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MATERIALS FOR ORGANIC ELECTRONICS: SYNTHESIS, SPECTROSCOPY AND THEORY

16 – 17 June, 2023
Heidelberg, Germany

Book of Abstracts

CONTENTS

Conference Chair

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Prof. Dr. Markus Enders, Heidelberg University

Registration Desk Opening Hours

Friday, June 16: 08:45 am – 12:30 pm
Saturday, June 17: 09:00 am – end of the symposium

Venue

Heidelberg University
Chemistry Lecture Hall Building
Im Neuenheimer Feld 252
69120 Heidelberg, Germany

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Programme

FRIDAY, June 16th, 2023

8:45 AM	**Registration**
9:30 AM	**Opening**
9:35 AM	Session 1 Chair: Milan Kivala **Opening Keynote Lecture** **Graphene Nanostructures 3.0: Nanoelectronics, Quantum Phenomena & Properties** *Xinliang Feng, Technische Universität Dresden*
10:20 AM	**Tuning electronic and optical properties of small-molecule semiconductors by processing and optical cavities** *Jana Zaumseil, Ruprecht-Karls-Universität Heidelberg*
10:50 AM	Coffee Break
11:20 AM	Session 2 Chair: Michael Mastalerz **New Materials for Energy Storage and Conversion** *Colin Nuckolls, Columbia University*
12:05 PM	**Gold Catalysis: A Modular Approach to N-Heteroacenes** *A. Stephen K. Hashmi, Ruprecht-Karls-Universität Heidelberg*
12:35 PM	Lunch
02:00 PM	Session 3 Chair: Claudia Backes **N-Heterocyclic Carbenes (NHCs) as Conductive and Stable Anchors for Au-based Hybrid Materials and Devices** *Franziska Lissel, Leibniz-Institut für Polymerforschung Dresden e. V.*
02:45 PM	**Designing Functional Polymers for 3D and 4D Microprinting** *Eva Blasco, Ruprecht-Karls-Universität Heidelberg*
03:15 PM	Coffee Break
03:35 PM	Session 4 Chair: Oriol Vendrell **Charge and Exciton Transport in the Transient Delocalization Regime** *Jochen Blumberger, University College London*
04:20 PM	**Computational Analysis and Design of N-Heteropolycycles** *Andreas Dreuw, Ruprecht-Karls-Universität Heidelberg*
04:50 PM	**Polariton condensation and control of energy landscapes in organic semiconductor microcavities** *David Lidzey, University of Sheffield*
05:35 PM	Coffee Break and Poster Session
06:45 PM	Conference Buffet Dinner

SATURDAY, June 17th, 2023

09:45 AM	Session 5 Chair: Martijn Kemerink **Electron Catalysis** *Armido Studer, Westfälische Wilhelms-Universität Münster*
10:30 AM	**New Functional Dyes Based on a Tetraazaperylene Core** *Lutz H. Gade, Ruprecht-Karls-Universität Heidelberg*
11:00 AM	Coffee Break
11:20 AM	Session 6 Chair: Hans-Jörg Himmel **Electronic Properties of N-Heteropolycyclic Compounds** *Petra Tegeder, Ruprecht-Karls-Universität Heidelberg*
11:50 AM	**Physisorbed and chemisorbed molecular adsorbates on monolayers of MoS2 on Au(111)** *Katharina J. Franke, Freie Universität Berlin*
12:35 PM	Lunch buffet and Poster Session
01:45 PM	Session 7 Chair: Hagen Klauk **Unconventional Stabilization of Large Acenes and N-Heteroacenes: Stable Azaheptacenes and Nonacenes** *Uwe H. F. Bunz, Ruprecht-Karls-Universität Heidelberg*
02:15 PM	**From small molecules to conjugated polymer nanoparticles for organic photonics** *Alexander Jan-Christoph Kühne, Universität Ulm*
03:00 PM	**Concluding Remarks**
03:05 PM	End of the Symposium

SPEAKER ABSTRACTS

Graphene Nanostructures 3.0: Nanoelectronics, Quantum Phenomena & Properties

Xinliang Feng
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With the advances in emergent quantum technologies, such as quantum computing, quantum communications, etc., graphene nanostructures provide a unique molecular toolbox for accessing their unprecedented quantum phenomena and properties. In this lecture, we will introduce our recent efforts towards the precision graphene nanostructures as the defined quantum entities for the spin-spin coupling. Both in-solution and on-surface synthesis approaches will be discussed that provide synthetic access to this class of unique graphene nanostructures with controlled spin-orbital coupling behavior. Individual open-shell graphene molecules (Kekuléne, non-Kekuléne and concealed non-Kekuléne structure motifs) with controlled singlet, triplet, as well as high-spin states, will be developed. Next, we will discuss the collective carbon magnetisms in the dimers of open-shell graphene molecules. Spin-chains with fractional edge excitations will also be presented. In the final section, we will also present our recent efforts towards graphene nanoribbon-based nanoelectronics. Various robust graphene nanoribbons with controlled edge structures and topologies will be synthesized and demonstrated to show their unique electronic and optoelectronic properties. The integration of single graphene nanoribbons into the nanoelectronic devices will be particularly highlighted.

Tuning electronic and optical properties of small-molecule semiconductors by processing and optical cavities

Jana Zaumseil

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The electronic and optical properties of organic semiconductors (e.g., absorption and emission wavelength, electron affinity and ionization potential) are typically tuned and adjusted through variation of the conjugated core of the molecules or modification of their side-chains. However, for crystalline small-molecule semiconductors the precise packing in the solid state may also have a substantial impact on their properties and can be varied through processing conditions rather than changing the molecules.

Here, I will use the example of PDIF-CN_2 – a well-known perylene diimide derivative with high electron mobility – to demonstrate the role of thin-film deposition conditions to create different polymorphs and thus obtain different optical and charge transport properties. Zone-casting aligned ribbons of PDIF-CN_2 from different solvents and at different deposition rates can result in either J- or H-like aggregates with the associated narrow or broad absorption and emission bands that are also strongly polarization-dependent.

Furthermore, the previously unidentified thin-film polymorph of PDIF-CN_2 with J-aggregate-like properties can be employed for strong light-matter coupling in optical microcavities. These cavities with different detunings (i.e., film thickness) further enable optimization of the angle-dependent absorption and emission into and from the upper and lower polariton modes. Processing-induced polymorphism and polariton formation in cavities could be applied to a wide range of organic emitters to tune their properties without the need to change the molecular structure.

New Materials for Energy Storage and Conversion

Colin Nuckolls

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This lecture will present our research to put molecules in the electronic and optoelectronic devices. One area that will be described our efforts to tune the electronic structure, molecular structure, and degree of aggregation/crystallinity through molecular contortion. Using this approach, we have been able to create a design for high performance materials in organic solar cells, photodetectors, redox flow batteries, pseudocapacitors, and lithium ion batteries. The lecture will discuss the design principles, molecular assembly, device construction, and materials performance. Using this approach, we have made best in class n-type pseudocapacitors and a new type of cathode for lithium ion batteries with high power density and fast charge and discharge capabilities.

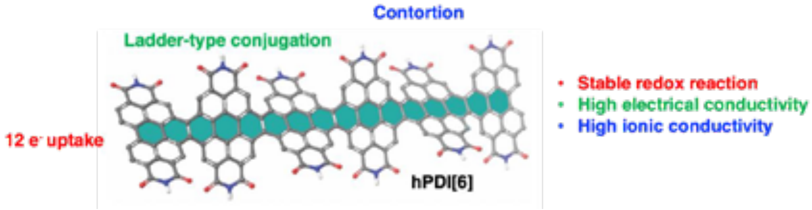

Figure 1. Contorted, twistacene oligomers have an unique combination of high lithium ion conductivity and high electrical conductivity that makes them excel in lithium ion batteries.

Gold Catalysis: A Modular Approach to N-Heteroacenes

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The first publications demonstrating a high increase in molecular complexity in gold-catalyzed organic reactions,[1,2] triggered the development of homogeneous gold catalysis to a frequently used tool in different sectors of organic synthesis, e.g. for total synthesis or materials science and related fields.[3,4] The reactivity patterns in the field are fascinating, reaching from π-coordination[5] for the acceleration of nucleophilic additions to "gold only" photoreactions[6,7] and even radical chains combined with gold-based catalytic cycles.[8]

The synthesis of conjugated, nitrogen-containing π-systems also can strongly benefit from gold catalysis. Highly modular and convergent routes allow a fast modification of the target molecules.[9] The presentation will address several of these strategies in detail.

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N-Heterocyclic Carbenes (NHCs) as Conductive and Stable Anchors for Au-based Hybrid Materials and Devices

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Gold nanoparticles (Au NPs) have unique surface plasmonic resonances (SPR) and promise a broad variety of optical applications in sensors and imaging,[1] while combining them with organic components can give electronically functional hybrid materials.[2] Protecting surface ligands, carrying one or more functional anchor groups with a high affinity for gold, are needed to stabilize the Au NPs and prevent their irreversible aggregation. Thiols are ubiquitously used, yet the thermal instability and comparably low conductance of the S−Au contact limit the applications of the resulting Au NPs.[3] *N*-heterocyclic carbenes (NHCs) have been used in surface chemistry as an high-performing alternative to sulfur-based ligands[4]: The NHC−Au linkage shows excellent stability under conditions that destroy the S−Au bond (e.g. high temperature, variable pH, and electrochemical redox), and is furthermore highly conductive.

We use NHC anchors as robust and conductive anchors to bind charge-conducting conjugated polymers (CPs) to Au NPs to obtain electronically functional hybrid materials.[5] Br-NHC-Au-X (X=Br, Cl) complexes were synthesized, converted to Grignard monomers and used for a chain-growth Kumada polymerization to obtain regioregular poly-3-hexylthiophenes (P3HT) with a low polydisperity index. Direct reduction gave spherical Au NPs with P3HT as surface ligands. The presence of the NHC on the surface was confirmed by XPS. The P3HT-NHC@Au NPs have a remarkable thermal stability up to 24 h in 100 °C toluene solutions, while Au NPs stabilized by sulfur-based PEG fully degrade under the same conditions. Also, continuous CV scans show only a slight decay of peak current after 50 cycles, indicating the good electrochemical stability of P3HT-NHC@Au NPs. To investigate the conductive linker, electrochromism (EC) experiments were carried out. P3HT is electrochromically active, and one can assume that binding the polymer to Au NPs *via* a conductive NHC anchor group will increase the electrochromic response speed, allowing to estimate the organic/inorganic electron transfer of P3HT-NHC@Au NPs. We found that blending 10% of P3HT-NHC@Au NP into an P3HT-NHC-Au films improves the responsive speed signiffcantly, from 1.21/1.05 s for neat P3HT-NHC-Au to 0.79/0.52 s for the blend.

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Designing Functional Polymers for 3D and 4D Microprinting

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3D, and more recently, 4D printing has gained much attention during the last years and become a promising tool for the fabrication of dynamic and adaptive structures with potential application in different fields ranging from biomedicine to optics to soft-robotics. The additional fourth dimension refers to the ability of a 3D printed object to change its properties over time. While great progress has been made at the macroscale, the continuous miniaturization of today´s devices has tremendously increased the demand for manufacturing at the smaller scales. Emerging technologies such as 3D laser printing (also known as two-photon lithography or direct laser writing) have enabled the precise printing of structures at the micro and nanometer scale.[1]

Our group has recently succeeded in the development of new functional materials for laser microprinting. In particular, we have focussed on the incorporation of new features such as conductivity, subtractive manufacturing (inks allowing printing and erasing), superresolution and more recently, stimuli response for complex actuation.[2,3] In this lecture, special attention will be paid to the design of inks based on polymeric materials for 3D/4D microprinting. The challenges as well as the potential and perspectives of the field will be highlighted, too.

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Charge and Exciton Transport in the Transient Delocalization Regime

Jochen Blumberger, Jan Elsner, Samuele Giannini

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London, WC1E6BT, UK

Recent computational and experimental studies on ordered organic semiconductors (OS) have shown strong evidence that charge carriers (holes or excess electrons) as well as excitons (bound electron-hole pairs) form partially delocalized quantum objects ``half way" between waves and particles (Fig. 1)[1-7] Strong thermal disorder between the weakly bound molecules in the crystal prevent full wave-like delocalization while sizable electronic couplings and small nuclear reorganization energies prevent full localization. The partially delocalized charge carriers and excitons were found to diffuse through OS via a novel transient delocalization mechanism[1-5,8-9], in a scenario that cannot be described with the standard tools developed for band transport in inorganic semiconductors or hopping transport in aqueous or biological systems. In this talk I will briefly present the quantum dynamical simulation methodology that has led to this picture[10] and I will review design rules extracted from these simulations that pave the way for development of materials with high charge mobilities or exciton diffusion constants. [3,10] I will also give an outlook on our current mechanistic understanding of thermoelectricity in the transient delocalization regime characteristic for ordered OS.

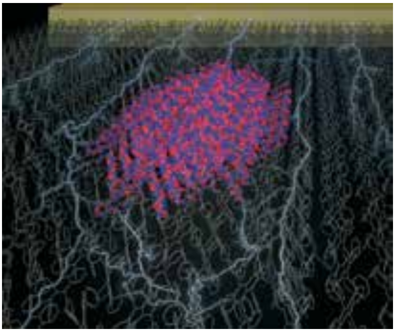

Fig. 1. Snapshot of the hole carrier wavefunction in rubrene at 300 K delocalising over about 5 nm (from Ref. 2).

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Computational Analysis and Design of N-Heteropolycycles

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Novel methods for the theoretical analysis and the computational design of electronic properties and spectra of N-heteropolycycles will be briefly introduced. We will analyze in detail how the isosteric substitution of C-H against N influences the UV/Vis absorption spectra, and derive simple chemical rules for the prediction of these changes. Also, the beauty of the analysis of excited states in terms of exciton properties will be highlighted by extending Platt's L_a/L_b nomenclature for polcyclic aromatic hydrocarbons to N-heteropolycycles.

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Polariton condensation and control of energy landscapes in organic semiconductor microcavities

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Microcavities are structures composed of two mirrors that are placed either side of a semiconductor thin film. Within the strong-coupling regime, a hybridization occurs between confined photon modes in the cavity and the semiconductor excitons, creating new types of quasi-particles called cavity polaritons. As cavity polaritons are bosons, they can undergo a 'condensation' process at high occupation density, creating a non-equilibrium condensate that is trapped at the bottom of the polariton dispersion curve. Although such condensates can be relatively large in size (10's of microns in diameter), they have a high degree of spatial and temporal coherence. When light is emitted from a condensate, it has the same coherence-properties as the condensate and thus constitutes a form of lasing (a so-called a polariton laser)[1,2].

In this talk, I discuss methods to spatially trap polariton condensates by optically imprinting a barrier region into a microcavity[3]. Here, we design microcavities that contain two molecular dyes; one that is strong-coupled to the cavity photon, the other out of resonance with the cavity mode and thus weak-coupled. By using an intense optical pump to create a transient bleach of the weak-coupled dye, we reduce its effective refractive index at the cavity mode wavelength which thus reduces the cavity optical path-length. This instantaneously 'blue-shifts' the energy of the polaritons in the pumped region by up to 8 meV in picosecond time-scales. This process can be used to create barrier regions that we have used to spatially-confine and manipulate polariton condensates. We expect that such techniques will allow us to create trapped lattices of polariton condensates, with such 'polariton simulator' devices being used in optical information processing schemes.

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Electron Catalysis

Armido Studer

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In the lecture the concept of using the electron as a catalyst will be discussed.[1,2] It will be shown that the electron is an efficient catalyst for conducting various types of radical cascade reactions that proceed via radical and radical ion intermediates.[3] It will be emphasized how a negative charge can significantly weaken the neighboring C-H bond and activate this bond towards H-atom transfer. Moreover, the activation of a C-H bond next to a C-radical towards deprotonation is a key point in the field of electron-catalysis. Extending that concept, the use of a negative charge to activate a C-C sigma-bond towards homolysis is also discussed. For example, electron catalyzed transition metal-free β-alkenylation-α-perfluoroalkylation of unactivated alkenes via radical 1,4 or 1,5-alkenyl migration will be presented. Finally, novel boron-based radical chemistry using the concept of electron catalysis will be presented.[4]

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New Functional Dyes Based on a Tetraazaperylene Core

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The synthesis of polycyclic aromatic hydrocarbons has been the focus of extensive research due to their applications in organic electronics. In the context of tuning their electronic properties the isosteric [CH→N] substitution of polycyclic aromatics provides a method to vary the electronic structure of the material while maintaining the molecular shape and rigidity of the π-system.[1] We applied this concept to perylene chemistry giving synthetic access to octaazaperopyrenes (**OAPPs**),[2] *peri* functionalized tetraazaperylenes,[3] and octaazaperopyrenedioxides (**OAPPDOs**).[4] Tetraazacoronenes were synthesized from bay-functionalized tetraazaperylenes inter alia via four-fold Suzuki-Miyaura cross coupling. The latter not only gives the tetraazacoronene target compound but also the condensed azacoronene dimer as well as higher oligomers.[5]

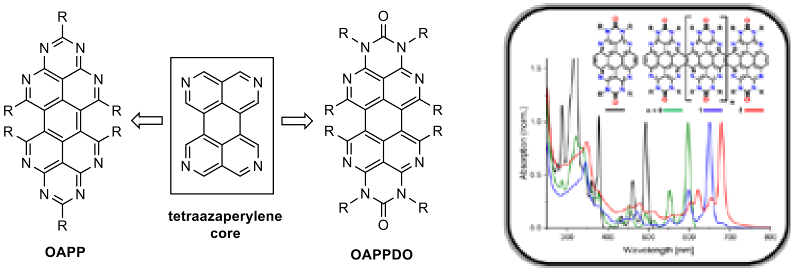

Figure 1. Left: Functional dyes based on a central *tetraaza*perylene unit, **OAPP**s and **OAPPDO**s. *Bay* functionalization leads to twisted chiral aromatic cores. Right: Tetraazacoronenes and their condensed dimers, trimers and tetramers.

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Electronic Properties of N-Heteropolycyclic Compounds

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N-Heteropolycycles represent a promising substance class for applications in functional organic materials, since their electronic structure and the resulting individual molecular properties are efficiently tuneable by number and position of nitrogen atoms in the aromatic structural backbone. The isosteric replacement of a C-H unit by N leaves the geometric structure unchanged, while ionization potential, electron affinity and absorption spectra are altered. By using two-photon photoemission spectroscopy (2PPE) and high resolution electron energy loss spectroscopy (HREELS) we determined quantitatively transport, singlet and triplet states as well as electronic spectra of serval N-heteropolycyclic molecules adsorbed on Au(111) (see Fig. 1).[1-4.] In addition charge transfer states between N-heterotriangulenes and strong electron acceptors have been identified. Furthermore, by means of two-photon absorption (TPA) the 3rd order nonlinear optical properties of diazaacene-bisthiophene compounds with high diradical character[5] have been analyzed. For these open-shell systems we found exceptionally large TPA cross-sections ranging from 4000 to 6000 GM over a broad wavelength range reaching values as high as 15000 GM.

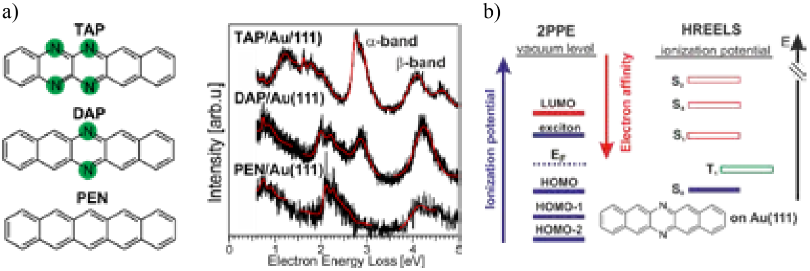

Figure 1: a) Influence of N-introduction in pentacene on the electronic structure. b) Electronic states of diazapentacene adsorbed on Au(111).

We acknowledge funding by the German Research Foundation through the SFB 1249.

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Physisorbed and chemisorbed molecular adsorbates on monolayers of MoS_2 on Au(111)

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Monolayers of transition-metal dichalcogenides are highly promising candidates for optoelectronic devices. Special attention has to be devoted to defects in these two-dimensional materials as already a minute amount dramatically influences the electronic properties, most notably by the introduction of subgap states.

Here, we grow monolayers of MoS_2 on a Au(111) surface and characterize their atomic-scale properties with scanning tunneling microscopy and spectroscopy at low temperature under ultra-high vacuum conditions. Hybridization of the S states with the metal substrate leads to a reduced semiconducting band gap as compared to a free-standing layer. We show that physisorbed molecules on a monolayer of MoS_2/Au(111) are well decoupled from the metal substrate owing to the bandgap of MoS_2. The molecules thus preserve their gas-phase properties and we resolve a multitude of vibronic states on single molecules using scanning tunneling spectroscopy.

To explore the influence of chemisorbed molecules on the properties of MoS_2, we introduce S vacancies into the top layer. These exhibit a Kondo resonance at the Fermi level reflecting the presence of an unpaired electron spin. We then deposit the thiol-based molecule CF3-3P-SH (tri-fluoro-methyl-p-terphenyl-thiol) on the defect-rich surface. Many of these molecules attach to the S vacancies. We find two categories of anchored molecules, those with and without a Kondo resonance. Density-functional theory calculations reveal that singly-occupied defects states persist when a dehydrogenated molecule is attached, while the hydrogen-terminated ones lead to doubly occupied defect states. These results explain the presence/absence of a Kondo resonance in experiment.

This work has been carried out in collaboration with many people, each one focusing on a different system. A great “Thanks” goes to: Juan Pablo Guerrero Felipe, Stefan Hecht, Nils Krane, Björn Kobin, Christian Lotze, Dmitrii Maksimov, Gael Reecht, Johanna Richter, Mariana Rossi, J. Rika Simon, Sergey Trishin, Paul Wiechers, Asieh Yousofnejad

From small molecules to conjugated polymer nanoparticles for organic photonics

Alexander J.C Kuehne

Universität Ulm

In this talk, I will present the concept of monodisperse conjugated polymer particles and their synthetic strategies,[1] along with their potential as laser gain media that can self-assemble into photonic crystal resonator structures.[2] However, the shortcomings and general limitations of electrically driven organic lasers will also be discussed.[3] In addition, I will introduce promising materials such as TADF emitters[4] and light emitting radicals[5] that could overcome the challenges that triplet states pose towards laser emission from electrically driven organic devices. By the end of the presentation, attendees will gain a comprehensive understanding of the opportunities and challenges in developing efficient and high-performance organic lasers.

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POSTER ABSTRACTS

1 These are the poster numbers under which you will also find the corresponding posters in the exhibition.

Fourfold TIPS-Ethynylation: Stabilizing Hexacene to Octacene

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The synthesis of higher acenes is challenging due to their reduced solubility and stability.1,2 Soluble acenes larger than hexacene are rare reported and their low stability complicates device application.3 The primary approach to enhance the stability of higher acenes involves functionalization with trialkylsilylethynyl substituents to prevent electrocyclic dimerization and oxidation.4 In addition, these functional groups increase the solubility and ensure easier processing of the material. In this study, we employed a modular synthetic method to produce fourfold TIPS-ethynylated acenes, ranging from hexacene to octacene. This series of acenes is important for fundamental research, and for comparing characteristic properties of acenes depending on their lengths. We investigate the transistor performance, frontier orbital positions (CV, DFT calculations) and the stability (UV/vis, NMR spectroscopy) as a function of the acene length. The enhanced stability enabled the application of the hexacene and heptacene in thin-film transistors. Furthermore, we examined the degradation of the octacene and characterized its butterfly dimer by time-dependent NMR spectroscopy and crystal structure analysis.

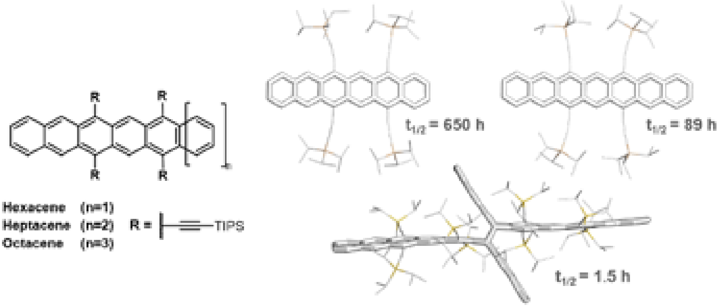

Figure 1. Structure and Substitution pattern of higher acenes (left). X-ray single crystal structures and half-life times of the reported acenes (right).

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Two-Photon 3D Laser Printing of Emissive Microstructures Using Tetraazaperylene Derivatives

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Light-based 3D printing technologies offer unique opportunities for the creation of highly customized, complex, and functional objects with greater efficiency and precision than traditional manufacturing methods.[1] Although luminescent materials have been widely applied in applications such as sensors, anti-counterfeiting devices or biomedicines, their use in 3D microfabrication, especially in high resolution two-photon laser printing, is still limited. In this work, a new class of fluorophores based on a twisted tetraazaperylene core in the fabrication of emissive organic 3D microstructures is presented (**Figure 1**). It was found the molecular design is critical to achieve compatibility with the two-photon printing as well as for the incorporation of the dye in the printable formulation. Various complex 3D microstructures were successfully printed and characterized using confocal fluorescence. These first results, render the further targeted modification of tetraazaperylene derivatives a promising strategy for developing printable dyes for the fabrication of high resolution fluorescent structures with defined photophysical properties.

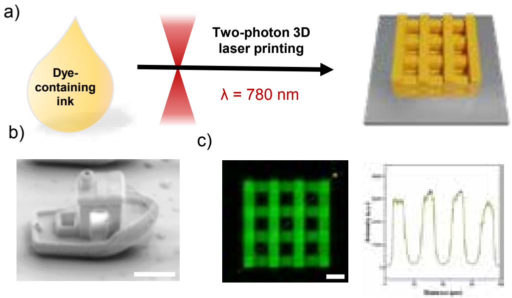

Figure 1. a) Schematic representation of two-photon laser printing using tetraazaperylene-containing inks; b) SEM image of an exemplary 3D printed microstructure, i.e., benchy; c) Confocal microcopy image and profile of a 3D printed woodpile microstructure. Scale bars = 10 µm.

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Machine learning on open-shell N-heteropolycycles

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Understanding the chemistry of open-shell N-heteropolycycles is crucial due to their use as organic semiconductors, OLEDs, catalysts, etc. Since the compound space of N-heteropolycycles is infinite, the researchers' ability to generate, synthesize, analyze, and compute the compounds limits their ability to shed light on and fully comprehend their structure-property relationship using computational chemistry and experimental findings. Machine learning is becoming a useful tool for discovering patterns in the compound space, identifying locations on which compounds with specific geometries rely and locating locations where the compounds populating the space have interesting properties. It is difficult to perform machine learning with open-shell compounds because the number of options for decoding the molecular structure into a numeric format is limited, as the majority of molecular representations are designed to deal only with closed-shell neutral compounds. The Matrix of orthogonalized atomic orbital coefficients[1] (MAOC) is a novel molecular representation that takes into account the charge, spin, and geometry of the molecular structures and is capable of distinguishing compounds with the same geometry but different charge and/or spin combinations. The ability of this novel representation in constructing the compound space of closed and open-shell N-heteropolycycles is evaluated using a novel database (N-HPC-1[1]) designed for the purpose of understanding the chemistry of N-heteropolycycles. In this study, the ability of kernel ridge regression models to predict properties of interest such as the LUMO energy and the H/SOMO-LUMO gap for N-heteropolycyclic compounds constructed by N-doping the skeletons below using the GANNA algorithm is evaluated.

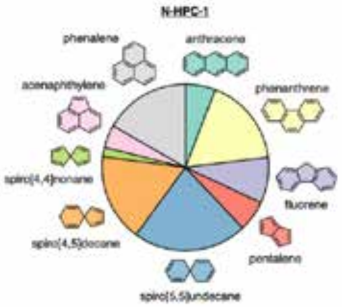

Figure 1. The type of skeletons and population with which the N-doped compounds are populating the dataset.

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Unusual Regioselectivity of the Diels-Alder-Reaction of TIPS-Ethynyl-Protected Acenes and 1,4-Bridged 1,4-Dihydro-naphthalenes

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Anthracene and pentacene act as dienes in a Diels-Alder reaction. They react with dienophiles such as vinyl carbonate[1] and epoxynaphthalene[2] at the central benzene unit furnishing barrelene-type structures. In 2001, Anthony et al. published a method to stabilize pentacene.[3] This involved the introduction of TIPS-ethynyl groups on the acene backbone, retarding oxidation and Diels-Alder reactivity at the central ring. As a result, dienophiles such as *para*-benzoquinone[4] or DMAD[5] no longer react at the central benzene ring but at the adjacent one. However, the Diels-Alder reaction of 6,13-bis(triisopropylsilyl)pentacene (TIPS-Pen) is virtually unexplored.

Herein, we investigate the regioselectivity of the Diels-Alder reaction of various dienophiles with TIPS-Pen and present two dienophiles with an unusual regioselectivity. The dienophiles can be divided into three different types: Type I dienophiles react as expected on the off-centered ring (red), corresponding to usual regioselectivity. Type II react at both the off-centered and the central benzene ring with a dominant attack at the off-centered ring, whereas Type III unusually prefers the central benzene ring of the TIPS-Pen in the Diels-Alder reaction. The reason for the unusual selectivity is the reduced width of the dienophile, lowering its steric demand and undermining the steric protection of the central ring.

Our current focus is on the simple design of an acene-based iptycene, using the unusual regioselectivity. This acene-based iptycene can be a potentially useful product for singlet fission.

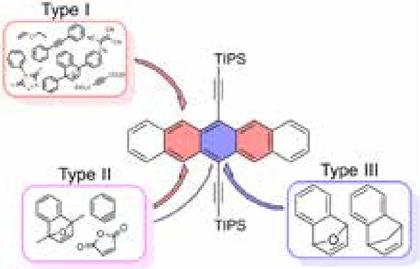

Figure 1. Visualization of the target benzene ring of various dienophiles with TIPS-Pen.

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Electron Microscopy and Related Techniques as Service Point for the Research in Materials Science

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In addition to the subproject proposed in the Collaborative Research Center 1249, we also play a role as service point for certain aspects of the characterization of materials for other groups. The functional imaging we provide offers a variety of material information, such as morphology, chemical components, crystallinity and element mapping *etc.* A collaborative network with internal and external research groups has developed in the last years. Figure 1 exemplifies the analytic methods we provide.

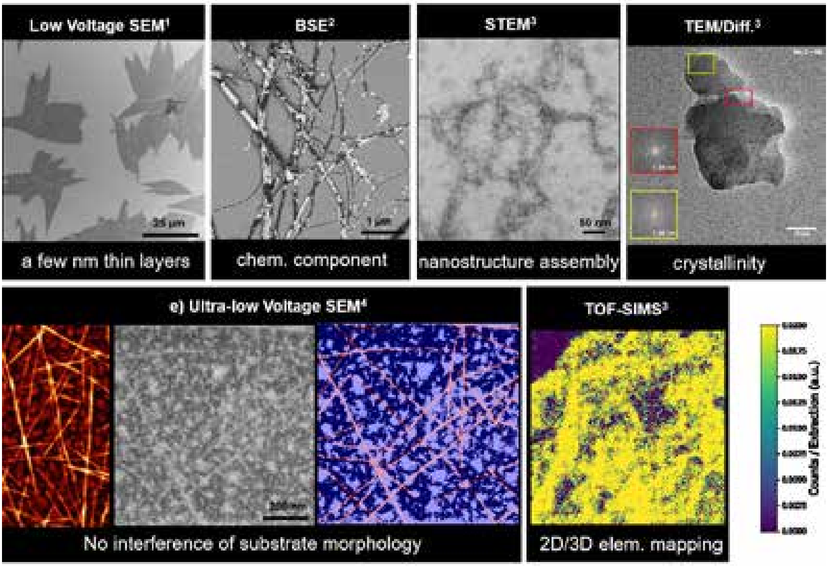

Figure 1 Scope of characterization methodologies for material researches provided from TP B05 as service point in SFB 1249.

Reference

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Controlling polymorphism in zone-cast PDIF-CN$_2$ thin films

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Differences in molecular packing, i.e., different polymorphs, can strongly influence the electronic and optical properties of crystalline organic semiconductors. Hence, being able to control the formation of different polymorphs during thin film deposition is important for optimized and reproducible samples and devices. PDIF-CN$_2$ is a well-known perylene diimide derivative and n-type semiconductor with high electron mobilities in both vapour-deposited thin films and single crystals. PDIF-CN$_2$ can form two different polymorphs (here named A and B). The single-crystal polymorph (A) is most stable and commonly observed but another thin film polymorph (B) of yet unknown structure has also been reported.

Here, we use zone-casting of PDIF-CN$_2$ from solution to create aligned films of different polymorphs by varying the organic solvent and casting conditions (temperature, speed). The two different polymorphs are easily identified by their characteristic low-wavenumber Raman modes and photoluminescence spectra reflecting their different intermolecular coupling (J- and H-aggregates). Based on polarization dependent UV-Vis absorption spectra, IR scattering near-field spectroscopy and GIWAXS data supported by quantum mechanical calculations, we propose a possible structure for the previously unidentified packing order of the additional thin film polymorph. Furthermore, we compare the electron transport properties of the two polymorphs in thin-film field-effect transistors.

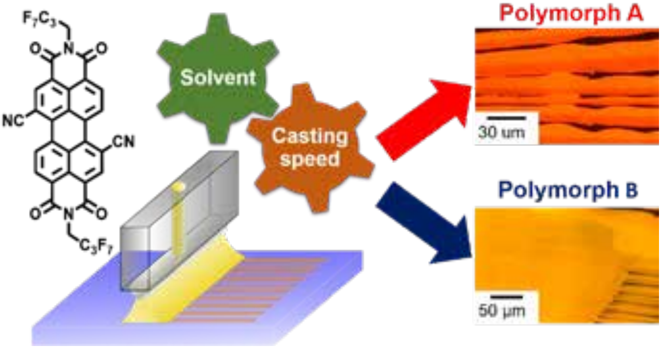

Figure 1. Molecular structure of PDIF-CN$_2$, zone-casting set-up for thin film deposition and fluorescence microscope images of the two zone-cast polymorphs.

Tetraazacoronenes and Their Twins, Triplets and Quadruplets

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The synthesis of polycyclic aromatic hydrocarbons (PAHs) has been the focus of research for many years due to their manifold opto-electronic applications. In this context of materials design the isosteric [CH→N] substitution plays an important role as it changes the electronic structure while maintaining the shape and rigidity of the π-system. Chemical modifications of the well-known PAH coronene have remained scarce due to limited synthetic accessibility, and the only fully characterized tetraazacoronene was described by Müllen and Li.[1] Recently, we applied the concept of "N-doping" to perylene chemistry[2a,b] giving synthetic access to octaazaperopyrenedioxides (OAPPDOs).[2c] Two synthetic concepts to laterally π-expand the OAPPDOs in its bay positions are presented, giving rise to tetraazacoronenes. In the first approach, two adjacent sp-hybridized carbon atoms are connected via Zr-mediated cyclization. An η^4-cyclobutadiene-zirconium(IV) coordination polymer was found to be the intermediate, which is in contrast to previously reported intermediates being zirconacyclopentadiene complexes.[3] In the second approach lateral conjugation is achieved by fourfold Suzuki-Miyaura coupling of sp^2 hybridized carbon atoms giving not only rise to the azacoronene parent compound but also to its extended two-, three- and four-fold condensed congeners.

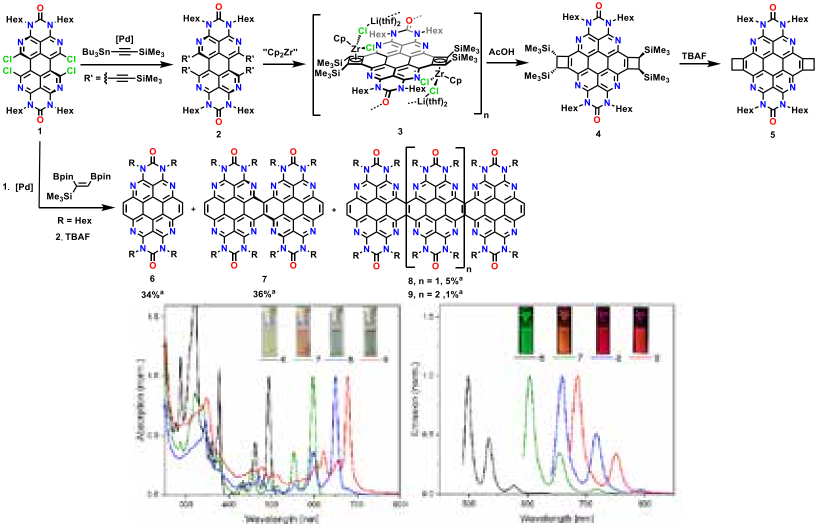

Figure 1. Synthesis of azacoronenes and their condensed congeners as well as their optical properties (in $CHCl_3$, ambient temperature).

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Enabling OF-DFT with Machine Learning? A novel ansatz for data generation

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Orbital-free density functional theory (OF-DFT) holds the promise to compute ground state molecular properties at minimal cost. Despite this, decades of research did not yield a kinetic energy functional with sufficient accuracy for general use in computational chemistry.[1]

Previously several ML models have been published that are able to predict the kinetic energy density and kinetic potential of Kohn-Sham ground state densities.[2,3] However no ML kinetic energy functional with sufficient generality for meaningful molecular calculation has been reported so far. A major computational obstacle is that it is insufficient to precisely predict the relevant quantities for the ground state only; instead it is necessary to estimate them accurately for all intermediate densities during a calculation.[3] Unfortunately, though, the kinetic potential can only be calculated from KS-DFT solutions.

As a consequence of this inverse DFT can be leveraged to calculate the external potential of those intermediate densities. This allows the calculation of the kinetic potential for those densities. Furthermore, we propose to overcome this limitation by not just training on standard KS-DFT ground states but also on ground states from perturbed external potentials. The novel equivariant network KineticNet has been trained accordingly and achieves OF-DFT calculations for two electron systems.

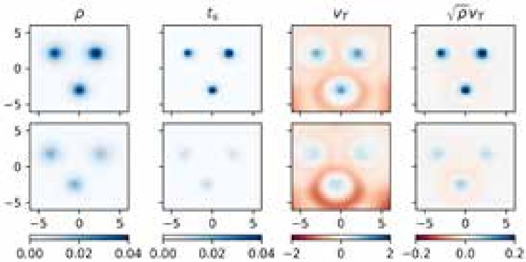

Figure 1. Electron density ρ, kinetic energy density t_s, kinetic potential v_T of H_3^+ with perturbed external potential.

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Revealing Different Interface Molecular Orientations of Isomorphic Organic Semiconductor by Dynamic Charging Map

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How molecular semiconductors orient themselves within thin-films is relevant for understanding electronic properties in a device configuration, such as charge-carrier mobility, exciton diffusion length, molecular quadrupole moments *etc.* To date, the reported methods to analyze molecular orientation of thin-films, including X-ray diffraction,[1] X-ray absorption spectroscopy,[2] high resolution electron energy loss spectroscopy,[3] are only able to provide global information without any site-specificity. In contrast, we present a novel method using spectral scanning electron microscopy (Delta-project SEM)[4] for a spatially resolved identification of the different molecular orientations. From these observations, deviation of experimental mobilities from calculations can be well explained.

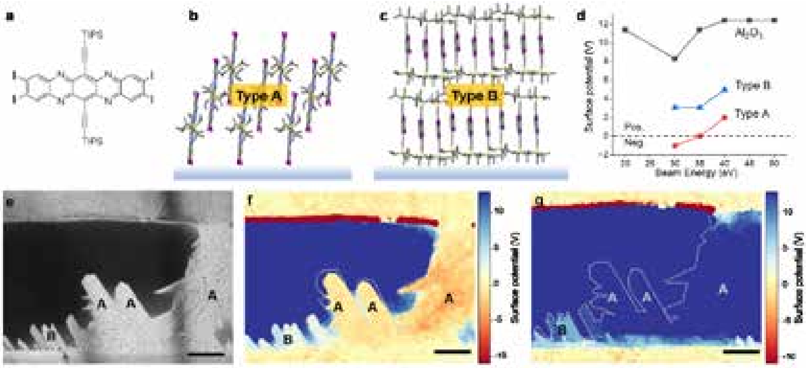

Figure 1. Two different molecular orientations of TIPS-TAP-I_4 formed on the surface of Aluminum oxides as dielectric for a OTFT device (Au/TIPS-TAP-I_4/Al_2O_3/SiO_2/Si): a) the molecular structure of TIPS-TAP-I_4, b) in Type A Iodine atoms standing up on Al_2O_3, where as c) in Type B TIPS-groups contact Al_2O_3 directly, d) surface potentials of related materials under various beam energies, e) SEM image of a channel section at 30 eV, f) dynamic charging map recorded at 30 eV, g) dynamic charging map recorded at 35 eV. The scale bars in e, f, g: 20 μm.

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On the Extraction of Contact Resistance in Organic Thin-Film Transistors

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Despite decades of research, the dynamic performance of organic thin-film transistors (TFTs) is still inadequate for most useful applications. Although the transit frequency of organic TFTs depends on a variety of parameters, it is limited mainly by the contact resistance, at least when the channel length is below about 10 µm and the intrinsic channel mobility is greater than about 1 cm^2/Vs, which is the case for many organic TFTs reported to date.[1] The contact resistance of organic TFTs reported in literature varies from 1 to 10^9 Ωcm, depending on the device architecture and the choice of materials for the source and drain contacts, the semiconductor, the surface functionalization, etc.

When it comes to determining the contact resistance of organic TFTs, especially if it is near the lower end of the aforementioned range, it is crucial to consider the strengths and weaknesses of the technique most commonly used for this task: the transfer length method (TLM). Here, the exact dimensions of the TFT's channel are just as important for a reliable result as the relation between the measured channel resistance and the extracted contact resistance.

Furthermore, measurements performed on nominally identical organic TFTs fabricated on several hundred substrates over the course of three years have revealed a relatively large substrate-to-substrate variation in the contact resistance, with extracted values ranging from 100 to 400 Ωcm for the semiconductor most frequently employed for this study (DPh-DNTT). The observed variation in the contact resistance does not appear to correlate with environmental factors such as the humidity in the lab during TFT fabrication. These findings suggest a certain degree of stochasticity that needs to be considered when reporting low (or even record) values for the contact resistance.

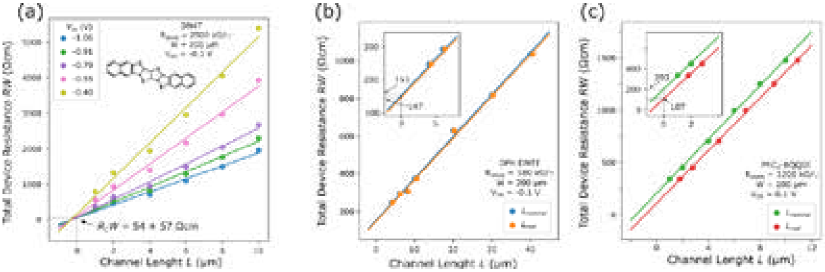

Figure 1. Extraction of the contact resistance via the transfer length method (TLM), illustrating how the accuracy of the method can be compromised if the semiconductors sheet resistance is unusually large (a), or if a deviation of the actual channel length from the nominal channel length is not properly accounted for in TFTs with small (b) or medium (c) sheet resistance.

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Aryne-Assisted Synthesis of Novel Pyrene-Based and Chiral 1,4-Dithiin Compounds

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Due to their incorporation of two sulfur atoms within a π-conjugated carbon scaffold, 1,4-dithiins are a special class of six-membered heterocyclic compounds of steadily growing interest.[1–3] Their unique properties, originating from their non-planar structures[4] are the primary incentive for their application in functional materials, e.g. as organic semiconducting materials[5] or cathode material for Li–S batteries[6]. Over the past decades, different synthetic methods to access 1,4-dithiins were developed.[7] Among dithiins, especially dibenzo-1,4-dithiin (thianthrene) is a popular structural motif in the construction of curved and sulfur-rich PAHs based on pyrene[3], corannulene[8] or nanobelts[2]. However, chiral dithiin compounds are rarely encountered. Here we present a series of 1,4-dithiin compounds containing stereogenic centers on the core dithiin moiety within a pyrene-based scaffold (see Figure 1).

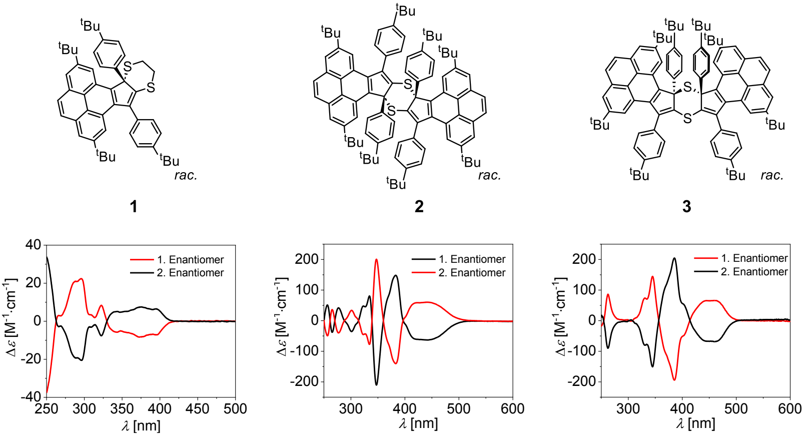

Figure 1. CD-spectra of chiral dithiins **1-3**, which are presented herein.

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Peri-Functionalized Tetraazaperylenes: A New Class of Strong Emitters

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The interest in the chemistry surrounding polycyclic aromatic compounds has experienced a revival as the result of the use of functional dyes as electronic materials, primarily due to the tunability of their photophysical and redox properties[1]. Among the plethora of published compounds, tetraazaperylene derivatives have distinguished themselves from other highly emissive and redox active functional dyes, because of its capability of independently modifying the peri and bay positions via nucleophilic substitutions and/or metal catalyzed coupling reactions[1]. This has led to the development of fluorophore systems such as octaazaperopyerene (OAPPs)[2] and octaazaperopyrenedioxides (OAPPDOs)[3]; in both cases limited structural variability (mainly in the peri positions) has led to significant impact on the electronic structures of these compounds[2,3]. Therefore, to expand on the chemistry of functionalizing the tetraazaperylene core and more precisely to understand the effect on the electronic structure of different substituents reactions were carried out using mild and strong electron donating groups[1]; and an electron withdrawing group. This work will show the synthesis, structural characterization and photophysical properties of the compounds shown in **figure 1**.

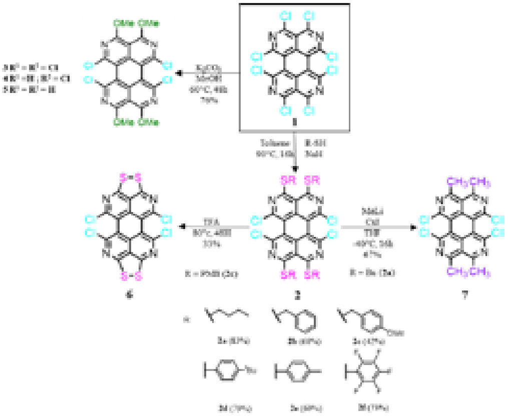

Figure 1. Diagram of the synthesized derivatives of the Octaclorotetraazaperylene

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Exploring the Properties of Thin Films of OAPPDO Emitters Inside and Outside Optical Cavities

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Molecules based on octaazaperopyrenedione (OAPPDO) cores are a new class of emitters that form amorphous films when processed from solution. Amorphous thin films are often advantageous compared to polycrystalline films as they offer much smoother surfaces, homogeneous and isotropic charge transport and emission properties. Amorphous OAPPDO films show absorption spectra similar to isolated molecules in solution, and for some derivatives even solution-like photoluminescence (Figure 1a) with high quantum yield and fluorescence lifetimes in the nanosecond range. These thin-film properties make OAPPDO derivatives interesting for application in light-emitting devices.

We can further tune the emission properties of these materials by placing them in optical cavities. When organic molecules are placed in resonant optical microcavities, they may experience a strong interaction with light. In this regime, the exciton resonance and the cavity photon exchange energy faster than their individual dissipation rates leading to the formation of hybrid light-matter states called exciton-polaritons. These polaritons, composed of excitons and photons, offer a unique way to modify the angle-dependent absorption and emission properties of an emitter (Figure 1b). They offer an additional method to tune the properties of OAPPDO films without molecular engineering.

Here, we investigate eight different OAPPDO derivatives to identify suitable candidates for application as solid-state emitters in devices. Their photophysical properties and variations in photostability and photoluminescence quantum yield will be presented. Furthermore, the ability of OAPPDOs to enter the strong coupling regime in cavities is demonstrated.

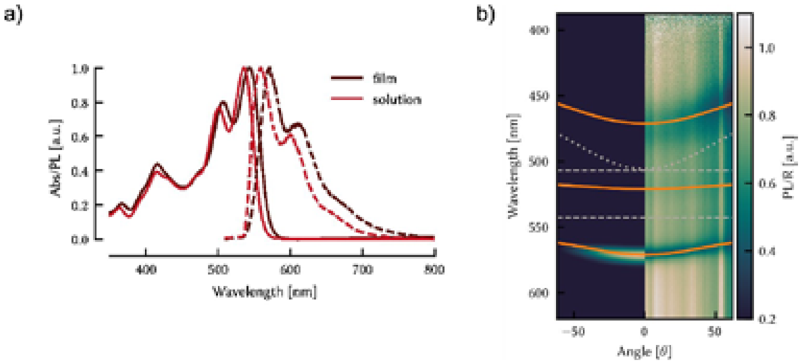

Figure 1. a) Absorption and emission spectra of one OAPPDO derivative in solution and thin film. b) Angle-resolved reflectivity and photoluminescence of a microcavity containing the OAPPDO derivative. The dashed lines indicate the absorption maxima of the molecule, the dotted line is the cavity mode and the orange lines are the energies of the polaritonic states.

Functionalization of a C_2-symmetrical Tripyrenylene for the Synthesis of Propeller-shaped Extended Polycyclic N-heteroarenes

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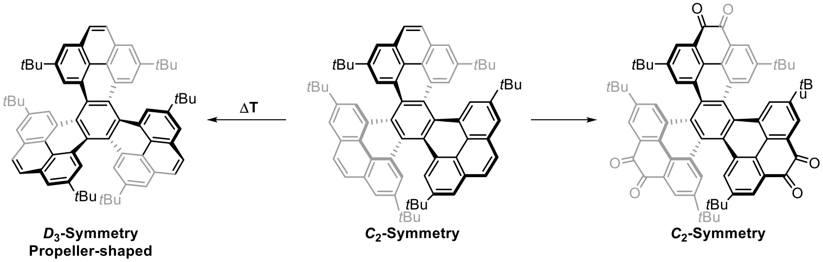
With a strained triple-bond-like character, arynes tend to be versatile reaction intermediates that can be generated by multiple different precursors and activation conditions and are employed in a plethora of different reaction types for the construction of otherwise challenging organic molecules.[1] One of these reactions is the palladium-catalyzed aryne-trimerization, that was discovered in 1998 and led to a variety of PAHs with three- or even hexapole helicity. [2, 3] The downside of this method is the dependency of the product on the scaffold of the monomer. After previously discovering higher oligomers of a di-*tert*-butylpyryne upon palladium-catalysis containing unsubstituted K-regions, increasing the cat loading led to an increased yield of C_2-symmetrical trimer.[4] The post-functionalization of this trimer into a C_2-symmetrical trimer-hexaone, as well as a propeller-shaped D_3-symmetrical trimer is presented herein.



Scheme 1. Synthesis and post-functionalization of a C_2-symmetrical Tripyrenylene.

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Enabling Electrical Readout of Molecular Qubits

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Organic semiconductors offer a promising platform for studying spin transport due to their weak spin-orbit and hyperfine interactions, resulting in much longer spin lifetimes compared with most inorganic semiconductors (1). Molecules with unpaired electron spins are interesting candidates for quantum bits. They can be easily tailored via chemical synthesis and can have considerable coherence even at room temperature (2). Here, we investigate a model system consisting of a semiconducting polymer and a molecular quantum bit (MQB) as a novel platform for enabling an electrical readout of the qubit. Such a coherent electric control has the potential to increase the detection sensitivity, in principle, down to the single-qubit limit (3). The readout mechanism would be based on the spin-dependent interaction between the spins of the qubits and the spins of the charge carriers of the polymer.

We chose the polymer poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene] (PBTTT) due to its high charge carrier mobility, and the molecule molybdenum tris[1-(methoxycarbonyl)-2-(trifluoromethyl)ethane-1,2-dithiolene] [Mo(tfd-CO$_2$Me)$_3$] because of its potential as both an MQB and a dopant for the polymer. We performed organic field-effect transistor (OFET) measurements on the polymer film and, pulsed electron paramagnetic resonance (p-EPR) spectroscopy on the MQB over a wide temperature range to characterize the conductivity and the spin coherence times of the polymer and the qubit, respectively.

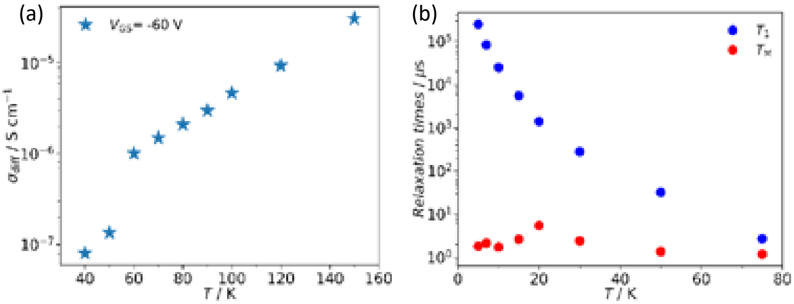

Figure 1. (a) Differential conductivity as a function of temperature for pristine PBTTT (b) spin relaxation times of [Mo(tfd-CO$_2$Me)$_3$]-NEt$_4^+$ measured using p-EPR at 35 GHz.

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Electronic Excitation Spectra and Calculated Structures of Matrix-Isolated Non-Covalently Bonded Dimers of Benzo[*a*]- and Benzo[*c*]acridine in Comparison with Dimeric Units Observed in their Solid-State Packings

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The electronic properties of acenes and their core substituted N-analogs play a crucial role in the design of organic electronics. To develop a better understanding of the intermolecular electronic interaction of multiple molecules in spatial proximity, non-covalently bonded dimers are created in solid neon using the matrix isolation technique and studied spectroscopically. Such weakly bonded dimers have already been characterized for the inversion-symmetric molecules tetracene,[1] pentacene and 6,13-diazapentacene.[2] In order to better control dimer aggregation, derivatives of acridine that exhibit a permanent dipole moment were now investigated. In accordance with the experimental data, structures of these dimers could be calculated with DFT. Different dimeric units can be found in the solid state and calculations based thereon resulted in very different electronic excitations. The results thus highlight how sensitive the electronic spectra of matrix-isolated dimers are to their structures.

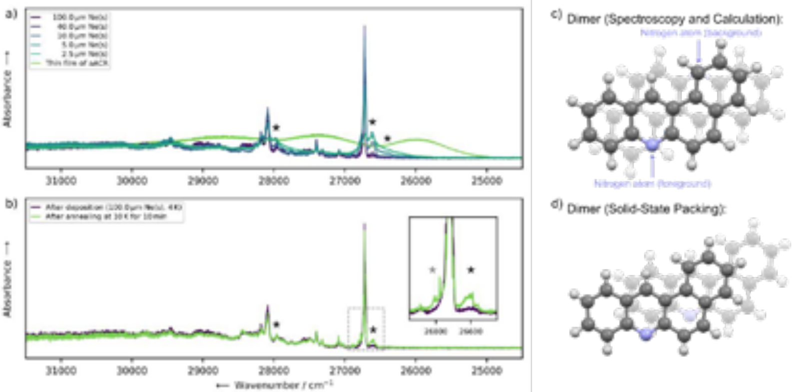

Figure 1. Experimental and theoretical results for benzo[*a*]acridine (aACR). a) Electronic absorbance spectra in solid Ne matrices of different concentrations at 4 K. b) Spectra after annealing at 10 K for 10 min. Additionally formed absorbance bands (asterisks) are assigned to dimers. c) Minimum energy structure of the corresponding aACR dimer, according to DFT calculations (BHLYP). d) Dimeric unit observed in the solid-state packing of aACR (CCDC-Code 1902433).[3]

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Highly anisotropic magnetoresistance of OLEDs at geomagnetic field strengths

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Polymer OLEDs can show extraordinary magnetoresistance (MR) and magnetoelectroluminescence phenomena, arising from hyperfine-field effects, spin-orbit coupling and macroscopic spin polarization.[1] At geomagnetic field strengths, OLEDs also exhibit a giant MR angular anisotropy of up to 35 %.[2] Comparison of the effect arising from a protonated and an analogous perdeuterated material, in combination with semiclassical quantum-stochastic modelling, demonstrates that microscopically anisotropic hyperfine-field distributions, on the level of the individual molecules, constitute the primary cause for this effect. For this microscopic anisotropy to emerge in the ensemble there must also be some degree of macroscopic ordering, which may arise from the structural anisotropy of the polymer. The theory predicts a critical field range, for which the anisotropy transitions from a twofold to a fourfold and back to a twofold angular functionality with increasing field strength, over a field range of only a few microtesla. Such a transition is indeed found experimentally, although it spans over a somewhat larger field range, suggesting a level of material disorder that is not accounted for in the simulations. Through the combination with microscopic modelling, anisotropic MR can serve as a sensitive probe of macroscopic molecular ordering in organic semiconductors. The inclination compass effect in OLEDs also offers a potential route to probe the radical-pair mechanism of spin chemistry in the solid state, and the associated coherent and incoherent electronic and nuclear spin dynamics, and could point to an intriguing analogy to avian magnetoreception.

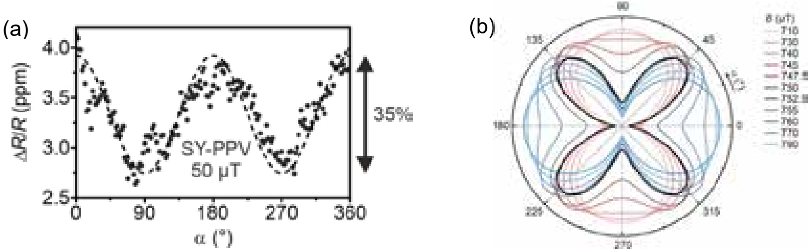

Figure 1. (a) The relative magnetoresistance (MR) exhibits an angular dependence with a $35\ \%$ modulation. The dashed line shows a $\cos^2 \alpha$ dependence. (b) Simulated, normalized MR anisotropy for different magnetic field values in the region where the anisotropy transitions between twofold, fourfold and twofold.

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Strongly Curved Suberenone-Pyracylene Hybrids and Their Cations

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Polycyclic aromatic hydrocarbons have gained significant interest in the field of organic electronics.[1] Especially the introduction of non-hexagonal rings, like five- and seven-membered rings allows fine-tuning of the optoelectronic and structural properties of the material by inducing curvature into the π-system.[2] By combining the electron-accepting properties of the pyracylene structural motif with the electron-donating abilities of seven-membered rings, distinct redox-active polycyclic scaffolds can be generated.[3]

The synthesis and characterization of strongly curved suberenone-pyracylene hybrids from commercially available 5-dibenzosuberenone over a seven-step synthetic route is described. Successive oxidative cyclodehydrogenation leads to stepwise enlargement of the π-system, resulting in altered optoelectronic and structural properties depending on the level of π-expansion. By functionalization of the keto-group, stable tropylium cations were accessed, which were analyzed by X-ray crystallography and UV/Vis spectroscopy.

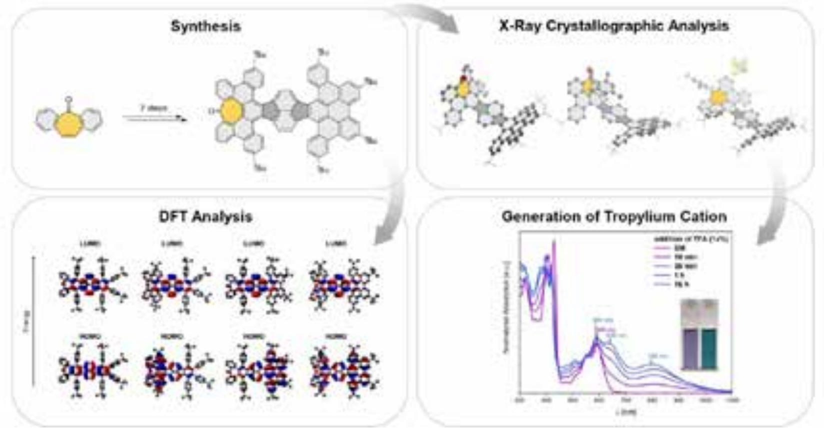

Figure 1. Curved pyracylene-suberenone hybrids and their optoelectronic and structural properties.

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Aggregation induced emission of *N*-Heteropolycycles

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During the last decades, scientists in different disciplines observed enhanced emissive behavior of small molecule organic solid-state materials, which were not expected from their molecular characteristics. Often this observation is denoted as aggregation induced emission (AIE).[1,2]

In this project, novel N-heteropolycyclic solid state luminogens are investigated which are formed through aggregation of dissolved molecules through the addition of antisolvent. In the first part of this project, we want to learn more about the role of the solvent/antisolvent system and follow aggregation kinetics of organic molecules *via* optical spectroscopy to systematically investigate the aggregate formation. This includes the use of different solvents, different volume fractions of antisolvent, different aggregation times, etc. By using different microscopy techniques (optical, AFM, SEM) the morphologies of the aggregates are systematically studied, in order to obtain an indication whether crystalline or amorphous aggregates, respectively, can be selectively produced and in which way the morphology plays a role for the emissive properties.

In the second step, a size selection of the different aggregates is targeted. Centrifugation-based techniques are well known in the context of size-selection techniques of nanomaterial dispersions,[3] while the effect of such techniques concerning aggregate sorting for size/morphology/etc. has not been explored in detail to date.

Typically, AIE research focused on achieving high PLQYs from films of aggregates, but inhomogeneous size/morphology distributions in samples and difficulties to create homogenous films hampered further progress. By using optimized aggregation conditions, remove undesired types of aggregates and exploiting adapted established deposition methods (Spray Coating, Spin coating, Langmuir-type deposition, Micro-filtration) we try to fill this gap.

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Influence of N-introduction on the adsorption geometry and the electronic structure of pentacene derivatives

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N-heteropolycyclic aromatic compounds are a class of organic electron-transporting (n-channel) semiconductors, which have high potentials for use in a variety of (opto)electronic applications. As such, in this study, the influence of N- introduction in pentacene on the adsorption geometry and electronic structure of two derivatives, namely 6,13-diazapentacene (DAP) and 6,7,12,13-tetraazapentacene (TAP) within thin films and at the interface with Au(111) are investigated by temperature-programmed desorption (TPD), vibrational and electronic high-resolution electron energy loss spectroscopy (HREELS) in combination with quantum-chemical calculations [1, 2]. The obtained results indicate that the introduction of nitrogen atoms in the aromatic backbone of parent pentacene (PEN) leads to a narrowing of the optical gap ($S_0 \rightarrow S_1$ transition) from 2.1 eV for PEN to 2.0 eV for DAP and to 1.6 eV for TAP as well as to an increase in the first triplet state energy from 0.9 eV for PEN and DAP to 1.2 eV in TAP. Additionally, in the series PEN, DAP, and TAP, the α-band ($S_0 \rightarrow S_2$ transition) gains significantly in intensity due to change in the transition dipole moment of the corresponding molecules upon nitrogen introduction [1, 2].

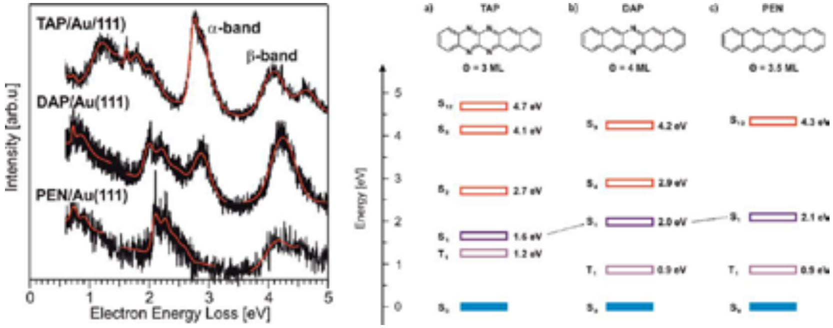

Figure 1. Electronic HREELS spectra of adsorbed TAP, DAP and PEN (left) on Au(111) and the associated energy level diagram (right).

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Pronounced Two-Photon Absorption Cross Sections in Diazaacene-Bisthiophene Diradical Compounds

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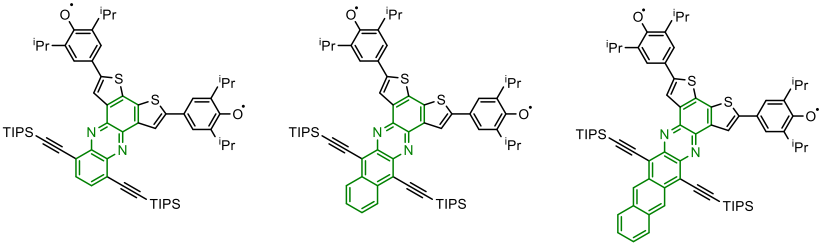
We present a study investigating the 3rd order nonlinear optical properties of diazaacene-bisthiophene (DAx-y-BT, see Fig. 1) compounds with high diradical character[1]. By employing the Z-scan technique[2] with a picosecond laser system, we identified a pronounced two-photon absorption (TPA) of these open-shell systems in the near-infrared regime. Our findings unveil an exceptionally large TPA cross-section ranging from 4000 to 6000 GM over a broad wavelength range (1200-1700 nm), even reaching values as high as 15000 GM. These results underscore the enormous potential stemming from the unique electronic structure and spin properties of diradicals. The remarkable nonlinear optical properties observed in the DAx-y-BT diradicals position them as highly promising candidates for various applications in the realm of nonlinear optical devices, encompassing optical limiters, three-dimensional imaging, and photodynamic therapy[3-4].



DA**A**-**f**-BT
Di**A**za**Anthra**cene-
forward-
Bis**T**hiophen

DA**T**-**f**-BT
Di**A**za**Tetra**cene-
forward-
Bis**T**hiophen

DA**P**-**f**-BT
Di**A**za**Penta**cene-
forward-
Bis**T**hiophen

Figure 1. Molecular structures for the studied diazaacene-bistiophene compounds. The annotation 'forward' denotes the direction the sulfur atoms are facing. Alternative configurations are 'asymmetrical' and 'backwards'.

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Polaron Spin Dynamics in Thin Films of Chemically Doped Semiconducting Polymers

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Semiconducting polymers and molecular doping have significantly advanced the field of electronic and opto-electronic devices, including organic field effect transistors, organic light-emitting diodes, and organic solar cells. Furthermore, the spin properties of polarons in semiconducting polymers hold potential for applications in spintronics and quantum computation.[1,2] However, the preparation plays a critical role in determining the conducting and spin properties of the material.[3,4] In this study, we investigated the spin dynamics properties of thin films of Poly(3-hexylthiophen-2,5-diyl) (P3HT) doped with the electron acceptor molecule 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ). Using a multi-frequency Electron Paramagnetic Resonance (EPR) spectroscopic approach, we elucidated the impact of morphology and doping strength on the spin properties of the material.

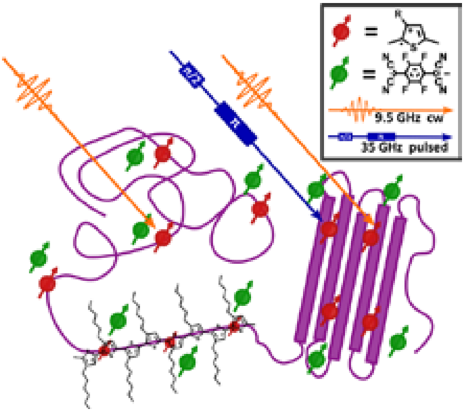

Figure 1. EPR spectroscopy can be used to access the spin properties of polarons in semiconducting polymeric materials. Additionally, by utilizing various EPR techniques, valuable information can be obtained regarding the film morphology and dopant distribution.

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Spiro-bridged *N*-Heterotriangulenes as Building Blocks for Advanced Functional Materials

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In 2020, our group presented a nitrogen-centered trispirocyclic *N*-heterotriangulene. The molecular design of this scaffold includes bridging of triphenylamine with sp^3-carbon spirofluorene units and protection of the reactive *para*-positions with *tert*-butyl groups.[1] The compound was prone to a facilitated one-electron oxidation and displayed aggregation-induced emission in the solid state. Nevertheless, at that time further functionalization of this appealing multispirocyclic scaffold was not possible.[2]

To investigate the impact of functionalization on the optoelectronic and structural properties we have established herein novel brominated spirocyclic building blocks to provide for selective synthetic transformations. Through this approach a series of compounds differing in the number and position of electron-withdrawing cyano-groups have been realized. Depending on the substitution pattern the compounds display dramatically altered optoelectronic and redox properties which were studied in detail by optical spectroscopy and quantum chemical calculations. Due to the inherent rigidity of the brominated spirocyclic scaffolds nickel-mediated *Yamamoto* couplings led to novel electron-rich microporous polymers with impressive thermal and structural stability and unique photophysical properties.

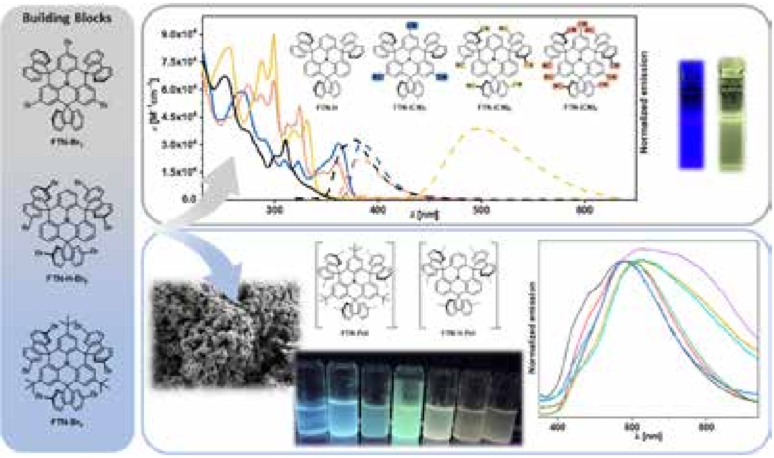

Figure 1. Evolution of the novel series of spirofluorene-bridged *N*-heterotriangulenes as building blocks for functional molecular and polymeric materials.

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PERTURBATION THEORETICAL APPROACH TO STRONG LIGHT-MATTER COUPLING

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In recent years experiments in chemistry, physics and material science have shown to be capable of coupling photons and matter in a way, that cannot be described by the classical interaction of electromagnetic fields with matter. In this so-called strong coupling regime light and matter form hybrid states, which alter the properties of the initial state of matter. While experiments made tremendous progress, consistent theoretical approaches capable of describing these effects within reasonable computational effort are still barely developed.

On this poster a short introduction to strong light-matter coupling phenomena is given along with a short motivation and a detailed example for an experiment[1]. Furthermore, some basic concepts of the theory are visualized[2], as shown in figure 1, and perturbation theoretical results for ground and excited states are shown[3] in comparison to other theoretical data[4], whenever possible. In the end a short outlook for the possibility of approximation schemes is presented along with an example.

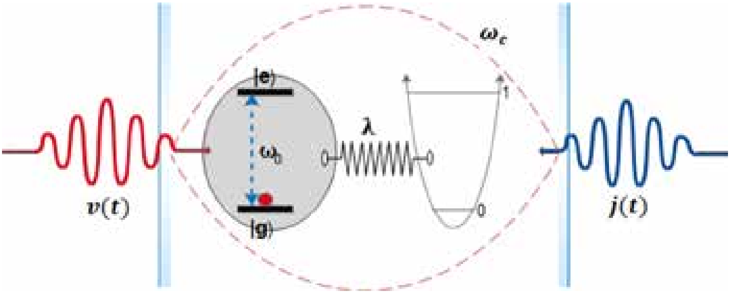

Figure 1. Graphical representation of the linear response of a polaritonic 2 x 2 level system.[2]

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Ferroelectric behavior and surprising conductivity in C6H6F5O-Cx-Amides

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The switchable polarization and concomitant pyroelectric and piezoelectric properties of ferroelectric materials enable a plethora of applications, ranging from memory devices over thermal and mechanical sensors to energy harvesters. Although current applications are dominated by inorganic materials, organic ferroelectrics offer a flexible, cheap and solution processable alternative.

Here, we present experimental research on the ferroelectric behavior and the conductivity of the liquid crystalline C6H6F5O-Cx-Amide[1] molecules. Electrical measurements of the ferroelectric properties were conducted, the current response to a triangular voltage pulse (figure 1a) exhibits a shape commonly observed for ferroelectrics. Integration of the current response yields ferroelectric-like hysteresis loops (inset figure 1a), however, these loops do not saturate with electric field, indicating the presence of substantial background currents. DC conductivity measurements (figure 1b) show an increase in conductivity by four orders of magnitude when heating from 300K to 360K-380K. This conductivity increase is not directly correlated to the temperature increase, as the conductivity remains on a high level when cooling down again, but results from a reversible alteration of the material itself. Capacitance-voltage measurements exhibit the characteristic butterfly shape expected from ferroelectric materials, caused by a pronounced increase of the dielectric permittivity of the material in the vicinity of the coercive field. Atomic force micrographs suggest a morphological restructuring and partial alignment of the molecular fibers under application of elevated temperatures and fields.

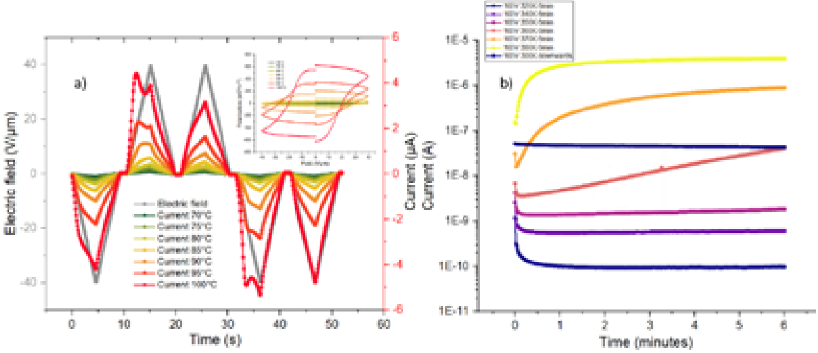

Figure 1. a) Measured current response to a triangular voltage pulse for varying temperatures. Inset: Resulting hysteresis loops. b) Temperature dependent current measurements showing a conductivity increase over multiple orders of magnitude.

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N-Heteroacene based rotaxanes

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Rotaxanes are mechanically interlocked species which consist of a dumbbell shaped molecule threaded through a macrocycle.[1] The formation of rotaxanes is a novel strategy to improve stability of nanographenes[2] without changing its covalent structure. Here we report the synthesis of mechanically interlocked N-heteroacene based rotaxanes obtained by clipping tetralactam macrocycles around azaanthracenes. The encapsulation prevents dimerization under irradiation and leads to an increase in stability. This was demonstrated by UV-vis measurements for a phenazine based rotaxane. In the same time period in which the phenazine dumbbell molecule completely decomposed the rotaxane absorption remained unchanged. An approximately 200-fold increase in the half life time from $t_{1/2}$= 8 min for the phenazine dumbell to $t_{1/2}$= 1600 min for the rotaxane was observed. Additionally, three further rotaxane structures based on tetraazaanthracene scaffolds were obtained and characterized via crystal structure analysis. Our current focus is applying this stabilization strategy to longer N-heteroacenes.

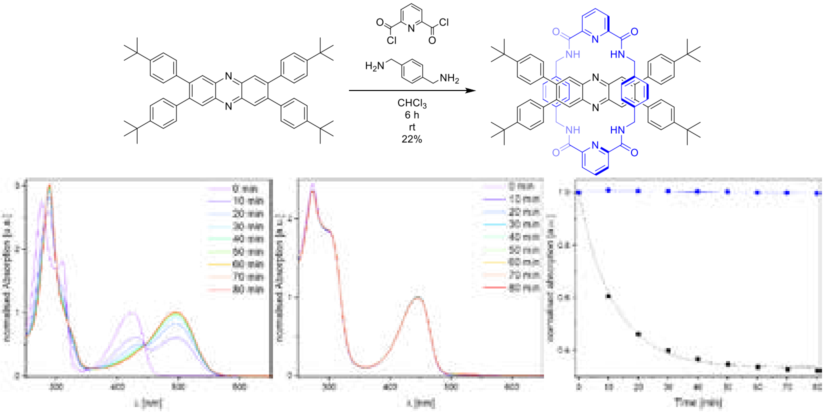

Figure 1. (a) Synthesis of a phenazine based rotaxane (top), (b) stability measurement of the phenazine dumbbell molecule (c = 10^{-5} mol L^{-1}, in DCM, λ_1 = 365 nm, λ_2 = 254 nm) (left), (c) stability measurement of the phenazine rotaxane (c = 10^{-5} mol L^{-1}, in DCM, λ_1 = 365 nm, λ_2 = 254 nm) (centre), (d) change in the absorption maxima of the *p*-band (left).

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Contact resistance of low-voltage n-channel organic thin-film transistors based on perylene diimide and tetraazaperopyrene derivatives

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Many applications envisioned for organic thin-film transistors (TFTs) are mobile devices for which a low power consumption is one of the most critical requirements. From a circuit-design perspective, the most effective approach to minimize the power consumption is to combine p-channel and n-channel transistors in a complementary design. However, the performance of even the best n-channel organic TFTs still lags behind that of p-channel organic TFTs. Here, we compare the performance of low-voltage n-channel organic TFTs based on three promising small-molecule semiconductors. The TFTs were fabricated on silicon or flexible plastic substrates using a hybrid gate dielectric composed of a thin, plasma-grown aluminum oxide layer and a tetradecylphosphonic acid self-assembled monolayer. We fabricated TFTs both in the staggered (top-contact) and in the coplanar (bottom-contact) device architecture. In the coplanar TFTs, the surface of the gold source and drain contacts was treated with one of four chemisorbed thiol interface layers (Fig. 1).

For each of the three semiconductors, the TFTs fabricated in the coplanar architecture were found to have a smaller contact resistance than the staggered TFTs. Regardless of the semiconductor, the best TFT performance was obtained by functionalizing the contacts with 4-(methylsulfanyl)-thiophenol (MeSTP). Flexible coplanar TFTs based on the semiconductor PhC_2-BQQDI with MeSTP-functionalized contacts have an intrinsic channel mobility up to 0.8 cm^2/Vs, an on/off current ratio up to 10^6, a subthreshold slope as small as 85 mV/decade, and a contact resistance as small as 210 Ωcm (a record for n-channel organic TFTs).

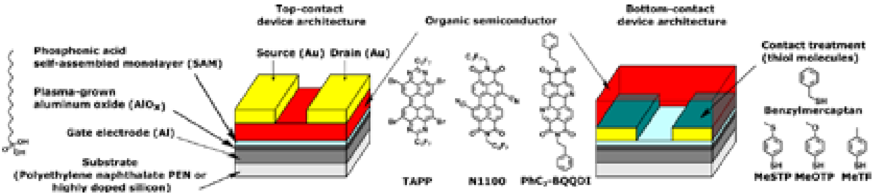

Figure 1. Schematic cross-sections of the TFTs in the top-contact and bottom-contact architecture, and chemical structures of the organic semiconductors (TAPP [1], N1100 [2], Ph_2C-BQQDI [3]), of the alkylphosphonic acid employed as part of the gate dielectric, and of the thiols employed for the contact treatment in the bottom-contact TFTs.

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The Pyridine Dimer - A Model for Weakly Interacting N-Heterocyclic Compounds

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N-heterocyclic aromatic molecules, in general, are used in a variety of applications. For applications in organic electronics, the interaction between these molecules is of central importance. Therefore, it is of interest to study the interaction between molecules of the prototype N-heterocyclic compound pyridine. Despite the assignment of a larger number of absorption bands to pyridine dimers, there has been yet no conclusive experimental evidence concerning the structure of pyridine dimers.

Matrix isolation is a means to prepare samples of isolated molecules surrounded by an inert environment of, for example, noble gases like Ne or Ar at low temperature. These samples can be investigated by standard spectroscopic techniques, namely absorption (IR, vis, UV) or emission spectroscopy. Thereby it is possible to investigate molecules at conditions that reduce the interaction with the environment and approximate gas-phase conditions. This also allows for the study of the formation of small aggregates, that is dimers.

To study in particular the formation of dimers, samples of pyridine in solid Ne have been generated and investigated by IR spectroscopy. Accompanying quantum chemical calculations yield information about different types of dimers and are the key to the assignment of the observed spectra. The spectra show the presence of hydrogen-bonded, T-shaped, and stacked forms of weakly bound pyridine dimers. Among these, the hydrogen bonded isomer is identified as the lowest-energy form.

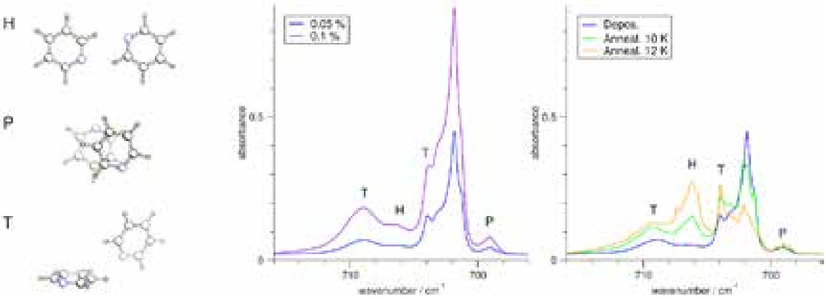

Figure 1. Absorption bands of pyridine, assigned to different isomers of the dimer.

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Tuning energy transfer in organic multilayer cavities

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Strong light-matter coupling arises when the exchange of energy between an excitonic transition and a resonant optical mode surpasses the competing dissipation processes. Strongly coupled optical microcavities enable the formation of exciton-polariton modes, which can be described as a linear combination of cavity photons and the constituent excitons and thus exhibit mixed light-matter properties. A notable feature of these hybrid states is their delocalized nature. This delocalization enables polariton-mediated non-radiative energy transfer between spatially separated molecular layers (donor and acceptor) in an optical cavity. The range of this energy transfer in the strong coupling regime was shown to be much larger (hundreds of nanometers) than for other types of non-radiative energy transfer, for example, FRET (limited to few nanometers). Nevertheless, a comprehensive understanding of the parameters that influence this long-range energy transfer is still outstanding.

Here we investigate the influence of different energy offsets between the donor and acceptor absorption and emission bands on polariton-mediated energy transfer in strongly coupled multilayer cavities. We use a multilayer structure consisting of two different ATTO dyes in PVA matrix separated by a PMMA spacer and sandwiched between two silver mirrors (see structure in Figure 1). The chosen donor molecules, various carborhodamine and oxazine dyes, along with a carbopyronine dye as the acceptor, have been widely used in super-resolution microscopy and feature narrow absorption and emission bands, high photoluminescence quantum yields and good photostability. By coupling these dyes with the cavity mode, exciton-polariton states are formed. Angle-resolved spectroscopy (reflection, fluorescence) is used to characterize these strongly coupled systems and to understand the impact of the energy offset between donor and acceptor dyes on polariton-mediated long-range energy transfer.

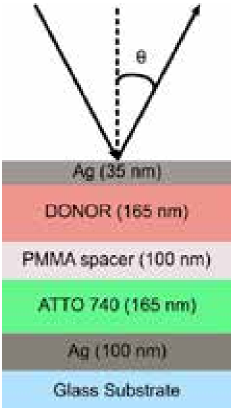

Figure 1. Schematic layout of a multilayer film embedded in the microcavity structure. Reflection and emission from the cavity are measured as a function of angle.

Dip coating of organic piezo- and ferroelectric materials

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Organic ferroelectric materials are of great interest due to their switching properties. However, the extensive procedures that are often required to achieve saturation polarization limit their possible applications. A possible solution is to pre-align the molecules. Previously, we analyzed the effect of dip coating parameters on the alignment of the prototypical supramolecular ferroelectric trialkylbenzene-1,3,5-tricarboxamide (BTA) and the resulting changes in the ferroelectric switching behavior of the resulting thin films. We established that dip coating, in general, allows for enhanced ferroelectric switching in BTA-C_8.[1] Hence, we now applied the technique to further materials. Firstly, we investigated the piezo- and ferroelectricity of two tritridecanamides. While we were not able to find any ferroelectric behavior, those materials are still expected to exhibit piezoelectric properties. However, due to high film roughnesses, this was impossible for us to investigate using a piezoelectric force microscopy. While dip coating allowed us to partially align the molecules, indicating that a long-range order can be established within of the material, it did not solve the film roughness problem. However, a newly synthesized derivative of the molecules may be a promising candidate for piezo- or even ferroelectricity. Secondly, a side project was introduced to find out whether pre-aligning P3HT molecules could enhance their electrical conductivity and Seebeck coefficient. Similar to BTA, Landau-Levich and evaporation regimes were established for P3HT via the formation of different morphologies in the dip-coated films and compared to other results.[2] The P3HT films were then sequentially doped with F4CNTQ and measured at our Seebeck setup. While it is still work in progress, we were able to verify a significant increase of conductivity in dip coated samples compared to the spin coated ones, which may be a promising sign for an improvement in thermoelectric properties.

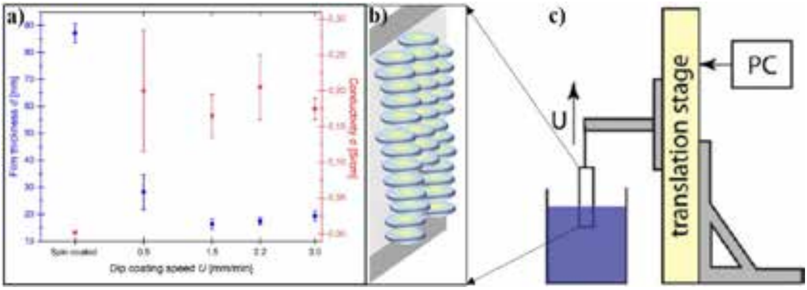

Figure 1: A) A film thickness and conductivity measurement of a spin- and multiple dip coated samples. **B)** A dip coated film which was aligned via a **c)** dip coating setup. Figure 1c is taken unchanged from [2]. Permission for usage granted by ACS Publications.

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Wavefunction frozen-density embedding with one-dimensional periodicity: Electronic polarization effects from local perturbations

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Tetraazaperopyrenes (TAPPs) show promising semiconducting properties. To describe the semi-conducting properties, both the geometries of the molecular crystals as well as the electronic structure of the charge transport need to be addressed.

We report an approach to treat polarization effects in a one-dimensional (1D) environment using frozen-density embedding (FDE), suitable to compute response to electron loss or attachment as occurring in organic semiconductors during charge migration, providing two key developments: Local perturbations are computed avoiding an infinite repetition thereof and a first-order equation-of-motion ansatz is used to compute polarization effects due to electron loss and attachment, ensuring an efficient calculation by avoiding open-shell calculations.

In a first step, an unperturbed 1D molecular chain is equilibrated using FDE by translation of the center molecule. In a subsequent second step, long-range contributions are frozen and a local perturbation is introduced in the center subsystem. Freeze–thaw iterations are used to relax the electronic wavefunction of both the center subsystem and subsystems in an active region around the center subsystem, avoiding the need to translate the perturbation. Due to its efficiency, the new method is capable of providing wavefunction-based reference data relevant for electronic couplings in complex environments.

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Facile two-step Synthesis of *para*-Dithienopyrazines

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N-heteropolycyclic compounds are valuable building blocks in organic electronic devices. In general, the introduction of nitrogen atoms into the π-conjugated system of polycyclic aromatic hydrocarbons results in a stabilization of its frontier orbitals,[1] an enhanced electron affinity and therefore often in an increased performance regarding its optoelectronic properties.[2] Recently, our group contributed the synthesis of dipyrrolopyrazines by a gold-catalyzed approach.[3] The targets have optical band gaps down to 2.80 eV and quantum yields up to 56%, properties, which make them attractive for usage in optoelectronic devices. However, the approach was limited to N-aryl-substituted dipyrrolopyrazines, making an orderly assembled crystal packing difficult to realize, which can be a drawback for a potential use as organic material. As possible approach to withdraw this problem, we envisaged the introduction of sulfur as replacement for the pyrrole N-units to get the corresponding planar dithienopyrazine systems. In this work, a convenient route for the synthesis of *para*-dithienopyrazines from readily available starting materials is described.[4] A cascade of nucleophilic aromatic substitution and subsequent bidirectional hydrothiolation of alkynes was used as a key step. In total, seven new compounds were synthesized and investigated regarding their photophysical properties. In solution, these molecules act as blue emitters, which turn to green upon addition of acid, which demonstrates a potential use as proton sensors.

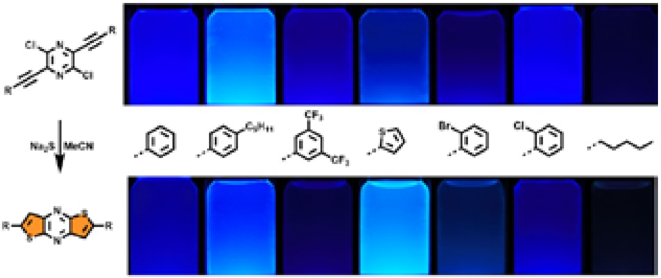

Figure 1. Synthesis of *para*-dithienopyrazines by nucleophilic cyclization starting from dialkynyl pyrazine precursors and photographs of the compounds as solution in DCM under irradiation by UV light (365 nm).

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Electronic Properties of N-Heterotriangulene Derivatives Adsorbed on Au(111) Investigated with Two-Photon Photoemission

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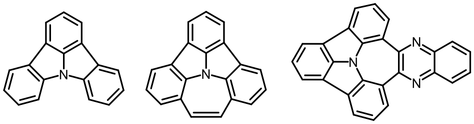
In many organic opto-electronic devices donor-acceptor-systems (D-A-systems) play a crucial role, for example as the emitting layer in organic light emitting diodes (OLEDs)[1] or to enhance charge separation in organic photovoltaics (OPVs).[2] Triphenylamine derivatives are a promising class of electron donors that can be utilized in D-A-systems.[3] Planarization of triphenylamine leads to *N*-HTA-550 (see Fig. 1). The introduction of an etheno bridge closes a seven membered ring in *N*-HTA-557 (see Fig. 1) and strongly modifies the electronic structure of the molecule while retaining its steric demands. By oxidation of the C_2H_2-bridge and subsequent condensation with quinoxaline-2,3-diamine *N*-HTA-557-P (see Fig. 1) is synthesized. This molecule can be classified as an intramolecular D-A-system.[4]

In the present contribution we investigate the electronic structure of *N*-HTA-550 (1), *N*-HTA-557 (2) and *N*-HTA-557-P (3) adsorbed on Au(111) with two-photon photoemission spectroscopy (2PPE). In agreement with the results of UV/Vis-absorption spectroscopy we found the optical gap of 1 and 3 to be 3.7 eV and 2.6 eV respectively.[4] For 2 the electron affinity level and occupied molecular states have been determined, yielding a fundamental gap of 2.9 eV. By means of femtosecond time-resolved 2PPE the exciton decay dynamics in thin films of compound 3 have been investigated. Thereby two coverage-dependent exciton decay pathways have been identified.



1 2 3

Figure 1. *N*-HTA-550 (1), *N*-HTA-557 (2) and *N*-HTA-557-P (3) investigated in the present study.

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Triptycene End-Capping as a Crystal Engineering Tool

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Controlling the arrangement of π-planes during crystallization is challenging but necessary to fine-tune the properties of polycyclic aromatic compounds (PACs) such as charge transport.[1] In an earlier work we presented that the introduction of one triptycene end-cap leads to a unique packing motif, which provides a brick-wall arrangement of π-planes.[2] With this in mind, we took the triptycene-end-capping approach to the second dimension[3] and found a π–π-interaction based dimer formation with high dissociation energies, resulting in materials with interesting properties. Furthermore, we used a dibenzo-barrelene derivative as an end-cap to decrease the steric demand of the end-cap. The influence on the packing will be discussed herein.

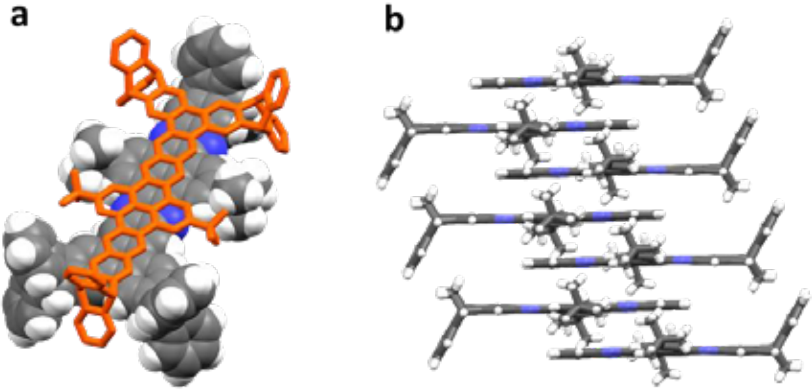

Figure 1. Single crystal X-ray structures of tri-triptycene-end-capped QPP (a) and dibenzo-barrelene-end-capped QPP (b).

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Modification of Intramolecular Singlet Fission dynamics with strong light-matter coupling

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Singlet Fission (SF) is a spin-allowed process in which a singlet exciton, S_1 splits into two triplet excitons $2T_1$. A limited number of molecular systems possess the necessary conditions to facilitate singlet fission. If a system shows an energy gap where, $E_{S1} < 2E_{T1}$, the SF process is not optimal or in some cases not possible[1]. This work, through quantum dynamics simulation using the MCTDH package, demonstrates that in a not-optimal SF system, the energy transfer to the $^3(T_1T_1)$ state can be modified by coupling the S_1 state strongly to a cavity mode. Our findings indicate that through the upper polarition (UP) a channel to the $^3(T_1T_1)$ state can be established and consequently improve the energy transfer.
Additionally, the size of the molecular ensemble coupled to the cavity mode was varied to investigate the collective effects.

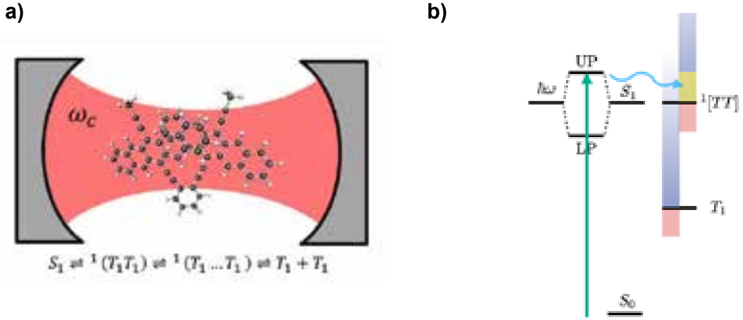

Figure 1. **a)** o-Bis(13-(methylethynyl)pentacen-6-yl)ethynyl)benzene dimer (o-TIPSPm)[2] investigated in this work and the SF mechanism[3]. The optical cavity, indicated graphically, is not to scale. **b)** Scheme of the energy transfer channel established by the strong coupling to a cavity mode[1].

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Synthesis of Pyrazine-based Materials: Catalysis, Functionalization & Applications in Materials Science

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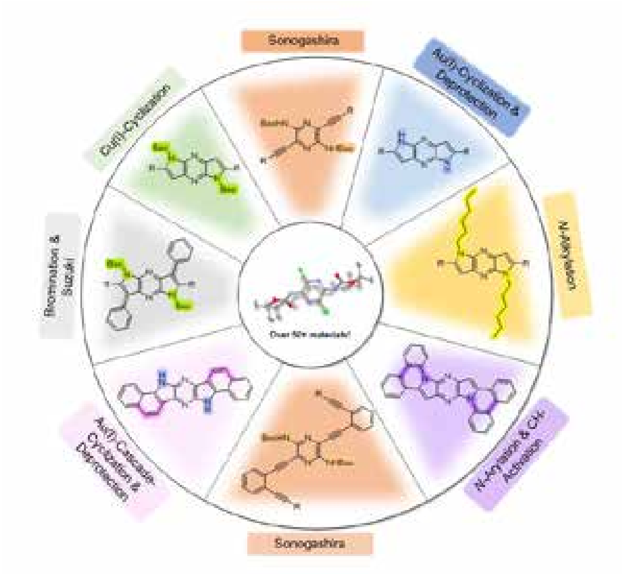

Figure 1: Variable substrate wheel derived from di-*tert*-butyl (3,6-dichloropyrazine-2,5-diyl)dicarbamate.

Herein we describe the synthesis of dipyrrolopyrazines *via* a selective *Sonogashira*-coupling followed by a direct cyclization. Di-*tert*-butyl (3,6-dichloropyrazine-2,5-diyl)dicarbamate was established as a key precursor towards the alkyne starting materials. This new building block was available in multigram scale *via* a short two step sequence. After subsequent bidirectional cross-couplings either diyne/tetrayne or dipyrrolopyrazine scaffolds were afforded in a selective modular fashion. The direct cyclization by the aid of Au-(I)-NHC complexes was possible and an *in situ* cleavage of the *Boc*-group was observed. Additionally, substitution of the indole-CH or NH-moiety *via* nucleophilic *N-arylation-& alkylation* allowed to further fine tune solubility and bandgaps. Extensive characterizations imply extraordinary UV-stabilities, thermal stabilities of up to 400 °C and excellent quantum yields of up to 93%. Further investigations are underway to explore potential applications in OFETS & sensor materials.

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The Impact of a Vinylene Bridge on the Properties of Planarized Triphenylamine

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Planarization significantly enhances the donor properties of triphenylamine.[1] In this contribution, a family of doubly pentagon-fused triphenylamines is presented, starting with the smallest member without a third bridging moiety,[2] in direct comparison to structures with an additional ethylene[3] or vinylene bridge.[3,4] The compounds were obtained in high-yielding synthetic protocols. Their electronic, structural, photophysical, and donor properties were thoroughly analyzed both in experiment and theory, while the donor properties were highlighted by co-crystallizations with several paradigmatic cyano-based acceptors. Particularly the vinylene bridge supports efficient π-conjugation and allows for further functionalization and thus π-expansion.

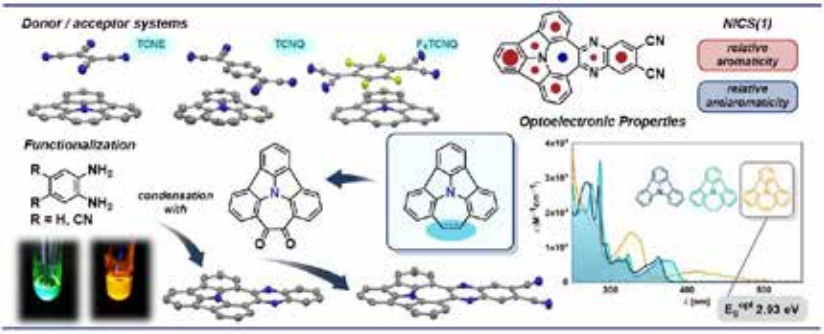

Figure 1. Tailoring the properties of fully bridged triphenylamine with a 7-membered ring.

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Wrinkling in Multilayered Systems: Experiment and Model

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In multi-layered organic electronics, surface structures like wrinkle structures[1-3] may become a problem and deviated the functionality of a device. Nevertheless, wrinkles as surface modification can be used in optics for random lasing[4-5] and mechanics for measuring material properties[6]. This poster will give an overview to the practical approach of generating such a structure in the lab and in a simple form with Monte-Carlo-Simulation using Truchet tiles on the one hand and the Ising-Modell on the other (see figure 1).

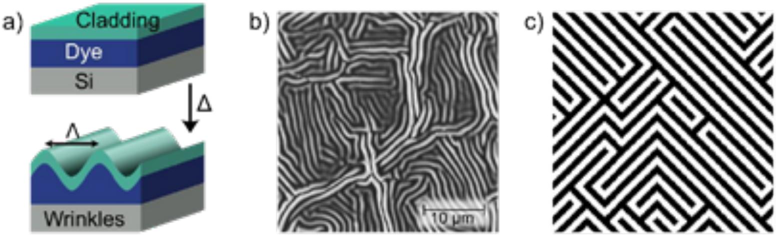

Figure 1 The wrinkling phenomenon in multilayers shown schematically in a), an optical image of a wrinkle experiment of two spiro-compounds in b) and a simulated wrinkle pattern at $T = T_{\mathrm{crit}}$ of the Ising-modell in c).

Generating structures with the given model offers two possibilities to aim the goals of this project. First, methods for profile characterization can be tuned and tested on well-defined structures with a given degree of structural order. Second, the structural order and morphologies will be linked to the optical properties of the wrinkled structures and their ability to show random lasing[4,5].

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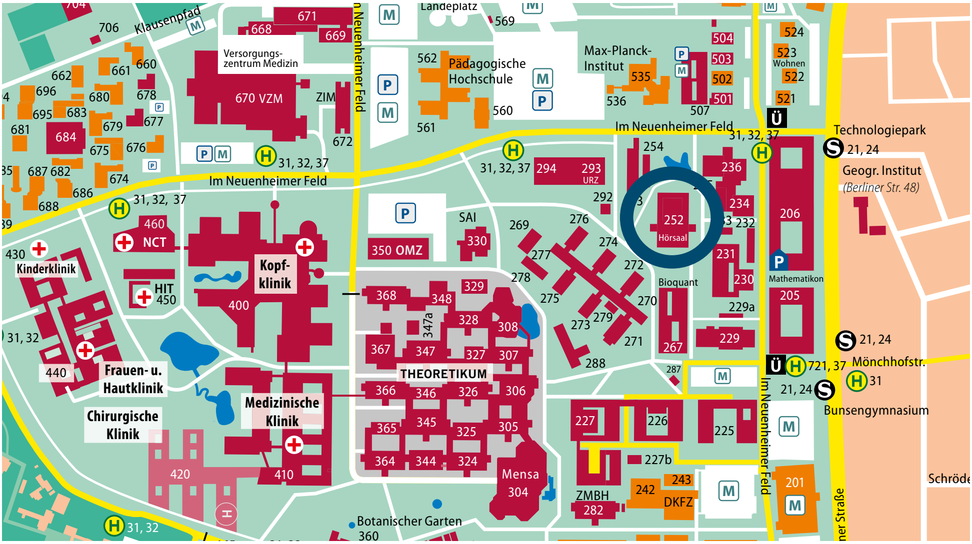

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