortho-substituted TBTQ derivatives are limited, [6] due to increased steric strain experienced at this position, but this position is important for the construction of larger TBTQ containing polyaromatic hydrocarbons. TBTQs 3 and 4 are synthetic aims of this work, where the Scholl reaction [7,8] of suitable precursors is the key step.



3 **4**

Figure 2: *Target molecules TBTQ 3 and 4.*

[1] D. Kuck, A. Schuster, B. Ohlhorst, V. Sinnwell, A. de Meijere, *Angew. Chem.* **101**, 626 (1989). [2] R. Haag, B. Ohlhorst, M. Noltemeyer, R. Fleischer, D. Stalke, A. Schuster, D. Kuck, A. de Meijere, *J. Am. Chem. Soc.* **117**, 10474 (1995). [3] J. Tellenbröker, D. Kuck, *Angew. Chem. Int. Ed.* **38**, 919 (1999). [4] D.Kuck, *Angew. Chem. Int. Ed. Engl.* **23**, 508 (1984). [5] H. Hopf, G. Markopoulos, L. Henneicke, J. Shen, Y. Okamoto, P. G. Jones, *Angew. Chem. Int. Ed*. **51**, 12884 (2012). [6] Y. Kirchwehm, A. Damme, T. Kupfer, H. Braunschweig, A. Krueger, *Chem. Comm.* **48**, 1502, (2012) [7] R. Scholl, C. Seer, *Justus Liebigs Ann. Chem.* **394**, 111, (1912). [8] K. Kawasumi, Q. Zhang, Y. Segawa , L.T. Scott, K. Itami, *Nat. Chem.* **5**, 739, (2013).

Transient Absorption Spectroelectrochemistry of a (6,5) Carbon Nanotube Thin Film

Klaus Eckstein, Holger Hartleb, Daniel Schilling and Tobias Hertel

The electronic and optical properties of low-dimensional semiconductors like quantum wells (2D), quantum wires (1D) or quantum dots (0D) strongly differ from their three dimensional counterpart because of increased electron confinement [1]. Furthermore, it has been shown that strong electric fields generated in field effect transistor structures using ionic liquids or solvent based electrolytes as a gate can efficiently manipulate the charge carrier densities in these low-dimensional systems [2-4].

In charge-neutral quasi-1D semiconducting carbon nanotubes (CNTs) the optical properties are governed by strongly bound excitons (H-atom like electron hole pairs) rather than uncorrelated electron hole pairs due to enhanced coulomb interaction and reduced dielectric screening [5].

Here, we report on an investigation of exciton dynamics by femtosecond pump-probe transient absorption experiments (VIS pump/NIR probe) in an electrochemically gate-doped (6,5) carbon nanotube film fixed at the working electrode. We find that the photobleach (PB) signal of the first subband exciton is strongly reduced upon charging the CNTs positively or negatively. Additionally, the ground state recovery was found to be accelerated in gate-doped carbon nanotubes (Fig. 1).

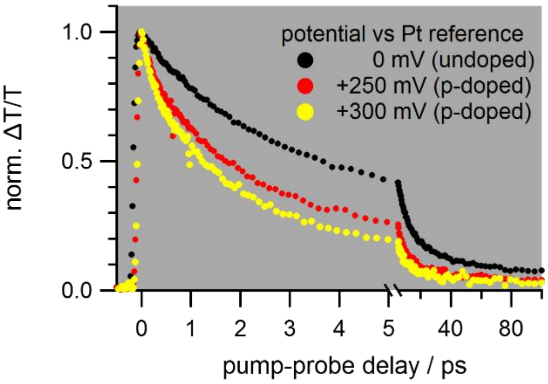


Figure 1: *Dynamics of the ground state recovery at different applied potentials.*

[1] H. Davies, *The physics of low-dimensional semiconductors,* Cambridge University Press (1998).

[2] D. Vanmeakelbergh, A. Houtepen and J. Kelly, *Electrochim. Acta,* **53**, 1140 (2007).

[3] A. Goldman, *Annu. Rev. Mater. Res.*, **44**, 45 (2014).

[4] W. Shi *et al.*, *Scientific Reports*, **5**, 12534 (2015).

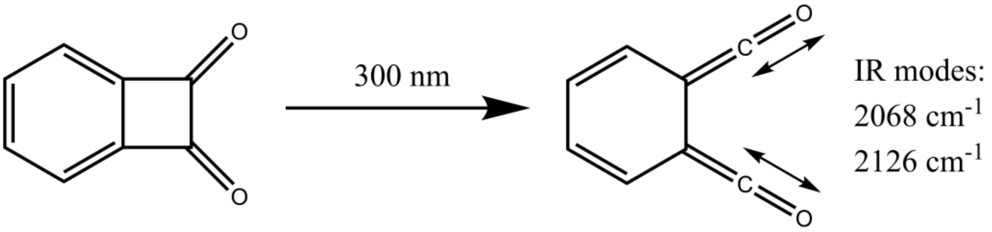
[5] F. Wang *et al.*, *Science*, **308**, 838 (2005).

A fs time-resolved UV/IR Study of Benzocylcobutene-1,2-dione

Marco Flock, Hans-Christian Schmitt, Ingo Fischer, Xianon Ma and Tobias Brixner

Benzocylcobutene-1,2-dione (**1**) is a common precursor for the generation of the biradical o-benzyne. As we know from matrix isolation [1] and liquid-phase [2] studies the bisketene formation of **2** is the first step in the photolytic generation of the biradical, that is followed by the loss of C=O moieties.

In this study we examine this key step with ultrafast time resolution. The formation of **2** could nicely be followed by its symmetric and asymmetric C=O stretching modes, which appear with a time constant of 6.6 ps. Besides, a blue-shift of the occuring bands is visible that is assigned to vibrational cooling. Global and target analysis fits reveal a time constant of 11.2 ps for the cooling process.



1 **2**

Figure: Photolytical generation of the bisketene

In addition to the expected signals we observed the formation of a new species that absorbs around 1731 cm^{-1}.

[1] A. Schweig, *Chem. Phys. Lett.,* **170**, 187–192 (1990).

[2] J. C. Scaiano, *J. Am. Chem. Soc.,* **112**, 8858–8863 (1990).

Exciton transport and dissociation at organic single crystal surfaces

S. Hammer, T. Schmeiler, J. Pflaum

The analysis of exciton transport and charge transfer processes at interfaces is a key interest in research of organic semiconductor devices. Optically excited states can travel by diffusion inside an organic material before relaxing into the ground state [1]. For an efficient conversion into free charge carriers it is therefore necessary that the electron-hole-pair reaches a suited donor/acceptor interface for separation within its lifetime. A possible dissociation pathway occurs via formation of a charge transfer (CT)-state at this organic-organic junction [2] (Figure).

This work will examine exciton transport in organic single crystals as well-defined model systems and will analyze CT-state formation and dynamics at organic-organic interfaces composed of such crystallographically aligned facets. In close collaboration with the AG Engels theoretical models will be compared with the experimental data for selected materials.

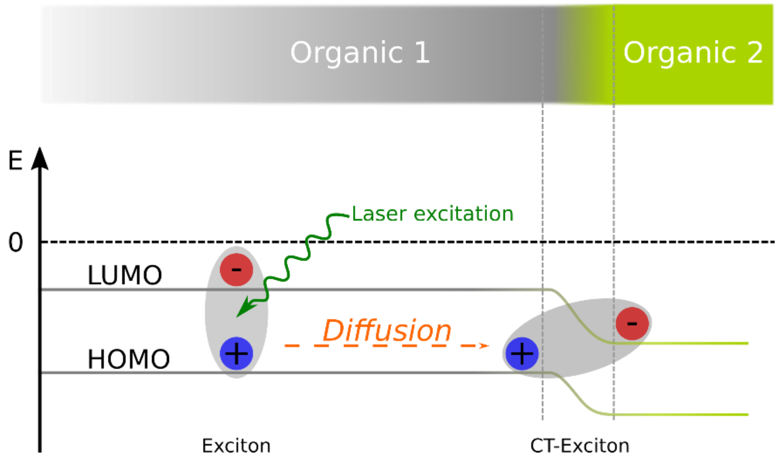


Figure: *Exciton diffusion and CT-state formation at an organic-organic interface.*

[1] Swenberg, Charles E., and M. Pope, *Oxford University Press.* (1999).

[2] Brédas, Jean-Luc, et al., *Acc. Chem. Res.* **42**, (2009)

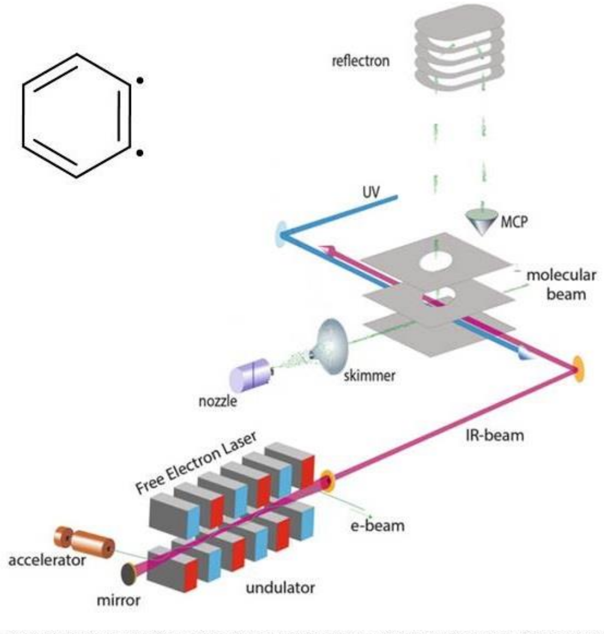
Study of the self-reaction products of o-benzyne radicals via IR/UV ion-dip-spectroscopy

Florian Hirsch, Philipp Constantinidis, Ingo Fischer, and Anouk M. Rijs

The self-reaction products of o-benzyne radicals produced by flash pyrolysis have been studied by ion-dip-spectroscopy in a free jet. As recent studies suggest, these molecules might play an important role in the even numbered growth of polycyclic aromatic hydrocarbons (PAH's) and consequently soot, as they can serve as a source of acetylene and diacetylene in combustion processes.

The spectroscopic method utilized in this study is capable of providing mass selective infrared spectra, which can be used for unambiguous identification of the formed molecules. The radicals have been generated by flash pyrolysis from the benzocyclobutendion precursor and ionized at fixed wavelengths at 265 and 275 nm. A tunable free electron laser provided infrared radiation in the range of 550 – 1750 cm-1. Subsequent analysis of the differences in ion signals, with and without infrared excitation, resulted in the sought after infrared spectra. Eventually comparison with theoretical and experimental data was performed for identification of the various reaction products.

This poster will provide a fundamental overview of methodology and results of this study, executed at the Free Electron Laser for Infrared eXperiments (FELIX) (Nijmegen, Netherlands).



A. Rijs and J. Oomens, Gas-Phase IR Spectroscopy and Structure of Biological Molecules, Springer International Publishing, 2015

Figure: *Scheme of the IR/UV-FELIX-setup in Nijmegen.*

Highly Efficient Mechanochromic Luminescence of Structurally Simple Cu(I) NHC Complexes

Benjamin Hupp, Jörn Nitsch, and Andreas Steffen*

Despite the simple structure of linearly coordinated dinuclear Cu(I) NHC complexes, the full potential of these compounds has yet to be discovered. They could show great promise as luminophores, as their high efficiencies and complex photophysics have already been hinted at[1]. To investigate the properties of such compounds, we synthesized a series of new dinuclear Cu(I) complexes. They show a strong, dual emission from blue to yellow, of which the relative intensities change upon mechanical stimulation; a phenomenon known as mechanochromic luminescence [2].

Our photophysical and theoretical studies suggest that in some cases, intermolecular Cu-Cu interactions are responsible for the low energy emission band. Most recent studies, however, indicate that in other cases, the F-substituted anion might have a significant influence on the emission of the compound. The untreated dinuclear Cu(I) complex **1**, for example, shows blue emission in the solid state, whereas after grinding, the solid exhibits 10-fold increased yellow luminescence; luminescence in solution is negligible. The BF_4^- compound, on the other hand, exhibits a quantum yield of over 20 % in solution.

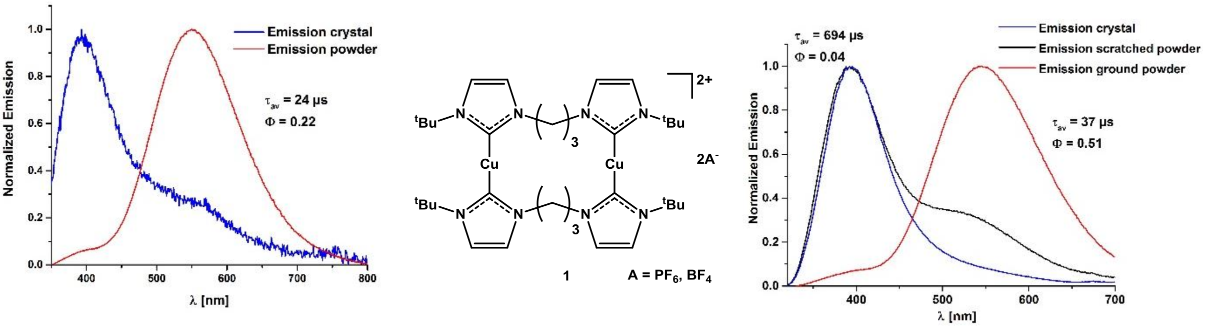


Figure1: *C3-bridged dinuclear Cu(I) NHC complex* **1** *(middle) and the emission spectra of the* BF_4 *salt (left) and the* PF_6 *salt (right) in the solid state.*

[1] T. Tsubomura et al., *Dalton Trans.*, 6795 (2009).

[2] A. Steffen et al., *in preparation* (2016).

Theoretical Studies On The Water Oxidation Mechanism in Ruthenium Macrocyclic Systems

J. Lindner, M. I. S. Röhr and R. Mitric

We used the QM/MM approach to simulate the spectroelectrochemistry of Ruthenium water oxidation catalysts by calculating UV/VIS spectra in different catalyst oxidation states. As absorption spectra are highly dependent on structural changes, averaged ensemble spectra were identified to be an appropriate model.

Furthermore, molecular dynamics simulations were used in order to give insights on the reaction mechanism with priority to the outstanding turnover frequency of the macrocycle compared to the corresponding monomer [1]. We found different reasons for the enhanced activity, including H-bonding networks between the three catalytic moieties of the macrocycle.

[1] M. Schulze, V. Kunz, P. D. Frischmann, and F. Würthner, *Nat. Chem.* **8**, 576 (2016)

Synthesis of new borole compounds based on thiophene deriatives

Michael Meier, Holger Braunschweig

Boroles are intensely colored, five-membered heterocyclic systems with four π-electrons delocalized through an empty boron p_z orbital.[1,2] Isoelectronic to the cyclopentadienyl cation, these compounds are antiaromatic according to Hückel's concept of aromaticity.[3] Our goal is the syntheses of an array of multithiophene-functionalized borole systems (**1**) and the investigation of their physical properties, with particular emphasis on the shapes and energies of their frontier orbitals. Furthermore, our interest is also focused on boroles serving as potential electron acceptors in push-pull systems (**2**), comparing them to other well-established acceptor groups such as mesityl-substituted, three-coordinate boron groups (-$BMes_2$)(**3**).[4]

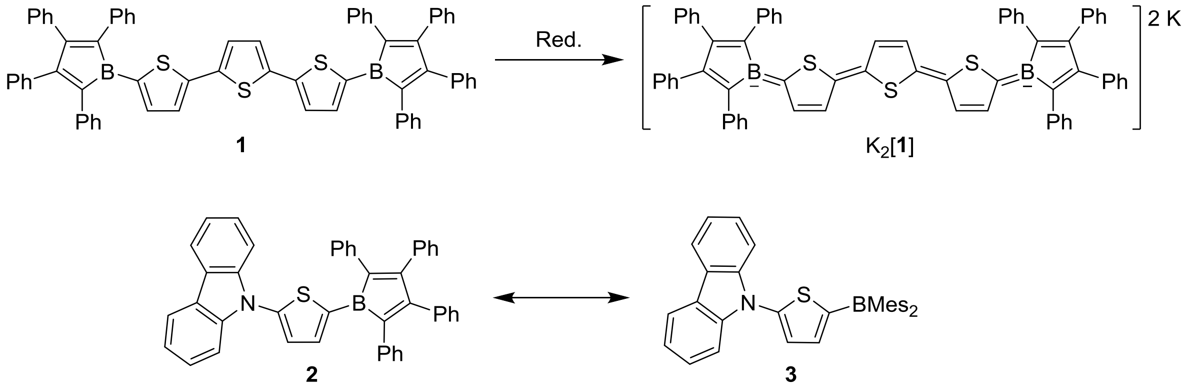


Figure: *Thiophene-functionalized borole systems.*

[1] J. J. Eisch, J. E. Galle, S. Kozima, *J. Am. Chem. Soc.* **1986**, *108*, (379).
[2] V. Gogonea, P. v R. Schleyer, P. R. Schreiner, *Angew. Chem. Int. Ed.* **1998**, *37*, (1945).
[3] M. K. Cyranski, T. M. Krygowski, A. R. Katritzky, P. v. R. Schleyer, J. Org. Chem. **2002**, *67*, (1333)
[4] Z. Yuan, C. D. Entwistle, J. C. Collings, D. Albesa-Jové, A. S. Batsanov, J. A. K. Howard, N. J. Taylor, H. M. Kaiser, D. E. Kaufmann, S.-Y. Poon, W.-Y. Wong, C. Jardin, S. Fathallah, A. Boucekkine, J.-F. Halet, T. B. Marder, *Chem. Eur.* **2006**, *10*, (2758).

Synthesis of a novel Donor – Sensitizer – Acceptor Triad for the Investigation of Magnetic Field Effects

David Mims, Christopher Schwarz, and Christoph Lambert

Triads with small $B_{1/2,hfc}$ values, which are about one magnitude larger than the earth's magnetic field have already been investigated by Lambert *et. al* [1]. These triads comprise of triarylamine donors containing a nitrogen atom with a nuclear spin of I = 1. Since the magnetic field effect is dependent on the nuclear magnetic moment of the donor- and acceptor moiety, a substitution of these donors with the sulfur (I = 0) bearing building block tetrathiafulvalene should lead to a charge separated state with a decreased effective magnetic moment and thus should give rise to triads that are sensitive to the earth's magnetic field.

Yet the synthesis of the desired complex proves to be difficult due to the electronrich tetrathiafulvalene building block. Hence detailed information on planed and already realized synthesis is given in this study.

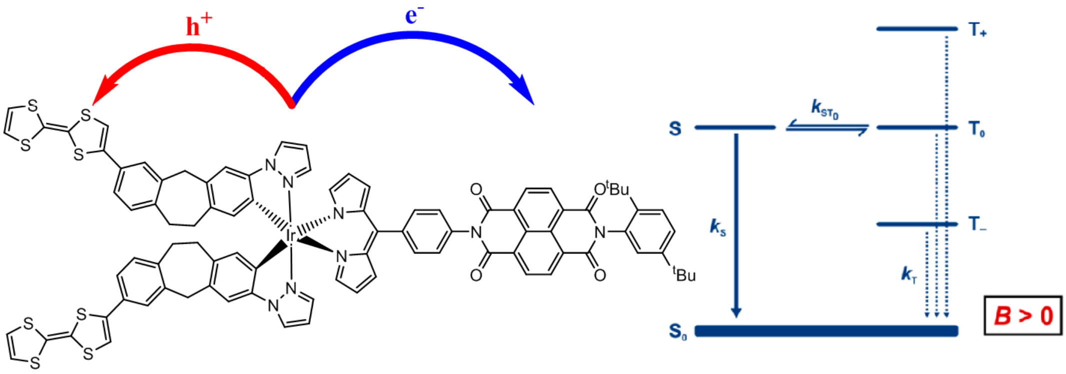


Figure: *After absorption of visible light a charge separated state occurs. The triplet splitting of the cs-state and its kinetics are dependent on the external magnetic field [1].*

[1] Johannes H. Klein, David Schmidt, Ulrich E. Steiner, and Christoph Lambert, *J. Am. Chem. Soc.* **137**, 11011–11021 (2015).

Perylene Bisimide Radicals and Biradicals: Synthesis and Molecular Properties

D. Schmidt, M. Son, J. M. Lim, M.-J. Lin, I. Krummenacher, H. Braunschweig, D. Kim, and Frank Würthner

Polycyclic aromatic hydrocarbons (PAH) with open-shell biradicaloid ground states have attracted continuous interest due to their critical role in understanding the fundamental nature of chemical reactions and versatile applicability in organic (opto)electronic devices. Despite the inherent instability of such open-shell molecules several classes of stable π-conjugated biradicaloids have been realized by designing a quinoidal PAH framework which is in resonance with a singlet biradical structure. In this regard, perylene bisimides (PBIs) with an electron deficient aromatic core should in principle offer another promising scaffold for constructing stable functional open-shell systems. In this contribution, we communicate the first example of a stable PBI-centered biradical (Figure 1) with an open-shell singlet biradical ground state with a relatively small singlet triplet energy gap of 0.041 eV and a large singlet biradical character of y = 0.72.[1]

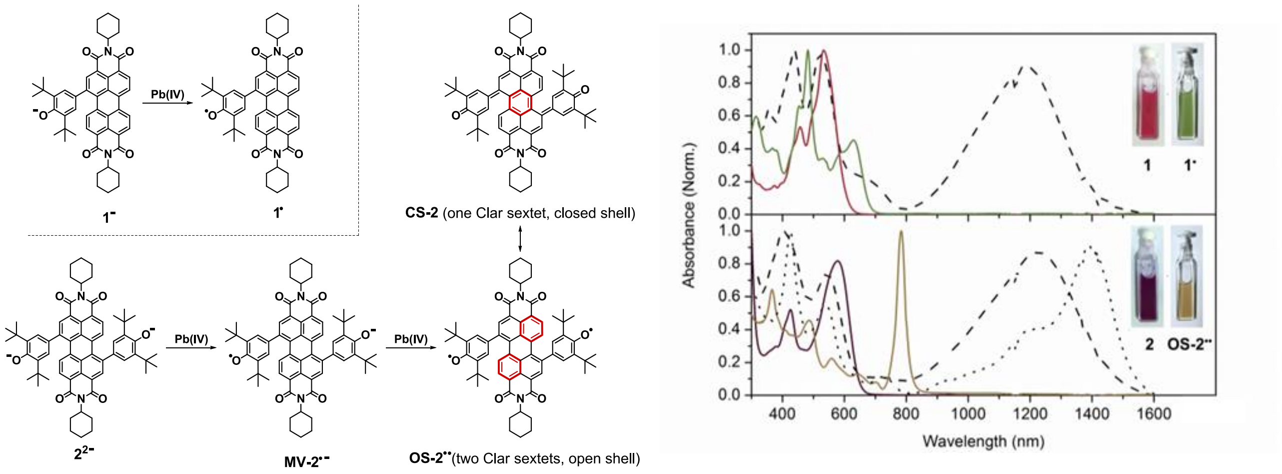


Figure: *Synthesis of PBI (bi)radicals 1• and 2•• and their optical properties in dichloromethane soultions.*

[1] D. Schmidt, M. Son, J. M. Lim, M.-J. Lin, I. Krummenacher, H. Braunschweig, D. Kim and Frank Würthner, *Angew. Chem. Int. Ed.* **54**, 13980 (2015).

Defined Electron-Poor Nanographenes: One-Pot Synthesis and Single Crystal Structure Analysis

S. Seifert, K. Shoyama, D. Bialas, D. Schmidt and F. Würthner*

Polycyclic aromatic hydrocarbons (PAHs) are an outstanding class of organic molecules that are characterized by extended carbon-rich sp^2-hybridized scaffolds with high thermal stability and interesting electronic properties. Therefore, this type of compounds has attracted continuous interest during the last decades as promising candidates for applications in organic electronics and photovoltaics. The synthesis of electron rich PAHs is often realized by multistep procedures including C-C coupling reactions and oxidative dehydrogenations,[1] while the synthetic access to electron-poor systems is generally underdeveloped presumably due to the instability of electron-deficient carbocations which are integral intermediates in oxidative dehydrogenation reactions.

In our contribution we report the one-pot synthesis and full characterization of core extended pyrenes bearing multiple dicarboximide substituents that can be regarded as electron-poor nanographenes.[2] We efficiently combined palladium catalyzed Suzuki-Miyaura cross coupling and dehydrohalogenation to synthesize large sized multiple imide containing chromophores with up to ten new C-C bonds formed in a single reaction. The molecular structures of these π-extended systems have been elucidated by single-crystal X-ray analysis confirming the formation of multiple C-C bonds and planar geometry of the scaffolds. Moreover, the optical and electrochemical properties of these electron-poor PAHs have been characterized and show their relevance for potential applications in (opto)electronic devices.

[1] a) A. Narita, X.-Y. Wang, X. Feng and K. Müllen, *Chem. Soc. Rev.* **44**, 6616 (2015); b) M. Grzybowski, K. Skonieczny, H. Butenschön and D. T. Gryko, *Angew. Chem., Int. Ed.* **52**, 9900 (2013).

[2] S. Seifert, K. Shoyama, D. Schmidt and F. Würthner, *Angew. Chem. Int. Ed.* **55**, 6390 (2016).

Synthesis and Characterization of Squaraine-Squaraine Copolymers

A. Turkin and C. Lambert

For the application of polymers as organic semiconductors high exciton diffusion rates and lenghts are desired. Based on earlier works on indolenine squaraine copolymers three copolymers as well as a monomolecular model compound are synthesized with molecular weights of M_n = 5.000, 10.000 and 20.000 g·mol^{-1} *via Suzuki* coupling for direct measurements of diffusion rates [1]. The used squaraines are prepared *via* a condensation reaction of the bromine functionalized indolenines with square acid (SQA) and squaric acid dicyano ester (SQB), respectively. SQA is then provided with a boron ester function. In order to determine the diffusion constant the copolymer is provided with a terminal exciton trapping moiety consisting of SQA and NDI. Together they form a charge transfer state [2]. The SQA-NDI end group is previously synthesized and then added during the polymerization. The lifetime of the excited state is examined *via* transient absorption spectroscopy. In addition other measurements like (spectro)electrochemical, UV/Vis/NIR absorption and fluorescence spectroscopy are carried out.

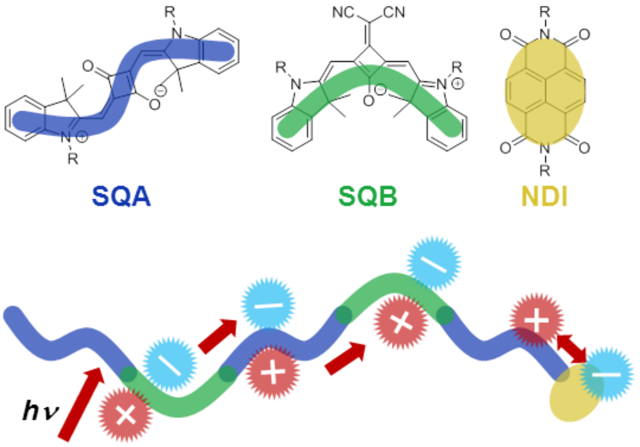


Figure: *Indolenine squaraine copolymer with a naphthalene diimide end group.*

[1] S. F. Völker, A. Schmiedel, M. Holzapfel, K. Renziehausen, V. Engel and C. Lambert, *J. Phys. Chem.* **118**, 17467–17482 (2014).

[2] S. F. Völker, A. Schmiedel, M. Holzapfel, C. Böhm and C. Lambert *Phys. Chem. Chem. Phys.* **15**, 19831–19844 (2013).

Two-Dimensional Spectroscopy of Homo- and Hetero-Dimers

Johannes Wehner

We theoretically compare the two dimensional photon-echo spectra of homo- and hetero-dimers taking angular average effects into account. The basic features of the spectra are analyzed analytically within an electronic level model. Numerically determined spectra of vibronic dimers reveal a complex vibrational sub-structure [1].

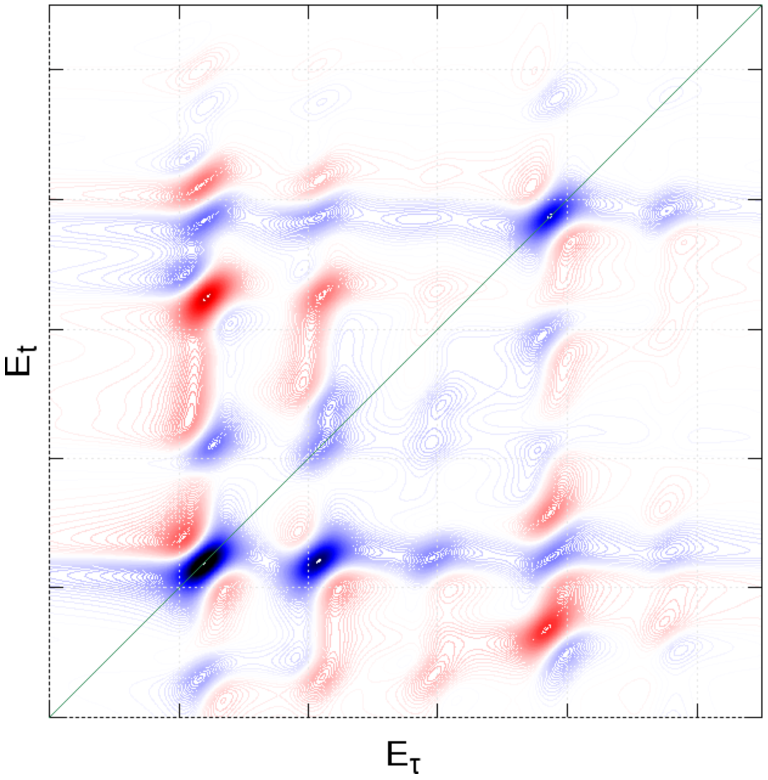


Figure: *Absorptive 2D-Photon-Echo-Spectrum of a hetero-dimer.*

[1] J. Wehner, V. Engel, *Phys. Chem. Chem. Phys.* (submitted)

Theoretical investigations of o-benzyne and the benzyne cation radical

Eileen Welz and Bernd Engels

Biradical compounds show interesting chemical and electronical features. However, due to their high reactivity experimental data are hard accessible. Theoretical analysis of these compounds can provide essential insights in this area. However highly accurate approaches are necessary. The o-benzyne molecule and the related radical cation are sufficiently small for a benchmark study about biradicals.[1] In this way it can be identified which methods work for the closed-shell system and may fail for the biradicals. Special attention is given to the efficiency of density functional theory, because they are applicable to large system.

The experimental photoelectron spectrum [2] and recent theoretical investigations show the presence of two ionization potentials. Using the CASPT2 method it is shown that the kind of radical, which is generated, depends on whether the electron is emitted from either the σ or the π orbital.

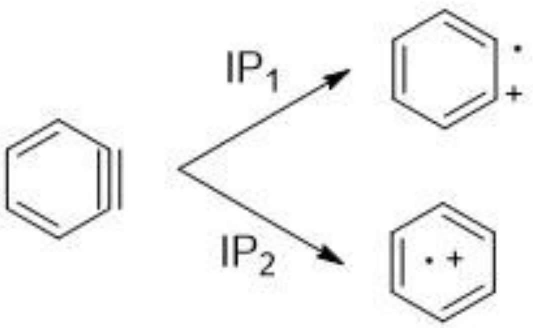


Figure 1: *The two different ionization potentials depending on the generated cation radical.*

[1] H. Li, S. Yu, M. Huang, Z. Wang *Chem. Phys. Let*. **450**, 12 (2007).

[2] X. Zhang, P. Chen, *J. Am. Chem. Soc*. **114**, 3147 (1992).

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