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MATERIALS FOR ORGANIC ELECTRONICS: SYNTHESIS, SPECTROSCOPY AND THEORY

10 – 11 June, 2022
Heidelberg, Germany

Book of Abstracts

CONTENTS

Conference Chair

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Registration Desk Opening Hours

Friday, June 10: 08:30 am – noon
Saturday, June 11: 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 10th, 2022

8:30 AM	Registration
9:30 AM	Opening
Chair: Jana Zaumseil (Universität Heidelberg)	
9:40 AM	**Keynote Lecture** **Charge transport and thermoelectric physics of high mobility conjugated polymers** *Henning Sirringhaus, University of Cambridge*
10:30 AM	**High-Frequency Flexible Organic Thin-Film Transistors** *Hagen Klauk, Max-Planck-Institut für Festkörperforschung Stuttgart*
11:00 AM	Coffee Break
Chair: Lutz H. Gade (Universität Heidelberg)	
11:30 AM	**Imide-functionalized Nanographenes: Synthesis, Supramolecular Chemistry and Functional Properties** *Frank Würthner, Universität Würzburg*
12:10 PM	**Investigating Mixed Conduction in Conjugated Polymers for Bioelectronics Applications** *Sahika Inal, King Abdullah University of Science and Technology*
12:50 PM	Lunch
Chair: Uwe Bunz (Universität Heidelberg)	
02:00 PM	**Humidity & Electrochemical Switching of Mixed Conducting Polymer Films** *Sabine Ludwigs, Universität Stuttgart*
02:40 PM	**Novel organic ferroelectrics** *Martijn Kemerink, Universität Heidelberg*
03:10 PM	Coffee Break
Chair: Andreas Dreuw (Universität Heidelberg)	
03:40 PM	**Energy and Charge Transfer between Organic Molecules and Semiconductor Nanocrystals** *Troy Van Voorhis, Massachusetts Institute of Technology*
04:20 PM	**Ultrafast Spectroscopy of N-heteropolycycles** *Tiago Buckup, Universität Heidelberg*
04:50 PM	**Ultrafast dynamics of energy transfer in molecular dyads and multichromophoric systems** *Josef Wachtveitl, Universität Frankfurt*
05:30 PM	**Poster Session**
07:00 PM	Conference Buffet Dinner

SATURDAY, June 11th, 2022

Chair: Petra Tegeder (Universität Heidelberg)	
9:30 AM	**Keynote Lecture** **High Performance Organic Electronics** *Karl Leo, Technische Universität Dresden*
10:20 AM	**Controlling aggregation of N-heteropolycycles** *Claudia Backes, Universität Kassel*
10:50 AM	Coffee Break
Chair: Stephen Hashmi (Universität Heidelberg)	
11:20 AM	**Bridged Triarylamines Incorporating 7-Membered Rings as Versatile Electron Donors** *Milan Kivala, Universtät Heidelberg*
11:50 AM	**Monkeysaddles and other Contorted Polycyclic Aromatic Compounds** *Michael Mastalerz, Universität Heidelberg*
12:20 PM	Lunch buffet and **Poster Session**
Chair: Marcus Elstner (KIT Karlsruhe)	
01:30 PM	**Structural and Reactivity Patterns in N-Heteropolycyclic Radicals** *Ganna Gryn'ova, Heidelberg Institute for Theoretical Studies*
02:00 PM	**Molecular quantum dynamics in the strong coupling regime** *Oriol Vendrell, Universität Heidelberg*
02:30 PM	**Porphyrin-based molecular wires and nanorings** *Harry L. Anderson, University of Oxford*
03:10 PM	**Concluding Remarks**
03:30 PM	End of the Symposium

SPEAKER ABSTRACTS

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POSTER ABSTRACTS

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

An Efficient Short-Wave Infrared Organic Photodetector Realized by Intermolecular Charge Transfer Mediated Coupling Based on Squaraine Dye

Jin Hong Kim,[†] Andreas Liess,[†] Matthias Stolte,[†] Ana-Maria Krause,[†] Vladimir Stepanenko,[†] Chuwei Zhong,[‡] David Bialas,[†] Frank C. Spano,[‡] Frank Würthner*,[†]
[†]*Institut für Organische Chemie and Center for Nanosystems Chemistry, Universität Würzburg, Am Hubland, 97074 Würzburg, Germany*
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A highly sensitive short-wave infrared ($\lambda > 1000$ nm) bulk heterojunction organic photodiode (OPD) composed of a self-assembling dicyanovinyl-functionalized squaraine dye (SQ-H) donor and $PC_{61}BM$ acceptor is investigated.[1] By thermal annealing, dipolar SQ-H dyes aggregate into nanoscale slipped stack structure with intermolecular charge transfer mediated J-type coupling, resulting in a red-shifted and narrow absorption band at 1040 nm.[1,2] The optimized OPD exhibits an external quantum efficiency of 12.3% and a full-width at half-maximum of only 85 nm (815 cm^{-1}) at 1050 nm under 0 V. Taking advantage skin penetrating ability of infrared light, transmission mode photoplethysmography application for heart-rate monitoring is successfully demonstrated with a self-power operating SQ-H flexible OPD.

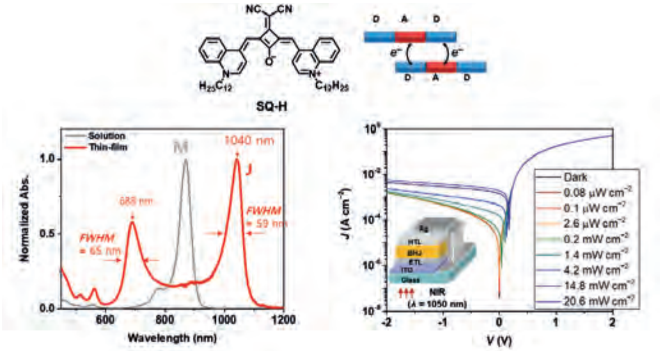

Figure 1. (Top) Chemical structures of SQ-H and schematic intermolecular charge transfer mediated J-type coupling molecular packing structure of SQ-H. (Bottom left) Normalized UV-Vis-NIR absorption spectra of the SQ-H solution and annealed thin film. (Bottom right) representative *J*-*V* characteristics of the SQ-H:$PC_{61}BM$ bulk heterojunction OPD under 1050 nm light illumination

Reference

(1) J. H. Kim, A. Liess, M. Stolte, A.-M. Krause, V. Stepanenko, C. Zhong, D. Bialas, F. Spano, F. Würthner, *Adv. Mater.* **2021**, *33*, 2100582.
(2) J. H. Kim, T. Schembri, D. Bialas, M. Stolte, F. Würthner, *Adv. Mater.* **2021**, 2104678.

Dimerization Leading to Fourfold Formation of σ-CC-bonds and Cumulenization

Kathleen Fuchs[a], Samara M. Rivero[b], Frank Rominger[a], Jan Freudenberg[a], Juan Casado Córdon[b], Uwe H. F. Bunz[a]

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Diradicals are molecules with two unpaired electrons characterized by the diradical index y_0 (y_0=0 closed shell, y_0=1 100% open-shell structure).[1] Some diradicals with small to medium diradical character form a quinoid/aromatic resonant hybrid structure, whereas others form long and therefore weak intermolecular sigma CC-bonds[2] and can undergo dynamic covalent chemistry (DCC).

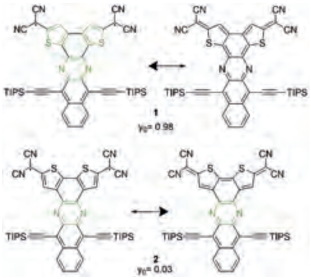

Figure 1: Mesomeric structures of target molecule **1** and **2** and their calculated diradical character.

We prepared two dicyanomethylene substituted benzodithienophenazines regioisomers in which the relative orientation of the sulfur atoms is critical to turn on the diradical character - an variation of a design strategy previously reported with azaacene-extended phenoxyylbithiophene.[3] Figure 1 shows two mesomeric structures and the calculated diradical character of the desired molecules **1** and **2**. Target **2** is a closed shell system - the *para*-quinodal segment is cross-conjugated to the azaacene core. The calculated diradical character for the *ortho*-isomer **1** is as high as y_0=0.98 due to a fully integrated electronically system. The generation of three Clar sextets provide the driving force for the diradical ground state. Instead of the diradical we isolated dimer **1a** after oxidation of its dihydro precursor. The *ortho*-isomer dimerized under formation of four elongated C-C bonds (1.6 Å) to a covalent cage, exhibiting a quinoid-cumulene structure (see Figure 2).

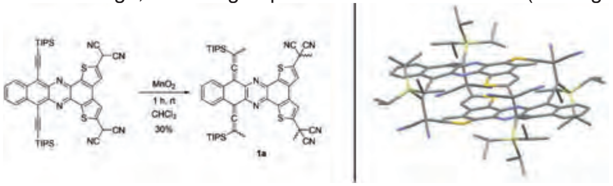

Figure 2: Reaction towards dimer **1a** (left). Crystal structure of **1a** at 200 K (right).

References

(1) a) K. Yamaguchi, *Chem. Phys. Lett.* **1975**, *33*, 330. b) D. Döhnert, J. Koutecky, *J. Am. Chem. Soc.* **1980**, *102*, 1789.
(2) J. L. Zafra, L. Qiu, N. Yanai, T. Mori, M. Nakano, M. Pena Alvarez, J. T. López Navarrete, C. J. Gómez-Garcia, M. Kertesz, K. Takimiya, J. Casado, *Angew. Chem. Int. Ed.* **2016**, *55*, 1463-14568.
(3) S. N. Intorp, M. Hodecker, M. Müller, O. Tverskoy, M. Rosenkranz, E. Dimitrieva, A. A. Popov, F. Rominger, J. Freudenberg, A. Dreuw, U. H. F. Bunz, *Angew. Chem. Int. Ed.* **2020**, *59*, 12396-12401.

Ultranarrow Bandwidth Semitransparent Organic Photodiodes by Social Self-sorting of Merocyanine Dyes

Tim Schembri, Jin Hong Kim, Vladimir Stepanenko, Matthias Stolte, Frank Würthner*
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Two dipolar merocyanines consisting of the same π-conjugated chromophore core but different alkyl substituents are investigated.[1] These dyes adopt different packing arrangements due to the sterical demand of their donor moieties in their respective solid state with either H- or J-type exciton coupling. This leads to ultranarrow absorption bands at 477 nm and 750 nm, respectively, due to exchange narrowing.[2] The social self-sorting behavior of these push-pull chromophores in their mixed thin films is evaluated and the impact on morphology as well as opto-electronical properties is determined. The implementation of this well-tuned two-component material with tailored optical features allowed us to optimize planar heterojunction organic photodiodes with **C_{60}** fullerene with either dual or single wavelength selectivity in the blue and NIR spectral range with ultranarrow bandwidths of only 11 nm (200 cm^{-1}) and an external quantum efficiency of up to 18% at 754 nm under 0 V bias. The application of these photodiodes as low-power consuming heart rate monitors was demonstrated by reflectance pulse oximetry photoplethysmography.

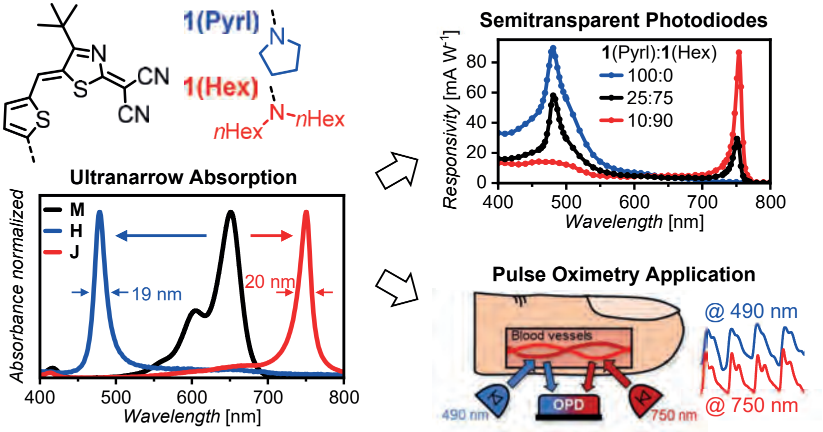

Figure 1. Chemical structures of the investigated merocyanine dyes **1(Pyrl)** and **1(Hex)** including their solid-state absorption spectra in annealed thin films as well as the resulting ultranarrow responsivity spectra of their semitransparent photodiodes and a schematic depiction of the demonstrative application of these photodiodes for pulse oximetry.

Reference

(1) T. Schembri, J. H. Kim, A. Liess, V. Stepanenko, M. Stolte, F. Würthner, *Adv. Opt. Mater.* **2021**, *9*, 2100213.
(2) A. Liess, A. Arjona-Esteban, A. Kudzus, J. Albert, A.-M. Krause, A. Lv, M. Stolte, K. Meerholz, F. Würthner, *Adv. Funct. Mater.* **2019**, *29*, 1805058.

High Resolution Electronic Excitation Spectra of Benz[a]- and Benz[c]acridine Monomers and Noncovalent Dimers by Matrix Isolation Spectroscopy

Stefan Germer, Olaf Hübner and Hans-Jörg Himmel

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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 linked 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 are now being investigated. For benz[a]- and benz[c]acridine, it has been observed that they indeed show a higher tendency to form dimers. This finding will allow future studies to investigate the electronic properties of such dimers more specifically.

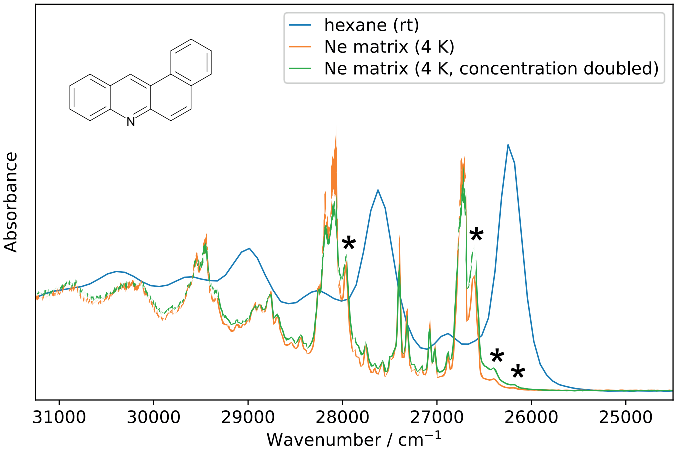

Figure 1. Comparison of electronic excitation spectra of benz[a]acridine in hexane at room temperature and two solid Ne matrices of different concentration at 4 K. With less neon used and thus a higher concentration of the analyte, an increase in the intensity of the absorbance bands associated with dimers can be observed (asterisks).

References

(1) J. Thusek, M. Hoffmann, O. Hübner, O. Tverskoy, U. H. F. Bunz, A. Dreuw, H.-J. Himmel, *Chem. Eur. J.* **2019**, *25*, 15147-15154.
(2) J. Thusek, M. Hoffmann, O. Hübner, S. Germer, H. Hoffmann, J. Freudenberg, U. H. F. Bunz, A. Dreuw, H.-J. Himmel, *Chem. Eur. J.* **2021**, *27*, 2072-2081.

Synthesis and Study of Spiro-bridged *N*-Heterotriangulenes with Multiple Cyano Functions

Angelina Jocic[a], Svenja Höhne[a], Frank Rominger[a], Thomas Oeser[a],
Andreas Dreuw[a], and Milan Kivala[a]*

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In 2020, our group presented a nitrogen-centered trispirocyclic *N*-heterotriangulene.[1] 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. The compound underwent a reversible one-electron oxidation to form a nitrogen-centered radical cation with considerably enhanced stability.[2] Nevertheless, at that time further functionalization of this appealing multispirocyclic scaffold was not possible due to the blocking *tert*-butyl groups. To investigate the impact of functionalization on the optoelectronic and structural properties, we have established herein a reliable methodology providing for selective cleavage of the *tert*-butyl groups followed by various synthetic transformations. A series of compounds differing in the number and position of the electron-withdrawing cyano groups was realized through this approach. Depending on the substitution pattern the compounds display dramatically altered optoelectronic and redox properties which were studied both in experiment and theory.

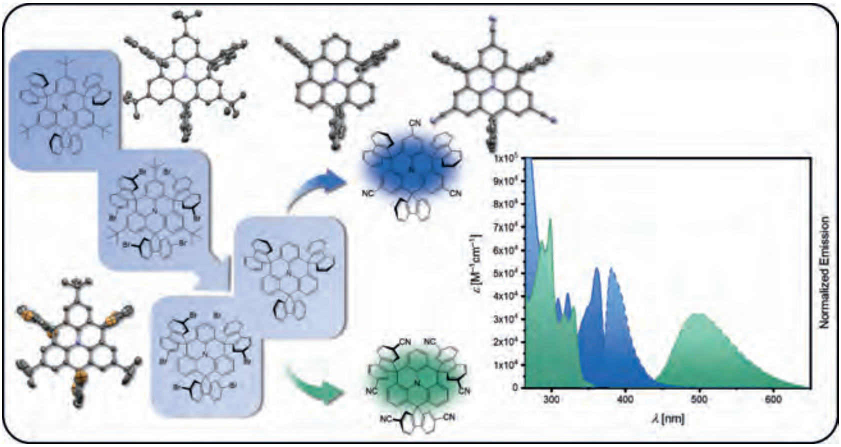

Figure 1. Evolution of the novel series of functionalized spirofluorene-bridged *N*-heterotriangulenes and their UV/Vis absorption (solid lines) and emission (dashed lines) spectra recorded in THF at room temperature.

Reference

(1) M. Krug, M. Wagner, T. A. Schaub, W. Zhang, C. M. Schüßlbauer, J. D. R. Ascherl, P. W. Münich, R. R. Schröder, F. Gröhn, P. O. Dral, M. Barbatti, D. M. Guldi, M. Kivala, *Angew. Chem. Int. Ed.* **2020**, *59*, 16233.

(2) T. A. Schaub, T. Mekelburg, P. O. Dral, M. Miehlich, F. Hampel, K. Meyer, M. Kivala, *Chem. Eur. J.* **2020**, *26*, 3264.

Tetraazaperopyrenes: towards molecular properties in crystals II

M. T. Wachter-Lehn, K. Fink, S. Höfener

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Tetraazaperopyrenes (TAPPs) show promising semiconducting properties. In particular, the crystallization and the resulting overlap leads to a significant impact on the 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.

To investigate the electronic properties, we present the development of a 1D periodic extension of wavefunction methods combined with frozen-density embedding (FDE).[1] The convergence in the periodic chain is obtained smoothly within a small number of relaxation cycles. The FDE method for a 1D environment can be used in combination with all methods available in the KOALA program.

Introducing perturbations such as excited states or charges leads to a perturbation of the target subsystem, e.g. a TAPP dimer. This perturbation polarizes an active region around the target subsystem within the 1D periodic environment.[2] In this new approach, the polarized subsystems show only little dependence with respect to the size of the active region, allowing for small active regions and avoiding the periodic repetition of the perturbation.

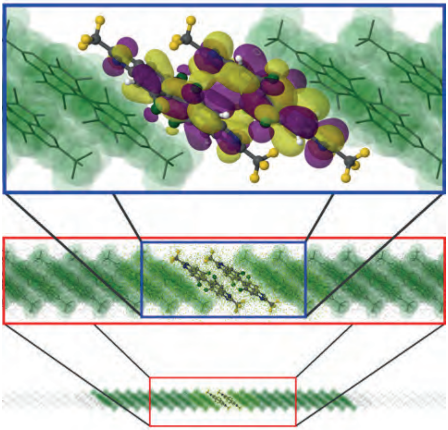

Figure 1. TAPP dimer located in a 1D environment. Green spheres show effective potentials employed on the environment atoms to prevent excited-state charge spill out.

Reference

(1) K. Fink, S. Höfener, *J. Chem. Phys.* **2021**, *154*, 104114.
(2) M. T. Wachter-Lehn, K. Fink, S. Höfener, *submitted for publication*.

Tetraazaperopyrenes: towards molecular properties in crystals I

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Tetraazaperopyrenes (TAPPs) show promising semiconducting properties. In particular, the crystallization and the resulting overlap leads to a significant impact on the semi-conducting 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.

To identify relevant geometries, we investigate molecular crystals of various TAPP compounds in different crystal packings using density functional theory (DFT) with periodic boundary conditions.[1] The accuracy is assessed for those compounds which were obtained experimentally earlier, while most of the theoretically investigated compounds were not obtained experimentally so far. The stable geometries are explained not only in terms of thermodynamic stability, but also short contacts are analyzed, serving as a measure for the kinetic stability.

In most cases, energy differences between different crystal systems are rather subtle and a definite prediction remains challenging. To illustrate properties beyond geometry and energy, the electronic gap is computed for the optimized bulk phase geometries, serving as a qualitative measure for the semi-conducting properties of the molecular crystals.

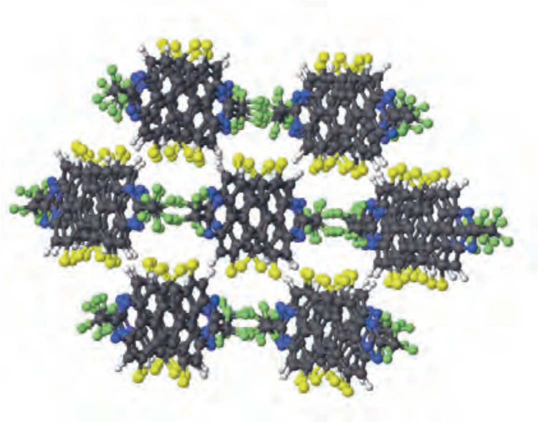

Figure 1 Extracted cluster from a bulk DFT optimization.

Reference

(1) J. Liu, S. Höfener, *manuscript in preparation.*

Polarization Dependent Photoinduced Supramolecular Chirality in High-Performance Azo Materials

Sekvan Bagatur, Marcel Schlesag, Thomas Fuhrmann-Lieker

Physical Chemistry of Nanomaterials
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Here, we report about photoinduced supramolecular chirality (PSC) using *l*-EPL on high-performance azo polymers, which are known for their high optical birefringence.[1,2] For this purpose, we investigate the temporal progression of azimuthal rotation upon exposure and its dependence on film thickness. By polarimetric measurements, we found out that the azimuthal rotation gets higher with layer thickness. The comparison of literature values for the azimuthal rotation in relation to its layer thickness *d* shows that our measured value of $\Delta\psi$ = 112.5 °/µm is, to our knowledge, the highest measured azimuthal rotation in amorphous PMMA-backboned side-chain azo polymers. The inscribed chirality was stable for several days.

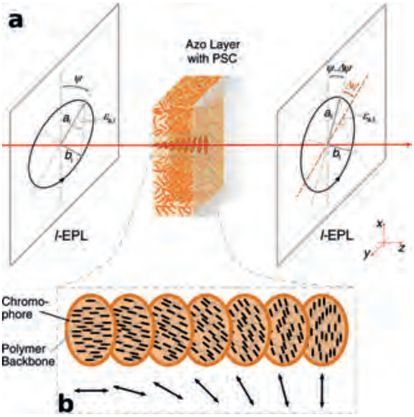

Figure 1. Schematical visualization of optical rotation and a possible explanation for molecular rearrangement upon irradiation with excitation beam.

We can assume that light-treatment with EPL results in supramolecular chirality (Fig. 1). Therefore, the azimuthal angle of analysis beam rotates while traversing the PSC (Fig. 1a). We can imagine this as twisted layers of azo groups with the same mean orientation (Fig. 1b)—comparable with a director in liquid crystals. The time dependency may be explained by a two-step process: (1) fast *trans*-*cis*-isomerization resulting in photo-orientation and (2) slow photo-induced mass flow.

Reference

(1) S. Bagatur, M. Schlesag, T. Fuhrmann-Lieker, *Molecules* **2021**, *26*, 2842.
(2) S. Bagatur, T. Fuhrmann-Lieker, *J. Eur. Opt. Soc.* **2019**, *15*, 12.

Switching behavior of dip-coated organic ferroelectric trialkylbenzene-1,3,5-tricarboxamide (BTA)

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Organic ferroelectrics 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 prealign the molecules. 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. Dip-coated films were characterized for different BTA concentrations and dip-coating velocities. The ferroelectric switching behavior was investigated using the Double Wave Method (DWM). The effect of dip-coating on the ferroelectric switching speed was analyzed. Furthermore, the change of the temperature at which ferroelectric switching starts was investigated. Landau-Levich and evaporation regimes were established via the formation of different morphologies in the dip-coated films and compared to other results.[1] The analysis of the ferroelectric switching revealed that dip-coating perpendicular to the electrodes leads to an almost perfect in-plane alignment of the supramolecular polymers. The observed ferroelectric switching behavior was equal to films which were aligned via the conventional field-annealing. Furthermore, a significant reduction in temperature needed for the ferroelectric switching to start was observed for slower dip-coating velocities. Hence, dip-coating allows for enhanced ferroelectric switching in BTA-C8, which we anticipate can be applied to other molecular ferroelectrics.

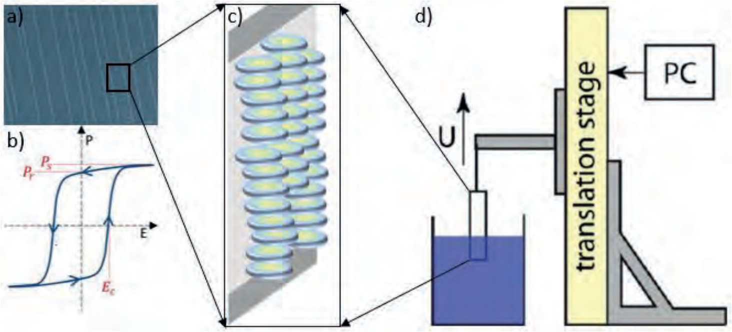

Figure 1. A typical **a**) polarization image of a dip-coated film and **b)** hysteresis curve of ferroelectric switching measurement obtained from a **c)** BTA film which is aligned in-plane via a **d)** dip-coating setup. Figure 1d is taken unchanged from [1]. Permission for usage granted by ACS Publications.

Reference

(1) R. Z. Rogowski, A. A. Darhuber, *Langmuir* **2010**, 26, 11485.

Tetra(*peri*-naphthylene)anthracene revisited: A reliable access to a new family of four-stage amphoteric near-IR fluorophores

Sabine Frisch,[a] Christian Neiß, Sebastian Lindenthal, Nicolas F. Zorn, Frank Rominger, Andreas Görling, Jana Zaumseil, Milan Kivala[a]*

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Back in 1959, Maximilian Zander described the synthesis and attractive properties such as bathochromically shifted UV/vis absorption and red fluorescence of tetra(*peri*-naphthylene)-anthracene (**TPNA**).[1] However, the originally described synthesis used hazardous picric acid and extremely harsh reaction conditions, which most likely precluded further studies of **TPNA** in the context of optoelectronic materials.[1,2]

We have developed an alternative facile synthetic strategy towards a soluble **TPNA** derivative bearing triisopropylsilyl- (TIPS)-ethynyl moieties at the anthracene core, which opened the way for detailed investigation of the optical and electrochemical properties of **TPNA** scaffolds. **TIPS-TPNA** shows bathochromically shifted absorption bands with λ_{max} at 702 nm. Interestingly, the emission maxima are also bathochromically shifted into the near-infrared region with two maxima at 718 nm and 786 nm and a tail reaching to 930 nm. The fluorescence is characterized by a surprisingly narrow Stokes shift of 317 cm^{-1} and a photoluminescence quantum yield of 0.19. Moreover, the emission was also observed in thin films fabricated by spin-coating. The newly gained solubility of **TIPS-TPNA** pioneers the evaluation of the electrochemical properties, revealing a four-stage amphoteric redox behavior of the compound.[3] With these appealing features, **TIPS-TPNA** is considered to be a highly interesting scaffold for the development of new optoelectronic materials.

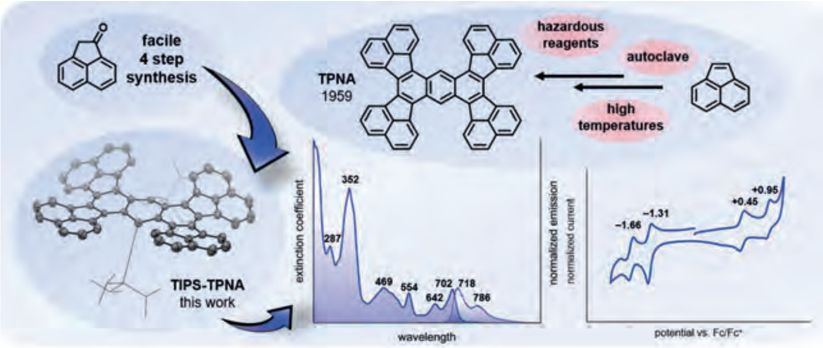

Figure 1. Schematic overview of the improved synthesis towards **TPNA** scaffolds together with the unusual photophysical and redox properties of **TIPS-TPNA**.

References

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Matrix isolation of N-heteropolycyclic compounds

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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.

N-Heteropolycyclic molecules are promising candidates as constituents of organic semiconductor materials. Therefore, their characterization is of particular interest. Samples of 6,13-diaza-pentacene enclosed in solid Ne at 4 K have been prepared, and absorption spectra in the visible region as well as emission spectra have been recorded[1] (see Figure 1). For 6,13-diaza-pentacene, a vibrationally resolved electronic transition has been observed at 17664 cm^{-1} and could be assigned by quantum chemical calculations. Furthermore, there is evidence for the formation of dimers.

Pyridine is a prototype N-heterocyclic compound. To study in particular the formation of dimers, samples of pyridine in solid Ne have been generated and investigated by IR spectroscopy. The spectra indeed furnish evidence for dimer formation. Quantum chemical calculations yield information about different dimer structures and support the assignment of the observed spectra.

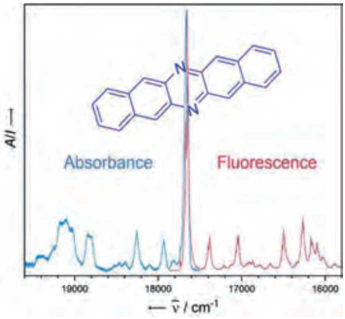

Figure 1. Absorption and emission spectra of diaza-pentacene isolated in solid Ne.

Reference

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Bridged triarylamines incorporating a seven-membered ring: The evolution of structural and electronic properties

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Effective π-conjugation represents a promising approach to influence the electron-donor properties of triphenylamine-based compounds.[1,2] In this contribution, a class of doubly pentagon-fused triphenylamines is presented, starting with the smallest member without a third bridging unit,[3] continuing with an ethylene-bridged compound incorporating a seven-membered ring, up to a fully planar vinylene-bridged system.[4] The compounds were obtained in high-yielding synthetic protocols and their electronic, structural, and photophysical properties were thoroughly analyzed both in experiment and theory. Particularly the vinylene bridge does not only support efficient π-conjugation but also allows for further functionalization, as to a 1,2-diketone, enabling subsequent condensation reactions with 1,2-phenylenediamines. The vinylene-bridged compound with its promising electron-donor properties was successfully co-crystallized with the paradigmatic acceptor molecules TCNE, TCNQ, and F_4TCNQ and the resulting charge-transfer complexes were characterized.

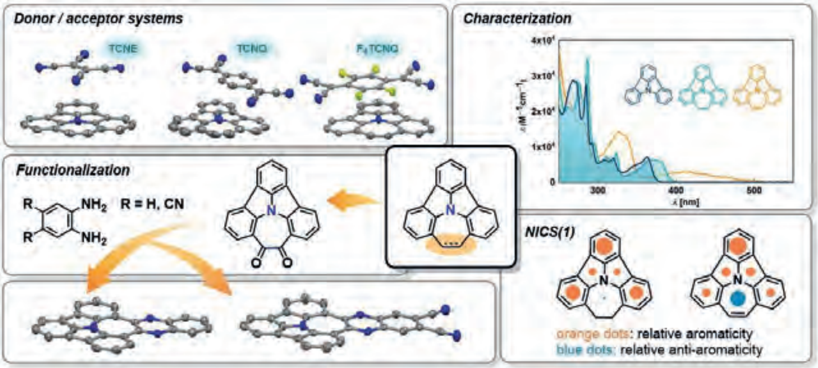

Figure 1. A newly established family of fully bridged triphenylamines.

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Hybrid Spintronic Materials from Conducting Polymers with Molecular Quantum Bits

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Alexander Allgaier,[a] Yannic M. Gross,[b] Stefan Bechler,[c] Hannes S. Funk,[c] Li-Te
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Hybrid materials consisting of organic semiconductors and molecular quantum bits is a promising platform for quantum spintronic applications. For this aim, it is fundamental to investigate such materials to elucidate both the electrical and quantum dynamical properties of the same material. Here we present the preparation of a prototype hybrid material, composed by the incorporation of a molecular spin qubit in a conducting polymer. Organic field-effect transistor measurements demonstrate that the favorable electrical properties are preserved in the presence of the qubits. Chemical doping introduces charge carriers into the material, and variable-temperature charge transport measurements reveal the existence of mobile charge carriers at temperatures as low as 15 K. Importantly, quantum coherence of the qubit is shown to be preserved up to temperatures of at least 30 K, that is, in the presence of mobile charge carriers.[1]

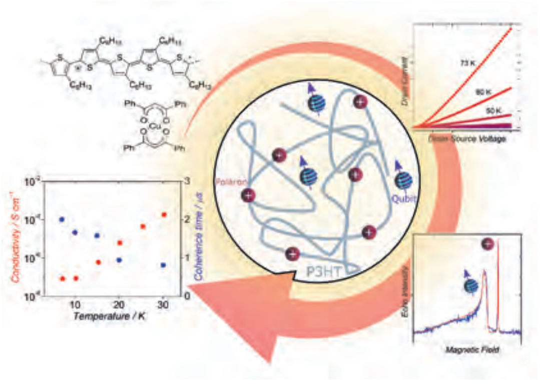

Figure 1. Schematic overview of the work presented. The molecular spin quantum bits, [Cu(dbm)$_2$], are dispersed into a conducting polymer, P3HT, which is chemically doped with F4TCNQ. The transport properties as a function of temperature, as well as the spin dynamics of the resulting hybrid material are investigated.

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Stabilizing Heptacenes

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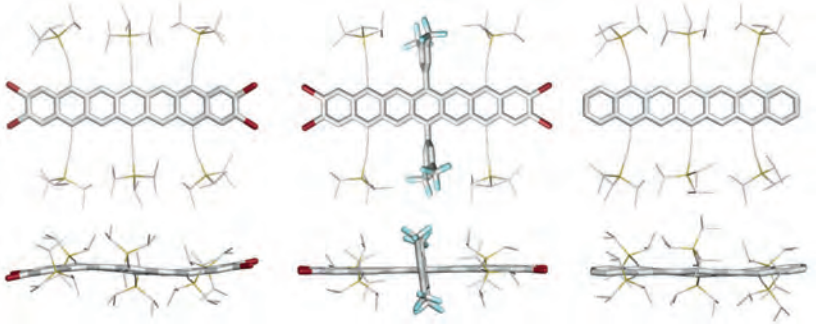
Synthesis of larger acenes is challenging due to their decreased solubility and increased tendency to decompose.[1-2] Soluble acenes larger than hexacene are rare, and they are not stable enough for device applications.[3]

The predominant strategy to stabilize the higher acenes is functionalization with trialkylsilylethynyl substituents.[4] In this contribution, we employed a modular synthetic approach to access a sixfold TIPS-ethynylated and fourfold brominated long-lived, soluble heptacene and compare it to its non-halogenated or diphenylated congeners. The substitution pattern prevents electrocyclic dimerization and oxidation under ambient conditions and leads to a huge increase of stability. This was not only demonstrated via UV/vis measurements but also by the first application of a soluble heptacene in thin-film transistors as well as the first postfunctionalization of a heptacene via Stille coupling. This π-extension led to a persistent tetrabenzononacene, which also has a longer lifetime than its arylated homolog reported previously.[5] Additionally, we investigated the redox chemistry of one of the heptacenes and characterized its monoanion and monocation.



Scheme 1. X-ray single crystal structures of the reported heptacenes (top and side view).

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Synthesis of chiral Octaazaperopyrenediones (OAPPDOs)

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Octaazaperopyrenediones (OAPPDOs) are a new class of highly emissive perylene derivatives. In contrast to the perylene based PDIs,[1,2] the aromatic core is reversely connected to the amide function in the peri position (C-NCO instead of C-CON). The synthesis of the OAPPDO parent compound as well as its bay chlorinated derivatives with different N substitution patterns (H, alkyl, benzyl) is reported. Furthermore, access to a series of bay arylated OAPPDOs was gained through Suzuki cross coupling which resulted in the formation of helically chiral OAPPDO derivatives. The electrochemical and photo physical properties were investigated by UV/Vis and fluorescence spectroscopy as well as cyclic voltammetry. The *P*- and *M*-enantiomers of a phenylated OAPPDO were isolated by semipreparative HPLC column chromatography and could be analyzed by CD-spectroscopy. The experimental data were supported by DFT-modeling as well as the mechanism of the isomerization and the CD spectrum (TDDFT). The stable radical cation of an alkylated OAPPDO was generated through 1e$^-$ oxidation and characterized by EPR spectroscopy. The reversible redox process was investigated by UV/Vis spectroscopy in a spectroelectrochemical cell.

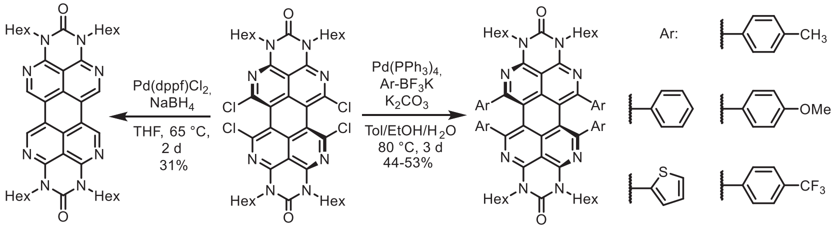

Figure 1. Synthetic route towards the OAPPDO parent compound and its bay arylated derivatives.

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Investigation of a hybrid spintronic system for electrical readout of molecular spins

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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. Presently, such qubits are mostly controlled and manipulated by using electron paramagnetic resonance (EPR) techniques, which is inherently insensitive because of the limited energy content of a microwave photon (tens of μeV). An electrical detection of such qubits can increase the spatial sensitivity of detection, in principle down to the single-qubit limit and shall also allow easy integration with the external control electronics[1]. Here, we investigate a hybrid system consisting of molecular qubits (MQBs) and semiconducting polymers as a platform to enable an electrical readout. We choose poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b] thiophene] (PBTTT), a conjugated polymer with large charge carrier mobility (~1 cm^{2}V^{-1}s^{-1}) as our conductive host and a molybdenum-based complex as the MQB. We perform Organic Field-Effect Transistor (OFET) measurements to assess the influence of the MQBs on the charge transport and pulsed EPR measurements to measure the phase coherence of the qubit in the presence of charge carriers. Preliminary results of OFET measurements on pristine polymer films are shown below.

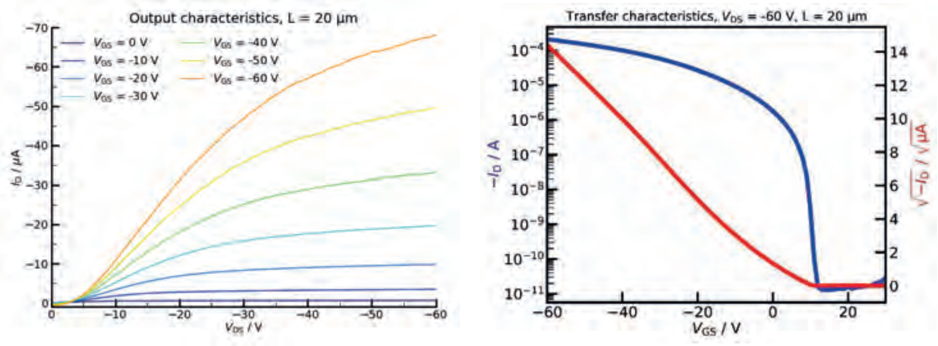

Figure 1. Output (left) and transfer characteristics (right) measured on PBTTT films deposited on OFET substrates of channel length, L = 20 μm by spin-coating.

In this system, the interaction between qubit spins and charge carriers is based on the spin-dependent recombination of charge carriers[2]. This provides a mechanism to enable electrical addressing of the qubit.

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Synthesis and Characterisation of a Stable, Carbon-centred Helical Radical

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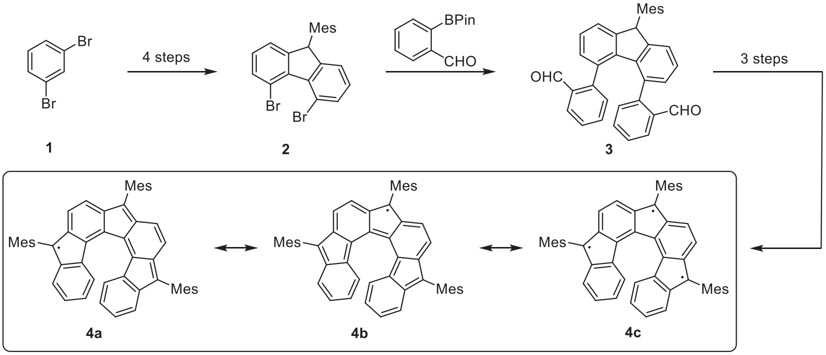
Polycyclic aromatic hydrocarbons (PAHs) have since long been the subject of research in organic chemistry. Their discovery and investigation contributed with aromaticity itself to a fundamental concept of chemistry that is still discussed today. Due to special optoelectronic properties, they also offer many possibilities in terms of material science. The incorporation of five-membered cyclopentane rings into PAHs, which are most generally composed of fused benzene rings leads to cyclopenta-fused polyaromatic hydrocarbons (CP-PAHs). If an odd number of these five-membered rings is present, a radical structure inevitably results for the neutral compounds.[1]

We have synthesized and examined a helical CP-PAH built from three five-membered and four six-membered rings.[2]



Scheme 1. Synthetic route to a helical radical.

Starting from 1,3-dibromobenzene (**1**) the assembly was achieved by double *Suzuki* coupling of fluorene **2**, introduction of the mesityl groups by nucleophilic addition, and ring closure. The fully conjugated helicene **4** was obtained by final oxidation. The structure was confirmed by X-ray crystallographic analysis and physical and spectroscopic properties were investigated by EPR, UV/Vis and cyclic voltammetry. Accompanying quantum chemical calculations were performed to determine further features (e.g. spin densities, orbital energies, aromaticity).[2]

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Modeling Charge Transport in Organic Semiconductors

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The trajectory surface hopping (TSH) method is nowadays widely applied to study the charge/exciton transport process in organic semiconductors (OSCs). In the present study, we systematically examine the performance of two approximations in the fewest switched surface hopping (FSSH) simulations for charge transport (CT) in several representative OSCs. These approximations include (i) the substitution of the nuclear velocity scaling along the nonadiabatic coupling vector (NCV) by rescaling the hopping probability with the Boltzmann factor (Boltzmann correction (BC)) and (ii) a phenomenological approach to treat the quantum feedback from the electronic system to the nuclear system (implicit charge relaxation (IR)) in the OSCs. We find that charge mobilities computed by FSSH-BC-IR are in very good agreement with the mobilities obtained by standard FSSH simulations with explicit charge relaxation (FSSH-ER), however, at reduced computational cost. A key parameter determining the charge carrier mobility is the reorganization energy, which is sensitively dependent on DFT functionals applied. By employing the IR approximation, the FSSH method allows systematic investigation of the effect of the reorganization energies obtained by different DFT functionals like B3LYP or ωB97XD on CT in OSCs. In comparison to the experiments, FSSH-BC-IR using ωB97XD reorganization energy underestimates mobilities in the low-coupling regime, which may indicate the lack of nuclear quantum effects (e.g., zero point energy (ZPE)) in the simulations. The mobilities obtained by FSSH-BC-IR using the B3LYP reorganization energy agree well with experimental values in 3 orders of magnitude [1]. The accidental agreement may be the consequence of the underestimation of the reorganization energy by the B3LYP functional, which compensates for the neglect of nuclear ZPE in the simulations (Figure 1).

This method is used to calculate electron mobility for n-type material. The development of n-type materials still largely lags behind p-type ones because of the deficiency of the high-performance materials. To the best of our knowledge, only four n-type organic semiconductors have been reported to exhibit field effect mobility higher than 10 cm2 V−1 s−1. One of them is 6,13-bis((triisopropylsilyl) ethynyl)-5,7,12,14-tetraazapentacene (TIPS-TAP), which is also the most successful member of the N-heteroacene family for applications in OFETs [2]. Recently, many theoretical and experimental studies have shown that the introduction of electron-withdrawing groups through, for example, halogenation (–Br and –Cl), is a promising way to transform p-type semiconductors into n-type ones. The rationalization of the change in the charge transfer is under debate, and so far there has been no evidence that modifying organic molecules with electron-withdrawing groups has a direct impact on the charge transfer properties. The question then becomes: what is the intrinsic impact of the changes in charge transfer in the first place? Structural rearrangements or the kinds and positions of the substituent groups? Understanding the natural mechanism of the charge transport process in these materials is important for the design of better organic materials.

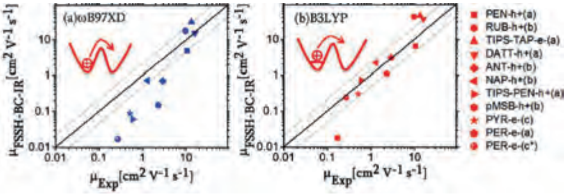

Figure 1. Experimental measured mobilities versus FSSH-BC-IR mobilities obtained using input reorganization energies.

Reference

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Two Dimensional Triptycene End-Capping and Its Influence on the Self-Assembly of Quinoxalinophenanthrophenazines

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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 for 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] The introduction of two triptycene-end-caps on the contrary suppresses a π-π-interaction and leads to an improvement of the solubility.[3] With this in mind, we were interested in expanding the triptycene-end-capping approach to two dimensions, to see how it influences π-stacking properties.

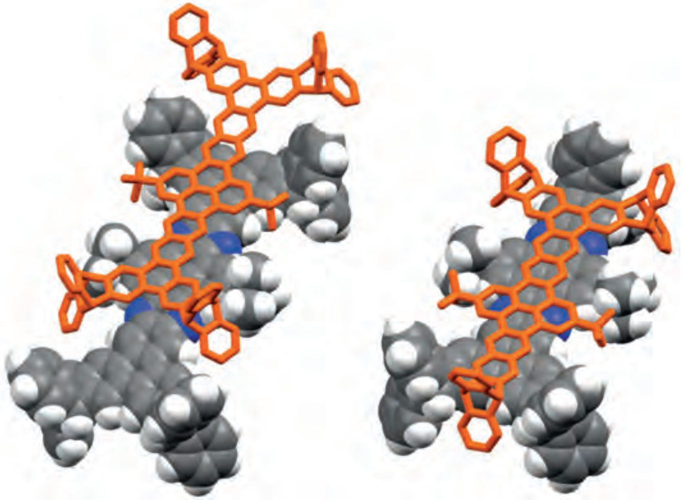

Figure 1. Single crystal X-ray structures of *tetra*-triptycene-end-capped (left) and tri-triptycene-end-capped (right) QPP.

Reference

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N-Heterotriangulenes Donors and Charge Transfer Complexes formed with strong Electron Acceptors investigated with Two-Photon Photoemission Spectroscopy

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Many opto-electronic devices such as organic photovoltaic cells or organic light emitting diodes utilize donor-acceptor-systems (D-A-systems). Triphenylamine derivatives are promising candidates for donors in D-A-systems.[1] The introduction of an etheno-bridge in the planar triphenylamine derivative indolo[3,2,1-jk]carbazole (*N*-HTA-550) creates a seven membered antiaromatic ring in the resulting *N*-HTA-557 (see Fig. 1). While the molecular geometry is mostly preserved, the electronic structure is strongly modified by this additional -C=C-moiety.[2] In the present contribution we study the electronic properties of *N*-HTA-550 and *N*-HTA-557 on a Au(111) surface using two-photon photoemission (2PPE) spectroscopy and temperature programmed desorption (TPD). Furthermore the formation of charge transfer complexes with strong electron acceptors (TCNQ and F4TCNQ) is investigated utilizing both 2PPE and TPD.

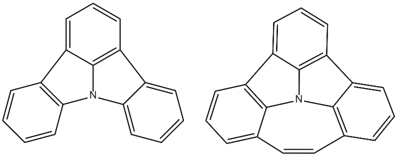

Figure 1. Indolo[3,2,1-jk]carbazole (*N*-HTA-550) and *N*-HTA-557 investigated in the present study.

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N-Heterotriangulenes as Donor Molecules in Charge Transfer Complexes

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N-heterotriangulenes (*N*-HTAs, see Fig. 1 (a) and (b)), are a class of organic electron-transporting semiconductors that belong to *N*-heteropolycyclic aromatic compounds, which are promising candidates for a variety of (opto) electronic applications such as field effect transistors and solar cells.[1, 2]

In this study, temperature-programmed desorption (TPD), vibrational and electronic high-resolution electron energy loss spectroscopy (HREELS) in combination with quantum-chemical theory are utilized to investigate the adsorption and electronic properties of two *N*-HTA derivatives, *N*-HTA-550 and *N*-HTA-557 (see Fig. 1) on Au(111). In addition, formation of charge transfer complexes (CTCs) with *N*-HTAs, acting as donor molecules in combination with two well-known cyano-based electron acceptor molecules, TCNQ and F_4TCNQ (see Fig. 1) is identified.

Our findings indicate that in monolayer and multilayer coverage regime, the *N*-HTA derivatives adapt a planar adsorption geometry parallel to the gold substrate. The identified transition energies of singlet and first triplet states of the molecules show that formation of the 7-membered ring in *N*-HTA-557 by adding the -C=C- bridge leads to a narrowing of the optical gap size by 0.9 eV and a decrease in the first triplet state energy by 1.2 eV. Moreover, all donor/acceptor bilayer systems on Au(111) exhibit low-lying electronic transitions between 0.9 and 2.2 eV, which are attributed to the formation of CTCs.

The results from this study provides important insights into the adsorption geometry and electronic structure of investigated molecules, at the interface with Au(111), within thin film and the formed CTCs. These properties are crucial for optimizing and improving the performance of electronic devices based on the given organic semiconductors.

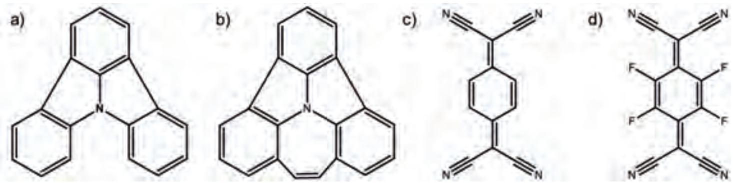

Figure 1. a) *N*-HTA-550 and b) *N*-HTA-557 as the electron donor molecules, c) TCNQ and d) F_4TCNQ as the electron acceptor molecules are investigated in this study.

Reference

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Contact resistance of low-voltage n-channel organic thin-film transistors

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While the performance and stability of p-channel organic thin-film transistors (TFTs) are already sufficient for certain applications, the performance and stability of n-channel organic TFTs are still comparatively poor. We compare the electrical characteristics of low-voltage n-channel organic TFTs based on three promising small-molecule semiconductors with low-lying lowest unoccupied molecular orbital (LUMO) levels, N,N'-bis(2,2,3,3,4,4,4-fluorobutyl)-(1,7 & 1,6)-dicyano-perylene-tetracarboxylic diimide (ActivInk N1100), 2,9-bis(heptafluoropropyl)-4,7,11,14-tetrabromo-1,3,8,10-tetraazaperopyrene (TAPP) and diphenylethyl-3,4,9,10-benzo[de]isoquinolino[1,8-gh]quinolinetetracarboxylic diimide (PhC_2-BQQDI).[1,2,3]

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 both staggered (top-contact) and coplanar (bottom-contact) TFTs. In the coplanar TFTs, the surface of the gold source and drain contacts was treated with one of four chemisorbed thiol interface layers. Overall, the contact resistance (measured using the transmission line method) is smaller in the coplanar architecture due to the contact treatment with the thiols. The treatment with MeSTP results in the best TFT performance for all three semiconductors. Coplanar PhC_2-BQQDI TFTs with MeSTP as thiol for contact treatment provide intrinsic mobilities up to 0.6 cm^2/Vs, on/off ratios up to 10^6, subthreshold slopes as small as 100 mV/decade and a contact resistance as small as 90 Ωcm.

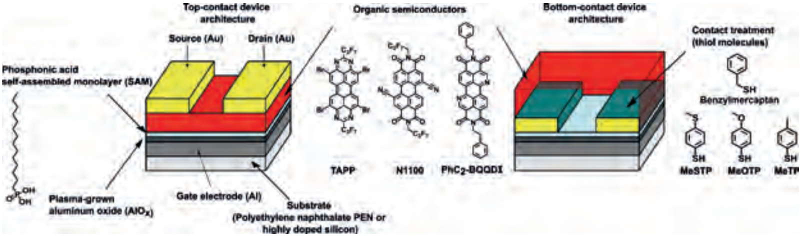

Figure 1. Schematic cross-section of the thin-film transistors in the top-contact (left) and bottom-contact architecture (right) and chemical structures of the three semiconductors (TAPP, N1100 and Ph_2C-BQQDI) as well as the chemical structures of the thiols used for contact treatment.

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Jahn-Teller effect on light polarization and ring currents in a cavity

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Molecular polaritonic states with mixed electronic, vibrational and photonic character are key to cavity-controlled chemistry of a single molecule and of molecular ensembles [1]. Recent contributions indicate that, additionally, the polarization degree of freedom of optical cavities can provide novel ways of controlling Chemistry [2]. Here, we discuss how vibronic couplings in molecules determine the degree of net polarization of polaritonic states. In particular, Jahn-Teller (JT) systems possess the necessary symmetry to couple simultaneously to the two orthogonal cavity polarizations and to mix them. We explore this effect by extending the paradigmatic (E x e) JT Hamiltonian to include the two orthogonal polarizations and show that the JT coupling strongly suppresses the net polarization compared to the photonic states of an empty cavity by at least one order of magnitude, already for moderate vibronic coupling strengths, as compared to the Born-Oppenheimer limit [3]. These mixed-polarization states of the molecule-cavity system can be excited by external circularly polarized light [4]. We study the effect of pulses ranging from a few up to hundreds of femtoseconds. The strong oscillations of the cavity polarization triggered by short (5 fs) pulses hint at the possibilities for attosecond cavity-controlled chemistry. We illustrate further that the ring currents of the polaritonic states undergo similar JT coupling mechanism.

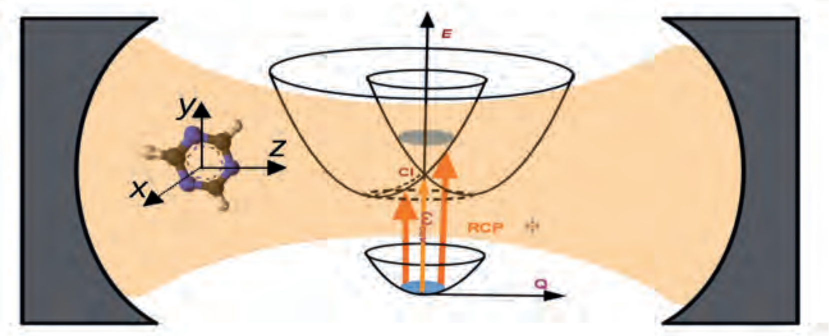

Figure: Schematic of x/y-polarized cavity interacting with JT active sym-triazine molecule. The cavity frequency is resonant with the energy of the JT-active doubly degenerate electronic excited-states from the non-degerate electronic ground state potential of the sym-triazine molecule.

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Synthesis of Imide-Functionalized PAHs Containing Heptagonal Rings by [5+2] Annulation

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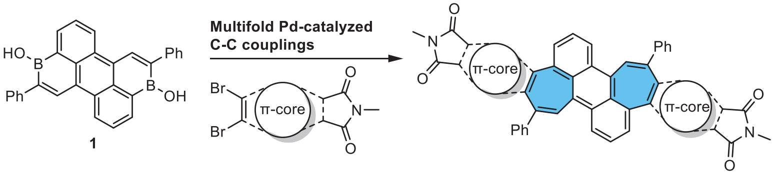
Imide-functionalized polycyclic aromatic hydrocarbons (PAHs) have attracted tremendous attention in various fields such as supramolecular chemistry and materials chemistry due to their intriguing properties. Most of them are based on a rylene core-structure where one or two dicarboximide moieties are attached on both sides of it.[1] Because of the planar rylene scaffold they are planar rigid molecules. Surprisingly, despite recent developments in negatively-curved PAHs,[2][3] there have been few examples of imide-functionalized PAHs with negative curvature. We conjectured that such non-planar imides might be prepared by introduction of odd-membered rings, which gives rise to curved molecules with remarkable optoelectronic properties and versatile topologies. Herein, we present the synthesis of novel imides featuring two heptagonal rings by a twofold Pd-catalyzed [5+2] annulation[4] of 3,9-diboraperylene **1**[5] and suitable dibromo-substituted precursors (Figure 1). X-ray crystallography as well as geometry optimization by DFT calculations revealed a highly warped *cisoid* saddle-shaped structure of the obtained imides. Their optical as well as electrochemical properties are strongly influenced by the imide moieties and were investigated by UV-Vis and cyclic voltammetry (CV) measurements. Theoretical studies by NICS(1)$_{zz}$ calculations and anisotropy of the induced current density (ACID) plots gave insight into the aromaticity of the examined imides. As a result, the unique electronic properties of the acenaphthylene-extended imide originating from its embedded azulene moiety were discovered.



Scheme 1. Synthesis of non-planar imides by two-fold Pd-catalyzed [5+2] annulation.

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Aggregation induced emission of *N*-Heteropolycycles

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In many physico-chemical molecular processes performed in the liquid-phase a common enemy of the experimentalist is aggregation. A standard fluorescence measurement of e.g., dissolved organic dyes is recommended at an adequate dilution (i.e., relatively low concentrations) and only with freshly prepared solutions, to rule out aggregation and related quenching effects. Explanations of these usually feature additional non-radiative decay channels of the aggregated species in contrast to the individual molecule. In 2001 interestingly an initially counter-intuitive observation was made, namely the aggregation induced emission (AIE).[1] Briefly, a substituted silole, which is non-emissive in diluted solution, starts to aggregate and fluoresce upon addition of antisolvent. Since then, many new compounds with analogue or similar fluorescence properties in the aggregated state were reported.[2,3] An additional factor affecting the fluorescence of these systems is the molecular packing in aggregates (i.e., crystalline *vs*. amorphous phases).

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 AIEgens *via* optical spectroscopy to systematically impact the aggregate formation in the first place towards a desired trend. This includes the use of different solvents, different volume fractions of antisolvent, different aggregation times, etc. By using different microscopy techniques (AFM, SEM) the morphologies of the aggregates will be systematically studied.

Centrifugation-based techniques are well known in the context size-selection techniques in 2D nanosheet dispersions,[4] while the effect of such techniques concerning aggregate sorting for size/morphology/etc. is yet to be explored as a second part of this project.

As an early outlook of AIE, synthetic chemists always focused on achieving high PLQYs from films of such aggregates, but inhomogeneous size/morphology distributions in samples and difficulties to create homogenous films hampered further progress. By using optimized aggregation conditions (part I), sort out contributions of undesired types of aggregates (part II) and exploiting a new Langmuir-type deposition method, recently established in our group, we try to fill this gap.

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Changing the excited-state dynamics of triphenylamine by planarization and solvent electron affinity

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Triphenylamine (TPA) and derived molecules are widely used in hole transport layers and donor materials in organic electronics.[1,2] In TPA, the propeller shaped orientation of phenyl groups around the central nitrogen limits π-conjugation between them. The introduction of linking groups at their *ortho*-positions forces the phenyl groups into a planar geometry. This enables π-conjugation through the lone pair at the nitrogen[3] and tunes photophysical properties (e.g. two-photon absorption cross-section) and aggregation behavior.[4-6] Here, the effect of planarization and solvent electron affinity on excited state dynamics of TPA derivatives was explored. Transient absorption spectroscopy covering 4 orders of magnitude in time and a spectral range from NIR to UV was applied to the archetype TPA and its dimethylmethylene- (DMM)-linked counterpart (Fig.1(b),(c)). In the absence of electron accepting solvents, DMM-TPA is found to be photo-stable, whereas the propeller-shaped TPA forms benzidine-like dimers. In halogenated solvents the excited state dynamics of both TPA and DMM-TPA are drastically changed though: An electron transfer to the solvent is observed which leads to formation of stable photoproducts. These are identified to be radical cations by comparison between chemical and photo-induced oxidation. The radical cations themselves are characterized by stationary (Fig.1(a)) and transient absorption spectroscopy.

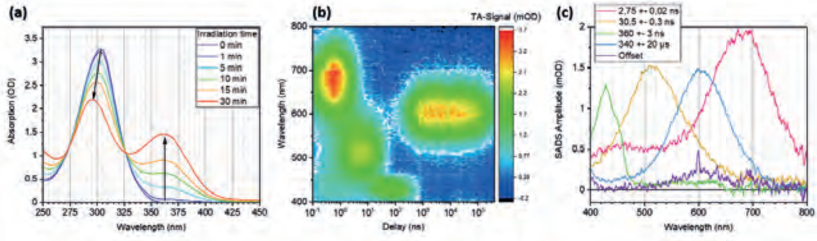

Figure 1. (a) Absorption spectrum of TPA in $CHCl_3$ at different irradiation times. (b) Transient spectroscopy data of TPA in n-hexane. (c) Species-associated difference absorption spectra retrieved after analysis of (b).

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2-D Electronic Spectroscopy for studying Singlet Fission

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Two-dimensional electronic spectroscopy (2DES) is a powerful four-wave-mixing technique, which provides an additional dimension for spectroscopic information. As such, spectral features that would be overlapped on either absorption or emission spectrum in conventional 1D measurements (e.g. transient absorption) can now be separated and identified.

Here, we develop and apply 2DES to spiro-conjugated dimers[1] to directly track the SF-process pathways. The additional excitation-energy resolution leads to less ambiguous assignments, allowing, for example, identification of population transfer or coupling between specific electronic states, if any.[2-3] With this newly built apparatus, we are able to track the ultrafast formation of the heterogeneous correlated triplet pair (^{1}(TT)), which can be populated impulsively, by characterizing cross-peaks that reveal the coupling between S_1 and ^{1}(TT). Furthermore, energy transfer processes between the hetero-chromic moieties occurring on similar timescales are disentangled from the SF-process, which will be elucidated in detail.

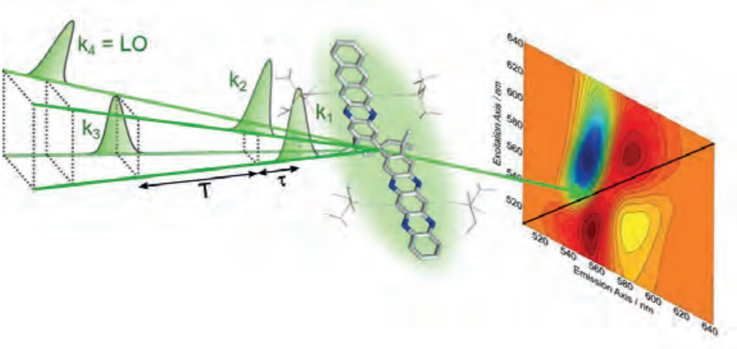

Figure 1. Four beams in a BOXCARS-geometry focused onto a sample of spiro-conjugated heterodimer DAP-TAP (left) and the corresponding 2D correlation map (dispersive component) acquired at the population time T = 200 ps.

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Synthesis of Nitrogen-Rich and Chalcogen-Substituted Organic Materials

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An access to π-conjugated **D**i**Q**uinolino**P**yrrolo**I**ndoles (DQPI) and **D**i**Q**uinolino**B**enzo**D**i**C**halcogenophenes (DQBDC) was developed by combining gold-catalyzed and classical cyclization reactions as well as the nucleophilic introduction of sulfur, selenium, and tellurium (Figure 1). Our recently introduced π-extended Indolocarbazoles[1] were electronically modified[2,3] by the isosteric replacement of CH-units by nitrogen atoms at the aromatic core next to the bisindole scaffold. The classical Pictet-Spengler-reaction enabled a last-step-cyclization approach.[3] Moreover, it was shown that the indolic nitrogen atoms can be replaced with chalcogen atoms using a strategy based on nucleophilic chalcogenide species.[4] The replacement of C-H by nitrogen and the substitution with chalcogens may have an effect on the electronic band gap which should allow new applications as organic functional materials.[5]

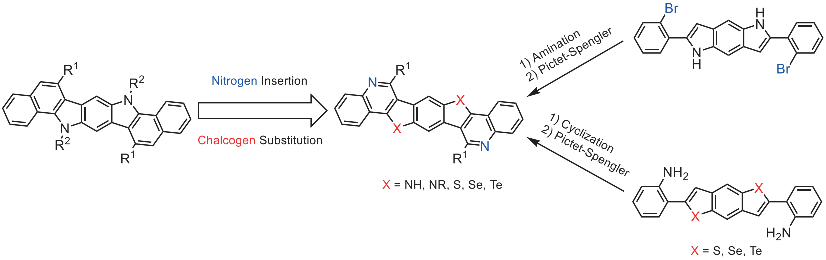

Figure 1. Modification of known benzo[a]benzo[6,7]indolo[2,3-*h*]carbazoles (BBICZs)[2] with additional heteroatoms to diquinolinopyrroloindoles (DQPIs) or diquinolinobenzodichalcogenophenes (DQBDCs).

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Iptycenes and Azaiptycenes with TIPS-Ethynyl Substituted Bridgehead Atoms

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Iptycenes, such as triptycene and its derivatives, have a unique structural design and a particularly rigid framework[1], which allows them to be used in many different applications, such as molecular tweezers[2], molecular motors[3] or with (aza-)acene-blades as materials for organic electronics[4]. Therefore, it is important to access the iptycene framework in a simple way.

We present a synthesis of noval iptycenes und azaiptycenes with TIPS-ethynyl substituted bidgehead atoms. The iptycene-precursor is accessed via Diels-Alder reaction between a TIPS-ethynyl substituted (aza-)acene and 1,4-dihydro-1,4-epoxynaphthalene. In a second reaction step, the respective (aza)iptycene is obtained by deoxygenating the precursor using tosylic acid in toluene or hydrochloric acid in acetic acid. Comparing the absorption spectra of the iptycenes **5**-**7**, no significant shifts in the absorption bands are observed. Substitution of one benzylic moiety of **6** with one pyrazine moiety results in iptycene **1** with red-shifted absorption. A red shift is also observed when hydrogen atoms are replaced by bromine atoms.

The blades of the brominated azaiptycenes can possibly be post-functionalized to higher azaacene-blades, which may make them suitable for applications in organic electronics, especially as light-emitting diodes[4] or in OPV cells[5]. The iptycene framework with the TIPS-ethynyl substituted bridgehead atoms should have a drastic impact on the intermolecular arrangement compared to their respective (aza-)acenes.

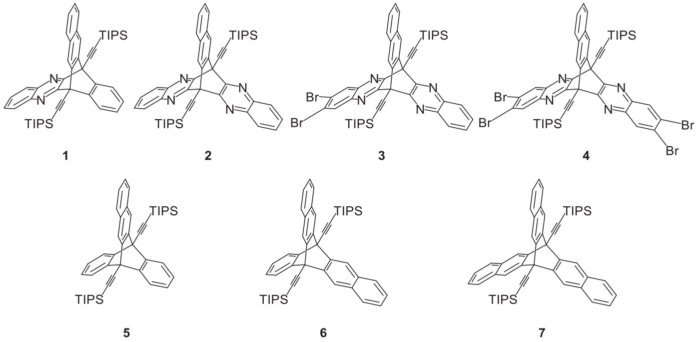

Figure 1. Structur of synthesized Iptycenes and Azaiptycenes with TIPS-ethynyl substituted bidgehead atoms.

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Intelligent Polymer Materials and Films for Electrochemical, Pharmaceutical & Soft Robotics Applications

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This poster will give insights into current research activities of the Ludwigs team. In our interdisciplinary and international research team of polymer chemists, physical chemists and materials scientists we are developing functional and intelligent polymer materials and devices for electrochemical, pharmaceutical and soft robotics applications. One of our aims is to control and manipulate structure-function relationships of hierarchical architectures from the molecular via the nanoscopic to the macroscopic scale such as block copolymer self-assembly and controlled crystallization of semicrystalline polymers.

Going beyond structure-function relationships stimuli-responsive polymers have come in the interest of our research, because their properties show a response when triggered by external environmental conditions such as change in relative humidity, temperature or electric fields, exhibiting great potential for the development of smart devices.

Conjugated (e.g. polythiophenes) and redox polymer (e.g. carbazole-bearing polymer) films are studied in terms of their electrochemical doping behavior[1,2] and with respect to electrochemical switching and doping between different redox states, e.g. for electrochromism or pore control in block copolymer templates.

In a recent paper, the mechanical properties of bilayer actuators as a function of relative humidity were examined in detail. By fabricating a bilayer out of a hydrophobic and a hydrophilic polymer (PDMS and PEDOT:PSS, respectively), our group managed to create a humidity-triggered actuator. Due to the fact that the mechanical properties of PEDOT:PSS depend strongly on the relative humidity (r.H.), it was possible to predict the curvature of the humidity-triggered bilayer actuators by the humidity-dependence of the mechanical properties.[3]

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Non-adiabatic exciton transfer simulation in organic semi-conductors using machine learning techniques

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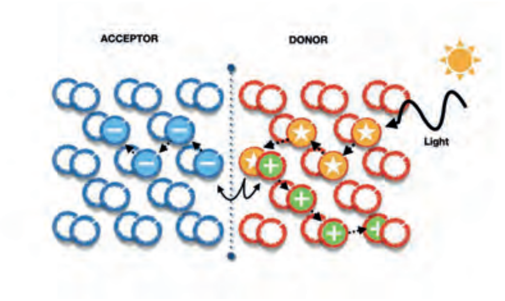
Exciton diffusion in molecular aggregates is mainly controlled by the excitonic coupling between the electronic excited states localized on the molecular units. We present an efficient multi-scale model to predict exciton diffusion length from non-adiabatic molecular dynamics simulations in bulk molecular systems [1]. In order to speed up the quantum chemical calculations, we use neural network based models to predict the value of the site energy and exciton coupling, trained on fast semi-empirical density functional tight binding (DFTB) method. The models are employed to simulate exciton propagation in, Perylenediimide and Pentacene crystal based on fewest switches surface-hopping approach. Resulted diffusion constants are in good agreement with experiments and other computational studies.



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Investigation of ferroelectric-like behavior in $C_6H_6F_5O$-C_3-Amide

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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, non-toxic and sometimes even biocompatible alternative.

Here, we present experimental research on the ferroelectric-like behavior of the novel liquid crystalline molecule $C_6H_6F_5O$-C_3-Amide[1] (Inset figure 1b)). To screen for a possible para- to ferroelectric phase transition, dielectric spectroscopy was employed. While the for ferroelectric materials characteristic Curie-Weiß behavior could not be observed, dielectric features around 80°C suggest a possible phase transition coinciding with a peak in differential scanning calorimetry traces.

With this in mind, 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 an incomplete background correction. Ionic contributions to the switching current are a possible culprit. Capacitance-voltage measurements (figure 1b) exhibit the characteristic butterfly shape expected from ferroelectric materials, caused by a strong increase of the dielectric permittivity of the material in the vicinity of the coercive field.

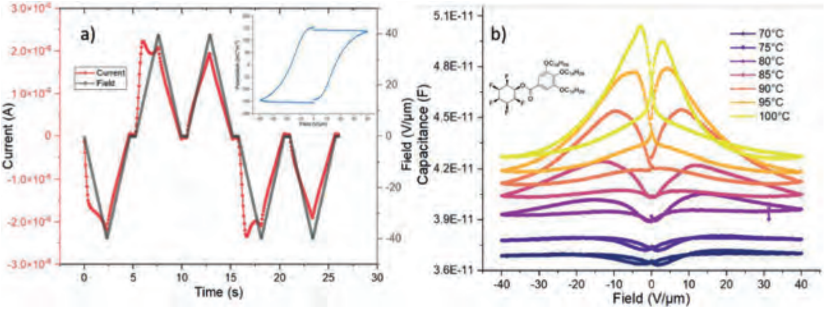

Figure 1. a) Measured current response to a triangular voltage pulse at 100°C. Inset: Resulting polarization against electric field. b) Measured capacitance against applied electric field at various temperatures.

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Synthesis of Diaza[5]helicenes by *ortho,ortho'*-Fusion of *ortho*-Terphenyls

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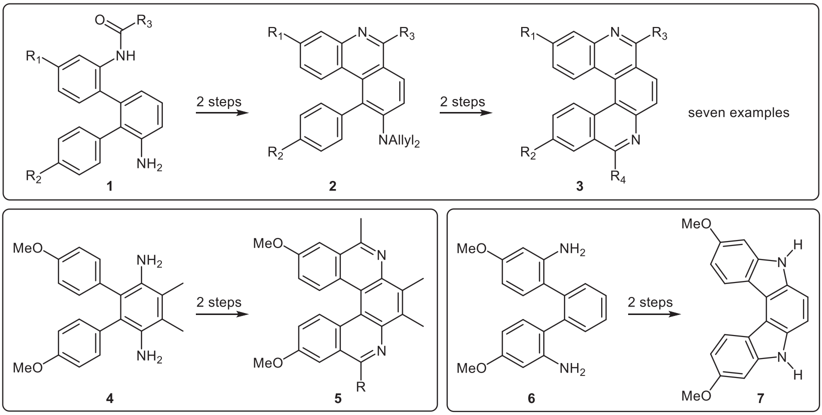
Helicenes are *ortho*-fused aromatic polycycles that exhibit special physical and optical properties due to their helical structure and intrinsic chirality. Therefore, they are promising compounds for a wide range of applications, e.g. as catalysts in asymmetric synthesis, molecular sensors, switches and (opto-)electronic devices.[1]
We noticed that there are numerous methods for the cyclization of *ortho*- and *ortho,ortho'*-biphenyls that lead to various tricyclic compounds such as phenanthrenes, fluorenes, fluorenones, carbazoles, or benzo[*c*]cinnolines. Based on this approach, we succeeded in synthesizing three different types of pyridine- and pyrrol-containing diaza[5]helicenes by double *ortho*-fusion in suitably substituted *ortho*-terphenyls (Scheme 1).



Scheme 1. Synthesis of pyridine- and pyrrol-containing diaza[5]helicenes.

Terphenyls **1**, **4**, and **6** were obtained by *Suzuki* couplings from biphenylamine and 1,2-benzene derivatives, respectively. 5,9-Diaza[5]helicenes **3** were then synthesized by two consecutive ring closure reactions using Eaton's reagent (P_4O_{10} in $MeSO_3H$). Allyl protection was required to prevent the formation of unreactive phenanthridine derivatives.[2,3] In contrast, acylation of diamine **4** and conversion with Eaton's reagent in two steps directly led to the symmetric 6,9-diaza[5]helicene **5**. Five-membered rings were accessible using a different strategy: Conversion of diamine **6** into a diazide followed by thermal cyclization yielded 5,8-dihydroindolo[2,3-*c*]carbazole **7**.[3]

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Photophysics of Singlet Fission in Acene Dimers

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Increasing the efficiency of solar energy harvesting has been one of the main goals of the ongoing research for novel singlet fission (SF) sensitizers. Heteroatom-substituted condensed aromatic polycycles such as acenes and peropyrenes have been shown to be promising materials, capable of efficient triplet generation via SF. Time-resolved spectroscopy has identified several SF features and competing relaxation pathways like oxygen-catalyzed sequential SF,[1] diffusion-controlled homogeneous SF,[2] molecular packing effects on SF[3] and excimer formation as loss channel.[4]

In this work, we investigate the photophysics of intramolecular singlet fission (iSF) in dimers in solution with time-resolved spectroscopy over 9 orders of magnitude. iSF in such systems is highly dependent on the spatial separation of monomeric units and on the orientation of conjugated π-systems.[5,6] Triplet yields are limited mostly by recombination events such as triplet-triplet annihilation, due to missing exciton diffusion. iSF in dimer systems with spiro-conjugation (Figure 1) does not promote the annihilation of nascent triplet pairs and undergo efficient iSF with triplet yields up to 199%.[7]

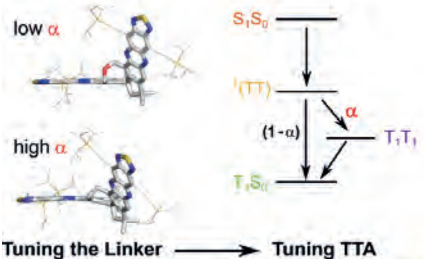

Figure 1: Overview of the singlet fission mechanism in differently-bridged spiro-homodimers. Selection of different linkers (left) affects the quantum yield for the dephasing of the correlated triplet pair (shown in the mechanism on the right). Reprinted with permission from L. Ahrens *et al.*, *The Journal of Physical Chemistry B* **2021**, *125*, 13235. Copyright 2021 American Chemical Society.

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Carrier dynamics in TIPS-pentacene optical microcavities

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Singlet fission (SF) is the process of generation of two triplet excitons from a single singlet exciton.[*1*] It has been considered promising to overcome the Shockley-Queisser limit of a single-junction solar cell.[*2*] Although the process of SF is relatively easy to understand conceptually, its high-yield implementation in real molecular systems appears extremely challenging due to various competing processes. A novel experimental way to shed more light on the ultrafast photo-induced pathway between the singlet to the triplet manifold is by the strong coupling between light and molecules (polariton formation) in optical microcavities.[3-5] Tuning the cavity properties allows one to modify the energy landscape of the active layer and to potentially select specific parallel reaction pathways competing between the singlet and triplet manifolds during SF.

Here we study TIPS-pentacene (TIPS-Pn) molecules in polystyrene matrix embedded into an optical microcavity where N exciton bands split into N+1 polaritonic branches. From transient-absorption (TA) experiments (Fig. 1a) we find that there are no drastic differences in SF dynamics between the open (Fig. 1b, left) and closed (Fig. 1b, right) microcavities of TIPS-Pn. However, we observe differences in relative amplitudes of the SF-related feature and singlet-related peaks indicating altered SF yield in the case of closed microcavities. Power-dependent splitting of polaritonic branches and faster sub-200-fs dynamics of SF for higher pump photon energies (at the S1v1 absorption band, ~590 nm) will be discussed.

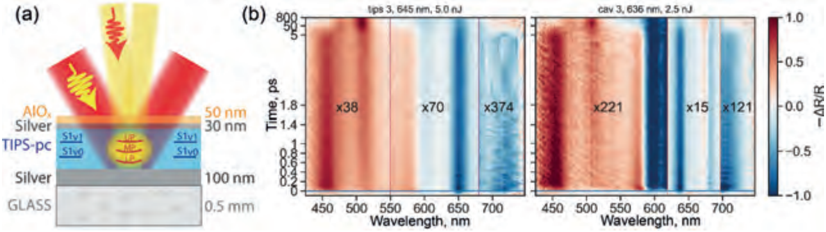

Figure 1. (a) Schematics of the pump-probe experiment on a TIPS-Pn optical microcavity. (b) TA spectra of a TIPS-Pn layer (left) and a TIPS-Pn optical microcavity (right).

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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, $2T_1$. This work, through quantum dynamics simulations, demonstrates how coupling between a pentacene dimer and an optical cavity mode can modify population transfer to the $^1(T_1T_1)$ multi-excitonic state. Our findings indicate that, for a single molecule, population transfer to the $^1(T_1T_1)$ state is suppressed for most photon mode frequencies but can be restored/enhanced when the cavity mode is in resonance with a high energy doubly excited (DE) state ($E_{DE} - E_{TT} = 0.2$ eV).
We also investigate the dependency of the dynamics on the bright singlet exciton energy level which gives insight into the mediated pathways that facilitate the population of $^1(T_1T_1)$. Future work in this project will include extending our model to include N dimers coupled to a cavity photon mode.

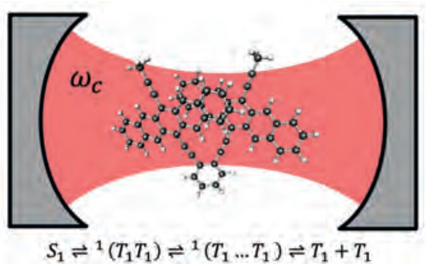

Figure 1. *o*-Bis(13-(methylethynyl)pentacen-6-yl)ethynyl)benzene dimer (*o*-TIPSPm)[1] investigated in this work and the SF mechanism[2]. The optical cavity, indicated graphically, is not to scale.

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Probing quenching of triplet excitons by charge carriers in dual-emitter OLEDs by phase-sensitive magnetic resonance

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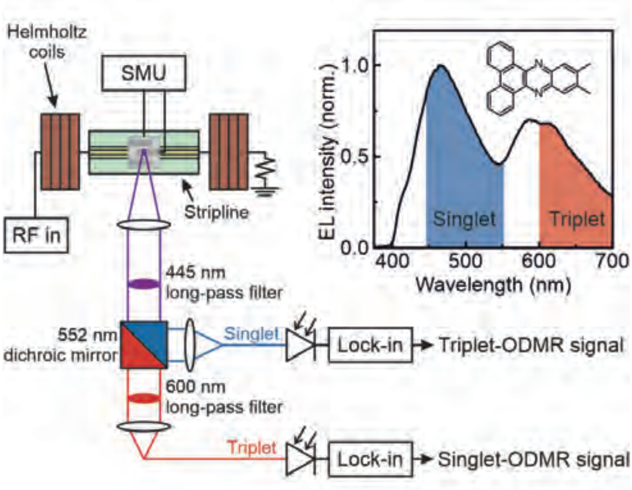
OLEDs exhibit strong sensitivity to magnetic fields due to spin-dependent electron-hole recombination. Employing a dual singlet-triplet emitting guest:host system, we can optically assess the spin-permutation symmetry of charge-carrier pairs by their magnetic-field dependent electroluminescence (EL) as illustrated in the figure[1]. Furthermore, due to the dual-emitting property of the material system used, we gain access to both singlet- and triplet-like states, allowing us to distinguish between singlet-triplet pair interconversion[2] and carrier-exciton quenching[3] processes.



We monitor the interconversion between singlet-like and triplet-like carrier-pair populations in the EL under electron paramagnetic resonance (EPR) conditions and observe deviations from the anticipated anticorrelation in the formation yields of singlet-like and triplet-like carrier pairs. We rationalize the optically detected magnetic resonance (ODMR) spectra using stochastic Liouville simulations of the spin-pair density matrix, based on an interplay between the conventional radical-pair model and an exciton-quenching mechanism. We exploit the extraordinary phase sensitivity of the lock-in quadrature detection technique used to gain insight into the temporal dynamics of the generation and recombination of the molecular triplet states. Using this approach, we observe a non-trivial phase dependence of the ODMR, revealing a dynamic interaction between host and guest molecule triplets.

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Random Modes in Random Structures

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Functional molecular glasses based on the spirobifluorene core have been applied in solar cells, organic lights emitting diodes, and lasers for a long time.[1,2] Here we investigate the stimulated emission behaviour of spiroquaterphenyl-doped polymer films in a disordered structure formed by self-organized wrinkling in stressed bilayers.[3] Within the stimulated emission gain profile, random laser modes evolve, with thresholds of around 10 µJ/mm². The mode formation can be explained by in-plane scattering within the corrugated monomode waveguide.

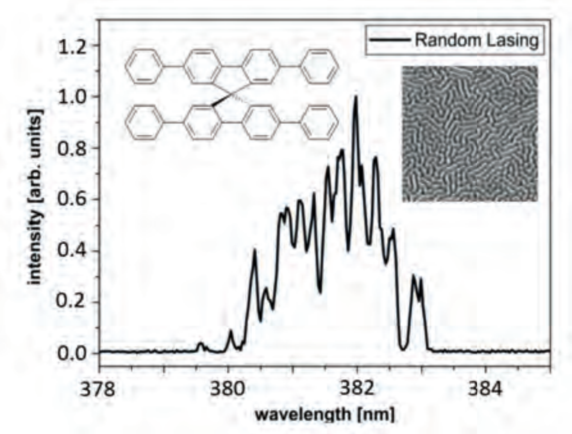

Figure 1. Emission spectrum above threshold of a spiroquaterphenyl-doped polystyrene between an oxidized silicon wafer and a cladding layer of *m,m*-spirosexiphenyl². The active chromophore (left) and the wrinkling morphology after annealing (right) are displayed as insets.

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Bending Pyracyclene upon π-Expansion

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Pyracyclene, a planar antiaromatic hydrocarbon composed of a naphthalene unit and two annealed five-membered rings, comprises a 12 electron π-system with a central double bond and can be considered as a fragment of fullerene.[1]

Herein, we disclose a stepwise π-expansion of pyracylene. Successive oxidative cyclodehydrogenation of octaphenyl-substituted dibenzopyracyclene (**OPP**) towards boat-shaped congeners tetraphenyl-substituted dibenzopyracyclene (**TPP**) and hexa-*peri*-hexabenozocoronene-pyracyclene-hybrid (**HPH**) resulted in unique structural features which were characterized by X-ray crystallographic analysis.[2] Depending on the extent of π-expansion the compounds are prone to several redox events as documented by cyclic voltammetry and display intense bathochromically shifted absorption bands in their UV/Vis spectra. The experimental observations are in line with the computational studies on the (CAM-)B3LYP level of theory, suggesting progressive narrowing of the HOMO–LUMO gap and distinct evolution of the electronic structure and aromaticity.

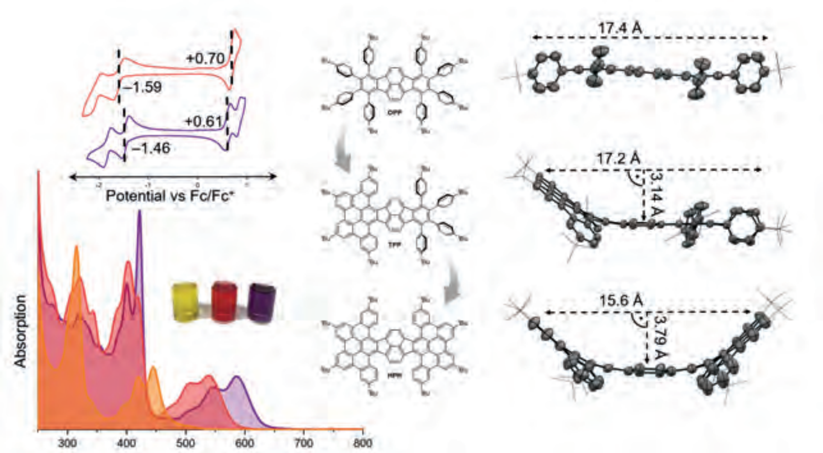

Figure 1. π-Expanded pyracyclenes **OPP**, **TPP** and **HPH** with their optoelectronic and structural characteristics.

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Control of polymorphism in zone-cast PDIF-CN_2 thin films

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Differences in molecular packing can strongly influence charge carrier mobilities and optical properties of crystalline organic semiconductors. Thus, polymorph-selective thin film formation is important for optimal and reproducible electronic devices such as field-effect transistors. PDIF-CN_2 is a well-known perylene derivative and n-type semiconductor with very high electron mobilities in vapour-deposited thin films and single crystals. PDIF-CN_2 can form two different polymorphs, with one being only rarely found in polycrystalline films produced by thermal vapour deposition.

Here, zone-casting of PDIF-CN_2 from solution was employed to create aligned films of different polymorphs (A and B, see Figure 1) in a controlled manner by varying the organic solvent and casting conditions (temperature, speed). The obtained polymorphs were investigated by 2D X-ray diffraction, Raman microscopy, fluorescence and UV-Vis absorption spectroscopy confirming the phase purity of the respective films. The two different polymorphs could be easily identified by their characteristic low-wavenumber Raman modes and their photo-luminescence spectra. Furthermore, field-effect transistors were fabricated to study charge transport properties depending on the polymorph.

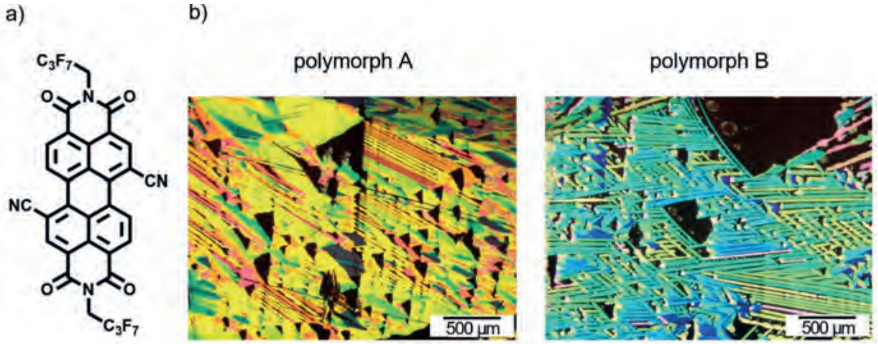

Figure 1. a) Molecular structure of PDIF-CN_2, b) cross-polarized microscope images of zone-cast, aligned films of the different polymorphs.

Cyclooligomeriziation of a Pyrene-based Kobayashi Aryne Precursor

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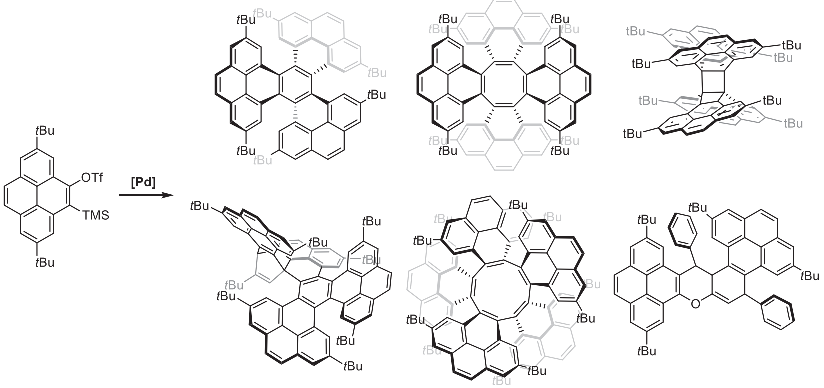
With a strained triple-bond-like character, arynes tend to be versatile reaction intermediates that can not only be generated by multiple different precursors and activation conditions but also employed in a variety of different reaction types for the construction of otherwise challenging organic molecules.[1] With access to higher yields of trimerization products of arynes by making use of palladium catalysts, over the years a plethora of PAHs were synthesized, many of which showed three- or even hexapole helicity that was manipulated and investigated in detail.[2, 3] While studying the cyclotrimerization of a mono-aryne Kobayashi type precursor of di-*tert*-butylpyrene, an unprecedented complex product mixture of higher oligomers was acquired.[4] The synthesis and characterization of these products are presented herein.



Scheme 1. Isolated products of a palladium-catalyzed oligomerization of Pyryne.

Reference

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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 in comparison to other theoretical data[3], whenever possible. In the end a short outlook for the possibility of approximation schemes is presented along with an example.

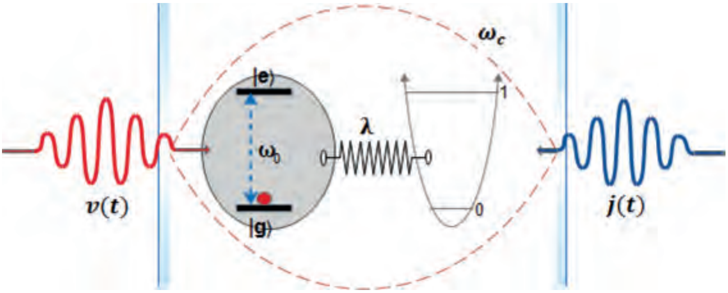

Figure 1. Graphical representation of the linear response of a polaritonic 2 x 2 level system. The electronic system is perturbed by a classical field **v(t)** and the photonic system is perturbed by a classical current **j(t)**, while both systems themselves are coupled via a constant **λ** multiplied with the transition dipole moment, represented by a spring.[2]

Reference

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Property Patterns in *N*-Heteropolycyclic Radicals

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Open-shell *N*-heteropolycycles are attracting growing interest from the area of functional electronic materials due to the increased stability of nitrogen-centered radicals and radical cations, their easily customisable multi-electron redox properties, as well as the propensity of extended polycyclic aromatic systems to exist in high-spin ground states.[1] Infinite structural variability of these systems necessitates rational property prediction protocols and design guidelines to guide the experimental efforts.[2]

In this project, we combine computational chemistry and data science to extract the patterns in the physico-chemical properties of *N*-heteropolycyclic radicals and establish their structure-property relationships. For a set of over 1000 structures comprising diverse organic skeletons and *N*-containing motifs, we map their chemical space and elucidate the patterns in their key properties, including the singlet-triplet gaps, ionisation potentials and electron affinities, radical stabilities, etc. Finally, using advanced machine learning techniques we are able to predict these properties with a high degree of reliability.[3] These results illustrate the intricate structure-property relationships in open-shell *N*-heteropolycycles and exemplify the possibility of assessing their properties without the need for costly quantum-chemical computations.

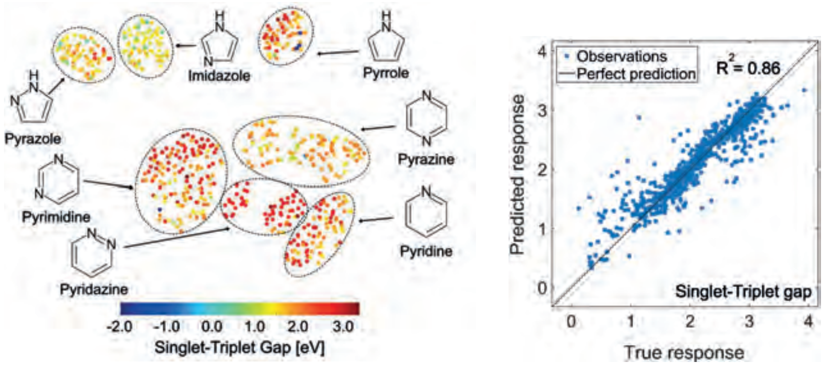

Figure 1. t-SNE plot grouped by *N*-containing motifs and colour-coded by the computed S-T gap values (left), and a plot of predicted (supervised machine learning) *vs.* true response (density functional theory) S-T gaps of neutral *N*-heteropolycycles (right).

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Quantum Chemical Investigation of Tetraazapentacenes as Organic Semiconductors

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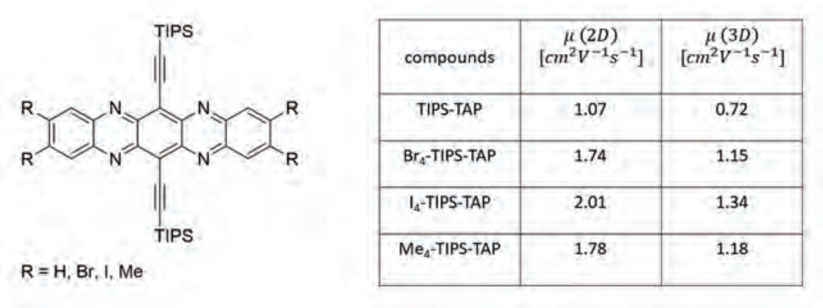
Both in basic research and in applications, organic semiconductors based on conjugated π-systems have proven to be fascinating systems that offer new possibilities for the design of devices. The class of N-heteroacenes has emerged as a promising candidate for n-channel semiconductors, of which only few reports can be found in the literature, despite their significant role in the development of organic electronics.[1] A series of symmetrically substituted triisoproylsilylethynyl-pentacenes (TIPS-PEN) and -tetraazapentacenes (TIPS-TAP) are investigated regarding their n-channel charge mobilities using quantum chemical methods at DFT and TDDFT level of theory.[2,3] The n-channel charge mobilities μ are evaluated using Marcus theory and show an increase of the mobility compared to TIPS-TAP for all its investigated functionalized derivatives Br_4-TIPS-TAP, I_4-TIPS-TAP and Me_4-TIPS-TAP, with the iodine-derivative showing the highest calculated mobility. Based on these results, all three compounds are suitable for an application as n-channel organic semiconductors. Analysis of the reorganization energies shows that stronger bonds of the functional group to the acene core (C-R) lead to larger reorganization energies and therefore lower mobilities. Furthermore, the results indicate that the functional group influences the transfer integral by altering the relative orientation of the molecules and by changing the shape of the LUMO (lowest-unoccupied-molecular-orbital). Since the transfer integral is larger with better overlap of the LUMOs, smaller functional groups that can be part of the π-system are a rational choice for future investigations on the n-channel mobility.



compounds	$\mu\,(2D)$ $[cm^2V^{-1}s^{-1}]$	$\mu\,(3D)$ $[cm^2V^{-1}s^{-1}]$
TIPS-TAP	1.07	0.72
Br_4-TIPS-TAP	1.74	1.15
I_4-TIPS-TAP	2.01	1.34
Me_4-TIPS-TAP	1.78	1.18

Figure 1. Left: Investigated TIPS-TAP derivatives, Right: Calculated n-channel electron mobilities using Marcus theory.

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π-Extended Indolopyrazines as Structural Motif for Materials Science

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Herein we describe the convergent synthesis of π-extended indolopyrazines as new substrate class for potential applications in materials science.[1] 3,6-Dichloropyrazine-2,5-diamine was established as key precursor towards the alkyne starting materials. This new building block was available in large scale via a short reaction sequence. After subsequent bidirectional cross-couplings, diyne and tetrayne scaffolds were obtained in modular fashion. In the final step, with the aid of a NHC-gold(I)-catalyst, π-extended pyrazine systems were constructed in a cascade cyclization.[2] In addition, the NH-moiety of the indole enables postfunctionalizations that allow to further fine tune the properties especially with the focus on solubility issues.[3]

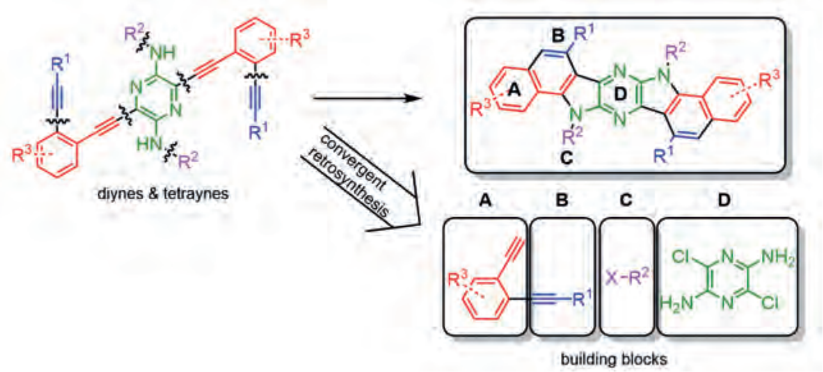

Figure 1. Convergent approach towards indolopyrazines.

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Singlet Fission in the Strong Coupling Regime

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Strong light-matter interaction of organic molecules in optical microcavities results in the formation of hybrid light-matter states, known as polaritons (lower (LP) and upper (UP) polariton). These newly formed states inherit properties from both light (photons) and matter (excitons), thus offering a new way to manipulate the energy landscape of organic molecules by altering their photophysical properties by modifying their electromagnetic environment without the need of molecular engineering.

Singlet fission is a process, in which a singlet excited state is converted into two triplet excited states (a triplet pair), that can result in two electron-hole pairs per absorbed photon. This process could be applied in solar cells to increase the external quantum efficiency beyond the Shockley-Queisser limit. However, the formation of the triplet pair state is the rate-limiting process and depends on the energy offset between the singlet and triplet-pair state. By making use of the tunability of polaritonic states, we aim to change the energy of the excited state (LP) in a controlled manner and thus the singlet fission rate of a given molecular system.

In the present study, we use TIPS-pentacene as singlet fission material and designed six different metal-clad microcavities with different energy gaps between the LP and the triplet pair state. With this model system, we can explore how the change of the LP position may affect the rate of singlet fission. Both steady-state (angle-resolved) and transient reflection spectroscopy are used to characterise these strongly-coupled systems and determine the rate of singlet fission depending on detuning, coupling strength and excitation energy. The influence of strong coupling on singlet fission processes (yield, amplitudes, rates…) will be presented.

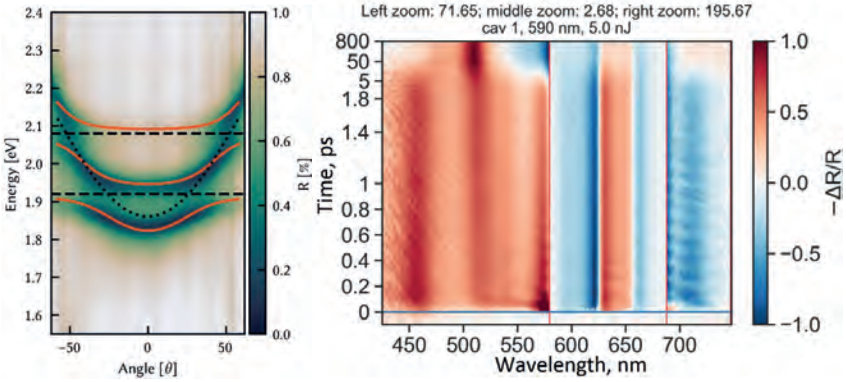

Figure 1. (left) Angle-resolved reflectivity of a microcavity containing TIPS-pentacene embedded in a polystyrene matrix. The dashed lines indicate the absorption maxima of bare TIPS-pentacene, the dotted line is the energy of the cavity and the orange lines are the energies of the polaritonic states (lower, middle and upper polariton). (right) Transient reflectivity data from such a microcavity.

Towards Nitrogen-Rich *N*-Heteropolycycles: Synthesis of Octaazaperopyrenes

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Ortho [CH→N] substituted octaazaperopyrenes (OAPPs) are a new class of functional dyes characterized by their strong electron-accepting behavior.[1] The OAPP target was prepared via selective nucleophilic substitution at the *peri* position of a *bay* chlorinated tetraazaperylene by introduction of four amino-substituents. The resulting tetraminoperylene was subsequently reacted with different acyl chlorides and anhydrides to give the twisted *bay* chlorinated OAPP derivatives which were isolated in their reduced dihydro-form. The OAPP target could be obtained via a palladium catalyzed dehalogenation and a subsequent oxidation. The eightfold isosteric [CH→N] replacement within the peropyrene core structure results in a large decrease of the frontier orbital energies, rendering the target compound a potent oxidant while preserving the planarity of the aromatic core. The radical anion was obtained by reduction of the OAPP with KC_8 and characterized by EPR spectroscopy. A general discussion of the number and location of [CH→N] replacements in peropyrene structures and their frontier orbital energies is provided.[1-3]

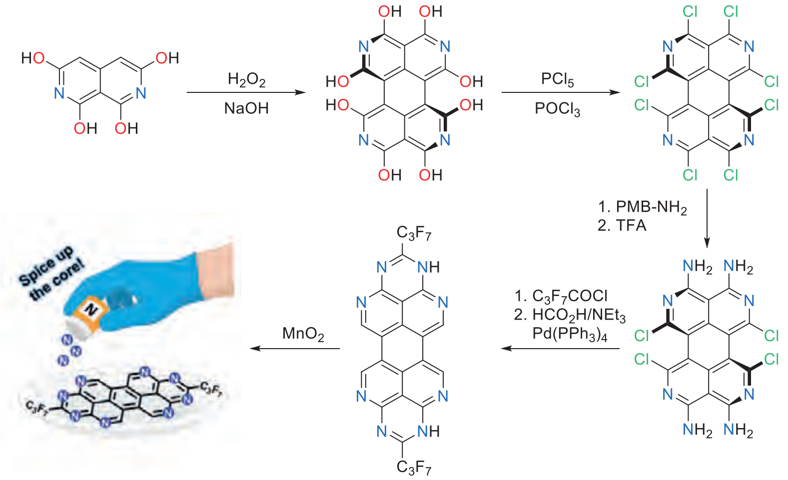

Figure 1. Synthesis of an *ortho* substituted octaazaperopyrene (OAPP).[1]

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Strong Light-Matter Coupling in Optical Cavities with Thio-functionalized tetraazaperylene derivatives

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Strong light-matter coupling results from the interaction between light (photons) and matter (excitons) in an optical micro-resonator. The fast energy transfer between photonic and excitonic states at resonant frequencies leads to the formation of new hybrid states called exciton-polaritons. These hybrid states inherit properties from both components making them interesting for numerous applications in optoelectronics and for externally tuning the photophysics of molecules.

Here, we investigate strong light-matter coupling in metal-clad microcavities with three thio-functionalized tetraazaperylene (TFTAP) derivatives with different solubilizing substituents: butyl, benzyl, and p-methoxybenzyl (PMB). This new class of emitters is characterized by high photoluminescence quantum yield in solution. Thin films of TFTAPs embedded in polystyrene matrices were sandwiched between two semitransparent silver mirrors, thus forming an optical cavity whose resonant cavity mode depends on the film thickness (Fig. 1a). Fitting the angle-resolved reflection spectrum (Fig. 1b) with a coupled oscillator model, confirmed strong coupling and the formation of lower, middle, and upper polariton branches. Among the three TFTAP derivatives, the PMB-substituted derivative showed the highest solubility and best film quality, enabling a high concentration of emitters in the molecular layer to increase the coupling strength further.

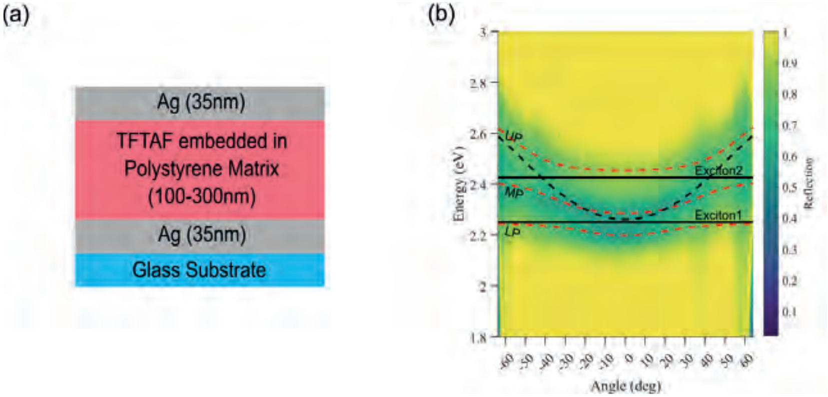

Figure 1. (a) Schematic of optical microcavity. (b) Angle-resolved reflection spectrum with lower (LP), middle (MP), and upper (UP) polariton branches.

Synthesis of Dithiahelicenes by Transition Metal-Catalyzed Cycloisomerization

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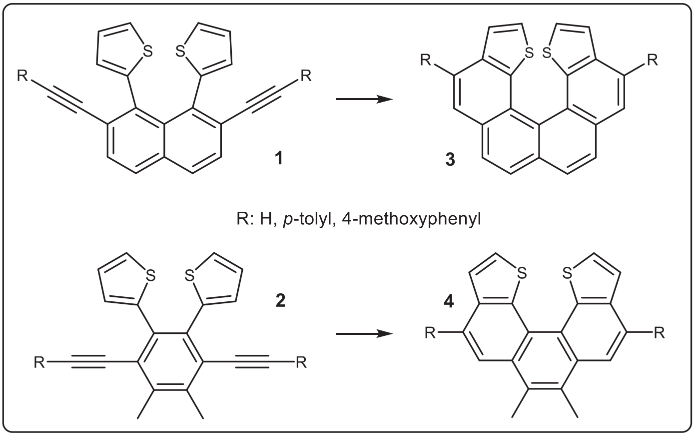
Thiahelicenes are unique within the helicenes due to the presence of thiophene rings, which confer specific chemical, geometric, and electronic properties. The modulation of specific properties in order to exploit the possible application fields can be achieved not only by specifically substituted precursors, but also by regioselective functionalization of the terminal thiophene rings. This allows for applications in materials sciences, optoelectronics, catalysis, polymer chemistry, biology and other fields.[1]

Here we describe the synthesis of dithiahelicenes starting from two core building blocks, which were appropriately functionalized and reacted with suitable coupling partners in Sonogashira and Suzuki couplings, respectively, to yield the teraryl precursors **1** and **2** The final helicenes **3** and **4** are obtained by *ortho* fusion of the alkynylated intermediates (Scheme) using transition metal-catalyzed cycloisomerizations, method which has been developed by Fürstner et al.[2]



Scheme. Synthesis of dithia[5]- and [6]helicenes.

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Fermi-Level Pinning at the Source/Drain Contacts in Organic Thin-Film Transistors

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One of the potential applications of organic semiconductors is in the development of thin-film transistors (TFTs) for flexible electronics, and significant progress in this direction has indeed been made.[1] However, the static and dynamic performance of organic TFTs is greatly influenced not only by the choice of the organic semiconductor and by the way it is processed into ordered films, but also by a variety of other aspects, such as the properties of the gate dielectric, the parasitic resistances associated with the source and drain contacts, and the various interfaces between the transistor components.[2] It can be shown that when the channel length of organic TFTs is made sufficiently small so that operation at frequencies greater than a few megahertz becomes feasible, the TFT characteristics are determined almost entirely by the contact resistance.[3]

The contact resistance of organic TFTs is determined mainly by the energy alignment at the interface between the organic semiconductor and the source/drain contact metal. Treating the surface of the source/drain contacts with a chemisorbed monolayer is often helpful in adjusting the Fermi level of the contact metal, with the intent of reducing the contact resistance by lowering the Schottky barrier between the highest occupied molecular orbital (HOMO) of the organic semiconductor and the Fermi level of the contact. In practice, however, the alignment between the semiconductor's HOMO energy and the contact's Fermi level is often prevented due to a pinning of the Fermi level to localized electronic states in the organic semiconductor.

Strategies to lift this Fermi-level pinning often focus on the introduction of interlayers to decouple the electrons in the contact metal from these localized states. Interlayers in p-channel TFTs need to have a large ionization energy (*IE*).[4,5] Here, we show that a high *IE* alone is not sufficient for reducing the contact resistance.

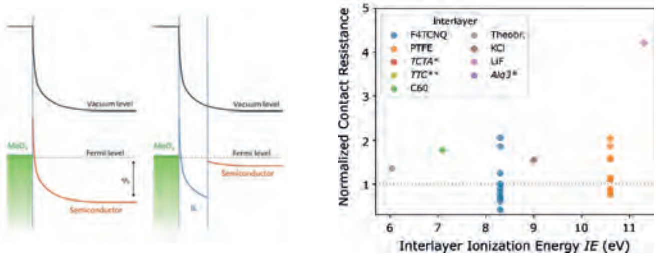

Figure 1. Strategy for Fermi-level depinning enabling energetic alignment between contact metal and organic semiconductor by introducing high-*IE* interlayers (left). Comparison of contact resistance of devices with and without interlayers for a variety of ionization energies (right).

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List of Speakers

Harry L. Anderson	University of Oxford
Claudia Backes	Universität Kassel
Tiago Buckup	Universität Heidelberg
Ganna Gryn'ova	Heidelberg Institute for Theoretical Studies
Sahika Inal	King Abdullah University of Science and Technology
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