



BOOK OF ABSTRACTS

12/16 FRIDAY

ESAA IN OPTICALLY AND MAGNETICALLY ACTIVE
MOLECULES AND MATERIALS: THEORY AND EXPERIMENT

Triplets, Rules, and Radicals: A Personal History

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The story by which the aromaticity rules for excited states were developed and popularized over time is related in this informal presentation. Pretending that the π -electron networks of conjugated hydrocarbon triplet states result from the interaction of two free radical π systems was central to my thinking, a fantasy that proved quite productive in both qualitative and semi-quantitative fashions. With the advent of calculated spin densities for polybenzenoid systems. I have returned to this topic recently, and I will describe the new results recently published.

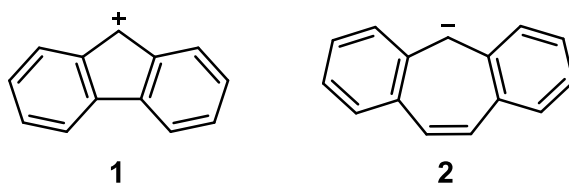
Generating Ground State Antiaromatic Systems in the Excited State and Related Work

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This presentation will provide a *historical perspective* of our work on the discovery of the ease in photogenerating intermediates that are formally ground state antiaromatic ($4n$) systems that contain in the cyclic array 4π or 8π electron counts (**1** and **2**). Our entry into these systems arose from work on studying polar photochemical reactions where the aromatic benzene ring is no longer preserved on electronic excitation, resulting in photochemical reactions that are initiated by highly polarized non-benzenoid structures. Most of the results are inferred from photochemical product (structure-reactivity) studies but one spectroscopic “proof” of an excited state $4n$ aromatic system has also been obtained.



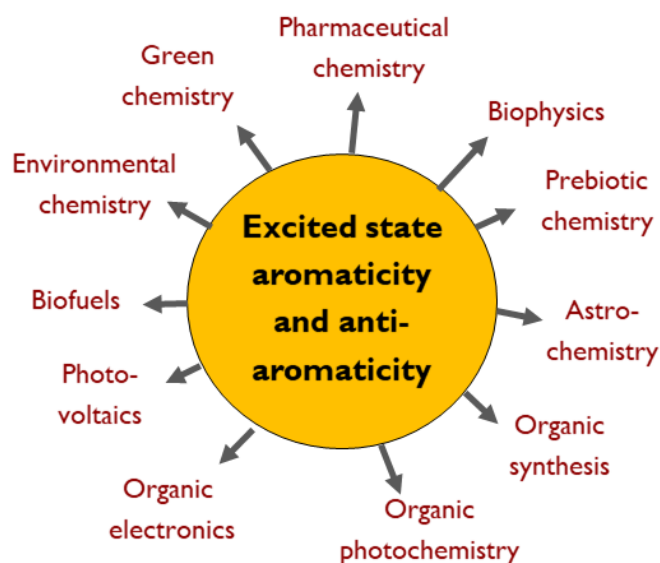
Excited State Aromaticity and Antiaromaticity: The Next 50 Years

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The use of excited state aromaticity and antiaromaticity (ESA & ESAA) to rationalize excited state properties and processes has grown rapidly in recent years. Now, 50 years after Baird's paper, it is timely to ponder on where the field is going and how it is growing. There are limitations, complications and pitfalls of the ESA & ESAA concepts. Instead of Baird-aromatic, some molecules are Hückel-aromatic or Hückel-Baird hybrid aromatic in their lowest excited states, while some other molecules are excited at different functional moieties than at the conjugated rings. Singlet excited states are more numerous than the triplet states, and they are (often) more complicated computationally. There are also differences between various computational methods and aromaticity descriptors. Likely, many unknown and exciting hurdles are awaiting to be discovered through future research. By exploring aromaticity and antiaromaticity effects in excited states we may also unravel what are aromaticity and antiaromaticity as phenomena, making them less fuzzy. Simultaneously as the fundamentals are uncovered, the ESA & ESAA concepts are being applied in a variety of areas; from prebiotic chemistry to organic electronics. Yet, for the research area to grow properly there needs to be ample interactions between many different researchers as knowledge gained from fundamental studies on ESA & ESAA should be transferred to the applied areas. To conclude, there are a lot of exciting research on ESA & ESAA to be done in the next 50 years!



Molecules in a hurry to get rid of excited-state antiaromaticity

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In this presentation, I will show that the drive for molecules to get rid of excited-state antiaromaticity triggers all sorts of photochemical reactions that are relevant for processes such as photosynthesis, photocatalysis, and energy conversion. This work was inspired by Baird's 1972 work¹ showing that the Hückel π -electron-counting rule for aromaticity $[4n+2]$ and antiaromaticity $[4n]$ reverse in the first triplet excited states. This means that aromatic compounds can become excited-state antiaromatic upon photoexcitation. Benzene, for example, is ground state aromatic and can stay trapped in a bottle for years, but becomes antiaromatic and highly reactive upon photoexcitation, rearranging to the strained and explosive benzvalene among other interesting structures.² I will present the importance and the mechanistic implications of excited-state antiaromaticity on photochemical reactions of proton,³ electron,⁴ and proton-coupled electron transfer.⁵

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Modulations of a Metal–Ligand Interaction and Photophysical Behaviors by Hückel–Möbius Aromatic Switching

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In organometallic complexes containing π -conjugated macrocyclic chelate ligands, conformational change significantly affects metal-ligand electronic interactions, hence tuning properties of the complexes. In this regard, we investigated the metal–ligand interactions in hexaphyrin mono-Pd(II) complexes Pd[28]M and Pd[26]H, which exhibits a redox-induced switching of Hückel–Möbius aromaticity and subsequent molecular conformation, and their effect on the electronic structure and photophysical behaviors. In Möbius aromatic Pd[28]M, the weak metal–ligand interaction leads to that the π electronic structure of the hexaphyrin ligand remains almost intact, which undergoes efficient intersystem crossing (ISC) assisted by the heavy-atom effect of Pd metal. In Hückel aromatic Pd[26]H, the significant metal-ligand interaction results in ligand-to-metal charge-transfer (LMCT) in the excited-state dynamics. These contrasting metal-ligand electronic interactions have been revealed by time-resolved electronic and vibrational spectroscopies and time-dependent DFT calculations. This work indicates that the conspicuous modulation of metal-ligand interaction by Hückel–Möbius aromaticity switching is an appealing approach to manipulate molecular properties of metal complexes, and further enabling the fine-tuning of metal–ligand interactions and the novel design of functional organometallic materials.

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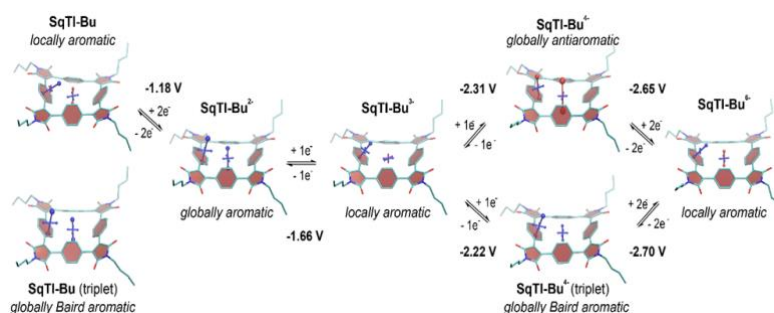
Aromaticity and antiaromaticity in conjugated macrocycles with locally aromatic subunits and a formal $4n$ π -electron system

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Conjugated macrocycles provide an exciting playing field for the discovery of effects and properties that cannot usually be attained. Among other interesting properties, they can sustain global aromatic or antiaromatic ring currents, which offers exciting opportunities for fundamental and applied research. Studying conjugated macrocycles that feature locally aromatic subunits as well as a formal $4n$ π -electron system, we have found that such molecules can help to address the issues of degradation and unsatisfying long-term cycling performance of organic battery electrodes, as their doubly reduced states are stabilized by global aromaticity.¹⁻³ We could also show that the tetraanion of a structurally related conjugated macrocycle with imide groups features a globally Baird aromatic triplet ground state according to EPR measurements and computations.⁴ The computations further indicate that the neutral molecule is Baird aromatic in its lowest triplet excited state (see Figure). In my talk, I will present our work on macrocycles as an introduction to molecular systems that feature both, locally aromatic subunits with $4n+2$ π -electrons and a formal $4n$ π -electron system. Following this first part of my talk, I will propose a solution to the current discussions on the use of the terms aromatic and antiaromatic for such molecules.



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Photoinduced Charge Transfer induced promoted by Excited-State Aromatization

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Molecular excited-state aromaticity and its application have attracted much attention based on the critical role of ground-state aromaticity in organic chemistry. Since structural changes and stabilizations in photosynthesis are dominated by the excited state aromaticity, controlling the excited state aromaticity became essential for designing a new synthetic pathway of photoactive materials. In regarding to this issue, we discovered an intramolecular CT process provokes the aromatization of TMTQ¹ in the excited state. The analysis of C≡N stretching modes by the time-resolved IR spectroscopy revealed that the intramolecular CT process accompanies the shift of electron density towards the dicyano groups (Figure 1). The qualitative analyses of C=C stretching modes and geometry optimization results showed that the CT process leads to a local [8] π formally dicationic M10A core, which becomes aromatic in the excited state by Baird's rule.² This observation obviously demonstrates the concept of excited state aromaticity in the annulene system. Furthermore, the CT induced aromatization provides a direct insight into the role of aromaticity in the modulation of excited state properties and designing photoactive materials.

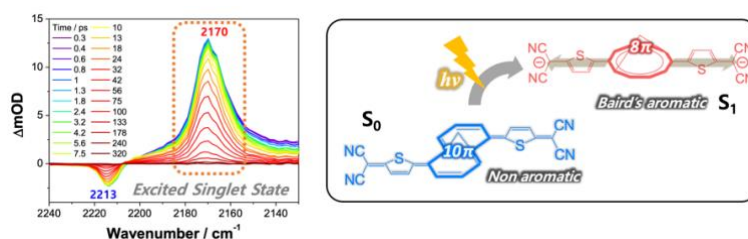


Figure 1. TRIR spectra of C≡N stretching mode in toluene (left) scheme of the aromatization induced by intramolecular CT process in the S_1 state (right).

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Quinoidal annulenes as Hückel-Baird hybrids (with a bit of Möbius almost added in)

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Several years ago, we discovered a new example of a π -electron diradical with an unusually small singlet-triplet gap that was built from the classic methano[10]annulene scaffold developed by Emmanuel Vogel. In this molecule, we conjectured that the small gap was driven by an ionic resonance structure due to charge transfer which resulted in an 8π electron annulene, thus destabilizing the singlet diradical state in a Hückel sense and stabilizing the formally excited triplet diradical state in a Baird sense. In the time since, we have challenged this finding structurally and recently reported spectroscopic observations of the Baird excited state upon photoinduced charge separation. In this contribution, the story of this Hückel-Baird hybrid will be presented along with recent efforts to extend this finding to other unusual conjugation topologies.

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Manipulating Multiexciton Mechanisms in Molecules and Macromolecules

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Organic materials offer a rich palate to be decorated with functional units in order to tune various properties. For example, the ability to generate multiple excitons from a single photon (singlet fission in molecular materials) has the potential to significantly enhance the photocurrent in single-junction solar cells, and thus raise the power conversion efficiency from the theoretical limit of 33% to 44%. However, there is a paucity of materials that undergo efficient singlet fission. Our group is interested in designing building blocks that are capable of generating triplet pairs in modular small molecules and macromolecules. In this vein, the reverse process of singlet fission – triplet-triplet annihilation upconversion (TTAUC) – provides the ability to upconvert low energy unabsorbed infrared photons into visible energy that can be used to improve the light absorption in solar cells. This talk will provide an overview on our approach to the design, synthesis, and evaluation of the materials for singlet fission and TTAUC.

New Representations for Polybenzenoid Hydrocarbons Enable Interpretable Machine and Deep-Learning

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Polybenzenoid hydrocarbons (PBHs) – molecules made up of multiple benzene rings – are the quintessential polycyclic aromatic species. In addition to their importance for a variety of functionalities, these molecules serve as model systems for the much larger and more heterogeneous space of polycyclic aromatic systems and provide the opportunity to investigate the effect of annulation geometry on different molecular properties. The structure-property relationships of PBHs have both conceptual and practical implications; understanding them can enable design of new functional compounds and elucidation of reactivity in a broader context. We interrogated these compounds using a combination of traditional computational techniques, including characterization of their aromatic character in the S_0 and T_1 states (described with the NICS metric), their spin density in the T_1 state, and their S_0 – T_1 energy gaps. Regularities were revealed that allowed for simple and intuitive design guidelines to be defined.¹ To verify these guidelines in a data-driven manner, we generated a new database – the COMPAS Project²– which contains the calculated structures and properties of all PBHs consisting of up to 11 rings. Further, we developed and implemented two types of molecular representation to enable machine- and deep-learning models to train on the new data: a) a text-based representation³ and b) a graph-based representation.⁴ In addition to their predictive ability, we demonstrate the interpretability of the models that is achieved when using these representations. The extracted insight in some cases confirms well-known “rules of thumb” and in other cases disproves common wisdom and sheds new light on this classical family of compounds. In addition to corroborating domain-experts’ interpretation, the different models also highlight additional relationships that are harder for the human eye to discern.

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Ultrafast Nonadiabatic Phenomena by MRSF-TDDFT

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As nonadiabatic Molecular Dynamics (NAMD) has been matured significantly over the past decades, it has become an essential method that can characterize the strong vibronic couplings between electronic states and vibrational degrees of freedom in the optically active materials. These processes typically involve multiple electronic states with various characters, which requires quantum mechanical theories with a good balance in terms of dynamic and nondynamic electron correlation treatments. The popular CASSCF as well as conventional LR-TDDFT and SF-TDDFT do not fully meet this requirement. On the other hand, it has been proven that the recently developed MRSF-TDDFT can be useful in this regard. Here, we show the advantages of MRSF-TDDFT and its applications in NAMD studies on nucleobase photo-decays, chromophore relaxations of Green Fluorescence Protein and aromatization dynamics of dihydrozylene. To highlight some, MRSF-TDDFT (a) accurately reproduced the experimental lifetime constants of thymine as well as GFP chromophore for the first time revealing their excited state dynamics, (b) discovered an unusual photo-intermediate of uracil providing a plausible hydration mechanism, and (c) revealed an ultrafast excited state aromatization dynamics of dihydroazulene.

Baird aromatic supramolecular adhesive

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The importance of Baird aromaticity¹ and related conformational planarization² become more pronounced in materials science. Stabilization energy in the excited state can be controlled by changing the degree of Baird aromaticity.³ The driving force can be used for photoinduced disorganization of the ordered molecular alignment.⁴ Here, A new application of Baird aromaticity will be introduced in a supramolecular platform. We have developed COT-based molecules that can construct tight columnar π -stacking and thus can be used for a highly cohesive, liquid crystalline adhesive. Exhibition of Baird aromaticity induces the rapid decrease of viscoelasticity of the material, while the mechanical properties immediately recover after stopping the UV excitation. The ultrafast dynamics proceeding intra- and intermolecular motions are monitored by transient absorption and transient IR, and time-resolved electron diffraction analyses, respectively. Small contribution of the photothermal effect is demonstrated by careful control experiments. As a result, real-time control of the adhesive performance has been realized using Baird aromaticity.

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BOOK OF ABSTRACTS

12/17 SATURDAY

**ESAA IN OPTICALLY AND MAGNETICALLY ACTIVE
MOLECULES AND MATERIALS: THEORY AND EXPERIMENT**

Ring currents in porphyrin nanorings: local or global (or both or neither)?

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We will present recent results describing how we can experimentally quantify the relative weights of local and global ring current pathways to the overall (anti)aromatic character of butadiyne-linked porphyrin nanorings in different oxidation states. These results are relevant for our understanding of aromaticity in polycyclic molecules, and to the design of ever larger ring-currents in molecules.

An All-organic Photomagnetic Switch

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Digital data storage relies on the change of a material's electrical, magnetic, or optical properties between two states, indicating 1 and 0. Smaller units of information storage are an interesting research target, because they could lead to higher-density storage. Molecular organic switches are interesting in this context.¹ However, the switching of spin states in all-organic molecules is challenging. This contribution will focus on the recently developed helical photochemical switch systems.² Configurationally stable dimethyl[5]helicenes were used in the design of a photochemical magnetic switch with bistable spin states (Figure 1).² When introducing quinoidal 4,11-substituents, such as oxo or dicyanomethylidene, the helicene undergoes rapid electrocyclicization which can be reversed using light as stimulus (77 K). Upon photochemical ring opening at cryogenic temperatures, the helicene favours a diradical configuration with a triplet ground state and a stable EPR signal. The process is fully reversible under thermal conditions and heating (to 93 K for R = C(CN)₂ or 127 K for R = O) recovers the diamagnetic closed-shell form via electrocyclicization. The system can be cycled without any significant degradation and represents a bistable photomagnetic switch that operates under chemical reactivity.

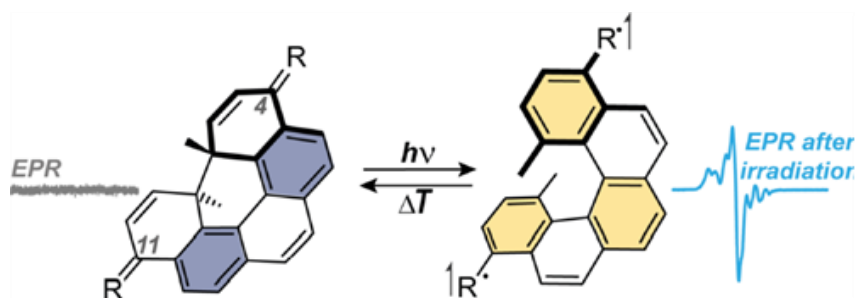


Figure 1. 4,11-Substituted dimethyl[5]helicene for photochemical magnetic switching.

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Tuning Antiaromaticity in Diarenoindacenes Leads to a Surprising Entry into Baird Aromaticity

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This talk will present our synthetic, structural, computational and materials studies of a class of carbon-rich semiconducting molecules based on the indeno[1,2-b]fluorene (IF) skeleton. Access to the fully conjugated, 20 π -electron, formally antiaromatic ring system is accomplished via a variety of intermediate diones. These molecules in turn can be prepared via a simple three-step process (Suzuki cross-coupling, benzylic oxidation, Friedel-Crafts acylation). Optimization of their syntheses now permits access to IF derivatives in multigram quantities. We have shown that thin films or single crystals of several different IF scaffolds can serve as an active layer in organic field effect transistors (OFETs). Current studies are focused on varying the antiaromaticity of the indacene core by systematic alteration of the outer benzene groups with other aromatic motifs to generate a wide variety of diarenoindacene structures. Study of other indenofluorene regioisomers resulted either in stable antiaromatic systems ([2,1-c]IFs), reactive molecules ([2,1-a]IFs) that rearranged to benzocyclobutadiene derivatives, or unstable compounds ([1,2-a]IFs) that only could be confirmed upon reduction with alkali metals. An unanticipated result was that this last unknown regioisomer was a Baird aromatic molecule based on NICS(1) calculations and ACID plots.

Unique Molecular Assembling Behavior of [4*n*]Annulene Derivatives

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Controlling molecular assembling events using light is one of the most important topics in developing photo-responsive materials. Previously, we reported the first experimental demonstration of the energetics of excited-state aromaticity (Baird aromaticity) using thiophene-fused cyclooctatetraene derivatives. This molecule undergoes ring inversion through a planar transition state. Under photo-irradiation, the inversion kinetics was significantly enhanced due to the emergence of aromaticity at the [4*n*]annulene core in the planar transition state. By comparing the activation barrier with and without photo-irradiation, we successfully estimated the energetic impact of Baird aromaticity to be 21–22 kcal/mol. By using this photo-responsive molecular motif, we successfully made the first example of an alternating heterochiral supramolecular polymer. As expected, this supramolecular polymerization can be initiated by photo-irradiation to the optically resolved monomer through racemization. Interestingly, we found that the polymerization can proceed only after the removal of the photo-irradiation, even the racemization was completed, due to the rapid fluttering motion of the monomer under photo-irradiation that prevent the monomers to interact with the growing end of the polymer. In fact, we can temporary suspend the polymerization by irradiating light even after the polymerization was initiated. This is the first example of photo-suspendable supramolecular polymerization.

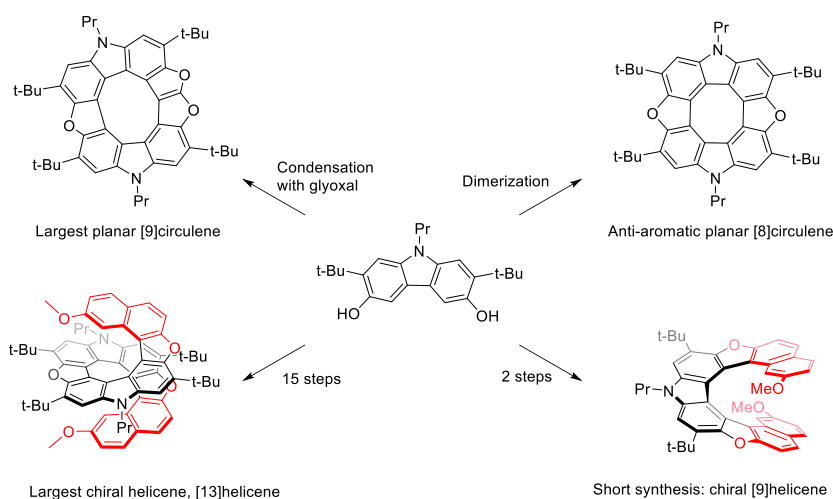
Synthesis and properties of circulenes and helicenes

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I will discuss the synthesis and properties of a range of aromatic-, anti-aromatic- and helical aromatic molecules.¹ The talk will feature molecules with 'weird' magnetic properties, helical chirality and abnormal reactivity due to close proximity. I will discuss some of the unusual properties (and some of the very trivial and unsurprising properties) of these large well-defined conjugated molecules. I will describe the journey from fundamental studies of the acid-mediated oligomerization of simple 1,4-benzoquinones to the controlled synthesis of heterocyclic [8]circulenes (featuring an antiaromatic planar cyclooctatetraene) and even a larger planar [9]helicene. In the simplest picture two units of benzoquinone gives a dihydroxy-dibenzofuran + water, thus forming a new furan ring. This sets up a 1+1=3 'logic' for elongation of the p-system. The synthetic methodology has allowed us to prepare a range of fully conjugated helicenes, including the longest known optically resolved chiral [13]helicenes. The helicenes and circulenes have been explored in a range of properties including as the blue fluorescent component in OLEDs, as G-quadruplex binding ligands and in fundamental studies of antiaromaticity and chirality.



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(1) See all publications from the group at: https://chem.ku.dk/research_sections/orgchem/pittelkow-laboratory/.

Excited States of Diradicals

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The properties derived from the unique structures of the low energy lying excited states of diradicals are rather unexplored. This is because of their full description is multi-configurational implying complications when it is dealt with “large” molecules. The key point on this is provided by the mixing of the ground state, or covalent state, wavefunction with that of one of the two ionic excited states. This mixing provokes a partial ionic contribution to the ground state and makes the second excited state to be a non-pure ionic state.

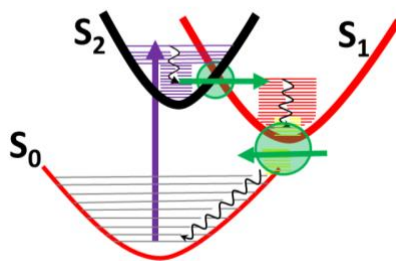


Figure 1. Diagram of the excited state processes taking place in diradical molecules.

These properties make a great impact in the final photophysical performance of diradicals and the interaction between the lowest energy lying excited states (Figure 1).¹⁻³ In this contribution, the basic properties of the excited state of diradicals is described and used to account for recent experimental studies in our laboratory concerning the properties of diradicals made from antiaromatic annulenes, their photothermal properties and electron-transfer and intersystem crossing in diradicaloid excited states. Compounds based on annulenes, anthathrene quinodimethanes and in bisphenoxy diradicals will be described in the present contribution.

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Non-Radicals as Radicals, Radicals as Non-Radicals, and Protons as Initiators

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Electrons usually prefer to be paired, and radical formation usually requires significant energy in the form of light or heat to homolytically cleave strong covalent bonds. Species with a single unpaired electron tend to be highly reactive, and species with even numbers of electrons tend to exist as ground state singlets. However, there are many exceptions: most famously, oxygen gas exists as a ground state triplet. Stable and persistent free radicals have important applications in both chemical synthesis and a wide range of materials applications, from spin labels to batteries and molecular electronics. We have been exploring the effect of electrostatics on radical stability, with view to devising methods of stabilizing radicals and controlling their chemistry.¹ In the course of this work we have uncovered a number of unusual behaviours including radicals in that react as non-radicals² and non-radicals that react as radicals.³ Moreover, we shown that the stability and reactivity of these species can be electrostatically tuned by remote charged functional groups – thus opening up the possibility of manipulating radical stability and reactivity through simple changes in pH.^{2,4} This talk will highlight some of these interesting features of radical and biradical molecule.

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On the Unique Behaviour of Azulenic Chromophores

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Azulene is one of the most peculiar small hydrocarbons. Being isoelectronic with colourless naphthalene, its blue colour has attracted the attention of chemists and was theoretically explained by Michl and Thulstrup already in 1976.¹ In addition, azulene disobeys Kasha's rule, which states that emission occurs exclusively from the lowest excited state of a given multiplicity. It has a strong emission from the S₂ state while the excitation by the visible light leads to the dark S₁ state. Unlike the absorption, anti-Kasha emission of azulene is understood merely on a phenomenological basis, which presents a fundamental obstacle in the generalization of the observed behaviour for rational design and property-tuning of analogical systems. In this contribution, we propose a model for the description of photophysical properties of the prototypical anti-Kasha fluorophore, azulene, based on its ground and excited state (anti)aromaticity. Our model reveals that the anti-Kasha properties of azulene are a consequence of: a) the contrasting aromaticity and electron configurations of the S₁ and S₂ states and b) the highly accessible unimolecular antiaromatic relief pathway of the S₁ state.

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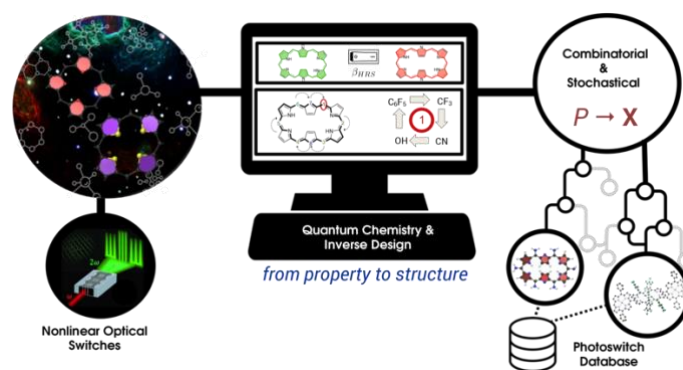
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Exploiting Excited-state Aromaticity for the Design of Functional Porphyrinoid Materials

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In this talk, I will first introduce a multidimensional approach to quantify Hückel and Möbius aromaticity based on global and local descriptors rooted on the energetic, magnetic, reactivity, structural and electronic criteria.¹⁻³ From the computed indices of a large dataset of porphyrinoid macrocycles, neural networks are proposed as an alternative approach to derive a truly multidimensional scale of aromaticity considering the different dimensions of the aromaticity.⁴ In the second part, I will focus on innovative inverse design strategies to explore the combinatorial chemical compound space of meso-substituted hexaphyrins to accelerate the search of high-contrast nonlinear optical switches.⁵ Ultimately, I will show how these computational strategies can be combined to assess excited-state aromaticity as a guiding principle to manipulate the excited-state energy levels and stability of porphyrinoid macrocycles to design promising building blocks as singlet-fission materials.



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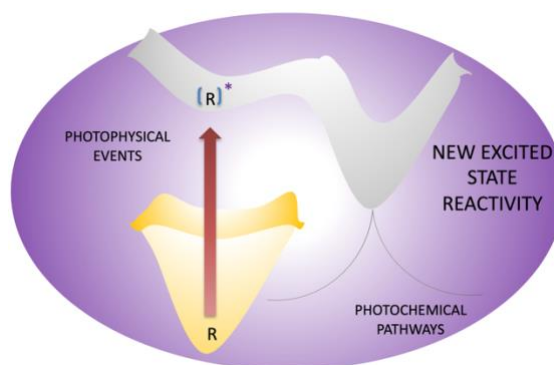
Exploring new photoreactivity through rational molecular design

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Uncovering new excited state reactivity provides opportunities to build complex molecular architectures often with unique stereochemistry. A fundamental challenge in such a process involves controlling excited state reactivity of organic molecules due to the short lifetimes of the reactive species leading to stereo-enriched products. We have been interested in developing strategies for controlling the stereochemistry of products where the reactants reach the excited state(s) upon UV and/or visible light irradiations. This presentation will highlight our methodology of employing UV and/or visible light for performing photoreactions with excellent control over reactivity and selectivity. Based on photochemical and photophysical investigations, the presentation will highlight novel excited state reactivity of organic molecules, how to influence their excited state behavior towards productive reaction pathways and provide a mechanistic rationale for the observed reactivity in different systems.¹⁻



5

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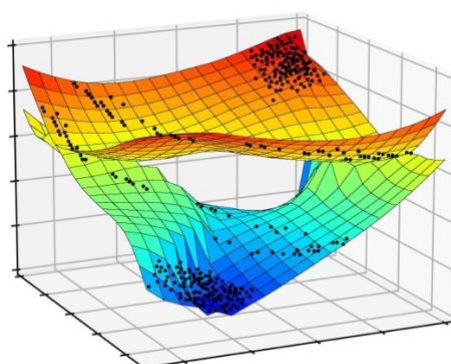
Machine-learning-accelerated photodynamics in complex environments towards new molecules and photomedicines

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Photochemical reactions are increasingly important for constructing value-added, strained organic architectures. Direct excitation and photoredox reactions typically require mild conditions to access therapeutic gases (e.g., carbon monoxide) and new synthetic methodologies. *A priori* design of photochemical reactions is challenging because degenerate excited states often result in competing reaction mechanisms to undesired products. Further, a lack of experimental techniques that provide atomistic structural information on ultrafast timescales (10^{-15} – 10^{-12} s) has limited general rules about these reactions. Computations, however, provide a path forward. I will discuss how my group has leveraged multiconfigurational complete active space self consistent field (CASSCF) calculations, non-adiabatic molecular dynamics, and machine learning (ML) techniques to understand reaction mechanisms and enumerate new reaction pathways. I will introduce our new open-access machine learning tool, Python Rapid Artificial Intelligence Ab Initio Molecular Dynamics (PyRAI²MD), which enables 100,000-fold longer simulations than current NAMD simulations with multiconfigurational quantum chemical methods. I will describe how PyRAI²MD has enabled the first ML-NAMD simulations with QM/QM (CAS/HF) training data. The presentation will explain the origins of the reactivities and selectivities of photochemical pericyclic reactions and CO-evolving reactions in aqueous environments.



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Photoreactivity of Corannulene Azide

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Over the past two decades corannulene and its derivatives have been utilized in numerous applications such as host-guest chemistry, metal-organic frameworks, porous organic polymers, organic field-effect transistors, and non-linear optical materials. However, lacking is a deeper molecular-level understanding as to the effect the curvature has on its chemical and physical properties. Corannulene and its derivatives provide a curved aromatic platform which remains largely unexplored regarding the reactions that are well-documented for planar aromatic hydrocarbons. Herein, we report the photoreactivity of corannulene azides, which upon direct photolysis in methanol yields 2-amino substituted hemiacetals. Transient and EPR spectroscopy allowed the direct detection of short-lived corannulene nitrene. DFT calculations were employed to explain why corannulene nitrene does not dimerize as other arylnitrenes do, but rather intersystem crosses to form the corresponding corannulene azirine. Analysis of the aromaticity of the triplet configuration of the corannulene azide and nitrene aids in a better understanding of the curved structure and how it affects their physical properties and subsequent reactivity.



BOOK OF ABSTRACTS

12/18 SUNDAY

ESAA IN PHOTOCHEMISTRY, PHOTOPHYSICS, AND
SPECTROSCOPY

Harnessing Baird aromaticity to improve fluorescence-based bioimaging

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Fluorescence-based imaging is vital to biomedical research, providing insight into a multitude of complex biological processes in live cells, biopsies, fixed tissue culture and in vitro. With technological advancements continuing to push the boundaries of bioimaging, fluorophore performance has been revealed as a key limiting factor to further progress. Through our team's efforts to advance single-molecule Fluorescence Resonance Energy Transfer (smFRET) imaging, we have shown that fluorophore performance can be markedly improved by tethering organic fluorophores to a single triplet state quencher (TSQ).¹⁻⁴ Cyclooctatetraene (COT) has proven particularly powerful as an intramolecular triplet state quenching molecule because of its ability to reduce the duration of long-lived, non-fluorescent fluorophore triplet states that are also prone to damaging chemical transformations. As a result, up to 100-fold improvements in total photon emission have been evidenced for chemically and structurally diverse organic fluorophores. COT's intramolecular triplet state quenching mechanism hinges on triplet-triplet energy transfer processes enabled by COT's excited-state Baird aromaticity. With this knowledge, we are currently pursuing electronic and steric functionalization of COT, and other Baird aromatic compounds, to optimize more broadly improve fluorescence-based imaging applications across the biomedical space.

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Off-nucleus magnetic shielding, aromaticity and bonding in the ground and excited states of cyclic and polycyclic conjugated molecules

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Chemists tend to recognize aromaticity using resonance structures, Frost-Musulin diagrams and electron-counting rules such as Hückel's $4n+2/4n$ rule. Aromaticity can be quantified using various aromaticity indices, numbers reflecting some experimentally measured or calculated molecular property, or some feature of the molecular wavefunction that may not have a visual interpretation or even direct chemical relevance. Computed isotropic magnetic shielding isosurfaces and contour plots provide pictures of aromaticity and bonding for the ground and excited states of cyclic and polycyclic conjugated molecules which are quantitative and easy-to-visualize and interpret. These isosurfaces and contour plots make good chemical sense as at atoms they are pinned to the nuclear shieldings which, in electronic ground states, are experimentally measurable through chemical shifts. Recent work includes investigations of aromaticity reversals in the S_0 , S_1 , and T_1 states of the smallest Möbius ring, $C_9H_9^+$,¹ of aromaticity and bonding in the S_0 , S_1 , S_2 and T_1 states of cyclooctatetraene² which, together with benzene and cyclobutadiene is amongst the classical examples of aromaticity and antiaromaticity, of aromaticity and bonding in corannulene and coronene,³ of the contest between aromaticity and antiaromaticity in norcorrole,⁴ the smallest cyclic tetrapyrrole porphyrin analogue, and in hydrogenated norcorroles.⁵

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Structure–Property Effects in Excited-State Isomerization and Applications in Protein Assay Development

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Excited-state intramolecular proton transfer (ESIPT) can lead to tautomeric structures that produce significant red-shift in emission relative to those expected by “normal” fluorescent pathways. We sought to exploit this unique mechanism to monitor the dynamic behavior of protein-protein interfaces. In an effort to improve the sensitivity of the fluorescent assay, we looked for structure-property rules to tune the wavelength and emission intensity of ESIPT fluorophores and inform the design of better fluorescent probes for the assay. None appeared to exist! We found that Baird’s rule provided a reliable metric to rationalize previously unexplained behavior of ESIPT fluorophores and pointed to excited-state aromaticity as a key principle in fluorophore design.

Anthracene Formation Through Unconventional Excited-State Reaction Dynamics

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Exploring the fundamental formation mechanisms of PAHs is crucial to understanding the molecular mass growth processes leading to 2D carbonaceous nanostructures in extraterrestrial environments (circumstellar envelopes, planetary nebulae, molecular clouds) and combustion systems. Reactions between hydrocarbon radicals in particular have been seen as critical steps in growth processes toward cyclization leading to these PAHs. Herein, we report on a combined computational and experimental study of the benzyl (C_7H_7) radical self-reaction to phenanthrene and anthracene ($C_{14}H_{10}$) through unconventional, isomer-selective excited state dynamics. Whereas phenanthrene formation is initiated via a barrierless recombination of two benzyl radicals on the singlet ground state surface, formation of anthracene commences through an exotic transition state on the excited state triplet surface through cycloaddition. These findings challenge conventional wisdom that PAH formation via radical-radical reactions solely operates on electronic ground state surfaces and open up a previously overlooked avenue for a more rapid synthesis of aromatic, multi-ringed structures via excited state dynamics in the gas phase.

Supramolecular Polymers of Photofunctional [4*n*]Annulenes: Chiral Superstructures and Chiroptical Properties

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Non-planar π -motifs are potential monomers to obtain new functional supramolecular polymers due to their chiral core and dynamic ring-inversion. However, less research has been done because of difficulties in synthesizing a suitable monomer and structural characterization of the polymer. Recently, we have developed supramolecular polymers of chiral thiophene-fused [4*n*]annulene (COT) derivatives, which brought the first example of an alternating heterochiral sequence of the polymer and photo-suspendable chain growth by photochemically fluttering monomers. Both phenomena were never seen in the previous supramolecular polymers. Notably, the COT monomers exhibit the excited-state aromaticity (Baird aromaticity) as we investigated in the previous work. Originated from these COT-based works, recently, we have focused on; (i) an optically active racemic supramolecular polymer, (ii) supramolecular depolymerization by enantiomeric polymer mixing, (iii) enhanced circularly polarized luminescence (CPL) upon supramolecular polymerization. In this presentation, we will report in detail the novel physicochemical properties of COT-based supramolecular polymers.

2-(4-Nitrophenyl)-1*H*-indolyl-3-methyl chromophore: A versatile photocage that responds to visible-light one-photon and near-infrared-light two-photon excitations

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Due to cell damage caused by UV light, photoremovable protecting groups (PPGs) that are removed using visible or near-infrared light are attracting attention. A 2-(4-nitrophenyl)-1*H*-indolyl-3-methyl chromophore (NPIM) was synthesized as a novel PPG. Various compounds were caged using this PPG and uncaged using visible or near-infrared light. Low cytotoxicity of NPIM indicates that it may be applied in physiological studies.

Pro-Aromaticity Induced Triplet Photochemistry in Acene-quinodimethyl Thioamides: Synthesis, Mechanism, and Photophysics

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Molecular systems containing pro-aromatic units such as *ortho*- or *para*-quinodimethyl ring are often presented to exist as a mixture of resonant species *viz.* closed- and open-shell structures. Recently, a number of strategies have been employed to isolate/stabilize either one of the resonant species/forms of quinodimethyl-based molecules. Yet, there are still queries regarding the characteristics and aromaticity of the photo-excited species of these exotic systems. To this end, our group developed new reactions *viz.* concomitant cycloadditions and reductive desulfurization that allowed to isolate novel acene-quinodimethyl thioamides starting from readily available acene diimides. Expectedly, upon photo-excitation ($S_0 \rightarrow S_1 \rightarrow T_1$), the acene-quinodimethyl thioamides of our interest will undergo local and global aromaticity enhancement and/or reversal in their lowest triplet excited state. Furthermore, we employed computational tools to devise the mechanism of the established reactions as well as evaluate the discrete/local and global/total aromaticity of the quinoidal-based systems.

The presentation will describe a rationale design and execution of the new quinodization reaction involving acene diimides. I will also discuss the mechanistic rationale which is based on computational modeling of the reactions trajectory and reactive intermediates. The discussion will also cover the photophysical properties of the new quinoidal chromophores

How aromatic are molecular nanorings? A perspective from electron delocalization and ring currents

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Large conjugated rings with persistent currents are novel promising structures in molecular-scale electronics. A six-porphyrin nanoring structure that allegedly sustained an aromatic ring current involving 78 π -electrons was recently synthesized.¹ We provide evidence that this molecule is either not aromatic or weakly aromatic, contrary to what was inferred from the analysis of ¹H-NMR data and computational calculations. The molecule does not present a largely delocalized circuit compatible with static global aromaticity. The main reason behind the absence of global aromaticity in these nanorings is the low delocalization in the transition from the porphyrins to the bridging butadiyne linkers, which disrupts the overall conjugated circuit.⁶ On the other hand, the presence of ring currents is highly dependent on the density functional approximation (DFA). The electron delocalization error - a common feature of DFAs with a low percentage of Hartree-Fock exchange - is responsible for the overestimation of response aromaticity.²⁻⁶ These results highlight the importance of choosing a suitable computational method to study large conjugated molecules and the appropriate aromaticity descriptors to identify the part of the molecule responsible for the loss of aromaticity.⁴⁻⁶

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Excited-state aromaticity and its influence on the photocyclization reactivity of diarylethene switches

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It is now well-established that the gain of excited-state aromaticity or release of excited-state antiaromaticity is a driving force for many different types of photochemical reactions. For electrocyclic reactions of molecular photoswitches, however, the presence of an aromatic moiety that changes character in the excited state has been attributed both positive¹ and negative² consequences, depending on the type of switch. Hence, it becomes of interest to explore whether such reactions can be controlled via differences in the excited-state aromaticity among a given type of molecular photoswitches. In this talk, I will describe how quantum chemical modelling and non-adiabatic molecular dynamics simulations have helped show that the photocyclization reactivity of diarylethene switches can be modulated through the excited-state aromaticity of their bridging π -linker.³ Specifically, using an archetypal diarylethene with a non-aromatic π -linker as reference, completely different outcomes are found when the π -linker is allowed to become either aromatic (no reaction) or antiaromatic (fast reaction) upon photoexcitation.

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Adaptive Aromaticity: From Fundamental to Application

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According to Hückel's and Baird's rules, cyclic conjugated species with $4n+2$ π -electrons are aromatic in the singlet electronic ground state (S_0) and antiaromatic in the lowest triplet state (T_1), and vice versa. Thus, species with aromaticity in both states (S_0 and T_1), termed as adaptive aromaticity, are particularly rare. Here we carry out density functional theory calculations to probe the origin of adaptive aromaticity in metallapyridiniums. Specifically, rhenapyridiniums and osmapyridiniums both exhibit adaptive aromaticity whereas iridapyridiniums do not. Further analysis reveals that the strength of metal-carbon and metal-nitrogen bonds in metallapyridiniums is the key factor to achieve aromaticity in the lowest triplet state. Blocking the spin delocalization in the six-membered ring of metallapyridiniums also help the persistence of aromaticity in the lowest triplet state. In addition, such a concept in the application of singlet fission will be discussed briefly. In most cases, species with adaptive aromaticity not only usually generate an intermediate $E(T_1)$ value (the energy gap of the singlet-triplet state) but also satisfy the thermodynamic requirements of the singlet fission process ($2E(T_1) < E(S_1)$ and $2E(T_1) < E(T_2)$). Thus, adaptive aromaticity could be an alternative strategy for experimentalists and theoreticians to design singlet fission materials.

Bringing Atomic Oxygen and Nitrenes to Life

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Photoinduced S–N and S–O cleavages of sulfilimines and sulfoxides, respectively, has been shown to generate nitrenes and an oxidant whose characteristics are consistent with ground state atomic oxygen [$O(^3P)$]. The reactivity of $O(^3P)$ is distinct from other reactive oxygen species generated by photosensitization, and thus, photodeoxygenation and photosensitization are expected to generate different oxidation products within a cell or tissue. To examine the types of oxidation products generated by $O(^3P)$ when released inside a cell, photoactivatable precursors of $O(^3P)$ capable of localizing within either the plasma membrane, mitochondria, or cell nucleus were prepared. Depending upon where the $O(^3P)$ -precursors localize within the cell, different oxidation products are observed upon irradiation. While irradiation of sulfilimines and sulfoxides can induce photocleavages, sulfones are typically more photo-inert. To determine if sulfoximines are photo-inert or susceptible to undergoing bond scission, the photochemistry of dibenzothiophene sulfoximine was examined. The irradiation of dibenzothiophene sulfoximine resulted in phodenitrentation followed by photodeoxygenation in a two-step, two-intermediate photorelease process.

Singlet Biradical Nature and Stacked Antiaromaticity Induced by π -Congestion of Two Acenes

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Highly π -congested aromatic dimers with short π -plane distance less than the sum of van der Waal's radii of carbon atoms have attracted much attention because of their unique electronic and magnetic properties expected from their unusual structures. Recently, benzo annulated anthracenophane (anthracene dimer) with close π -plane distance of 2.80 Å was found to exhibit a weak antiaromaticity within the space between anthracenes, that is, stacked antiaromaticity. Computational investigations of anthracene dimer revealed that the stacked antiaromaticity is observed at near the transition state of isomerization. In other words, this point is the transition state of bond order changing between sp^2 carbon and sp^3 carbon, which is also observed in the graphite-to-diamond transformation. Therefore, to further understanding of the nature of π -congestion of two aromatic rings, we evaluated benzene dimer and a series of acene dimers from naphthalene to pentacene with changing the distances between faced rings for evaluating the effect how the π -extension is reflected on its biradical character and stacked antiaromaticity. In this presentation, the singlet biradical nature and stacked antiaromaticity of acene dimers will be discussed in detail.



BOOK OF ABSTRACTS

12/20 TUESDAY

ESAA IN PHOTOCHEMISTRY, PHOTOPHYSICS, AND
SPECTROSCOPY

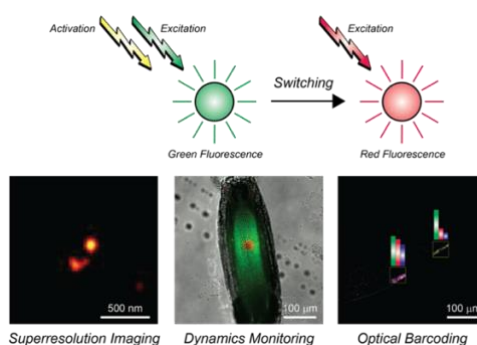
Photoswitchable Fluorophores for Bioimaging Applications

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The goal of our research program is the identification of operating principles to switch fluorescence under optical control in order to develop photoactivatable fluorophores for bioimaging applications.¹⁻⁴ We design molecules capable of interconverting between states with distinct emission properties upon illumination at an appropriate activation wavelength. Their photochemical transformations enable the activation of fluorescence within a defined region of space at a specific interval of time in a given sample of interest. Such a level of spatiotemporal control provides the opportunity to overcome diffraction and reconstruct fluorescence images with spatial resolution at the nanoscale. It also permits the monitoring of dynamic events in real time with the sequential acquisition of fluorescence images. We are particularly interested in adapting these mechanisms for fluorescence photoswitching to allow the visualization of intracellular targets with nanoscaled resolution in live cells as well as the tracking of translocating species in live organisms. Thus, our fundamental investigations on molecular switches can eventually lead to the realization of innovative fluorescent probes for a diversity of bioimaging applications.



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Aromatic Molecules - A Twisted Tale

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Planarity plays a crucial role in determining the electronic and optical properties of π -conjugated backbones. Here I will discuss two examples of non-planar and planar systems: twisted acenes and planar furan macrocycles. In the first part, the recent progress in the study of helically locked twisted acenes will be discussed. These acenes consist of anthracene backbone diagonally tethered by an n -alkyl bridge, which allows us to systematically monitor the effect of twisting on electronic, magnetic and optical properties. In particular, I will focus on the trends of excited-state properties upon increasing twist. In the second part, the first series of macrocyclic furans will be discussed. A combination of lower aromaticity and larger exo angle allows the introduction of small planar macrocycles, with $4n+2$ and $4n$ electrons, which display alternating properties such as emission maxima, oxidation potentials and chemical shifts.

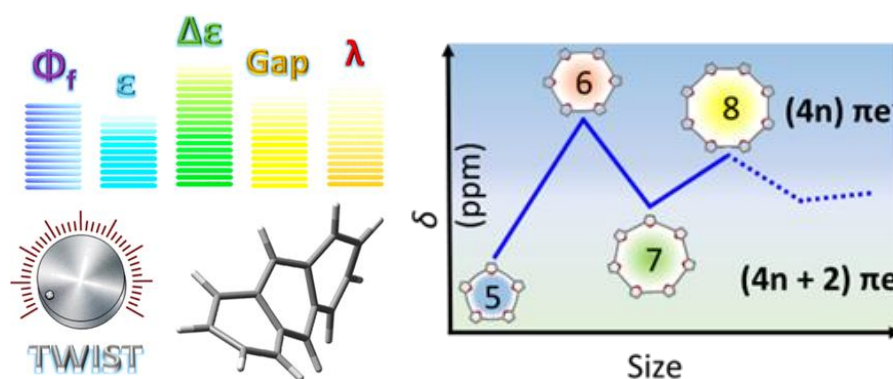


Figure 1: Twisted acenes (left) and macrocyclic furans (right).

"Aromaticity from first principles: the limits of Hückel's rule"

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Cyclic delocalization of electrons in planar molecular rings is often associated with unusual thermodynamic stability that can be rationalized by means of the $4n+2$ electron bookkeeping rule arising from the molecular orbital theory by Hückel. The $4n+2$ rule adequately relates topology, symmetry, and degeneracy of molecular orbitals containing cyclic arrangement of atoms, and it can be used to predict different ground-state and molecular-response properties. However, fulfilling the $4n+2$ rule is a necessary but not sufficient condition for a molecular ring to be stabilized by aromaticity. In this project, we provide a first-principle insight into the theoretical concepts of electron delocalization and the magnetically induced current density, and we propose a profound paradigmatic change for quantitative assessment of the aromaticity in the size- and topologically differentiated compounds from monocycles through poly- and macrocycles to nanorings.

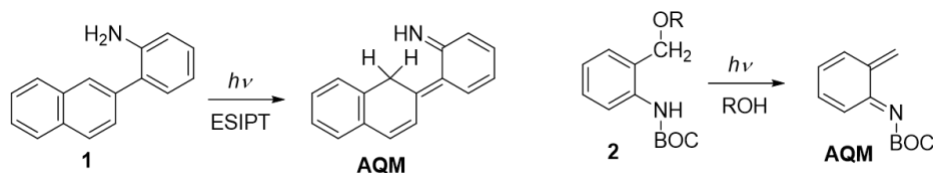
Photochemical Formation of Aza-Quinone Methides by Dehydration and ESIPT of Aminoarenes

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Aza-quinone methides (AQMs) are reactive intermediates that have attracted scientific interest owing to their application in organic synthesis.¹ AQMs can also be prepared in photochemical reactions,² which opens avenues to their potential applications in biological systems. However, contrary to the analogues phenolic intermediates quinone methides (QMs),³ reports on AQM photochemical generations are scarce. It has been demonstrated that the antiaromatic character of excited states of phenolic derivatives drives the excited-state intramolecular proton transfer (ESIPT), which relieves the excess energy by forming less antiaromatic keto-tautomers.⁴ We infer that analogous reasons initiate the photoreactions of phenols that deliver QMs such as photodehydration⁵ and photodeamination.⁶ Furthermore, we have recently extended the scope of investigation to photochemical reactivity of different anilines that undergo ESIPT to carbon atom,⁷ or photodehydration. In both cases AQMs are formed as reactive intermediates, as shown for the ESIPT reaction of **1**⁷ or elimination of ROH from **2**.



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The search for new Baird aromatic species to enhance fluorophore performance

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Single-molecule Fluorescence Resonance Energy Transfer (smFRET) imaging has emerged as a powerful tool for directly imaging complex biological systems in diverse biological settings.¹⁻⁵ A foundational element of these advancement is access to high-quality, spectrally diverse organic fluorophores species and the development of robust inter- and intra-molecular triplet state quenching strategies. Our team seeks to advance the fluorescence imaging and single-molecule fluorescence imaging by developing self-healing cyanine-class organic fluorophores utilizing Baird aromatic cyclooctatetraene (COT) as an intra-molecular triplet state quencher. These next-generation fluorophores exhibit dramatic enhancements in overall performance including increased brightness and lengthened duration of photon emission. To continue pushing the frontiers of this technology, as well as the fields of fluorescence-based imaging and single-molecule research, we have aimed to further modify COT with steric and electronic alterations and demonstrated that these derivations continued to increase fluorophore brightness. Beyond COT, we have also began studying other Baird aromatic species as solution-based TSQs, to broaden our range of potential fluorophores.

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Exploiting Gain of Excited State Baird Aromaticity to Drive Photoreactions

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This talk describes efforts to drive useful photoreactions by exploiting ground-state anti-aromaticity and excited state aromaticity in carbocations resulting from C-LG photoheterolysis reactions. It is hypothesized that a combination of ground-state carbocation antiaromaticity plus excited state aromaticity leads to a productive conical intersection along the reaction coordinate and lowers the barrier for formation. A variety of such carbocations are identified by computation, and the approach is evaluated by its application in new BODIPY-derived photocages that can be activated using visible to near-IR light.