Molecular biradicals: structure, properties and reactivity

Julius-Maximilians-
UNIVERSITÄT
WÜRZBURG

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Conference of the DFG Research Training School 2112
at the University of Würzburg

Molecular biradicals: Structure, Properties and Reactivity

February 27th till March 2nd, 2018
Würzburg, Residenz

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Photos on title page by Leonardo Regoli (Residenz), Thomas Huth (Marienberg fortress), Andreas Bestle (Prince's Garden) and CTW (Alte Mainbrücke)).
Pictures within the abstracts by the respective authors.
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Welcome to the International Symposium on Biradicals

Biradicals have been in the focus of chemical research for quite a while, motivated by their unusual electronic structure and the challenge to describe it properly. In recent years interest in this field experienced a renaissance, because new experimental and computational approaches permit to address both, unresolved issues and new questions. For example biradicals play an important role in the chemistry of reactive environments like combustion engines, the atmosphere or interstellar clouds. It was also realized that electronic states with a biradical character are key intermediates in the formation of light-emitting states in optoelectronic materials and have the potential to increase the efficiency of solar cells via singlet fission. To understand and correctly describe the dynamic processes in biradicals and biradicaloids as well as to reduce phenomena in complex open-shell systems to fundamental principles is therefore of relevance for many areas of chemistry, physics and material science.

To achieve these goals, an interdisciplinary approach is necessary, combing all areas of chemistry and selected parts of molecular physics. This motivated the DFG (Deutsche Forschungsgemeinschaft) in 2015 to fund the research training school GRK 2112 *Molecular Biradicals: Structure, Properties and Reactivity* for initially 4.5 years to investigate molecular biradicals with an electronic structure that is characterized by two unpaired electrons in degenerate or near-degenerate molecular orbitals. Primarily designed as an interdisciplinary training programme for participating PhD students, the GRK also addresses basic research topics. We combine the synthesis of novel compounds, spectroscopic techniques ranging from laser spectroscopy in the time- and frequency-domain to electron paramagnetic resonance and computational methods including quantum chemistry and surface hopping dynamics with the goal to study the structure, the reactivity and the properties of molecular biradicals.

We organize this Symposium to collect external expertise and an outside view, to strengthen cooperations within the GRK and to initiate new interactions with German as well as international research groups. It brings together scientists from all over the world working on various aspects of biradicals and related topics. We are particularly happy to welcome several leading experts in the field, who agreed to present invited talks. The program is complemented by oral and poster contributions from GRK members and external participants. The Würzburg Residenz World Heritage Site in the center of our university town provides a beautiful setting for stimulating discussions and scientific exchange between experienced researchers and the younger generation. We hope that it will be a memorable event for all of us.

Speaker GRK2112
Ingo Fischer

Dean of the Faculty of Chemistry and Pharmacy
Lorenz Meinel

Dean of the Faculty of Physics and Astronomy
Bert Hecht

Organizing Comittee
Ingo Fischer
Eileen Welz
Ursula Rüppel
Nicole Hemmert

Contents

Würzburg

History, Points of Interest, Art and Cultural Events

Würzburg – a town for looking and browsing, a historical and arthistorical picture-book with various views, but at the same time a jigsaw-puzzle of a joy of living, an art to live, cultural flair and Franconian way of life.

Marienberg fortress. Foto: Thomas Huth.

Würzburg started its history as a celtic shelter (around 1000 BC) and a Franconian duchy (650 AD) on the hill known today as Marienberg, which gave shelter to a settlement of fishermen in early times. In 689, the Irish missionaries Kilian, Kolonat and Totnan suffered a martyr's death here in Würzburg. Since the foundation on the bishopry in 742, Würzburg has been the clerical center of the area, with Charlemagne taking part in the consecration of the cathedral in 788. The privilege of holding a market dates back to 1030 when the king's town became the town of the bishop. In 1156, Frederick Bar-

barossa was married to Beatrice of Burgundy here in Würzburg. He also confirmed the duchy to the bishops of Würzburg in 1168. In 1397, King Wenceslas promised imperial immediacy, but was never able to keep this promise. During the Peasant's Revolt in 1525, the town sided with the peasants, who tried to storm the fortress, but failed. This sealed the fate of Würzburg's famous woodcarver, alderman and mayor, Tilman Riemenschneider, who died here in 1531 as a poor and broken man. In the following decades strong clerico-worldly sovereigns ruled the town, among them prince-bishop Julius Echter of Mespelbrunn, who founded the Juliusspital in 1576 and the second university of Würzburg in 1582. There, at the institute of physics, would Wilhelm Conrad Röntgen discover the X-Rays in 1895. The town reached its zenith under the leadership of the artloving family of Schönborn. For them, the architect Balthasar Neumann built the "castle of castles" – the Residenz – between 1719 and 1744 including the famous staircase, where the Venetian artist Giovanni Battista Tiepolo created the world's largest ceiling fresco. After various political quarrels, Würzburg finally became Bavarian in 1814. On March 16, 1945 the town was almost completely destroyed within 17 minutes in an air raid. It owes its reconstruction to the enormous commitment of the inhabitants.

Prince's Garden at Marienberg fortress.

Foto: Andreas Bestle.

Today, Würzburg has 134 000 inhabitants. The town, not only in the center of Germany, but also in the heart of Europe, has perfect traffic connections. Several highway exits close to the city connect it to a variety of routes in any direction. About 300 trains, among them 112 intercity high-speed trains stop over at Würzburg's main station every day. The airports of Nürnberg and Frankfurt are within reach in less than 2 hours without switching trains. The high-speed railway line between Hannover and Würzburg adds a special treat to the possibilities of reaching Würzburg by train. Flourishing river traffic on the river completes the picture.

Würzburg Residenz. Foto: CTW.

Würzburg is a town of tourism and conventions, and it has acquired a unique profile within German tourism. The best way to learn about Würzburgs points of interest is to follow the route that leads from the "Residenz", Balthasar Neumann's masterpiece (including Tiepolos famous frescoes, the court chapel and the court garden) and the former home of the prince-bishops, to the fortress Marienberg. This path covers St. Kilian's cathedral, the Neumünster church with the grave site of medieval poet Walther von der Vogelweide, the market square with the splendid ensemble of the chapel of St. Mary and the "House of the Falcon", a combination of Rococo and gothic style, and last but surely not least the city hall including the Grafeneckart, the Fountain of the Four rivers and the Old Main Bridge. From here, one can see St. Burkard's church and the pilgrimage church Käppele; looking down the river there is the Old Crane, the convention center and finally the vineyard "Würzburger Stein". Up the fortress hill, accessible for a pedestrian from the western side or – in summer – by bus, the "Mainfränkisches Museum" hosts, among other interesting collections, a huge selection of Riemenschneider's works. The church of St. Mary, the Renaissance well-temple and the fortress tower catch the eye of a visitor participating in a convention at the "Hofstuben" (400 persons) inside the Marienberg fortress, thus offering a strong contrast to the newly built "Congress Centrum" downtown.

The bridge "Alte Mainbrücke" was erected from 1473 to 1543 in place of an old Romanesque bridge. Foto: CTW.

As yet, not all interesting sights have been mentioned. Many profane and clerical buildings, such as Stift Haug with its Tintoretto, or the Old University church with its impressive Renaissance tower, Augustiner- and Franciscan church, St. Peter, St. Stephan, St. Johannis and many more buildings are within easy reach, and especially the attractive court yards and the famous "Bürgerspital zum Hl. Geist", founded in 1319, and the "Juliusspital", founded in 1576, where many a bottle of franconian wine, mild or dry, have been sampled and will be sampled again over the years. In addition, a lot of wine cellars, the most imposing being the cellar beneath the Residenz, winehouses and restaurants with a lot of local flair proudly represent Franconian hospitality, and about 60 lodging enterprises from simple guesthouses up to hotels of international standard provide more than 4 000 beds all together. The university and shopping town of Würzburg offers an interesting variety of cultural programmes althrough the year;

museums and galleries cater for various exhibitions and the theatre offers first class performances and concerts. Wine tasting sessions, wine- and beer-festivals as well as short trips by boat or coach complete the agenda for the tourist. Among the largest traditional events are the “Africa Festival” in May and the “Mozartfest” in June with more than 35 000 visitors per year.

Further information
Congress – Tourismus – Wirtschaft (Tourist Office)
Am Congress Centrum, 97070 Würzburg
Phone: +49 931 37 23 35
Fax: +49 931 37 36 52
Internet: http//www.wuerzburg.de
E-Mail: tourismus@wuerzburg.de

University of Würzburg

Past and Recent History

The University of Würzburg was founded in 1402 by Prince Bishop Johann von Egloffstein, making it the oldest university in today's Bavaria and the sixth oldest in the German-speaking world. Reconfirmed by papal and imperial decrees under Prince Bishop Julius Echter von Mespelbrunn in 1582, it has since developed a long tradition of successful science and research. Numerous famous scientists and scholars, including 14 Nobel prize laureates, have worked and taught here. Among them are Rudolf Virchow, Carl Siebold, Franz Brentano, the physicists Wilhelm Conrad Röntgen, who discovered the "X-rays" here in 1895, and Klaus von Klitzing, discoverer of the quantised Hall effect and laureate in 1985. The most recent one is Harald zur Hausen, who was awarded the Nobel prize in Medicine in 2008.

In 1895, the physicist Wilhelm Conrad Röntgen discovered the X-rays in Würzburg.

Immediately after the end of World War II, the reconstruction of the University was embarked upon, after it had been almost completely destroyed in the air raid on March

16. Since its completion in the 1960s, there has been a continuous extension of university sites which is still being carried out today. As a result, a modern campus, "Am Hubland", has come into being. It is situated on one of the hills at the outskirts of Würzburg and offers a magnificent view of the city and its surrounding vineyards. The University Library, a large refectory and brand-new university sports facilities are to be found here as well as a state-of-the-art microstructure laboratory and the *Biozentrum*, equipped with the latest biological technology.

The "Hubland", however, is not the only place of the university's expansion and development: In the urban district of Grombühl, for example, where the university hospital is situated, an extensive new surgical complex (ZOM) and a modern centre for internal medicine (ZIM) were opened in 2008 and 2009. They are run by the Faculty of Medicine and are closely cooperating with the 22 specialised clinics of the city's teaching hospital, where approximately 50 000 people receive inpatient treatment each year.

Campus Hubland, including sciences, philosophic faculty, main library and cafeteria. On the bottom right side, there is the center of chemistry with the pharmacy and food chemistry building; on the top edge, there is the building of theoretical chemistry on the new "Campus Hubland Nord".

The newest site is the "Campus Hubland Nord" which was established in April 2011. After US Army had abandoned their "Leighton Barracks" facilities situated right next to the Hubland campus and had handed over the area to German civil administration in 2008, a part of the site was turned over to the University. Today, the new campus offers a student's residential hall, office space – especially for researchers in theoretical natural sciences – seminar rooms, computer pools and libraries. Lots of new facilities for research and study, however, are about to emerge in the next couple of years, making that area another vital place of university life.

Having been closely linked to the history of the city for centuries, the Julius-Maximilians Universität has become an essential part of its cultural life and an important factor in the local economy. A Service Centre for Research and Innovation at the University has therefore been set up in order to ensure the legal protection and the application of inventions and the results of research. Another important task of this office is to introduce local firms and companies to partners of the University with whom they can enter into a cooperation, and to provide them with information about the latest technology developed in the University's laboratories, along with the achievements and potential of the University in general. With its numerous special research projects, research training schools, research groups and research centres focussing on various areas of the natural sciences and the arts, the University of Würzburg is one of the most successful universities in Germany today.

The University regularly holds a series of public lectures and organises open days for prospective students. It also stages concerts and organises exhibitions – most of them in its own university museum. Throughout the year, these events and a large variety of cultural and recreational activities such as theatre, music, open air concerts, and wine festivals offered by the city, turn Würzburg and its university into a highly attractive place to live and work.

Facts and Figures

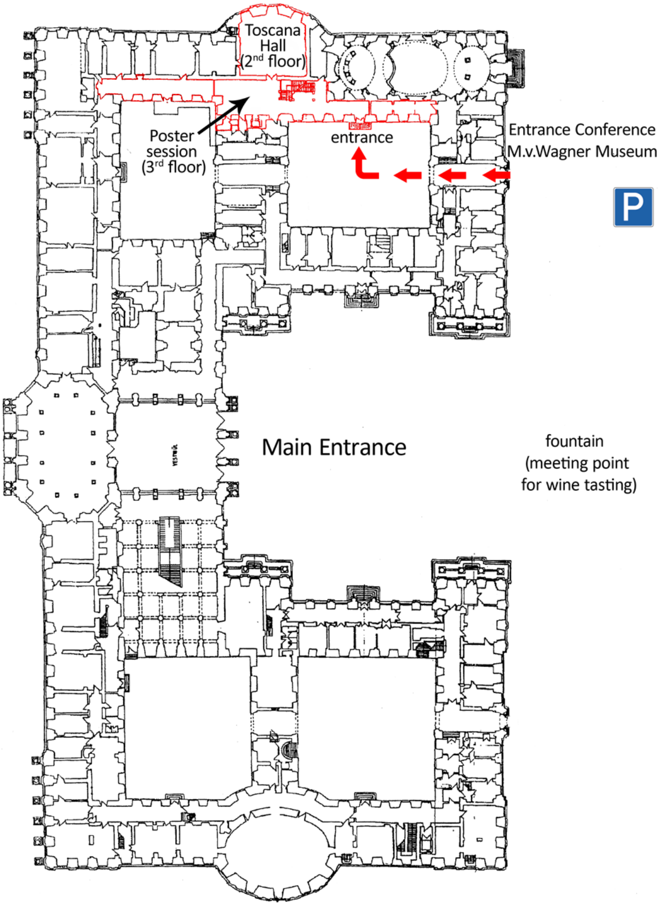
More than 28 000 students among them 2 750 internationals are enrolled at ten faculties, which can be classified into four main categories: Humanities, Law and Economics, LifeSciences and Science and Technology. Of the 4 270 academic people employed by the university, 437 are professors. The University of Würzburg maintains partnerships with 37 universities in many countries in western and eastern Europe as well as overseas.

The university offers 250 degree courses in all subsjects leading to university and/or state examinations. The traditional State Examination is required for Medicine, Dentistry, Pharmacy, Law, and Teacher Training for all categories of schools. New Bachelor and Master degrees have been introduced in nearly all other subjects of study, replacing the traditional Diploma or Magister degrees. For postgraduates, it offers a number of special courses and degrees, e. g. MBA in Business Integration, M. A. in German for

The university building at Sanderring in the city center.

non-native speakers, LL. M. Eur. in European Law, Licentiate in Roman Catholic Theology, and, of course, PhD studies in any subject taught.

Venue and Scientific Programme



Tuesday, February 27

		Arrival
16:30 - 17:50		**Registration**
17:50 - 18:00		**Ingo Fischer** Welcome and opening remarks
	Chairperson: Ingo Fischer	
18:00 - 19:00	I 1	**Josef Michl** *Magnetic circular dichroism of a planarized cyclooctatetraene*
19:00		Welcome mixer

Wednesday, February 28

	Chairperson: Bernd Engels	
09:00 - 9:50	I 2	**Manabu Abe** *The third isomer in bond-homolysis of 1,4 - diarylbicyclo [2.1.0]pentanes*
09:50 - 10:40	I 3	**Wolfram Sander** *Taming the beast – Controlling carbenes by light, temperature, and solvent interactions*
10:40 - 11:00		coffee break
	Chairperson: Anke Krüger	
11:00 - 11:50	I 4	**Holger Bettinger** *Alternating hydrocarbons with polyradical character*
11:50 - 12:10	O 1	**Julian Böhnke** *Reactivity of boron-boron multiple bonds and isolation of biradical products of twisted double bonds*
12:10 - 12:30	O 2	**Eileen Welz** *Theoretical investigations of inorganic biradicals,in particular diborenes, with an unique structure*
12:30 - 14:25		Lunch
14:25 - 15:45		**Residence tour** *Meeting point: Franconia Fountain in front of the Resicence* *Last Names: A-M*
14:40 - 16:00		**Residence tour** *Meeting point: Franconia Fountain in front of the Resicence* *Last Names: N-Z*
15:45 - 16:15		coffee break

Chairperson: Frank Würthner

16:15 - 16:45	O 3	**Mahesh Hariharan** *Strategies to reduce the rate of charge recombination*
16:45 - 17:25	O 4	**Michal Juríček** *Synthetic strategies to persistent biradicals of graphene fragments*
17:25 - 17:45	O 5	**Fabian Dinkelbach** *Inter system crossing from TDDFT-Amplitudes*
17:45 - 20:00		Poster session I

Thursday, March 1

Chairperson: Tobias Hertel

09:00 - 09:50	I 5	**Albert Stolow** *Conical Intersections: Transition states in the excited state*
09:50 - 10:15	O 6	**Jens Petersen** *Simulation of excited-state dynamics in organic radicals and biradicals*
10:15 - 10:35	O 7	**Anja Röder** *Exploring the excited-state dynamics of para- and meta- xylylene with photoelectron spectroscopy*
10:35 - 11:00		COFFEE BREAK

Chairperson: Roland Mitric

11:00 - 11:50	I 6	**Anna Krylov** *Electronic structure of single-molecule magnets: Lessons from theoretical studies of binuclear copper diradicals*
11:50 - 12:10	O 8	**Mathias Steglich** *Photoelectron spectrum and energetics of the meta-xylylene biradicals*
12:10 - 12:30	O 9	**Lena Roos** *Synthesis and properties of tetracene derivatives*
12:30 - 14:30		LUNCH

	Chairperson: Todd Marder	
14:30 - 15:20	I 7	**Suning Wang** *Intramolecular charge transfer driven structural transformation of organoboron compounds*
15:20 - 15:40	O 10	**Stefan Riese** *Photophysics and spin- chemistry in donor- acceptor substituted dipyrrinato- metal complexes*
15:40 - 16:00		COFFEE BREAK
	Chairperson: Tobias Brixner	
16:00 - 16:50	I 8	**Christopher Bardeen** *Exciton Fission and Fusion: Interconverting triplet pairs and singlets*
16:50 - 17:10	O 11	**Lena Grimmelsmann** *Impact of kbar pressures on ultrafast photoisomerization dynamics of a triacene and a thiacyanine system*
17:15 - 18:50		Poster session II
19:00		Wine tasting

Friday, March 2

Chairperson: Andreas Steffen

09:00 - 09:50	I 9	**Oliver Wenger** *Biradicals from Photoinduced Electron Transfer in donor-bridge- acceptors*
09:50 - 10:10	O 12	**Jan Maier** *Novel conjugated systems arising from HDDA generated benzyne-self- trapping via biradicals*
10:10 - 10:30	O 13	**Kazutaka Shoyama** *Synthesis of polycyclic aromatic dicarboximide by Pd- catalyzed annulation reaction*
10:30 - 11:00		COFFEE BREAK

Chairperson: Vladimir Dyakonov

11:00 - 11:50	I 10	**Thomas Prisner** *Probing magnetic interactions of biradicals: From model compounds to macromolecular complexes*
11:50 - 12:15	O 14	**Andreas Sperlich** *Difference between optical excitation and and electrical generation in donor- acceptor based OLEDs*
12:15 - 12:35	O 15	**Ulrich Müller** *Photon- correlation studies revealing the exciton- exciton interaction in single para- xylylene bridged perylene bisimide macrocycles*
12:35		**Ingo Fischer** Concluding remarks
		DEPARTURE

Invited Lectures

Magnetic Circular Dichroism of a Planarized Cyclooctatetraene

Josef Michl [1,3], Jin Wen[1], Takayuki Uto[2], Deb Casher[3], Gerhard Raabe[4], Joerg Fleischhauer[4], Takeshi Yanai[5], Hayato Tsuji[2], Koichi Komatsu[2]

[1]Institute of Organic Chemistry and Biochemistry AS CR, Flemingovo nám. 2, 16610 Prague 6, Czech Republic., [2]Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan, [3]Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215, U.S.A., [4]Institut für Organische Chemie, Rheinisch-Westfälische Technische Hochschule Aachen, Landoltweg 1, D-52056 Aachen, Germany, [5]Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Okazaki, Aichi 444-8585, Japan, and JST PRESTO, 4-1-8 Honcho, Kawaguchi-shi, Saitama 332-0012, Japan

An overview of magnetic circular dichroism (MCD) of π-electron systems derived from a 4N-electron perimeter is provided, with emphasis on the hypothetical parent D_{8h} cycloocta-1,3,5,7-tetraene (a perfect antiaromatic biradical) and its unaromatic biradicaloid D_{4h} derivatives. Absorption and MCD spectra of a D_{4h} symmetric cycloocta-1,3,5,7-tetraene planarized by fusion of four bicyclo[2.1.1]hexeno units are compared with expectations based on computations by (i) time-dependent density functional theory and (ii) extended multistate complete active space second-order perturbation theory, but most insight is obtained from (iii) an algebraic solution of the perimeter model. Signs of the MCD A and B terms of the two observed symmetry-allowed transitions obtained by the three theories all agree; three of the four also agree with observations.

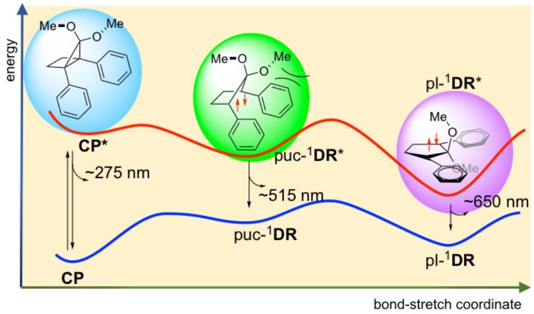
NOTES

Unusually Long-wavelength Emissions of Bicyclo[2.1.0]pentanes: New Insight into C-C Bond Homolysis

Manabu Abe[1]

[1]Department of Chemistry, Graduate School of Science, Hiroshima University

Bond homolysis (BHo) is a fundamental concept in chemical bonding phenomena. To date, research studies on the BHo concept have provided crucial information for understanding the nature of chemical bonding and reactions. Two potential energy minima, a σ bonding isomer and a singlet-diradical isomer, have been known to exist in carbon-carbon BHo. In the present study, a third isomer, that is, a puckered singlet diradical (puc-1DR) exhibiting unstructured long-wavelength fluorescence beyond 460 nm, was first observed in the excited states of 1,4-diarylbicyclo[2.1.0]pentane (CP) derivatives. The careful selection of appropriate substituents in the bicyclic structures enabled direct spectral detection. State-of-the-art ab initio quantum chemical calculations quantitatively reproduced the experimental observations. This novel finding provides new insight into carbon-carbon bond-breaking and forming processes.



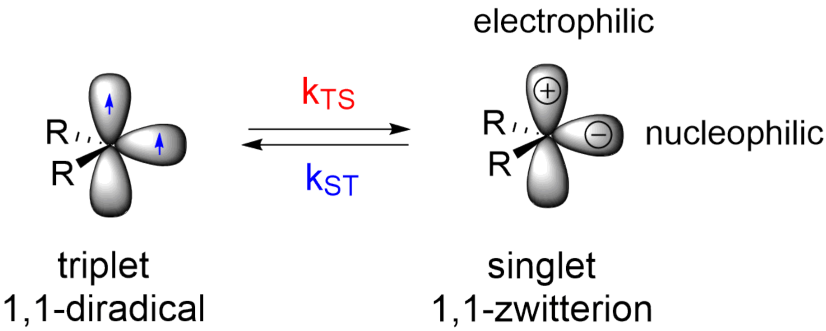
NOTES

Taming the Beast: Controlling Carbenes by Light, Temperature, and Solvent Interactions

Wolfram Sander[1], Paolo Costa[1]

[1]Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, Germany

Carbenes are among the most versatile reactive intermediates. The reactivity of these species is highly variable, ranging from the open-shell (triplet or singlet) reactivity expected for a 1,1-diradical to the extreme philicities of closed-shell (singlet) carbenes that resemble 1,1-zwitterions with both high electrophilicity and nucleophilicity. The stability of carbenes varies from fleeting intermediates with life¬times in the range of picoseconds to entirely stable compounds that can be isolated at room temperature. During the last years we learned to control the spin state, and thus the reactivity, of carbenes by weak intermolecular interactions, in particular by hydrogen[1]- and halogen bonding.[2] By carefully selecting reaction conditions it is even possible to synthesize carbenes that coexist in both their triplet and singlet states, resulting in magnetically bistable carbenes.[3,4] The mechanistic studies described in the lecture pave the ground for developing new carbene reactions and for applications such as switchable magnetic materials.



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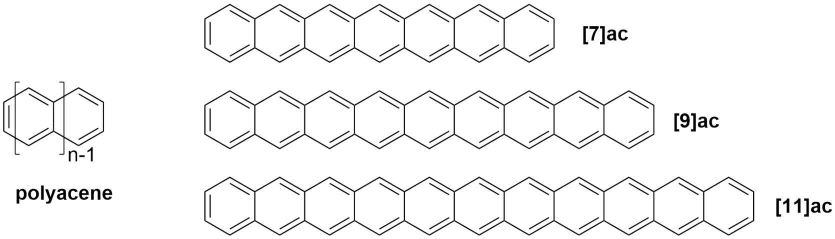
NOTES

The Higher Acenes: Alternating Hydrocarbons with Polyradical Character

Holger F. Bettinger[1]

[1]Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen,
Germany

The acenes, alternating hydrocarbons composed of linearly fused benzene rings, are of high importance in the context of organic electronics.[1-3] Having a width of only one benzene ring, they are also the narrowest 1D graphene nanoribbon4 of zigzag topology. The electronic structure of the 1D polymer, polyacene, was discussed controversially in the literature and predictions ranging from metallic,[5] Mott-type insulating behavior,[6] magnetic ordering,[7,8] and superconducting[6,9] behavior were made. More recently, band gap oscillations[10,11] have been predicted to occur in the length regime, [9]ac to [11]ac, that could be accessible experimentally.
We here report on our efforts of gaining access to acenes of unprecedented lengths following our earlier work on heptacene and nonacene.[12-15]



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NOTES

Conical Intersections: Transition States in the Excited State

Albert Stolow[1,2]

[1]Departments of Chemistry & Physics, University of Ottawa, [2]Molecular Photonics Group, National Research Council Canada

The conical intersection plays a role in excited state reaction dynamics much like a transition state in ground state dynamics. Perhaps we can find, for excited state polyatomic dynamics, a set of notions analogous to the Polanyi rules for ground states which guide our thinking about the topography and location of conical intersections relative to potential gradients, barriers and thresholds. Will there be notions such as ”early” or ”late”? Do the ”velocity” and ”direction” of passage through a conical intersection affect branching? We begin with a phenomenological approach by using the location and number of methyl substituents on unsaturated hydrocarbons as a ”variable” to tune motions near conical intersections. We introduce the concept of the “dynamophore”, an analogy with the concept of a chromophore. The dynamophore is the chemical moiety (e.g. a specific C=C bond) where the dynamics become localized. We experimentally probe excited state dynamics using time-resolved photoelectron spectroscopy, a method sensitive to both vibrational and electronic degrees of freedom.

Notes

Electronic structure of single-molecule magnets: Lessons from theoretical studies of binuclear copper diradicals

Anna Krylov[1]

[1]Department of Chemistry, University of Southern California

Molecular magnets can be used as building blocks in the fabrication of novel and structurally diverse magnetic light-weight materials. This lecture will present a theoretical investigation of the lowest spin states of several binuclear copper diradicals. In contrast to previous studies, we consider not only the energetics of the low-lying states (which are related to the exchange-coupling parameter within the Heisenberg-Dirac-van-Vleck model), but also the character of the diradical states themselves. We use natural orbitals, their occupations, and the number of effectively unpaired electrons to quantify bonding patterns in these systems. The performance of spin-flip time-dependent density functional theory (SF-TDDFT) using various functionals and effective core potentials against the wave function based approach, equation-of-motion spin-flip coupled-cluster method with single and double substitutions (EOM-SF-CCSD) will be compared and discussed. Visualization of frontier natural orbitals shows that the unpaired electrons are localized on copper centers, in some cases exhibiting slight through-bond interaction via copper d-orbitals and p-orbitals of neighboring ligand atoms. The analysis reveals considerable interactions between the formally unpaired electrons in the antiferromagnetic diradicaloids, meaning that they are poorly described by the Heisenberg-Dirac-van-Vleck model. Thus, for these systems the experimentally derived exchange-coupling parameters are not directly comparable with the singlet-triplet gaps. This explains systematic discrepancies between the computed singlet-triplet energy gaps and the exchange-coupling parameters extracted from experiment.

NOTES

Charge-Transfer Driven Structural Transformation of Organoboranes: Unusual Reactivity of Boriranes

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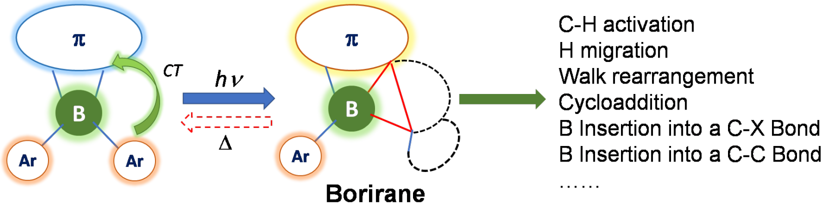
Photochemistry of organoboron compounds has attracted much research attention recently primarily because of the discoveries of a variety of new and interesting applications based on photoresponsive boron systems. A key discovery made by our team is new photochromic boron systems, which involve reversible B-C and C-C bond breaking/formation and distinct color change of the boron species. Internal donor-stabilized boriranes is the key species in the phototransformation process. Charge-transfer transition has been found to be the key driving force with biradical species being implicated in some examples of the transformation. Depending on the nature of the substrate and the aryl substituents on boron, the borirane species have been found to be capable of engaging in highly unusual bond activation chemistry, such as C-C bond cleavage of acenes, C-X bond cleavage of aromatic heterocycles with the boron center being intimately involved. This presentation will focus on the key knowledge and the latest findings we have obtained on charge-transfer driven photoreactive boron systems.[1][2]



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NOTES

Exciton Fission and Fusion: Interconverting triplet pairs and singlets

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Although most spectroscopically accessible states involve single excitations (i.e. the promotion of one electron to a new orbital), doubly excited molecular states have been the subject of increasing interest due to their roles in exciton fission and fusion. Fission is an energy downconversion process (1 high energy excitation -> 2 low energy excitation) while fusion is an energy upconversion (2->1) process. Both are of practical interest because they provide routes to boost solar energy conversion efficiencies by 30% or more. Organic semiconductors like tetracene and rubrene are uniquely well-suited to perform this energy repackaging because the Frenkel character of the excitons leads to energetically distinct singlet and triplet bands, which can exchange energy via spin-allowed fission and fusion processes.[1] We will describe efforts to understand the basic photophysics of singlet fission using time-resolved transient absorption, photoluminescence and magnetic field effects.[2] [3] [4] The roles of molecular packing and crystal morphology in controlling the fission rate will be emphasized.[5] [6] The reverse process, where a pair of triplet excitons fuse into a high-energy singlet state, is also studied. A new approach to triplet state sensitization involves absorption of low energy photons by semiconductor nanocrystals followed by energy transfer to the molecular triplet states.[7] When these triplet states fuse, we observe upconverted light. We find that upconversion via triplet fusion can occur in certain molecular crystals even in the absence of sensitizers, possibly due to the presence of low-energy intermolecular states. Finally, the importance of spin interactions in these processes is only beginning to be examined in a systematic way. For singlet fission, nonequilibrium spin state distributions can play an important role in both the ultimate triplet yield and the observation of experimental quantities like delayed fluorescence. We will describe time-resolved experiments and Monte Carlo simulations that look at how spin dynamics affect fission and triplet-triplet annihilation.

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NOTES

Biradicals from Photoinduced Electron Transfer in Donor-Bridge-Acceptor Compounds

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Photoexcitation of donor-bridge-acceptor molecules commonly induces the transfer of single electrons, leading to the formation of simple electron-hole pairs. In this talk, new systems that go conceptually beyond the transfer of single electrons will be presented. This includes long-range electron transfer reactions that are coupled to multiple proton transfers, attempting to mimic an entire series of primary events occurring in photosystem II. [1] A further focal point will be multi-electron transfer reactions leading to the accumulation of redox equivalents without the use of sacrificial reagents. [2] In one recent case study, we found evidence for circular electron transfer in a flexible donor-bridge-acceptor compound, leading to a system that can be considered a molecular circuit. [3]

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NOTES

Probing magnetic interactions of biradicals: From model compounds to macromolecular complexes

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Electron Paramagnetic Resonance can measure precisely the magnetic dipole-dipole and the exchange interaction between the two unpaired electron spins of biradicals with high precision for distances ranging from 1-10 nm. This can be used for obtaining structural constraints in large macromolecular complexes and to analyse in detail the spin-density distribution in biradicals. A detailed understanding of the magnetic coupling is for example important for optimization of biradicals used as dynamic nuclear polarization (DNP) agents. Another possibility is to use the measure of the magnetic interaction strength for structural studies in macromolecules, as proteins or synthetic polymers. In proteins, site-directed spin-labeling with nitroxides at two cysteine positions is an well established method. Paramagnetic transition metal ions, intrinsically bound to proteins are also interesting targets for such kind of measurements. They are more challenging because of the much larger spectral width, faster relaxation rates and high-spin effects, complicating the analysis of the magnetic coupling. In our group, we have synthesized a number of bi- and multi-radical molecules to evaluate and optimize the pulsed EPR methods used for such kind of investigations. Advances of the methodology and its potential to characterize structure and dynamics of protein complexes and nucleic acids will be shown.

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Oral Presentations

Reactivity of Boron–Boron Multiple Bonds and Isolation of Biradical Products of Twisted Double Bonds

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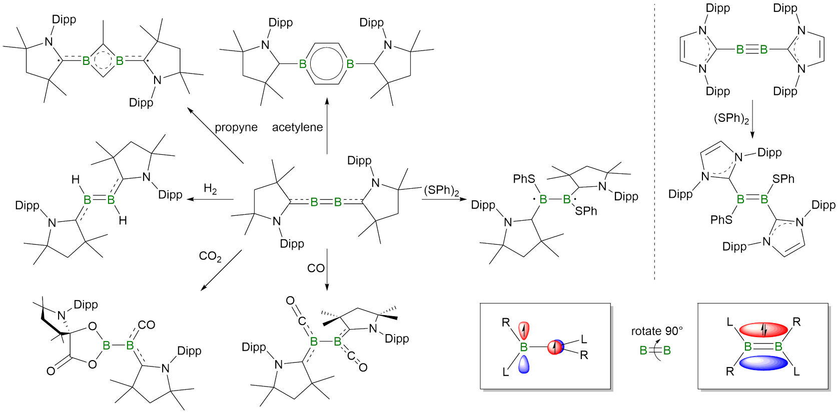
The utilization of cyclic (alkyl)(amino)carbenes (CAACs) to stabilize the highly reactive B_2 unit led to the formation of a diboracumulene ($R_2C{=}B{=}B{=}CR_2$), in contrast to the discrete B–B triple bond observed with NHC donors ($R_2C{-}B{\equiv}B{-}CR_2$).[1][2] The capacity of the CAAC ligands to withdraw π-electron density from the B–B bond has provided access to a range of compounds displaying unique bonding situations. Reactivity studies on this system led to base adducts (isonitriles, NHCs),[3] small molecule activation (CO, CO_2, H_2)[4][5] and cycloadditions (acetylene, propyne),[6] illustrating the synthetic potential of B–B-multiple bonds. Frequent attempts have been made to perturb the structure and reactivity of multiply bonded species through bending and twisting.[7][8] However, only modest success has been achieved in the quest to completely twist double bonds in order to homolytically cleave the associated π-bond. The 1,2-addition of a disulfide to a diboryne and a diboracumulene led in the first case to the formation of a diborene, and in the second to its fully twisted biradical congener.



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Theoretical investigations of inorganic biradicals, in particular diborenes, with an unique structure

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The CAAC ligated diborenes show an interesting behavior concerning their chemical reactivity. Depending on the sterical effects of the ligands, the molecules arrange either coplanar or orthogonal. In this case the CAAC ligand plays an important role, as its sterical and electronical effects very often result in an open shell structure. For the coplanar coordinated diborene it was already proven that the B-B bond is a B=B double bond. However, for the diborane with orthogonal coordinated ligands, a B-B single bond is found. The main interest of this work is now to figure out in what way it is possible to describe a biradical character with low cost DFT functionals and which functionals give the best performance compared to high level CASSPT2, MR-CI methods. Another interesting point is the influence of the ligand on the boron centres. Therefore, a closer look was taken at differently substituted boron systems and the influence of the ligands on the overall structure (see Fig. O2). In order to get an overview of the influence of the electronic behavior, the same basic molecular structure was used to verify the electronical behavior of the ligands.

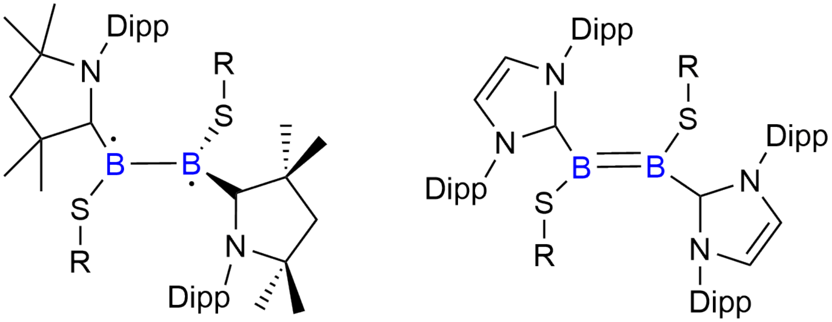

Figure O2: Orthogonal ligated diborane (left) and coplanar ligated diborene (right).

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Notes

Strategies to Reduce the Rate of Charge Recombination

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Molecules that produce charges when excited by light are useful for a variety of (bio-)organic electronic applications. To maximize the utility of these molecules, researchers work to keep the induced charges separate for as long as possible. Stacking the excitable molecules can extend the charge lifetime, but often the donor and acceptor parts of the molecule naturally alternate in the stack, which causes the charges to immediately recombine. Our group aim to minimize charge recombination[1] [2] [3] [4] [5] by separating the donor and acceptor portions of the molecule on different spatial planes. We have synthesized a naphthalimide-naphthalene dyad where the donor and acceptor units are twisted into different planes. The twisted monomers also assemble into a stacked tower. When illuminated by UV light, the charge separated state of the stack can last more than 1.2 ns, 10,000 times longer than in the monomeric dyad (Figure 1). This assembly could be a novel scaffold for light harvesting, molecular electronics, or new light-induced electronic applications. As opposed to the conventional view of modulating the redox properties and/or distance between donor and acceptor, our results encourage to focus on fine-tuning of spatial organisation of the donor and acceptor chromophores to hop the charges over long distances.

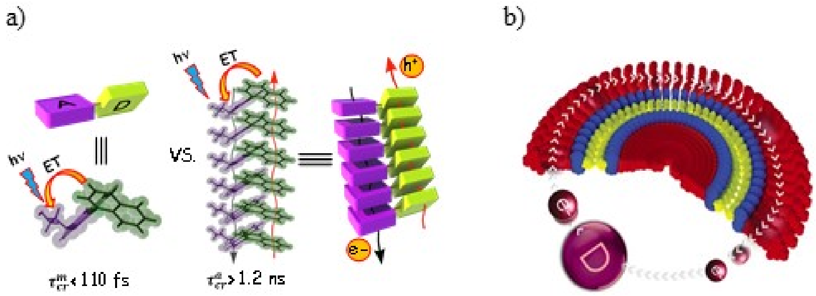

Figure O3: Representative strategies adopted in our group to spatially organize electron donors and acceptors for emergent properties.

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NOTES

Singlet diradicaloid cethrene: the chameleon of Woodward–Hoffmann Rules

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Electrocyclic ring-closure (EC) in singlet diradicaloid cethrene[1],[2] is shown to proceed both thermally and photochemically in a conrotatory mode. This feature is in stark contrast to most of other pericyclic reactions that proceed either thermally or photochemically in a given rotatory mode, depending on the orbital symmetry, and places cethrene among a rare type of molecules. In the case of cethrene, the thermal conrotatory EC is formally a "forbidden" process according to the Woodward–Hoffmann rules. Because of its diradicaloid character stemming from the small HOMO–LUMO gap, however, the LUMO is partially occupied in the ground state and the thermal process thus displays a surprisingly low activation energy (14 kcal mol−1). We argue and provide evidence that it is most likely due to decreasing the symmetry of the molecule along the reaction coordinate. Here, the C1-symmetric transition state, unlike the C2-symmetric one, allows for mixing of the lowest singlet excited-state configuration into the ground-state configuration and lowers the barrier.

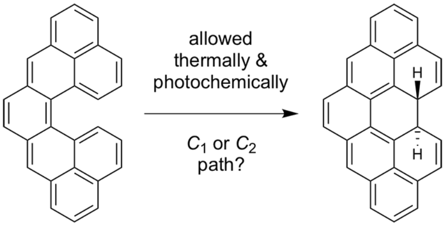

Figure O4: Electrocyclization of cethrene.

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NOTES

Intersystem Crossing from TDDFT Amplitudes

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To understand excited state processes, the ability to compute rate constants for intersystem crossing (ISC) or reversed intersystem crossing (RISC) is important.

Approaches to compute such rates depend on the spin–orbit matrix elements (SOMEs) between different states. The coupling can be calculated for small systems from wave function methods such as multireference configuration interaction (MRCI), multireference perturbation theory (MR-MP) or a combination of density functional theory with MRCI known as DFT/MRCI [1-3]. For large systems, these approaches are expensive. In contrast, time dependent functional theory (TDDFT) represents an inexpensive approach to calculate interstate couplings. While TDDFT is a fast method, it is important to mention that it is not applicable to problems involving double excitations, charge-transfer- or Rydberg states.

Our approach employs auxiliary many-electron wave functions (AMEW) [4] generated from left and/or right eigenvectors of Cassida's non-Hermitian TDDFT equation. Spin–orbit integrals are calculated using a spin–orbit mean field (SOMF) approximation [5].

In a recent benchmark, it could be shown that TDDFT-SOMEs calculated with B3-LYP and PBE0 density functionals are in good agreement with SOMEs at DFT/MRCI level [6].

After a brief introduction into the method, a few representative examples will be presented.

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NOTES

Simulation of excited-state dynamics and time-resolved spectroscopy in organic radicals and biradicals

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The ultrafast photodynamics and nonradiative relaxation of organic radicals and biradicals have been investigated theoretically in the framework of the quantum-classical field-induced surface-hopping method (FISH) [1]. This approach allows for the full-dimensional simulation of the coupled electron-nuclear dynamics in complex molecules under the influence of arbitrarily shaped laser fields, providing a detailed picture of photodynamic mechanisms at the molecular level.

Experimentally, such processes are frequently investigated using time-resolved spectroscopic techniques. In particular, time-resolved photoelectron imaging provides valuable information on energy and spatial distribution of the emitted photoelectrons, which in turn are sensitive probes for the temporal evolution of the nuclear and electronic quantum states.

The connection between such measurements and theoretical dynamics simulations is established by calculating the time- and angle-resolved photoelectron imaging signals along the nuclear surface-hopping trajectories. For this purpose, the differential ionization cross sections are determined using Dyson orbitals as initial and Coulomb waves as final states [2]. This methodology was employed to study the nonadiabatic photodynamics in selected organic radicals and biradicals, which are of interest both from a fundamental point of view as well as in the context of polymer formation, combustion processes, or astrochemistry [3, 4] .

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NOTES

Exploring the excited-state dynamics of para-xylylene with photoelectron spectroscopy

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Here we present the joint experimental and theoretical study of the excited-state dynamics of one xylylene-isomer in the gas phase, the *para*-xylylene. Xylylenes are major combustion intermediates, since xylenes (C_8H_{10}) are common fuel additives for jet fuels due to their high octane ratings. Even though xylylenes are frequently represented as biradicals (see fig. 1), for *ortho*- and *para*-xylylene the quinone (closed-shell) structure dominates, and only the *meta*-xylylene is a true biradical. *Para*-xylylene was produced from suitable precursors using flash pyrolysis. The molecule was excited using the third harmonic of a Ti:Sapphire laser (266 nm) and subsequently ionized with the fundamental of a Ti-Sapphire laser in a fs-time-resolved pump-probe experiment. Time-resolved mass spectra (TOF-ms) and time-resolved photoelectron spectra (TR-PES) were recorded using the velocity map imaging technique. The mass spectra were dominated by the *para*-xylylene signal, which shows a bi-exponential decay (τ_1<40 fs, τ_2=400 fs). The evolution of the second state can be directly followed in the evolution of two others, far less intense masses: benzene and the hydrogen abstraction product of *para*-xylylene. The time-resolved photoelectron spectra show a broad band issued from a [1+4'] process, whose structure changes over time. The experiments were accompanied by field-induced surface hopping (FISH[1]) dynamic calculations as to obtain a deeper understanding of the involved molecular states.

Acknowledgments: This work has the support of Laserlab Europe.

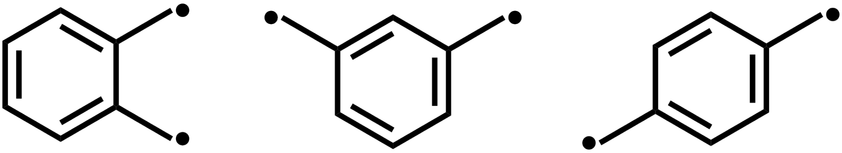

Figure O7: The three xylylene isomers (from left to right): *ortho*-, *meta*- and *para*-xylylene

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NOTES

Photoelectron Spectrum and Energetics of the *meta*-Xylylene Diradical

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The *meta*-xylylene diradical m-C_8H_8 is a prototypical organic triplet that represents a building block for organic molecule-based magnets and also serves as a model compound for test and refinement of quantum chemical calculations. Flash vacuum pyrolysis of 1,3-bis-iodomethyl-benzene (m-$C_8H_8I_2$) produces m-C_8H_8 in gas phase; we used photoelectron spectroscopy to probe the first two electronic states of the radical cation, and resolve the vibrational fine structure of the ground state band. The determined adiabatic ionization energy of m-C_8H_8 is (7.27±0.01) eV. Heat of formation of the diradical was established measuring C–I bond dissociation thresholds in the precursor cation and utilizing a thermochemical cycle to yield $\Delta H_{f,298K}$ = (325±8) kJ mol^{-1}, ca. 10 kJ mol^{-1} below the previous value.

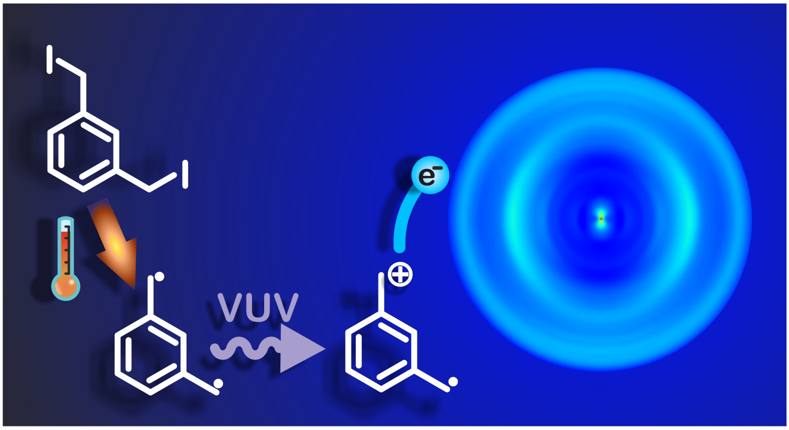

Figure O8: Photoelectron Spectroscopy of the *meta*-Xylylene Diradical

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Synthesis and Properties of Tetracene Derivatives

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Acenes have attracted enormous interest because of their potential application as luminescent and semiconducting materials. Tetracene, a polycyclic aromatic hydrocarbon which consists of four linearly fused benzene rings, is classified as an open-shell system. Due to its relatively small triplet excitation energies, tetracene is a promising candidate for singlet fission.[1] In this spin-allowed process a singlet state splits into two triplet states, the efficiency strongly depends on the relative orientation of the participating chromophores. 2,2'-Ditetracene [2] was synthesized in a 7-steps-synthesis by means of Diels-Alder cycloaddition, halogenation and transition–mediated coupling reactions. To demonstrate the effect of molecular conformation on the progress of singlet fission the optical properties of single tetracene molecules and covalently linked ditetracene chromophores were compared by forcing the chromophores into a particular conformation by the surrounding lattice (different crystalline and non-crystalline environments).

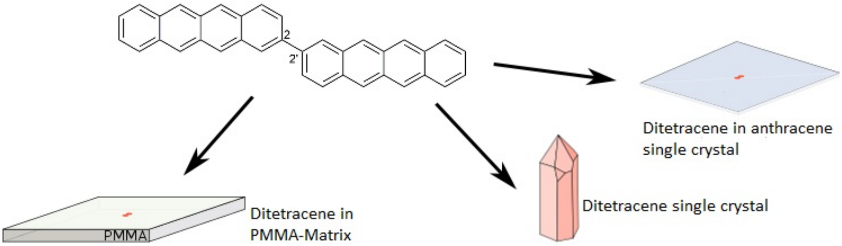

Figure O9: Ditetracene doped into different crystalline and non-crystalline environments.

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Photophysics and spin-chemistry in donor-acceptor substituted dipyrrinato-metal complexes

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Magnetic field dependent transient absorption measurements on triarylamine-iridium(III)-dipyrr naphthalene diimide triads could, for the first time, show a well defined biphasic magnetic field effect (MFE) on the decay-kinetics, which can be assigned to the transition from coherent to incoherent spin-motion.[1]

In this study we focus on the influence of the central metal ion on the formation of charge separated states and the MFE of their decay. Therefore we synthesized two additional sets of dipyrrinato-metal complexes with Pt(II) and Pd(II) as central ions, resulting in the three triads shown in figure 1. The compounds were examined by magnetic field dependent transient absorption spectroscopy on a nanosecond time scale at aprox. 90 fields between 0 mt and 1800 mT. The analysis of the experimental data according to the model depicted in figure 1 shows a clear influence of the central complex on the spin-chemistry of the triads. For example the MFE increases from a 6-fold increase in lifetime for Ir to a 90-fold increase for Pd.

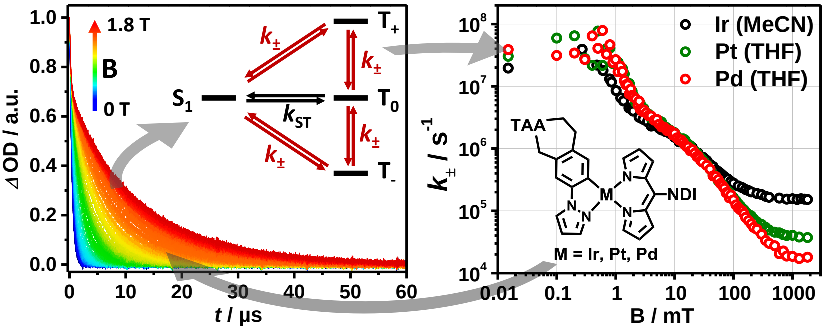

Figure O10: following the arrows: triads examined in this study, an examplary measurement, the underlying model and the resulting plots of the biphasic MFEs

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NOTES

Impact of kilobar Pressures on Ultrafast Photoisomerization Dynamics of a Triazene and a Thiacyanine System

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Photoinduced cis-trans isomerizations of carbon or nitrogen double bonds are of great importance for many fields of chemistry, biology, and technology. For example the primary step of vision involves the cis-trans isomerization of rhodopsin [1]. Numerous mechanisms for cis-trans isomerizations are known, the most common motions being rotation and inversion. Other mechanisms described in the literature comprise the hula-twist and the NN-twist which are discussed for azobenzene, and the bicycle-pedal motion proposed for rhodopsin. Depending on the molecular system and its characteristics, the dynamics of the isomerization differ remarkably when changing the viscosity or temperature. The triazene compound berenil (1,3-bis(4'-amidinophenyl)triazene) and thiacyanine compound NK88 (3,3'-diethyl-2,2'-thiacyanine) both exhibit extremely short fluorescence lifetimes of 0.46 ps in water and 1.80 ps in methanol, respectively, indicating a rapid non-radiative deactivation pathway. Previous liquid-phase studies at 1 bar in combination with quantum chemical calculations have shown that berenil isomerizes *via* a volume-conserving bicycle-pedal motion [2], whereas for NK88 a rotation mechanism with two competing excited-state pathways has been observed [3]. These studies also investigated the viscosity-dependence of the environment for a better understanding of the isomerization dynamics. For berenil a negligible dependence was found, whereas for NK88 a significant increase of the excited-state lifetime with viscosity occured. However, the variation of the viscosity was carried out by employing different solvents, thereby also varying solvent polarity, and thus possibly influencing the isomerization dynamics as well. An alternative for adjusting the viscosity is pressurizing the system or lowering the temperature of the system, hence keeping polarity changes low. In this study, we apply femtosecond fluorescence upconversion to berenil and NK88 dissolved in 2-propanol or water under pressure of 1 to 1500 bar. For berenil, a negligible impact of the viscosity on the fluorescence dynamics is found, in agreement with the bicycle-pedal motion. By contrast, the two fluorescence lifetimes of NK88 exhibit a prolongation scaling linearly with the viscosity, and their relative amplitudes indicate a pressure-dependent branching ratio for the two accessible photoisomerization pathways.

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NOTES

Novel conjugated systems arising from HDDA generated benzyne - self-trapping via biradicals

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Cyclisation reactions have long been a way of generating structures of high complexity in an elegant fashion. The hexadehydro-Diels-Alder (HDDA) reaction[1] – evolved from the classical Diels-Alder reaction – provides highly reactive benzyne intermediates, which can be utilized in a variety of follow-up reactions.[2] We report the unusual self-trapping of a benzyne derivative, generated *via* an HDDA reaction of one bis-(diyne) by a second bis-(diyne) molecule, wherein a C–C triple bond formally gets cleaved. We identified both a naphthalene and a benzindenopyrene derivative, among other reaction products, depending on which of the two chemically different triple bonds (and its orientation) is involved in the reaction with the benzyne. The calculated mechanism shows similar initial reaction steps, though on the way to the benzindenopyrene a strained enediyne is generated, facilitating a Bergman-cyclisation, which is followed by the formation of two new C–C bonds.

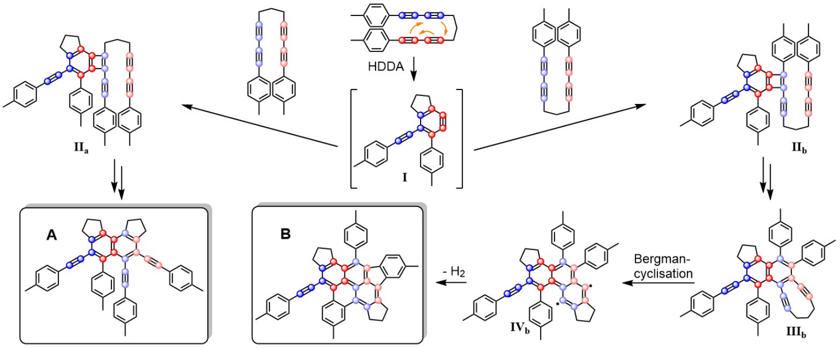

Figure O12: HDDA-induced C—C triple bond splitting leading to naphthalene **A** and benzindenopyrene **B** .

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Notes

Synthetic Method for Multi-Imide-Substituted Polycyclic Aromatic Hydrocarbons by Palladium Catalyzed Annulation Reaction

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Imide-substituted polycyclic aromatic hydrocarbons (PAHs) are an important class of functional materials due to their excellent optical and electrochemical properties as well as functionality that allows formation of various supramolecular structures. In particular the ability of imides to be reduced easily into stable radical anionic species appears to be most promising to clarify important questions with regard to the interaction of multiple spin centers, starting from biradicals and moving on to multiradical systems. With this goal in mind, we have been engaged in synthesis of new imide-substituted PAHs by palladium-catalyzed annulation reaction using naphthalene dicarboximide as a coupling component.[1] This allowed us to introduce imide-substituents to various planar π-conjugated scaffolds.[2] Furthermore we could also apply this method to synthesize bowl-shaped imide-substituted PAHs.[3] Our recent progress on the improvement of substrate scope will be also presented.

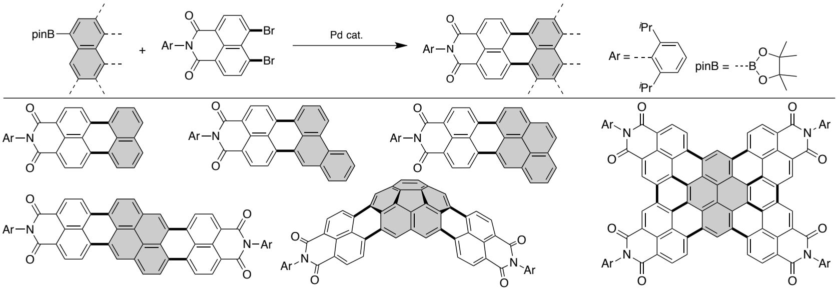

Figure O13: Pd-catalyzed annulation reaction of naphthalenedicarboximide and PAHs.

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NOTES

Difference between Optical Excitation and Electrical Generation in Donor-Acceptor based OLEDs

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The mechanism of thermally activated delayed fluorescence (TADF) emission in organic light emitting diodes (OLEDs) raised many questions about the mechanism of triplet-singlet up-conversion leading to emission. Yet, direct spin-sensitive measurements on OLED devices are scarce in literature. Here, we apply a combination of time-resolved optical spectroscopy and spin-sensitive magnetic resonance measurements based on electrical detection (EDMR), electroluminescence (ELDMR) and photoluminescence (PLDMR) to efficient TADF OLED devices based on several donor-acceptor systems. Our results show that the triplet state which is mainly responsible for the occurrence of TADF in donor:acceptor based systems is the exciplex triplet for both electrically driven devices as well as for optically excited samples. Molecular triplets however, appear only after optical excitation at low temperatures and don't play any role for electrical injection. We expect this picture to also be valid for further donor-acceptor exciplex emitters, which is why it is imperative to carefully distinguish between optical excitation and electrical generation as they may involve different intermediate excited states.

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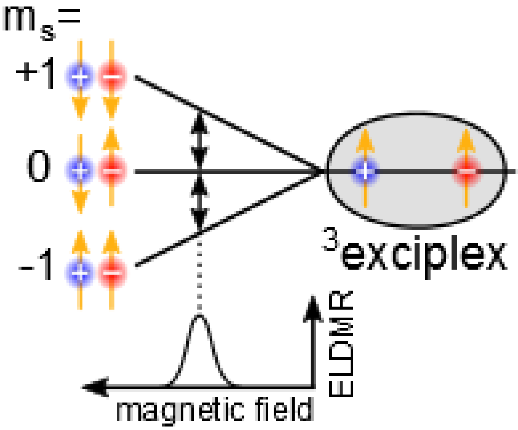

Figure O14: The properties of emissive exciplex excited states are studied using magnetic resonance spectroscopy.

Notes

Photon-correlation studies revealing the exciton-exciton interaction in single para-xylylene bridged perylene bisimide macrocycles

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Multi-chromophoric systems serve as strong links between free photons and excitonic excitations in nature and define promising compounds for non-classical light sources in quantum optics. In this context, we have identified Perylene Bisimides (PBIs) as a model system for strong absorption and efficient single photon emission at room temperature promoted by their chemical tunability and high photostability [1]. We utilize time-correlated single photon counting techniques to analyze the photon statistics of single fluorescent molecules. By comparing para-xylylene bridged PBI-macrocycles to single chromophores we find PBI-macrocycles acting as bright single photon emitters since ultra-fast exciton-exciton-annihilation significantly suppresses the simultaneous emission of two photons. By increasing the laser excitation above single-excited state saturation the co-existence of multi-excitonic states becomes more likely and opens up new channels to the triplet state. A stochastic Markov model consistently explains our observations and advances the understanding of excitation and relaxation processes in multi-chromophoric systems. We are grateful for the financial support provided by the GRK 2112.

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NOTES

Posters

Quantitative p-Doping and Electron Localisation in (6,5)-Single-Wall Carbon Nanotubes

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Defects and doping in Single-Wall Carbon Nanotubes (SWNTs) by (electro-) chemical methods is a highly important topic for future applications of SWNTs. Previous indirect all-optical techniques hypothesise charge carrier localisation in SWNTs due to adjacent $AuCl_3$ molecules, which is indicated by changing exciton dynamics [1]. Here, we present direct quantitative investigations of chemical p-doping by means of electron paramagnetic resonance (EPR), using a spin count reference sample. We estimated the p-doping concentrations on our SWNTs over a wide range, gaining new insight into the widely discussed topic of charge carrier confinement.

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Investigation of intra- and intermolecular TADF emission investigated by magnetic resonance methods

Nikolai Bunzmann[1], Benjamin Krugmann[1], Sebastian Weißenseel[1], Gintare Grybauskaite-Kaminskiene[2], Dmytro Volyniuk[2], Andreas Sperlich[1], Juozas V. Grazulevicius[2], Vladimir Dyakonov[1,3]

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Organic light emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) utilize molecules with a small energy splitting ΔE_{ST} between singlet and triplet states. This can either be realized in intramolecular charge transfer states of molecules with near-orthogonal donor and acceptor moities or in exiplex states formed between a proper combination of individual donor and acceptor materials. Here, we investigate 4,4'-(9H,9'H-[3,3'-bicarbazole]-9,9'-diyl)bis(3-(trifluoromethyl) benzonitrile) (pCNBCzmCF3), which shows intramolecular TADF but simultaneously can form intermolecular exciplex states in combination with 4,4',4"-Tris[phenyl(m-tolyl)amino] triphenylamine (m-MTDATA). In order to reveal which triplet states are involved in the RISC mechanism for both types of TADF emission, we apply electroluminescence and photoluminescence detected magnetic resonance (ELDMR, PLDMR). Thereby, we draw a comprehensive picture of which intermediate states are populated between optical or electrical excitation and light emission.

Neutral Captodative Stabilized Boron-Containing Biradicals

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Anionic boryl radicals have been investigated for decades,[1] whereas the field of the isoelectronic neutral compounds remained rather scarcely investigated. However, neutral boryl radicals have emerged in recent years and a few examples of Lewis-base-stabilized boryl radicals could be isolated and characterized.[2] N-heterocyclic carbenes (NHC) have been employed to stabilize the lone electron at boron by Curran and coworkers.[3] These neutral boryl radicals were recently applied to various organic radical reactions, such as radical deoxygenation of xanthates, radical reductions of alkyl halides and radical chain homolytic substitution reactions.

Based on these results, the first neutral boron-containing radicals stabilized by cyclic (alkyl)(amino)carbenes (CAAC) were synthesized and fully characterized by our group.[4] These radicals showed an extraordinary stability to high temperatures as well as a larger spin density on boron, compared to known boryl radicals. In this work, we show the first synthesis of a neutral boron-containing biradical stabilized by cyclic (alkyl)(amino)carbenes. 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.

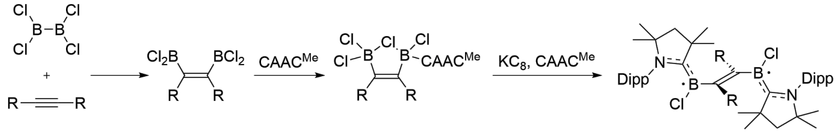

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Figure P3: Synthesis of neutral captodative stabilized boron-containing Biradicals.

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Evidence for charge localization in the spectra and dynamics of excitons in doped carbon nanotubes

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Doping of semiconductor nanostructures like carbon nanotubes providing freely moving, delocalized charges is essential for their application in electronic devices. Recent studies have focused on the assessment of electrochemical gate doping [1] [2] or chemical doping [3] [4] [5] of semiconducting single-wall carbon nanotubes (SWNTs) by absorption and photoluminescence spectroscopy. However, the character of surplus charges, being either delocalized or localized is still subject of current debate [4] [5] .

Here, we report on steady-state and femtosecond time-resolved spectroscopic investigations of electrochemically field-doped and redox-chemically doped carbon nanotube films. Upon moderate doping the absorption spectrum shows a reduction of excitonic oscillator strength accompanied by a blue-shift and asymmetry of the exciton absorption band. These changes are found to be well described by a random distribution of localized surplus charges, resulting most likely from poor dielectric screening of adsorbed counterions at the nanotube surface. Additionally, exciton decay dynamics recorded by femtosecond pump-probe spectroscopy reveal a doping induced acceleration which can be described by a diffusive exciton transport to these randomly distributed charge carriers acting as exciton quenching sites [6] . Furthermore, for highly doped carbon nanotubes with completely bleached excitonic absorption bands a Drude-like response in the Terahertz spectral regime can be observed. This metallic behavior is interpreted as a transition in the character of charge carriers from localized to delocalized.

Our results show that the integration of doped carbon nanotubes into electronic devices might be affected by charge localization which has to be considered and should be suppressed by appropriate choice of the surrounding medium, ideally with high dielectric constant.

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Utilization of Photoluminescent Molecular Probes for Investigation of Charge Carrier and Electric Field Distribution in OLEDs

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Charge carrier distribution in organic thin film devices is essential in optimizing their operation characteristics. Recently it has been shown that current densities can be determined in situ and on nanometer length scales by means of photoluminescence (PL) studies on single guest dye molecules. [1]

In this work we transfer this concept from single molecules to technologically relevant molecular ensembles. For this purpose we utilize Tetraphenyldibenzoperiflanthene (DBP) entities as molecular probes in well established Alq_3/α-NPD organic light emitting diode (OLED) structures. DBP is intentionally embedded as dopant (0.1 vol%) at defined depth within the Alq_3 emissive layer of the device via co-evaporation. Upon charge injection a reduction in dopant PL is observed which can be attributed to non-radiative electron - exciton interaction. The macroscopic current density required to achieve a certain amount of PL quenching scales with the distance between guest molecules and injecting electrode in qualitative agreement with a space charge limited current (SCLC) model. The validity of this model and thus, variations in vertical charge carrier distribution are studied as a function of current density.

Even at reverse bias PL quenching of DBP guest molecules in proximity of up to 5 nm to the Alq_3/α-NPD interface is observed. This can be attributed to strong localized electric fields at the interface caused by interface charges. The occurance of this significant interface effect is due to the giant surface potential (GSP) of Alq_3.[2][3] In addition to quenching measurements we aim at a comparative study on the integral interface charging by means of impedance spectroscopy.

Authors gratefully acknowledge funding from GRK 2112.

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A ps time-resolved photoelectron imaging study on the photophysics of Acenaphthylene

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Acenaphthylene is a member of the chemical group of polycyclic aromatic hydrocarbons (PAHs). PAHs are a toxic and cancerogen species and are emitted to the environment mainly through incomplete combustion processes. Thus, they are supposed to significantly increase the risk of human cancer diseases. Beside their toxicology, PAHs show interesting photophysical properties and are promising building blocks for devices like semiconductors or solar cells. In our studies, we investigated the excited state dynamics of the S1 and S2 state of Acenaphthylene. Time-resolved TOF photoionization and photoelectron imaging experiments showed an IC transition from the S1 state to the ground state with decreasing lifetimes from 480 ps at the S1 origin to 100 ps at a vibronic excess energy of 2700 cm-1. In further experiments, a monoexponential decay after excitation of the S2 state was detected. This can be explained by a very fast IC transition to the high vibronically excited S1 state, followed by another IC to the electronic ground state. The time constant of this second process further decreases to a value of around 55 ps. Besides, time resolved photoelectron images show a constant signal offset at long delay times, which indicates a competing ISC transition to the triplet manifold after S2 excitation.

Calculations on the photo-induced electron transfer in organic mixed valence systems: Transient absorption spectroscopy and relaxation dynamics

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In a former experiment [1], optically induced electron transfer in organic mixed valence systems was investigated using NIR transient absorption spectroscopy. The underlying relaxation dynamics was interpreted within the simplified Sulzer-Wieland model [2]. Here we re-interpret the time-resolved measurements in calculating transient absorption spectra. In doing so, the processes of internal conversion on one hand and cooling in the excited and ground state on the other, are disentangled.

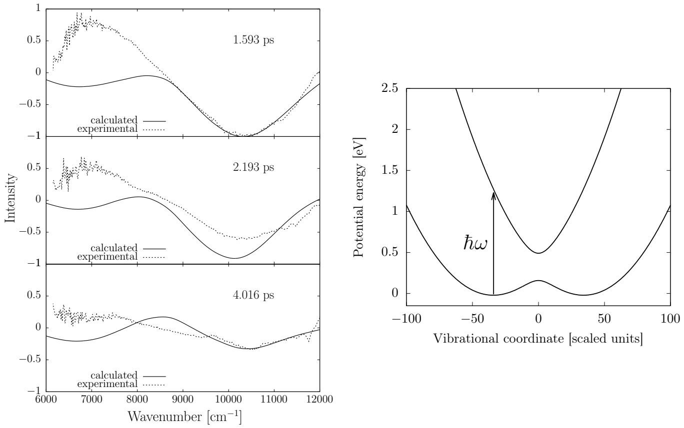

Figure P7: Left: Comparison between the calculated and the experimental transient-absorption spectra of the mixed-valence compound **2⁺** (see [2]) in MeCN for different delay-times. The broad band seen at 7000 cm^{-1} in the experimental spectra is due to excited-state-absorption, which is not included in the model-system. The employed adiabatic potential energy curves are shown on the right.

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Water-Soluble 3-Coordinate Boron Chromophores for One- and Two-Photon Excited Fluorescence Imaging of Mitochondria in Cells

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Triarylboranes have attracted a huge amount of interest due to their application in many different fields such as anion sensing, OLEDs and non-linear optical materials.[1] Over the last few years, we have studied the use of dimesitylboron-based π-acceptors (A) in two-photon absorption (TPA) chromophores. We designed dipolar, quadrupolar and octupolar compounds with exceptional TPA cross sections and high fluorescence quantum yields.[2] Furthermore, we reported structure-TPA cross section relationships for our quadrupolar A-π-A compounds.[3,4] Recently, we synthesized oligothiophene-$BMes_2$ chromophores, with significantly enhanced TPA cross sections of up to 1930 GM in the near-infrared region, the "biological transparent window".[5] We present herein the further functionalization of such chromophores with ammonium groups, an approach pioneered by Gabbaï,[6] in order to achieve hydrophilicity and biocompatibility, and our initial results of both one- and two-photon excited fluorescence (TPEF) microscopy allowing the imaging of mitochondria in cells with our chromophore.[7]

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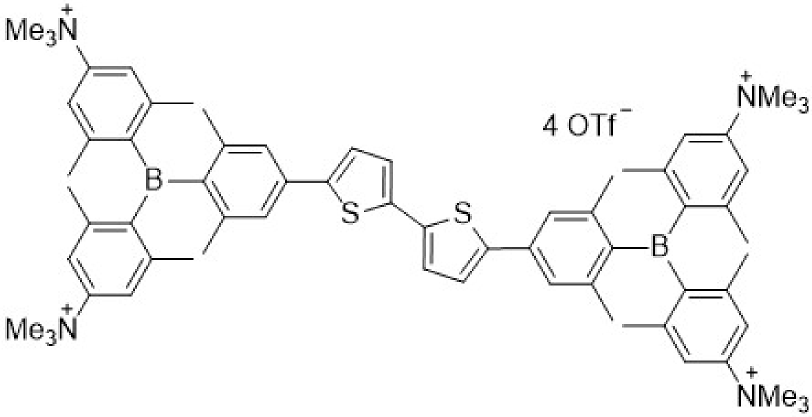

Figure P8: Mitochondrial imaging agent for two-photon excited fluorescence microscopy.

Photoinduced Current Increase at Pentacene/Perfluoropentacene Crystal Interfaces

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Pentacene-Perfluoropentacene (P:PFP) thin films have been used as a prototypical model systems for optical activated charge transfer states [1] and the influence of interfacial molecular packing on exciton dynamics have been studied [2]. Nevertheless, thin film boundaries limit possible effects on charge carrier transport at P:PFP-interfaces and thus, the examination of well defined crystal interfaces is essential. Therefore pentacene single crystals have been grown by horizontal physical vapor deposition and the crystallographic phase has been determined by XRD studies of the (001)-orientation. PFP layers with varying in thickness from 5 to 50 nm were deposited on the crystal's (001)-surface via evaporation and their morphology has been studied combining XRD and AFM measurements.

We report an increase of the interface conductivity as far as 50% with respect to the pristine pentacene crystal under 532 nm cw-laser illumination which is in good agreement with the prediction. Since the increase in the conductivity varies with layer thickness and the applied electric field, we discuss in which manner contact effects and interface states participate in the observed photoinduced current increase.

Authors gratefully acknowledge funding from GRK 2112

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Ultrafast 2D-Vis-Spectroelectrochemistry

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Ultrafast 2D-spectroscopy is a well established method to investigate dynamic processes with femtosecond time resolution and to observe coupling between different energetic states and electrochemistry is used to generate different oxidized and reduced molecule species in solution. We plan a combination of these two techniques, which is called ultrafast 2D-spectroelectrochemistry.

A setup using infrared light was successfully realized in the past [1,2], but so far not for the excitation in the visible spectral regime. This would be a great innovation due to the fact, that many interesting photoreactions like chemical reactions of biradicals, which are important for nature and have potential applications in optoelectronic materials, take place in this spectral range.

To investigate and understand these photoreactions, we want to use a new type of spectroelectrochemical cell, which we will integrate in an existing laser setup. With this powerful tool, it will be possible to study ultrafast reactions of molecules in their different redox states, which are generated in situ. First measurements for testing the setup are done with cresyl violet.

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Generating laser-pulse enantiomers

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We developed an optical setup capable of mirroring an arbitrary, potentially time-varying, polarization state of an ultrashort broadband laser pulse [1]. This is achieved by splitting up the incident beam in two separate beams of which one is mirrored by reflection off a mirror in normal incidence. Afterwards, both beams are recombined in time and space such that two collinearly propagating ultrashort laser pulses with mutually mirrored polarization, i.e., laser-pulse enantiomers, leave the setup. Via this approach, wave plates are not needed and broadband pulses in a large wavelength range can be processed.

Since the two beams travel separately through the optical system, shot-to-shot chopping and detection schemes can be applied. These capabilities are desired, e.g., for circular dichroism, ellipsometry, anisotropy or chiral quantum control experiments. As an application example, the latest progress on time-resolved circular dichroism and transient absorption spectroscopy on the early photochemistry of oxygenated myoglobin is presented.

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IR/UV Ion Dip Spectroscopy of Xylylenes

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Reactive species like radicals, carbenes and biradicals play an important role in a large variety of different chemical systems like combustion, atmospheric and interstellar chemistry. Due to their high reactivity regular analytic methods often cannot be applied and experiments must be performed in isolated environments.

Looking upon the composition of modern gasoline blends, the three xylene isomers (ortho, meta and para) are important aromatics for enhancing the performance in fuels , due to their high octane rating. Under these harsh conditions during combustion, reactive species like xylyl radicals and xylylene biradicals can be formed and are consequently available for further reactions.

In this study we apply IR/UV Ion Dip Spectroscopy to investigate the vibrational properties of xylylenes. The molecules are formed *via* pyrolysis from a suitable precursor and seeded in noble gas carrier to form a molecular beam. In a time of flight mass spectrometer the species are excited by a tunable Free Electron Laser (FEL), which is scanned over the fingerprint region from 550cm^{-1} to 1800 cm^{-1} and consequently ionized resonantly in a [1+1] process by a ns dye laser. Whenever the FEL excites a vibrational mode of a molecule in the jet, the ground state of the molecule is depopulated resulting in a decrease in ion signal. Analyzing the differences between the signal with and without FEL radiation leads to mass selected IR spectra for each individual mass visible at the given UV wavelength. Finally, comparison of the IR spectra with computed data allows for identification of the molecule masses in the experiment and in the case for xylylenes may lead to a better understanding of the biradical character of this species.

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

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Luminescent, responsive materials are of great interest for various applications. In the case of molecular organometallic compounds, responsiveness has typically been a result of metal-metal interactions or stacking effects of the ligand π-system[1]. It has been challenging, however, to establish an accessible structure-property relationship and therefore a reliable approach that enables the design of phosphorescent smart materials.

We have been able to synthesize a series of structurally simple, dinuclear Cu(I) compounds exhibiting mechano-, thermo- and vapochromism in the solid state. In contrast to previous studies, we suppose that upon grinding, an exciplex is formed between the coordinatively unsaturated Cu(I) centers and the fluorinated counterion instead of a second metal center. The resulting distortion from the linear coordination geometry leads to a bathochromic shift of the emission and a significant increase of the efficiency [2].

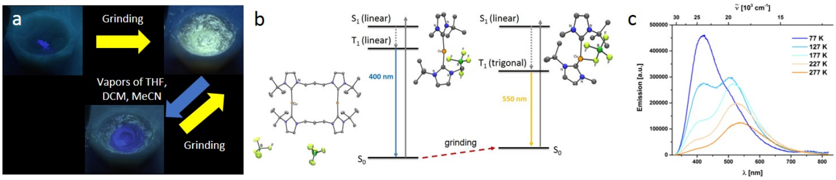

Figure P13: Mechanochromic and vapochromic behavior; b) Jablonski diagram of excited dynamics in linear and trigonal geometry; c) temperature-dependent emission spectra.

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Blue Thermally Activated Delayed Fluorescence from Acridan and Benzonitrile Based Emitter

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Thermally activated delayed fluorescence (TADF) opened the way to overcome the efficiency-limiting spin statistics in a new generation of organic light-emitting diodes (OLEDs). Intensity of intramolecular TADF is mainly ruled by conformation of the donor/acceptor parts within the emitter molecule and temperature. At the same time, the role of host matrix is poorly discussed in literature. Here, we report luminescent properties of novel TADF molecules studied in a broad range of temperatures in various types of solid films. We show that emission consists of three components: prompt fluorescence, delayed fluorescence and phosphorescence. Temperature and environment of the TADF emitters have crucial effect on lifetimes and relative amplitudes of the components. Hindering of the emitting molecules in a polymeric matrix suppresses phosphorescence, while increasing both TADF lifetime and intensity a hundredfold. All in all, we demonstrate that the molecular environment can significantly improve TADF efficiency, which is decisive for the resulting OLED performance.

Pyrene MO Shuffle – Controlling Excited State and Redox Properties by Changing the Nature of the Frontier Orbitals

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Pyrene is a polycyclic aromatic hydrocarbon (PAH) that has very interesting photophysical properties which make 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-positions by an iridium-catalyzed C-H borylation.[2] First investigations demonstrated that pyrene derivatives functionalized at the 2-position have different photophysical properties compared to the "traditional" functionalized pyrenes at the 1-position.[3] We report a series of novel pyrene derivatives substituted at the 2- and 2,7-positions with a julolidine-type moiety as a very strong donor, giving D-π and D-π-D systems, and with Bmes2 as a very strong acceptor leading to a D-π-A system. These compounds exhibit unusual photophysical properties such as emission in the green region of the electromagnetic spectrum in hexane, whereas all other previously reported pyrene derivatives substituted at the 2,7-positions show blue luminescence. Furthermore, spectroelectrochemical measurements suggest an unexpectedly strong coupling between the substituents at the 2,7-positions of pyrene in the D-π-D system. Theoretical studies show that these properties result from the very strong julolidine-type donor and Bmes2 acceptor coupling well to the pyrene HOMO-1 and LUMO+1, respectively. Destabilization of the former and stabilization of the latter lead to an orbital shuffle between HOMO and HOMO 1, and LUMO and LUMO+1 of pyrene. Consequently, the S1 state changes its nature sufficiently enough to gain higher oscillator strength, and the photophysical and electrochemical properties are then greatly influenced by the substituents.[4]

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The Magnetic Field Effect of PBI containing Donor-Acceptor-Dyads and Triads

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Photoinduced charge separated states (CSS) in some rigid, covalently linked donor-acceptor molecules are known to show a dependence of their lifetime on an external magnetic field, the so called magnetic field effect (MFE). In order to gain further insight into the spin chemistry of such radical pairs, a few donor-acceptor dyads and triads (comprising of a triaryl amine donor and naphthalene diimide acceptor moiety, as well as either an iridium complex photosenstizer or an all-organic bridge) have already been studied[1] using various methods, among which transient absorption spectroscopy in the ns to μs time regime was proven to be valuable. Substitution of the naphthalene diimide acceptor (NDI) with an analogous perylene bisimide (PBI) opens a new way of charge recombination via a low lying triplet state.

An overall increase in lifetimes is observed for all investigated structures comparing measurements at zero magnetic fields to those at large field (around 1.8 T), but the shape and behavior of the decay curves differ noteably at small fields (around 20 mT) due to the different energy gap 2J between ^{1}CSS and ^{3}CSS.

Additional characterization is done using UV/Vis- absorption and emission spectroscopy, cyclic voltammetry and spectroelectrochemistry and will be presented as well as the synthesis and the MFE.

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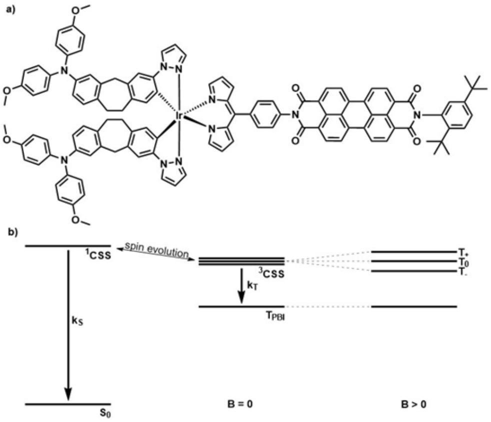

Figure P16: **a)** One of the investigated donor-acceptor molecules. **b)** The lifetime of the CSS is dependend on an external magnetic field due to the Zemann splitting of the triplett levels, which affects the rate constants of interconversion between ^{1}CSS, T_+ and T_-. Recombination of the ^{3}CSS is spin forbidden in systems utilizing NDI as an acceptor, but becomes possible after substitution with PBI.

Neutral and charged excitons in covalently functionalized Carbon Nanotubes

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Impurities in semiconductors often play a key role in providing essential functionality, for example by acting as donors of free charge carriers or by modifying photophysical properties in beneficial ways.

Covalent functionalization of semiconducting single-wall carbon nanotubes (s-SWNTs) by diazonium salts, for example is known to give rise to new emissive states by introducing sp3-defects into the curved sp2-graphene lattice [1].

Gate-doping of pristine SWNTs also yields new absorption and emission features which coexist with the well known intrinsic exciton bands. The trion (charged exciton) states appear at low doping levels while higher doping is associated with the formation of a broad absorption band in the Pauli-blocked region [2].

Here we present spectroelectrochemical measurements of covalently functionalized semiconducting (6,5)-SWNTs using a home built set-up, providing quasi simultaneously recorded absorption and photoluminescence spectra of covalently functionalized SWNTs under potentiostatic control.

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Synthesis of boron containing polycyclic aromatic hydrocarbons via metal-free Hydroboration/C-H-Borylation

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Polycyclic aromatic hydrocarbons (PAHs) are an important class of organic optoelectronic materials which are widely applied in organic field effect transistors, organic light emitting diodes and organic photovoltaic devices. One efficient strategy to specifically adjust the frontier molecular orbital energies as well as the charge-transport and photophysical properties of PAHs is concerned with the substitutional doping of the π-conjugated carbon framework with heteroatoms. Whereas nitrogen has primarily been used as "dopant" element due to the large variety of simple synthetic strategies towards N-doped PAHs, the synthesis of boron doped PAHs is rather underexplored. Obviously, the empty p_z-orbitals of three-coordinate B-doped PAHs account for their excellent electron accepting properties, but also significantly reduce their chemical stabilities. Aiming for new n-type semiconducting materials, we have recently developed a new one-pot synthetic strategy to prepare unprecedented boron-doped perylene derivatives with remarkable stabilities. Thus, boron-doped PAH **4** could be prepared in a tandem metal-free hydroboration/electrophilic C-H borylation using a N-heterocyclic carbene-borenium salt.[1] Doubly boron-doped perylene **4** exhibits visible range absorbance and fluorescence in chloroform solution ($\Phi = 0.63$) and undergoes two reversible one-electron reductions at moderate potentials of −1.30 and −1.64 eV vs. ferrocenium/ferrocene in DMSO. Currently, we are exploring the scope of this methodology and develop larger multiply boron-doped PAHs and nanographene derivatives.

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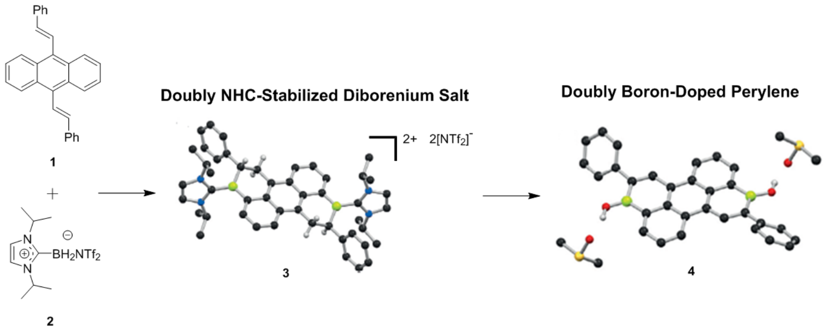

Figure P18: Synthesis of doubly boron-doped perylene **4**.

Reactivity of a 1,4-Diborabenzene towards Actinide Halides

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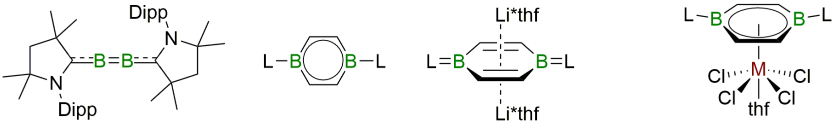
The CAAC-stabilized diboracumulene **1** [1] undergoes a spontaneous cycloaddition reaction with acetylene, yielding the first neutral 6π aromatic 1,4-diborabenzene compound (**2**).[2] Upon reduction with lithium sand, the corresponding dianionic, species **3** could be isolated.[3] During our efforts to synthesise sandwich-type complexes based on this dianion, unprecedented reactivity of the system was revealed. Instead of undergoing the expected salt-elimination reaction, the dilithiated compound **3** reacts as a strong reducing agent when exposed to transition metal halides, with regeneration of the neutral heterocycle **2**. When reacted with the Lewis-Base-stabilised adducts of the tetravalent actinides MCl4 (M = Th, U), heterocycle **2** cleanly adds to the metal, yielding novel half-sandwich complexes. Solid-state structures of **4** and **5** show a slight distortion of the boron atoms out of the C4 plane, away from the metal.



1 **2** **3** **4**: M=Th **5**: M=U

Figure P19: Chemical structures of the diboracumulene (**1**), the diborabenzene (**2**), its dianionic derivative **3**, and the novel half-sandwich compounds **4** and **5**.

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Conjugated Borane Dendrimers

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Triarylboranes are interesting building blocks in the synthesis of π conjugated materials. The empty p_z-orbital localized on the boron atom is a strong π-acceptor.[1][2][3] Using ortho methylated aromatic systems, the boron atom can be kinetically stabilized towards nucleophilic attack allowing borane-containing conjugated systems to be synthesized, which are stable towards air and moisture.[4][5]

We have developed a facile route towards new starburst borane dendrimers. (**Fig. 1** top) With that strategy, we have synthesized a series of *para* functionalized first generation borane dendrimers and investigated their photophysical as well as electrochemical properties. All derivatives show conjugation over the whole π-system and multiple reduction bands corresponding to the boron centers. This makes the borane dendrimers promising candidates for the application as electron storage or transporting materials. The solubility, however, is very low, which impedes the further expansion to a second generation dendrimer. To circumvent this problem, we have exchanged the ortho methyl groups of the outer aryl layer with trifluoromethyl groups. (**Fig. 1** bottom) The trifluoromethylated **BFG1H** exhibits strongly improved solubility in comparison to its methylated derivative **BG1H**. The conjugation, however, is slightly diminished. None the less, we consider this approach to be a promising route towards higher generation conjugated borane dendrimers.

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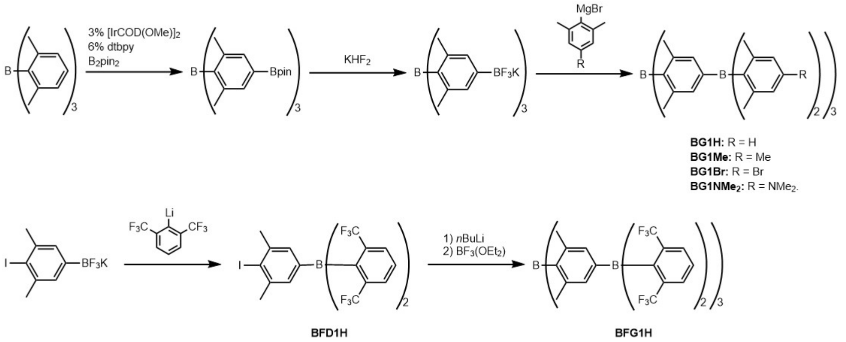

Figure P20: Synthesis of conjugated borane dendrimers **BG1H**, **BG1Me**, **BG1Br** and **BG1NMe$_2$** by a divergent approach. (top)

Synthesis of borane dendrimer **BFG1H** by a convergent synthesis. (bottom)

Stable Organic (Bi-)Radicals by Delocalization of Spin Density into the Electron-Poor Chromophore Core of Isoindigo

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The first isoindigo (bi)radicals were obtained by proton coupled oxidation of their 4-hydroxyaryl substituted precursors. Optical and magnetic spectroscopic studies revealed a singlet open-shell biradicaloid electronic ground state for the bisphenoxyl-isoindigo (<s2> = 1.1980) with a small singlet-triplet energy gap of 0.065 eV and a large biradical character of y = 0.79 that was corroborated by temperature-dependent EPR spectroscopy and quantum chemical calculations. The concept of kinetic blocking of the radical centers and delocalization of spin density into the electron-withdrawing chromophore core of isoindigo offers an entry into a new class of exceptionally stable open-shell functional materials based on organic colorants.

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Photoelectron Spectroscopy of Triplet Pentadiynylidene and Methylpentadiynylidene

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Highly unsaturated and carbon-rich chain molecules like Pentadiynylidene and Methylpentadiynylidene occur as unstable intermediates in harsh chemical environments. Particularly, in the chemistry of interstellar space [1], the atmospheric chemistry of Titan [2], the largest moon of Saturn, and in the combustion of fuel-rich hydrocarbon flames [3] this triplet carbenes are key components. They are well studied by various techniques like matrix isolated IR, EPR and UV/VIS spectroscopy [4]. Nevertheless, Threshold Photoelectron Spectra (TPES) of both with predominant carbene character at C3 didn't exist.

To obtain first insights we applied imaging Photoelectron Photoion Coincidence Spectroscopy (iPEPICO) in this study, which is capable to supply mass selective TPES. 1-Diazo-2,4-pentadiyne and 1-Diazo-2,4-hexadiyne, synthesized by the procedure of Bowling et al. [4], were selected as excellent precursors generating Triplet Pentadiynylidene and Methylpentadiynylidene. Ensuing the corresponding carbenes were produced by flash pyrolysis, stabilized in the gas phase and photoionized by tunable vacuum ultraviolet synchrotron radiation.

This poster will offer first results in the Photoelectron Spectroscopy of Pentadiynylidene and Methylpentadiynylidene, executed at the Swiss Light Source (SLS) for synchrotron radiation (Villingen, Switzerland).

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Reactivity of Boron-Boron multiple-bonds towards small molecules

Holger Braunschweig[1], Marcel Härterich[2], **Benedikt Ritschel**[2], Julian Böhnke[3], Tobias Brückner[3], Theresa Dellermann[3]

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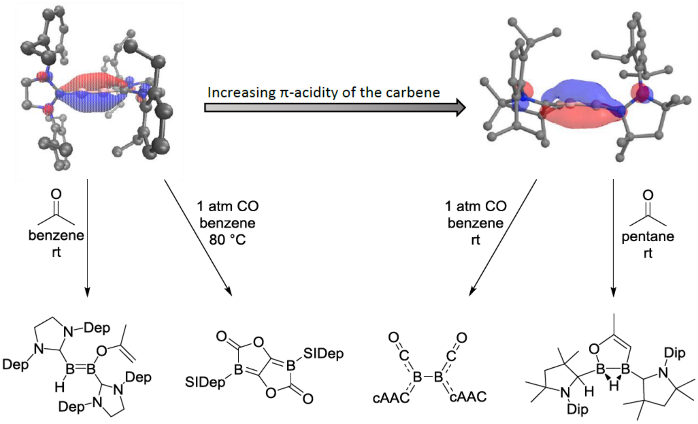
Compounds with the formula L–B_2–L, L being a cyclic (alkyl)(amino)carbene (cAAC) or a N-heterocyclic carbene (NHC), were synthesized, characterized and investigated with regard to their electronic properties and their subsequent reactivity. Whereas the electron density is fully localized between the two boron atoms of the NHC-stabilized diboryne, forming a B–B-triple bond, the electron density within the diboracumulene is delocalized over the entire C–B–B–C moiety owing to the increased π-acidity of the cAAC ligand compared to NHCs. Therefore the diboracumulene may be viewed as a diborene displaying a B–B-double bond, rather than a diboryne. As a consequence, differences between the various L–B_2–L compounds were determined in terms of reactivity (addition and insertion reactions) and structural properties.



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Yldiides as ligands for stabilizing electron-deficient reactive species

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Bisylides (**A** in Figure 1) have received great attention over the past years due to their unique reactivity and electronic structure. The structurally closely related methandiides (**B** in Figure 1) can be viewed as their dianionic congeners. A link between bisylides and methandiides would be a monoanionic yldiide, such as compound **1**. Such compounds are supposed to be strong σ- and π-donors and are of considerable interest as ligands, but examples of isolated and structurally characterized yldiides are rare.[1] [2] Here we report the synthesis of yldiide **1** directly from its protonated precursor by deprotonation with strong bases. The electronic structure of this compound is elucidated through X-ray analysis of its potassium and sodium salts as well as DFT studies. Reactivity studies demonstrate the unique reactivity of the yldiide which can be explained by its capability to act as σ- and π-donor. Additionally its ability to stabilize borenium cations as well as their synthesis, structure and reactivity are discussed.[3] [4]

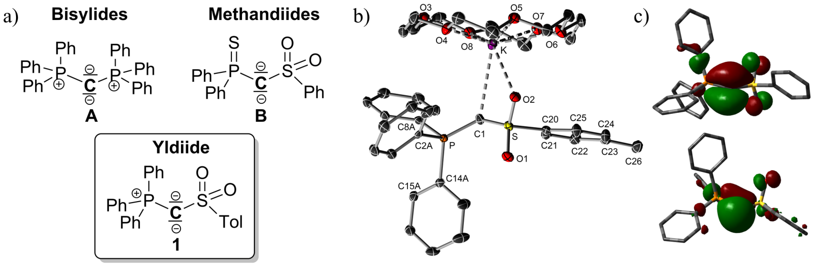

Figure P24: a) Comparison of bisylides, methandiides and yldiides; b) Molecular structure of yldiide **1**; c) Kohn-Sham orbitals of **1** (HOMO (top) and HOMO-1 (bottom)).

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Kinetics of the Allyl radical with oxygen, investigated by photoionization using synchrotron radiation.

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The allyl radical (a-C3H5) is the smallest resonance-stabilized radical. It can be found as an intermediate in combustion processes as well as in interstellar media, exoplanetary atmospheres, the troposphere and even in biological systems.[1] Its properties like excited state lifetimes and couplings, the ionization energy, unimolecular reaction rates and reaction energetics were measured by various techniques. Rissanen et al. studied the reaction of the allyl radical with oxygen using photoionization mass spectrometry.[2] However, the allyl peroxy product of this reaction could not be detected. We reinvestigated the reaction between the allyl radical and oxygen using CRF-PEPICO at the Swiss Light Source (SLS) in order to explore why the elusive allyl peroxy compound was not found in previous studies. Furthermore, we are interested in complementing the already existing data and the evaluation of different generation schemes for the allyl radical (see Figure 1). This presentation will offer first insights into the reaction kinetics of the allyl radical with oxygen using the CRF-PEPICO setup at the SLS.

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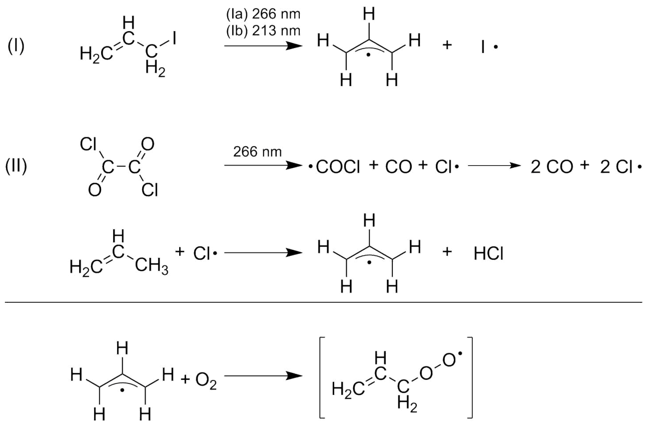

Figure P25: Different generation schemes used for the production of the allyl radical.

Mapping of exciton-exciton annihilation in a molecular dimer via 5-th order two-dimensional spectroscopy

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We present calculations on exciton-exciton annihilation (EEA) in a molecular dimer. This process is monitored using coherent two-dimensional spectroscopy as was recently proposed [1]. Using an electronic three-level system for each monomer, we analyze the different paths which contribute to the two-dimensional spectrum. It is shown that the decay of specific peaks directly monitors the annihilation and thus the proposed spectroscopy is able to uniquely characterize the relaxation mechanism.

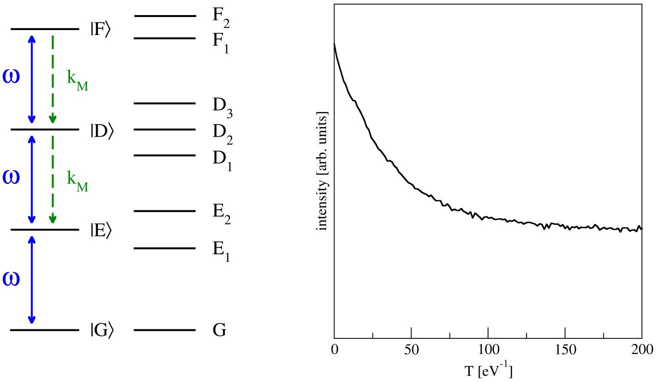

Figure P26: **Left**: Level scheme of the dimer model. The laser excitation (ω) couples the ground state $|G\rangle$ with the manifold of first excited states $|E\rangle$ and the latter with the manifold of second excited states $|D\rangle$. Absorption of another photon yields to the excitation of the higher states $|F\rangle$. The $|D\rangle$ and $|F\rangle$ states decay non-radiatively where the respective time-scale is determined by the monomer decay-rate k_M.

Right: Decay of the spectrum intensity monitoring the annihilation process as a function of the population time T.

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Synthesis of Precursors for Bowl-Shaped TBTQ Derivatives with Low Lying Triplet States

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Tribenzotriqinacene (TBTQ) is an interesting polycyclic aromatic framework with a particularly rigid, C3v symmetrical, bowl shaped core bearing three mutually fused indane wings. The transformation of TBTQ to tribenzacepentalene by multiple deprotonation creates an aromatic dianion (Figure 1) and examinations of the singlet and triplet states of the TBTQ core in the dianionic and the neutral state would provide important insights into the features of these molecules has already reported for the parent system [1, 2]. Moreover; TBTQ and its derivatives have been investigated in systematic studies of their chemistry in host-guest complexes [3, 4], self-assembly systems [5], optical resolution [6,7] and for various further applications [8-10]. With taking into consideration the properties of TBTQ we decided to synthesize precursors for bowl-shaped TBTQ derivatives with low lying triplet states using benzannulation and the formation of a larger conjugated periphery the electronic structure of the core can be modulated (Figure 2). In an attempt to synthesize PAH molecule based on TBTQ core, iodinated tribenzotriquinacenetriol was synthesized and the alcohol groups were protected. In a later stage the protecting groups and subsequently the OH groups will removed following the annulation reactions.

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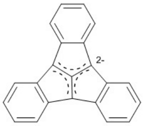

Figure 1: *Dianion structure of TBTQ by multiple deprotonation* [1]

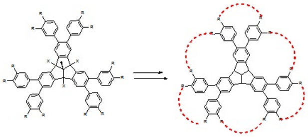

Figure 2: *Target molecules based on TBTQ*

Photodissociation dynamics of the trichloromethyl radical

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Chlorinated hydrocarbons are known to be responsible for the photochemical degradation of the stratospheric ozone layer, shielding the biosphere from harmful UV radiation emitted by the sun.[1] The human exposed CCl_4 molecule represents 12 percent of the chlorine containing molecules in the atmosphere and is the major photolysis source of trichloromethyl radicals (CCl_3).[2, 3] For a better understanding of the atmospheric reactions, it is important to understand the dissociation pathways introduced by photolysis. Therefore, the photodissociation products of the trichloromethyl radical were investigated by velocity map imaging.

From the precursor bromotrichloromethane the CCl_3 radical was generated by flash vacuum pyrolysis. The dissociation was observed in a one color experiment at 235 nm via [2+1]-REMPI to ionize the $Cl(^2P_{3/2})$ atoms. One primary dissociation channel, CCl_3 -> CCl_2+Cl, with an expectation value of f_T=0.29 for the fraction of excess energy released into translation could be observed, originated by a statistical dissociation process. The fraction of the CCl excess energy being released as translational possess a value of f_T=0.38, corresponding to CCl_2 -> CCl+Cl, caused by the absorption of a second photon.

The observed angular distribution of β=0.03 for slow chlorine atoms indicates a dissociation process slower than the rotational period of CCl_3. For fast chlorine atoms a β-value of 0.38 was determined, leading to the assumption that these chlorine atoms originate from different electronic states populated by multiphoton absorption.

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On the calculation of two-dimensional vibronic spectra using quantum diffusion wave-functions

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We apply the quantum diffusion wavefunction approach[1] to calculate vibronic two-dimensional (2D) spectra. We regard a system consisting of two electronic states $|g\rangle$ and $|e\rangle$ with harmonic oscillator potentials which are coupled to a bath. The bath induces vibrational cooling in the electronic states. The dissipative system interacts with three time-delayed laser pulses which gives rise to a third-order polarization. In addition to our former work[2] we take stochastically correlated dynamics in the electronic states into account. The impact on the third order-polarisation is shown in Figure 1. In comparison to the uncoupled stochastic results, the polarisation shows a physically intuitive behavior if correlated ground and excited state fluctuations are taken into account.

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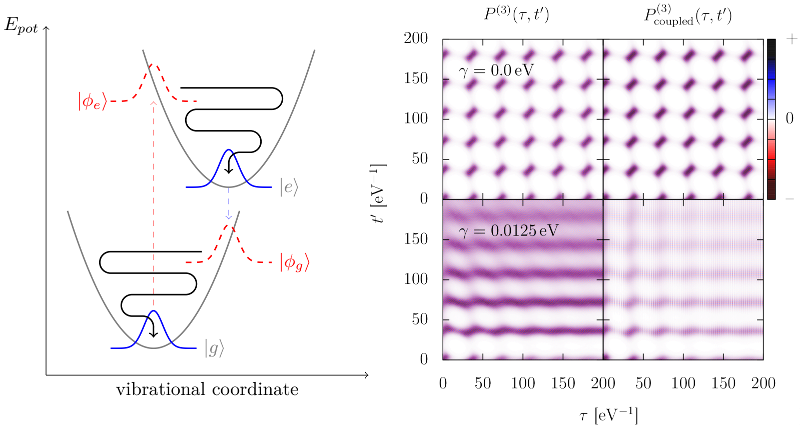

Left: Bath-induced vibrational cooling in a two electronic state system coupled to an environment. Field interactions are indicated by vertical arrows. The nuclear wave-packets $|\phi_g\rangle$ and $|\phi_e\rangle$ show dissipative dynamics until reaching the vibrational groundstates (solid lines).

Right: Third-order polaristations for the uncorrelated stochastics in ground and excited state (left panel) and for correlated ground- and excited state stochastics (right panel). The stochastically correlated dynamics lead to a symmetrical decrease of the polarisation along both time-axes.

Organic Light Emitting Diodes based on blue emitting TADF Materials

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Since the mechanism of thermally activated delayed fluorescence (TADF) emission was proposed for organic light emitting diodes (OLEDs), the OLED community experienced renewed enthusiasm. The molecular design of TADF materials omits the expensive heavy metal atoms needed for phosphorescence emitters and thus promises a cost reduction and sustainability. Here, we investigate novel blue emitting molecules, which exhibit intramolecular TADF mechanism. OLED devices are analyzed by means of current-electroluminescence-voltage characteristics, emission spectra and external quantum efficiency. We also apply direct spin-sensitive measurements on OLED devices to extract information about the involved spin states and shed some light on the TADF mechanism [1]. This may contribute to an overall better understanding of TADF, which is essential for further improvement of organic light emitting diodes.

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Author Index

Schedule: Molecular biradicals: structure, properties and reactivity

Tuesday *February 27th*	**Wednesday** *February 28th*	**Thursday** *March 1st*	**Friday** *March 2nd*
registration Welcome J. Michl welcome mixer	M. Abe W. Sander coffee break H. Bettinger J. Böhnke E. Welz lunch Residence tour coffee break M. Hariharan M. Juríček F. Dinkelbach poster session I	A. Stolow J. Petersen A. Röder coffee break A. Krylov M. Steglich L. Roos lunch S. Wang S. Riese coffee break C. Bardeen L. Grimmelsmann poster session II wine tasting	O. Wenger J. Maier K. Shoyama coffee break T. Prisner A. Sperlich U. Müller conclusion

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