



# Abstract Book

Solvay Workshop on “Charge, spin, and heat transport  
in organic semiconductors”

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# CONTENTS

## Poster Presentations

Alexandre Abhervé .....	5
<i>Molecular Hybrid Systems Based on Bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) and Anilate-based Molecules</i>	
Imane Arbouch .....	6
<i>Theoretical study of Type II Catechol-Thiophene Sensitizers for Dye Sensitized Solar Cells</i>	
David Curiel .....	7
<i>High Performance of Carbazolocarbazole-based Organic Thin-Film and Single-Crystal Field-Effect Transistors</i>	
Gabriele D'Avino .....	8
<i>Electronic states in bulk fullerenes and at their interface to polymers: charge delocalization and exciton hybridization effects</i>	
Kealan J. Fallon.....	9
<i>Indolo-naphthyridine-6,13-dione thiophene (INDT) Building Block for Conjugated Polymer Electronics</i>	
Kevin Felter.....	10
<i>Long-range exciton diffusion in perylene diimides mediated by singlet fission</i>	
Alexander Forster .....	11
<i>Spirocycle Containing Conjugated Polymers: Manipulating Excited States</i>	
David M. E. Freeman .....	12
<i>Manipulating the Singlet-Triplet Energy Gap – TADF in Organic Conjugated Polymers</i>	
Niall Goodeal.....	13
TBC	
Stefano Gottardi.....	14
<i>Kinetic Monte Carlo simulations for improving organic electronic device performance</i>	
Yunbin Hu .....	15
<i>Benzo-Fused Double [7]Carbohelicene: Synthesis, Structures, and Physicochemical Properties</i>	
Ryutaro Inaya .....	16
<i>Study on the synthesis of highly conjugated [1]benzothieno[3,2-b]benzothiophene derivative</i>	
Robby Janneck.....	17
<i>Single-crystalline organic thin films: A predictive model that enables fast process optimization</i>	
Outi Kontkanen.....	18

*Modeling of perylene monoimide based dye molecules and NiO (100) for p-type dye sensitized solar cells*

Vincent Lemaur.....	19
<i>On the origin of the high hole mobility in IDTBT conjugated polymers: a theoretical study</i>	
Anastasia Leventis.....	20
<i>Conjugated Materials for Organic Solar Cells</i>	
Clemens Liewald.....	21
<i>Imaging electronic bottlenecks in organic field-effect transistors with photocurrent microscopy</i>	
Aart Ligthart.....	22
<i>Analysis of triplet-triplet annihilation in organic phosphorescent materials</i>	
Feilong Liu.....	23
<i>Ab initio modeling of charge transport in amorphous molecular semiconductors</i>	
Kevin Martin.....	24
<i>Redox Active Helicenes for Molecular Materials</i>	
Miriam Más-Montoya.....	25
<i>Influence of H and J-aggregation of Small Thiophene-Pyridine-DPP Molecules on the Photophysical Properties and Photovoltaic Performance of Solution-Processed Solar Cells</i>	
Mastropasqua Talamo Maurizio.....	26
<i>Electrochemical study of EDOT-based polymers for cation sensing</i>	
Yuya Matsuta.....	27
<i>Modulation of open-shell character of triphenylamines having two phenoxy radicals via structural modification</i>	
Cristina Oliveras.....	28
<i>Chiral C<sub>3</sub> symmetric molecules suitable for charge transport processes</i>	
Alexandra F. Paterson.....	29
<i>Small Molecule / Polymer Blend Organic Transistors with Hole Mobility Exceeding 13 cm<sup>2</sup>/Vs</i>	
Marco J. Pereira.....	30
<i>Pressure sensor based on organic single crystal air-gap transistor</i>	
Eduard Preis.....	31
<i>Very high solid state Photoluminescence Quantum Yields of Poly(tetra-phenylethylene) Derivatives</i>	
Beth Rice.....	32
<i>Polaron states in Fullerene adducts by Coarse Grain Molecular Dynamics and Tight Binding</i>	
Audrey Richard.....	33
<i>New Challenges for Charge Transport: Isotropy</i>	

Gilles H. Roche .....	34
<i>Hybrid Field Effect Transistors (HFET), first example of a fully covalent transistor with a <math>\pi</math>-conjugated organosilica material</i>	
Sandra Rodriguez Gonzalez .....	35
<i>Pinning and Polarization Effects in Molecular Junctions</i>	
Janina Roemer .....	36
<i>Nanoscale C<sub>70</sub>-aggregates on pentacene for investigating the relation of charge carrier separation efficiency and crystallinity</i>	
Cedric Rolin.....	37
<i>The Gated van der Pauw Approach to Mobility: Taking The Contacts Out of the Equation</i>	
Xingyuan Shi.....	38
<i>Impact of Conjugated Polymer Chain Conformation on the Density of States and Charge Transport</i>	
Cansel Temiz.....	39
<i>Relation between supramolecular structure and the charge and excited state dynamics in organic materials</i>	
Yusuke Tsutsui.....	40
<i>Structure-Property Relationship of Thienoacenes Using Time-Resolved Microwave Conductivity</i>	
Thomas Weitz.....	41
<i>Role of grain boundaries for the electrical stability of organic n-channel transistors</i>	
Hui Yang .....	42
<i>Modelling Charge Transport in Organic Molecular Materials</i>	

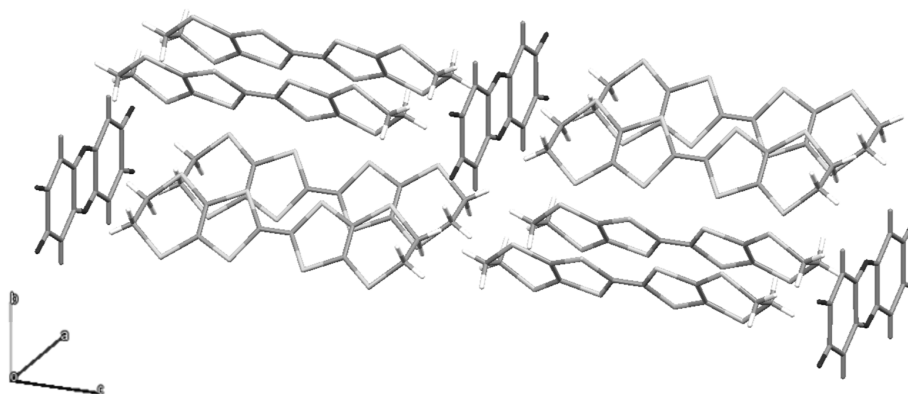
# Molecular Hybrid Systems Based on Bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) and Anilate-based Molecules

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Combination of electrical conductivity and magnetic properties in the same molecular material is one of the most active topics in chemical science. Since they can be prepared as radical cation salts, tetrathiafulvalene-based (TTF) molecules appear to be very interesting candidates for the design of new hybrid organic/inorganic compounds. The combination of TTF-based conductors with magnetic counterions have been largely explored in order to obtain  $\pi$ - $d$  hybrid systems with presence of magnetism from the  $d$  electrons and conductivity from the  $\pi$  electrons. As previously reported with oxalate-based metallic networks,<sup>1</sup> we have used the molecular building-block approach to combine the bis-(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) donor with molecules based on the anilate ligand (namely 3,6-disubstituted-2,5-dihydroxy-1,4-benzoquinone dianion;  $C_6O_4XY^{2-} = XYAn^{2-}$ ).<sup>2</sup> Here we present the synthesis and characterization of the new hybrid compounds obtained by electrocrystallization and layering techniques.



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# Theoretical study of Type II Catechol-Thiophene Sensitizers for Dye Sensitized Solar Cells

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Titanium dioxide is of great technological interest for photovoltaic applications. In dyes sensitized solar cells<sup>1</sup>, the TiO<sub>2</sub> nanoparticles are largely used as semiconductor, however, due to the large fundamental band gap of 3.2 eV<sup>2</sup>, the light absorption is slow in the visible region. This limitation has been overcome by sensitization of the TiO<sub>2</sub> by organic or organometallic compounds that absorb light in the visible region and optimize the absorption of the solar spectrum. It is important to establish a computational investigation on the interaction of adsorbates with TiO<sub>2</sub> anatase surface in order to control and improve the photovoltaic properties of TiO<sub>2</sub>.

Catechol is one of the smallest chromophores studied in dye sensitized solar cells<sup>3</sup>, the catechol-titania combination has been described as a Type II injection system where it is thought charge injection occurs directly from the highest occupied molecular orbital of the dye to states near the titania conduction band edge<sup>3,4</sup>. In this work, we have theoretically studied the adsorption of oligothiophene derivatives anchored on TiO<sub>2</sub> via catechol and investigated the surface electronic modification of TiO<sub>2</sub> anatase (101) surface by using Density Functional Theory (DFT) and Time-Dependent Density Functional Theory (TD-DFT).

The calculations established that the selected dyes present two photoinjection mechanisms: indirect mechanism of electron injection characterized by excitations with considerable intensity and involvement of the dye LUMO and second type of photoinjection which is an additional type with less intensity without the involvement of the excited state of the dye molecule. This last mechanism called type II photo injection is interesting because the absorption is in the visible region and may efficiently improve the performance of dye sensitized solar cells if we limit the recombination losses.

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# High Performance of Carbazolocarbazole-based Organic Thin-Film and Single-Crystal Field-Effect Transistors

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Among the enormous diversity of organic materials that have been studied as organic semiconductors in different types of optoelectronic devices, heteroacenes constitute one of the most promising families of compounds. Analogously, carbazole-based materials have been largely explored in organic electronics due to the good hole transporting ability of the carbazole unit. Therefore, the convergence of these two structural approaches has come into the synthesis of carbazole-based azaacenes. In this regard, it is worth highlighting the studies reported for indolocarbazole<sup>1</sup> and triazatruxene<sup>2</sup> systems as organic semiconductors. Nevertheless, despite the wide variety of derivatives prepared from these structures, and the good results reported for some of them, alternative carbazole-based azaacenes which expand the scope of these systems are not abundant in the literature. This has motivated our interest in the synthesis of new carbazole-fused systems, namely carbazolocarbazoles.<sup>3</sup>

Herein we report a novel carbazolocarbazole isomer which has been applied to the fabrication of thin-film and single-crystal organic field-effect transistors. The electronic structure of carbazolocarbazoles shows low lying HOMOs which makes them highly stable towards ambient oxidation. Nevertheless, this might also make more difficult to obtain ohmic contacts. Accordingly, contact doping<sup>4</sup> has enabled an improvement in the OFET operation when compared to previously reported results. Besides, several gate dielectrics have been evaluated, leading to excellent device performances. As a result, this new carbazolocarbazole represents one of the best carbazole-based azaacenes described in organic field-effect transistors.

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# Electronic states in bulk fullerenes and at their interface to polymers: charge delocalization and exciton hybridization effects

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Motivated by the prospects for high-efficiency organic solar cells, there have been considerable efforts to unveil the electronic processes taking place at organic donor/acceptor (D/A) heterojunctions.<sup>1,2</sup> The description of the electronic structure at the length scale pertaining to charge separation at D/A interfaces is a formidable task that we tackle with a multiscale approach grounded on a site-based model Hamiltonian fed with atomistic inputs, explicitly accounting for disorder, electrostatics and genuine quantum effects such as charge delocalization and exciton hybridization.

Our theoretical analysis show that in bulk fullerene derivatives, electrostatic disorder, mostly dipolar and static in nature, leads to fully localized charge carriers at room temperature in PC60/70BM quite irrespective on the sample crystallinity, while delocalized states are available for transport in pristine C60.<sup>3</sup> Yet, all fullerene derivatives sustain high-energy delocalized states that can play a role for solar cell application, as shown for a prototypical polymer/fullerene interface. In fact, at D/A interfaces bound localized charge transfer states are found to coexist with a large majority of thermally accessible delocalized space-separated charges.<sup>4</sup> The latter can be also reached by direct photoexcitation, thanks to their strong hybridization with singlet polymer excitons. These findings reconcile the recent experimental reports of ultrafast exciton separation ("hot" process) with the evidence that high quantum yields do not require excess electronic or vibrational energy ("cold" process). We further show that delocalization, by shifting the density of charge transfer states toward larger effective electron-hole radii, may reduce energy losses through charge recombination.

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# Indolo-naphthyridine-6,13-dione thiophene (INDT) Building Block for Conjugated Polymer Electronics

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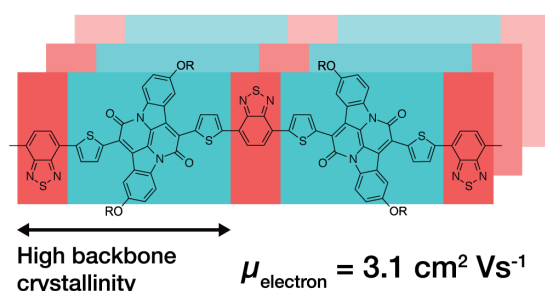
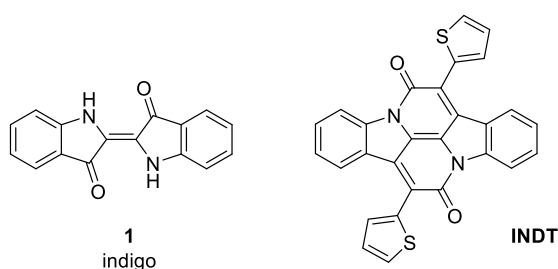
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We present our work on improving the strongly absorbing chromophore of indigo (**1**) dye in high performance organic electronics. Indolo-naphthyridine-6,13-dione thiophene, **INDT**, can be synthesized from indigoids via condensation reactions with functionalized acetyl chlorides and has a strongly absorbing, electron deficient character.

We have synthesized and characterized four conjugated polymers of INDT with common comonomers: thiophene, phenyl, benzothiadiazole and selenophene.<sup>1</sup> All four polymers exhibit extremely small band gaps of  $\sim 1.2$  eV, power conversion efficiencies up to 4.1% and charge photo-generation up to 1000 nm. The polymers showed ambipolar transport in organic field-effect transistors and notably, reliable<sup>2</sup> n-type mobility exceeding  $3 \text{ cm}^2 \text{ Vs}^{-1}$  in the benzothiadiazole-containing polymer **INDT-BT**.

Using grazing-incidence wide-angle x-ray scattering (GIWAXS) we were able to correlate the observed high n-type transport with remarkably high crystallinity along the polymer backbone, having a correlation length in excess of 20 nm,  $\sim 13$  repeat monomer units. Furthermore, computational calculations and crystallography<sup>3</sup> show the **INDT** molecule is not planar and the thiophenes are twisted slightly out of plane. Our findings suggest that high n-type transport is more dependent on polymer backbone crystallinity over backbone planarity and shines light on the inherent ability of the benzothiadiazole building block to increase polymer backbone crystallinity.



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# Long-range exciton diffusion in perylene diimides mediated by singlet fission

*Kevin Felter*

The favorable electronic coupling and energetics of perylene diimides (PDIs) allow efficient occurrence of the unconventional photophysical processes termed singlet exciton fission (SF) [1]. SF influences the observed exciton diffusion length ( $L_{exc}$ ) while molecular crystal packing affects both. This study aims to determine the  $L_{exc}$  in imid substituted PDIs and relate it to the extent of SF and crystal packing. To this end, physical vapor deposited planar heterojunctions of crystalline zinc phthalocyanine (ZnPc) and PDI are studied by flash photolysis time resolved microwave photoconductance (FP-TRMC) and transient absorption (fs-TA). FP-TRMC reveals PDI  $L_{exc}$  values over tens of nanometers that can be correlated to efficient singlet fission as deduced from fs-TA and improved crystal packing. These findings provide understanding of the role of singlet fission in charge carrier and excited state dynamics in organic solid state systems.

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# Spirocycle Containing Conjugated Polymers: Manipulating Excited States

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*Modified spirocycle unit showing orthogonal electron withdrawing groups.*

TADF has been demonstrated within small molecule systems<sup>2</sup> where it is used to enhance electroluminescent efficiencies, we wish to transplant this technology into polymeric materials. This necessitates the manipulation of the materials  $\Delta E_{s-t}$  allowing for the thermally activated conversion of triplet excitons into singlet excited states.

The structure of the spirocycle monomeric unit allows for the placement of electron withdrawing groups orthogonal to the polymer backbone.<sup>3</sup> This orientation induces the spatial separation of HOMO and LUMO orbitals upon the chain, lowering the singlet-triplet energy gap and fulfilling the prerequisite conditions for TADF to occur. The singlet-triplet energy gap of these materials is shown computationally to be modifiable by the substitution of the orthogonal groups within the materials.

*The separation of HOMO and LUMO orbitals*

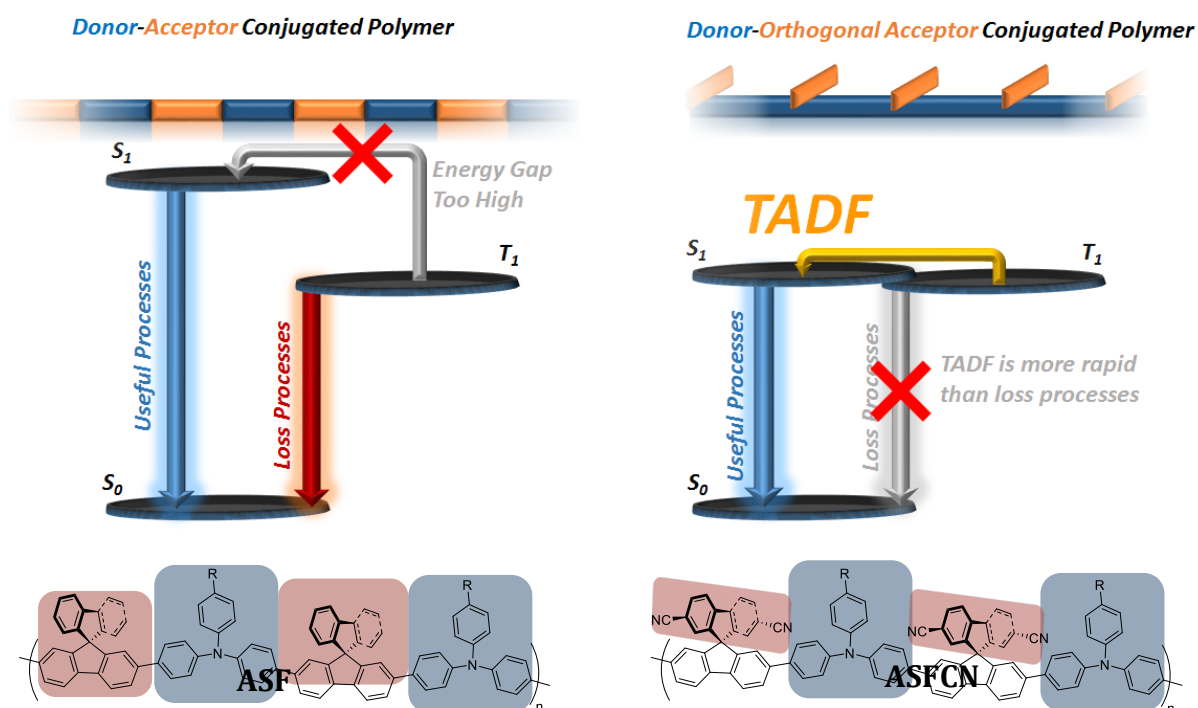
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# Manipulating the Singlet-Triplet Energy Gap – TADF in Organic Conjugated Polymers

David M. E. Freeman, Andrew Musser, Richard Friend, Hugo Bronstein

Triplet harvesting materials are an attractive field of study within the larger field of organic semiconductors, due to the efficiency boosting potential of utilising triplet excited energy states in a useful manner. **Thermally Activated Delayed Fluorescence (TADF)** has recently been reported in several small molecule based devices and leads in all cases towards highly efficient systems.<sup>1</sup> It has previously been **assumed that this would be impossible to achieve in polymers**, due to an almost constant  **$S_1$ - $T_1$  energy gap ( $\Delta E_{ST}$ ) of  $\approx 0.7$  eV** across all conjugated polymeric organic systems.<sup>2</sup> This assumption is based on the fact that conjugated polymers predominately have their frontier molecular orbitals located across the polymer backbone: a prerequisite for long range conjugation. By manipulating the **LUMO to a spatially distinct part of the molecule** however,  $\Delta E_{ST}$  may be manipulated well below the previously accepted value of 0.7 eV. This talk will outline the design, synthesis and physical data of a series of conjugated organic semiconducting polymers; ending with a polymer with  $\Delta E_{ST} \ll 0.1$  eV. This represents the first example of TADF in an organic conjugated polymer.<sup>3</sup>



Graphical representation of **ASFH** (left) and **ASFCN** (right) frontier orbitals. Through the addition of EWGs to an orthogonal moiety,  $S_1$  is effectively decreased in energy while  $T_1$  remains constant. This effect is large enough so that ambient thermal energy can promote an electron from  $T_1$  to  $S_1$ , thus all triplet excitons may be harvested as singlet excitons.

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**Niall Goodeal**

# Kinetic Monte Carlo simulations for improving organic electronic device performance

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Organic electronics is the state-of-the-art technology in displays and emerges as promising future technology for large-area lighting, photovoltaics and flexible electronics. However, optimizing and improving the efficiency and lifetime of these devices remains a challenging task due to the complex interplay between charges and excitations at the molecular scale. Without guiding tools, materials and device structures used are typically optimized in a trial-and-error approach, using expensive and time-consuming device fabrication techniques and experiments. We have developed a 3D kinetic Monte Carlo organic electronic device model<sup>1-3</sup> incorporating the latest scientific insights in charge transport and exciton dynamics in disordered organic semiconductors. The Bumblebee simulation tool,<sup>4</sup> based on this model, enables researchers to analyze, predict and improve the performance of new organic electronic device concepts.<sup>5,6</sup>

Here, we show predictions of the electrical characteristics, efficiency, color point and lifetime of state-of-the-art organic light-emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) materials.<sup>7,8</sup> Exciton loss processes like exciton-polaron quenching, exciton-exciton annihilation and non-radiative triplet states are included. We compare our predictions with experimental results and we provide research directions for OLEDs performance improvement.

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# Benzo-Fused Double [7]Carbohelicene: Synthesis, Structures, and Physicochemical Properties

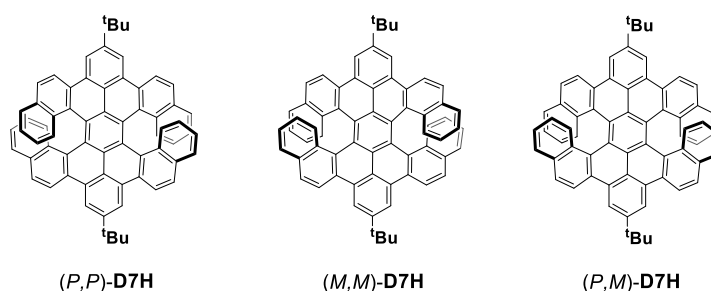
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ABSTRACT helicenes have attracted continuous attention due to their contorted  $\pi$ -systems, inherent chirality, and dynamic behavior, which render them promising application in asymmetrical catalysis, supramolecular chemistry, and organic electronics. [7]Carbohelicene is an interesting member in helicene family with double-layered helical structure that has led to its application in molecular tweezer and chiral organic surfaces. In the past two decades, double helicenes with a scaffold of two fused helicenes have emerged as a representative class of multihelicenes, demonstrating increased molecular distortions and multidimensional intermolecular interactions in the solid state. In particular, significant advances have been made in the synthesis of double heterohelicenes, and double [7]heterohelicene with a layered structure was constructed recently. However, double carbohelicenes are relatively rare because of their synthetic challenge, and double carbohelicenes with seven or more ortho-fused aromatic rings have never been achieved.



We demonstrate an efficient regioselective cyclodehydrogenation protocol towards benzo-fused double [7]carbohelicene (**D7H**). The three isomers of **D7H**, including two enantiomers in twisted form and one conformer in meso form, were separated by recrystallization and chiral HPLC. Their double-layered helical structures were clearly confirmed by X-ray crystallography, and a record-setting isomerization energy barrier of 46.0 kcal mol<sup>-1</sup> was estimated by DFT calculations, supported by the experimentally observed, remarkable conformational stability of **D7H**. The physicochemical properties of **D7H** were investigated, indicating modulation of the electronic structure upon conformational change. The highly stable double [7]carbohelicene might find applications in the growing field of chiral photonics, for example in chiral imaging and biosensing.

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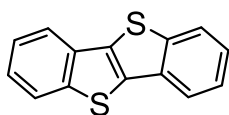
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# Study on the synthesis of highly conjugated [1]benzothieno[3,2-b]benzothiophene derivative

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To achieve high-performance organic field effect transistor, the investigation for new molecular structure is important. [1]benzothieno[3,2-b]benzothiophene (BTBT)<sup>1,2</sup> is one of the promising molecular structures which can realize high charge carrier mobility. The carrier mobility of some BTBT derivatives has been reported as higher than  $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>3-5</sup> In this study, the synthesis of highly conjugated BTBT derivative, BTTBTTBTTB has been investigated, because highly conjugated structure can contribute to obtain higher electron charge mobility due to its wide overlapped electron clouds.



BTBT



BTTBTTBTTB

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# Single-crystalline organic thin films: A predictive model that enables fast process optimization

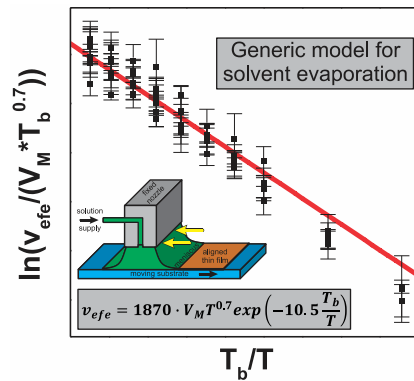
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Single crystalline organic thin film transistors (OTFTs) offer great potential for the realization of high-performance, low-cost flexible electronics. The most common methods to fabricate these layers directly on an inert substrate are all based on unidirectional solution coating techniques such as zone-casting, dip-coating or solution shearing. The quality of the resulting film strongly depends on the choice of solvent, coating speed and substrate temperature. So far, process optimization in literature has been conducted by trial and error methods, involving, for example, the variation of coating speeds over several orders of magnitude.

Here, we show our recently developed model that enables the prediction of the coating speed for a given solvent-temperature combination[1]. Thereby we are able to reduce the three dimensional parameter space by one dimension, enabling faster parameter screening and thereby process optimization. We show the validity of our approach by comparing it with results obtained by numerical simulations, experimental results published in literature and our own experimental results. We show the clear advantage of this approach in terms of processing steps needed to find a suitable process window[2]. In the case of C8BTBT, this leads to state of the art results with well-behaved OTFT characteristics with mobilities up to 7 cm<sup>2</sup>V/Vs and onset voltages close to zero volts.



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# Modeling of perylene monoimide based dye molecules and NiO (100) for p-type dye sensitized solar cells

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The interest for dye-sensitized solar cells (DSSC) has increased during the last few decades. This is due to their synthetic flexibility, wide lightcollecting spectrum, low cost, and high quantum efficiencies. [1] Our focus here is on p-type dye sensitized solar cells, in particular on the modelling of the electronic energy level alignment at the dye-oxide interfaces.

We have studied two dye molecules, both alone and on the NiO (100) surface, at the Density Functional Theory (DFT) level, using a localized basis set and a hybrid functional (B3LYP). The studied molecules are donor-acceptor dyes. In dye **1**, a terthiophene is used as donor and a perylene monoimide as acceptor and in dye **2** perylene monoimide moiety is the donor and naphthalene diimide is the acceptor. The anchoring group is carboxylic acid in both cases.

Calculations of the band structure and density of states of the dye molecules, NiO alone, and the dye-NiO full systems show that: i) the frontier orbitals are localized on the donor (HOMO, LUMO+1) and acceptor (LUMO) moieties in the isolated dyes, ii) the HOMO-LUMO gaps vary in the range 1.8 - 2.5 eV depending on the molecule, iii) the band gap of the NiO slab is 4.0 eV, in good agreement with experimental data, and iiiii) most importantly, the HOMO of the dye molecules lies above the Valence Band Maximum (VBM) of the NiO surface in all combined systems.

The predicted energy level alignment at the semiconductor-molecule interface is expected to result in an inefficient hole extraction from the photoexcited molecule to the NiO, in contrast to experimental evidence [2]. We speculate that this discrepancy arises from the presence of defects and doping of the NiO, known to enhance the p-type character of the oxide surface, while our calculations have been performed for the pristine semiconductors. We are now conducting additional theoretical investigations to check this hypothesis.

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# On the origin of the high hole mobility in IDTBT conjugated polymers: a theoretical study

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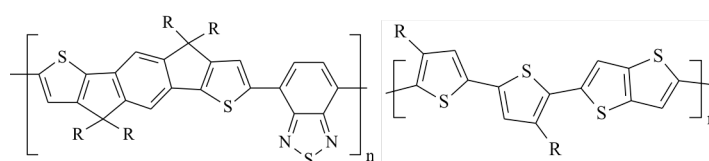
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The use of organic semiconductors in organic field-effect transistors has raised growing interests and efforts in the last decades which led to outstanding improvements of their performances; it becomes now common to find organic conjugated materials with charge mobilities larger than  $1\text{cm}^2/\text{Vs}$ . Throughout these years of intensive researches, the highest mobilities were always reported for single crystals of organic small molecules and it therefore boosted intensive works towards the design of ordered/crystalline materials since it seems that ordering in films is a key parameter to get high performances in field-effect transistors. Organic conjugated polymers are intrinsically not highly ordered materials since they are only weakly van der Waals bonded flexible macromolecules. They have therefore been the subject of many efforts to increase the amount of ordered/crystalline regions, i.e., to get semi-crystalline materials, and hence an increase of the long-range charge transport properties. But recently, this general belief that high crystallinity is required to get high charge mobilities broke down with the emergence of a new class of disordered or even seemingly amorphous organic conjugated polymers which also exhibit charge mobilities larger than  $1\text{cm}^2/\text{Vs}$  [1-2].

Understanding at the atomistic level the fundamental reasons of the outstanding properties of these disordered polymers is becoming crucial to design the next generation of polymers for field-effect

transistors since the link the microstructure and mobility is, so far, far clear. In this context, we the atomistic



Chemical structures of IDTBT (left) and PBTTT

between charge from probed

microstructure of two state-of-the-art polymers (IDTBT and PBTTT) by means of molecular dynamics simulations from crystalline to amorphous regions and demonstrated the subtle interplay between their structural properties and their electronic (DFT calculations) and charge transport properties.

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# Conjugated Materials for Organic Solar Cells

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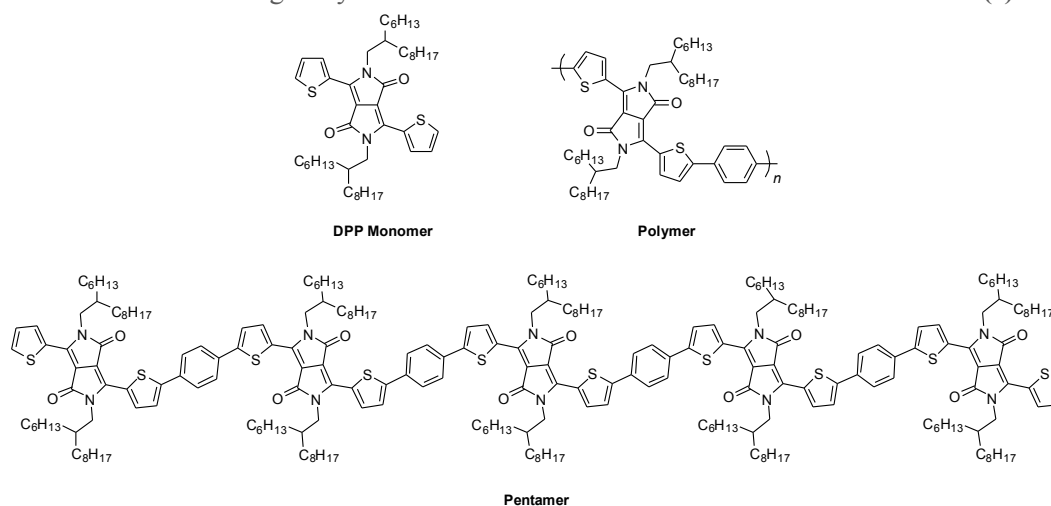
The most widely studied materials for organic photovoltaic (OPV) devices are conjugated polymers and conjugated small molecules. Both materials have the potential to offer cheap, lightweight and mechanically flexible devices with tuneable light-harvesting properties. However, **comparison of conjugated oligomers and polymers with relevance to solar cell applications has not been widely investigated**. As it is unknown which photoactive material results in the greatest efficiency of a solar cell, this became the focus of our research.

Our work focuses on the electron deficient lactam core of diketopyrrolopyrrole (DPP) which has been used to synthesise exceptionally narrow band gap materials suitable for use in OPV devices.<sup>1</sup> We have successfully synthesised a series of well-defined oligomers containing from two to seven units of a DPP monomer with alternating phenyl rings along the chains (*via* regular Suzuki-Miyaura cross-coupling and dibromination reactions), as well as the corresponding DPP-derived polymer.<sup>2</sup>

A fundamental feature greatly overlooked in literature is the **extinction coefficient ( $\epsilon$ )**. It is a measure of

how well a molecule can absorb light at a particular wavelength.

Initial studies on the optical properties of our oligomers have been performed using



density functional theory (DFT). We calculated that as the chain length increases, the extinction coefficients increase accordingly. However, normalising with respect to the number of  $\pi$ -electrons in each system shows us that as oligomer length increases,  $\epsilon$  also increases and then drops from trimer to pentamer. This can be attributed to the chain becoming more twisted (due to the introduction of phenyl groups between DPP units), which affects the conjugation length. This trend is also observed experimentally. Interestingly, as the chain length extends further from pentamer to polymer, the absorption onset only slightly becomes more red-shifted. We speculate that this could be due to aggregation, though further work to determine why this phenomenon occurs is ongoing.

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# Imaging electronic bottlenecks in organic field-effect transistors with photocurrent microscopy

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Improving the performance of organic electronic devices in terms of higher charge carrier mobility requires a detailed investigation of the electronic bottlenecks. These bottlenecks, e.g. contact resistance or charge carrier traps, obstruct the charge transport, leading to unwanted voltage loss in the active device regions. Here, we use scanning photocurrent microscopy (SPCM) to highlight the dominant voltage loss mechanism in pentacene transistors under ambient conditions.<sup>1</sup> We make use of a highly asymmetric transistor (voltage loss of >94% in the defective direction) in order to separate contact resistance from channel resistance within the same device. In the defective direction, SPCM maps highlight contact resistance at the source electrode due to charge separation. In the ohmic direction SPCM shows areas of high trap density deep within the transistor channel, caused by trap release.

In future, we are going to apply SPCM on transistors with the hydrogen-bonded semiconductor epindolidione. This promising material shows high mobility together with an exceptional stability of the device characteristics.

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# Analysis of triplet-triplet annihilation in organic phosphorescent materials

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The efficiency of phosphorescent organic light emitting diodes (OLEDs) shows a decrease with increasing luminance ("roll-off"). One of the contributions to the loss of efficiency at a large luminance is triplet-triplet annihilation (TTA). Triplet-triplet annihilation is the process of energy transfer from one exciton to another, after which the excited exciton decays non-radiatively to the lowest triplet state. Effectively, one exciton is lost. In literature, the mechanism of TTA is under debate<sup>1,2</sup>: what is the role of triplet diffusion and how can the diffusion process then be described (as a Förster type or a Dexter type process), and what is the role of the matrix material in which the phosphorescent emitter molecules are embedded?

In this study, the rate of the TTA process is studied for a large number of emissive materials consisting of a small concentration of phosphorescent molecules ("guests"), embedded in a non-emissive host material. Using a recently presented novel analysis method to analyze transient photoluminescence experiments,<sup>2</sup> it is possible to deduce for a single guest concentration whether TTA is a single-step or a multi-step (diffusion-mediated) process. A comparison is made with the results obtained from kinetic Monte Carlo simulations. From the simulations a Förster radius for TTA can be obtained and it can be shown that triplet diffusion can be described when disorder is taken into consideration in a mechanistic manner using a Dexter type process. For the studied system of CBP:Ir(ppy)<sub>2</sub>(acac) a Förster TTA radius of 4–4.5 nm is found.<sup>3,4</sup> The exciton diffusion is found to be described well using a Dexter process with an exciton wavefunction decay length of 0.3 nm and a rate to the first neighbor molecules of  $\sim 1.2 \times 10^{13} \text{ s}^{-1}$ .

Furthermore, we have investigated which to what extent the TTA efficiency loss can be minimized by choosing a host material with a triplet exciton energy which is much larger than the guest triplet energy, leading to strong confinement of the triplet states on the guest molecules. For Ir(ppy)<sub>2</sub>(acac), embedded in various matrix materials, differences of the TTA loss up to a factor of two were found.

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# *Ab initio* modeling of charge transport in amorphous molecular semiconductors

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Amorphous molecular semiconductors are key materials in the emerging organic light-emitting diode (OLED) technology. Understanding and predicting their charge transport properties is crucial. While commonly-used charge transport models use fit parameters, we present here an *ab initio* model.<sup>1,2</sup> The study is based on microscopic information obtained from atomistic simulations of the morphology and density functional theory calculations of the molecular hole energies, reorganization energies, and transfer integrals. Using stochastic approaches, the microscopic information obtained in simulation boxes at a length scale of  $\sim 10$  nm is expanded and employed in one-dimensional (1D) and three-dimensional (3D) master-equation (ME) modeling of the charge transport at the device scale of  $\sim 100$  nm. We consider electron and hole transport in several molecular semiconductors used in OLEDs, like  $\alpha$ -NPD and TCTA. Without any fit parameter, the predicted current-voltage and impedance spectroscopy characteristics of  $\alpha$ -NPD hole-only devices with different thicknesses obtained with the 3D-ME modeling agree well with experiment in a wide range of bias voltages, temperatures, and frequencies. Similarly good results are obtained with the computationally much more efficient 1D-ME modeling after optimizing a hopping prefactor. Refining the model by including energy correlations and superexchange between the molecules further improves the agreement.

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# Redox Active Helicenes for Molecular Materials

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Introduction of chirality in tetrathiafulvalene (TTF) has been investigated by our group since several years and has recently provided the first experimental observation of the electrical magneto-chiral effect in a bulk molecular conductor.<sup>1</sup>

Helicenes<sup>2</sup> are original helical screw shaped  $\pi$ -conjugated molecules with remarkable chiroptical properties.<sup>3</sup> The electroactive TTF moiety present two stable redox state and the association with helical precursors may the possibility to modify their chiroptical properties. Also, we can expect original architectures in the solid state, with the presence of  $\pi$ - $\pi$  stacking between helicene units and S...S interaction between TTFs.<sup>4</sup>

Besides, introduction of heterocycles such as thiadiazoles in the helical structure can provide luminescent properties.<sup>5</sup>

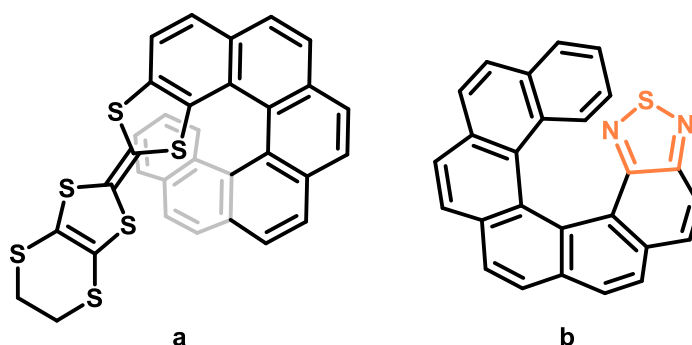


Figure 1 : a) EDT-TTF-[n]helicene (n = 4, 6), b) thiadiazole[7]helicene

Such chiral electroactive precursors are of great interest since they might allow the preparation of chiral conducting or luminescent materials.

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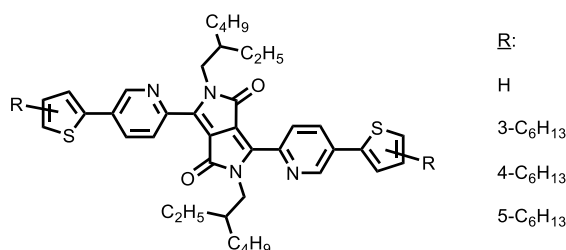
# Influence of H and J-aggregation of Small Thiophene-Pyridine-DPP Molecules on the Photophysical Properties and Photovoltaic Performance of Solution-Processed Solar Cells

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The performance of organic semiconductors in optoelectronic devices depends on the functional properties of the individual molecules and their mutual orientations when they are in the solid state.<sup>1-3</sup> Herein we present the effect of H and J-aggregation on the photophysical properties and photovoltaic behavior of four electronically identical, but structurally different thiophene-pyridine-diketopyrrolopyrrole molecules. By introducing and changing the position of two hexyl side chains on the two peripheral thiophene units of these molecules, we effectively tune their aggregation in thin films between H-type and J-type as evidenced from the characteristics of optical absorption, fluorescence, and excited state lifetime. The two derivatives that assemble into J-type aggregates exhibit a significantly enhanced photovoltaic performance, up to an order of magnitude, compared to the two molecules that form H-type aggregates. The reasons for this remarkably different behavior are discussed.



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# Electrochemical study of EDOT-based polymers for cation sensing

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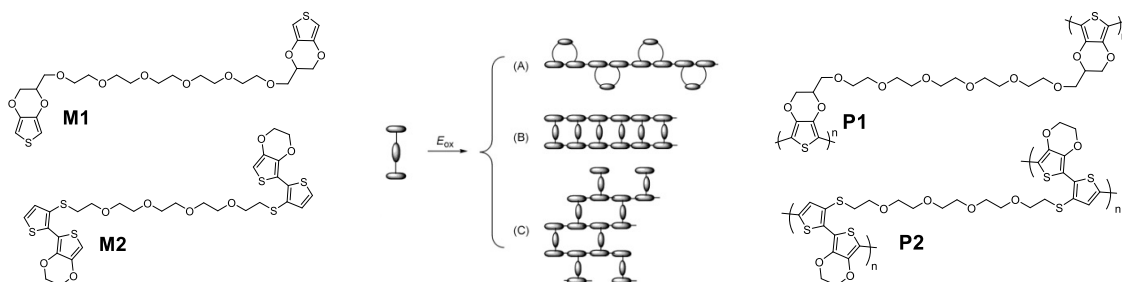
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PEDOT:PSS-based organic electrochemical transistors (OECTs) have received a considerable interest for chemical and biological sensing in aqueous media.<sup>1</sup> Since PEDOT:PSS displays poor selectivity toward cationic analytes, the fabrication of OECT that could be run as cation sensor has often required a cation selective membrane coupled to the active layer.

Electro-generated PEDOT-like materials with some intrinsic cation recognition properties can be obtained from precursors consisting of two electropolymerizable EDOT moieties bridged by an oligo(ethylene-glycol) (OEG).<sup>2</sup> Such a material consists of a 3D network with an electroactive conjugated backbone and hydrophilic cavities.<sup>3,4</sup> Replacing the EDOT core with a  $\pi$ -extended EDOT-thiophene electropolymerizable moiety in the precursor, is also possible to obtain analogous polymeric structures endowed with higher oxidation potentials, which can in turn be run in normally-off devices.

We have synthesized two OEG-bridged bis-EDOT (**M1**) and bis(EDOT-thiophene) (**M2**) precursors, and studied their electropolymerisation in different conditions. Subsequently, we investigated the electrochemical behavior of the corresponding polymers (**P1**) and (**P2**), in presence of different electrolyte cations, ranging from bulky tetrabutylammonium (TBA) to alkali ( $\text{Li}^+$  and  $\text{Na}^+$ ) and alkaline earths ( $\text{Ca}^{2+}$ ).



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# Modulation of open-shell character of triphenylamines having two phenoxy radicals via structural modification

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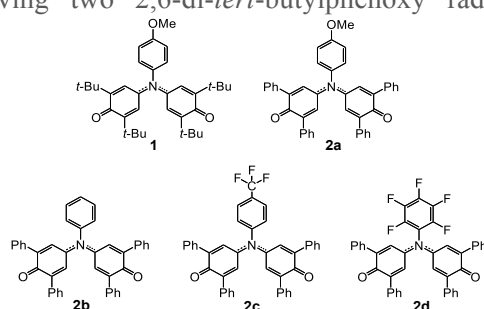
It is expected that the electron removal from the molecules with nonbonding HOMO less affects the bond lengths and then the reorganization energy could be decreased.<sup>[1]</sup> According to this principle, we have so far developed a triphenylamine derivative having two 2,6-di-*tert*-butylphenoxy radicals having nonbonding HOMO and a closed-shell electronic structure (1)<sup>[2]</sup>. In this study, we prepared derivatives of 1 with substituents (2a-d) and investigated their structures, properties and energy gaps between the closed-shell biradical states ( $\Delta E_{T-CS}$ ).

The structures of 2a-d were confirmed by the crystal X-ray analysis. 2a-d showed the characteristic bond length alternation (BLA) patterns precursors of 2a-d did not, suggesting the closed-ground states of 2a-d.

As shown in Figure 1, 2a-d exhibited ESR even at room temperature while 1 showed no ESR

The signal intensities decreased with decreasing temperature for 2a-d. These indicated that 2a-d have the singlet state, but 2a-d have smaller  $\Delta E_{T-CS}$  than also estimated  $\Delta E_{T-CS}$  from the temperature dependence of the signal and revealed 2a has largest  $\Delta E_{T-CS}$  and smallest  $\Delta E_{T-CS}$  in 2a-d.

These observations were supported calculations. The order of the calculated was 1 > 2a > 2b > 2c > 2d. For 2a, the density of the biradical state could be delocalized on the outer phenyl groups, therefore the biradical state of 2a could be stabilized compared to 1. The electron group on the nitrogen atom could stabilize the closed-shell state and make  $\Delta E_{T-CS}$  larger, and this may result in the order of  $\Delta E_{T-CS}$  of 2a-d.



Scheme 1. Triphenylamine derivatives drawn as closed-shell forms

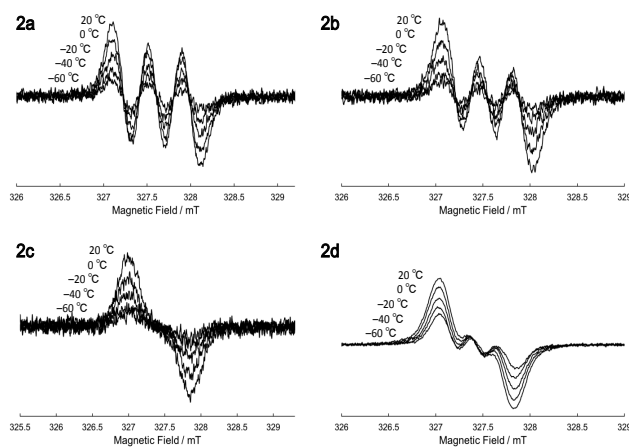


Figure 2. ESR spectra of 2a-d (1 mM in toluene)

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# Chiral $C_3$ symmetric molecules suitable for charge transport processes

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Organic  $\pi$ -conjugated molecules with columnar organization driven by a co-facial stacked aromatic cores surrounded by alkyl chains afforded a great number of nanomaterials showing energy or charge transport in organic electronic devices such as solar cells or organic field-effect transistor (OFETs).<sup>1</sup> Different rotational symmetries have been studied for discotic molecules, but the  $C_3$  symmetrical structures have become more attractive, especially those ones with 1,3,5-benzenetricarboxamide unit as a central core (Figure 1).<sup>2</sup>

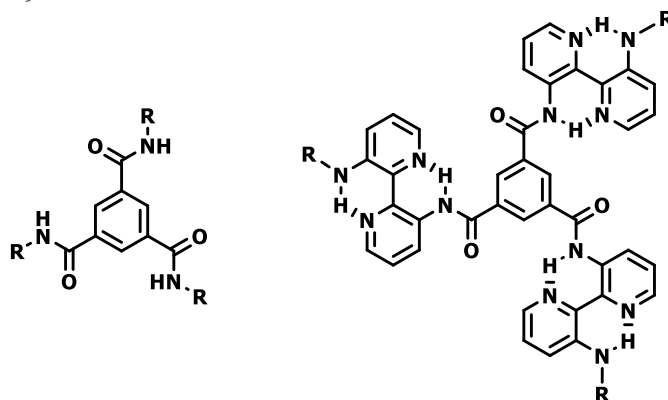


Figure 1.

The possibility to modify systematically the peripheral arms offers a great number of derivatives that easily tune their physical with tunable properties in order to be integrated in nanoelectronics<sup>3</sup> or optical devices.<sup>4</sup> Moreover, the introduction of chiral centers in the arms can influence the charge transport in the chiral aggregates.<sup>5</sup>

In this work,  $C_3$  molecules compounds based on the electroactive chiral TTF and chiral porphyrins have been synthesized and their self-assembly and morphology have been studied by CD and AFM studies.

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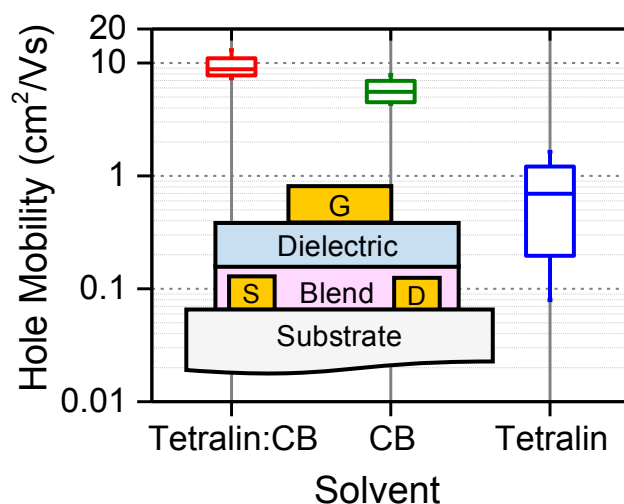
# Small Molecule / Polymer Blend Organic Transistors with Hole Mobility Exceeding 13 cm<sup>2</sup>/Vs

Alexandra F. Paterson<sup>1</sup>), Neil D. Treat<sup>1</sup>), Weimin Zhang<sup>2</sup>), Zhuping Fei<sup>1</sup>), Gwenhivir Wyatt-Moon<sup>1</sup>), Hendrik Faber<sup>1</sup>), George Vourlias<sup>3</sup>), Panos A. Patsalas<sup>3</sup>), Olga Solomeshch<sup>4</sup>), Nir Tessler<sup>4</sup>), Martin Heeney<sup>1</sup>) and Thomas D. Anthopoulos<sup>1</sup>)

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Plastic electronics that can be manufactured using solution-based methods are the subject of great interest due to their potential for low-cost, large-area electronic applications. The interest in this field has led to considerable research and subsequent advances in device performance. To this end solution-processed organic thin-film transistors (OTFTs) have shown impressive improvements in recent years, mainly through the increasing values of charge carrier mobility.

Here we report the development of 3<sup>rd</sup> generation organic blend systems for spin-coated OTFTs with hole mobilities exceeding 13 cm<sup>2</sup>/Vs (please see Figure below). These high performance devices have been achieved using a novel ternary semiconducting blend system comprising of an amorphous-like conjugated polymer, a highly crystalline small molecule and a fluorinated fullerene which plays the role of a molecular dopant. The polymer binder that has been used is indacenodithiophene-benzothiadiazole (C<sub>16</sub>IDT-BT), which belongs to the family of indacenodithiophene-based copolymers which are renowned for their high carrier mobilities regardless of their apparent structural disorder. 2,7-Dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C<sub>8</sub>-BTBT) has been carefully selected as a complementary small-molecule to blend with the C<sub>16</sub>IDT-BT and – most importantly – the inclusion of C<sub>60</sub>F<sub>48</sub> as a molecular dopant within this system is seen to greatly improve device characteristics. The improvement in the performance of the OTFTs due to the addition of a dopant demonstrates the potential of this novel ternary blend system.



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## Acknowledgements:

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# Pressure sensor based on organic single crystal air-gap transistor

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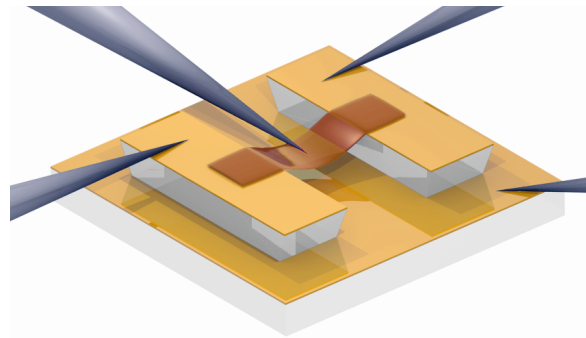
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Despite past efforts on Micro ElectroMechanical Systems (MEMS) low-pressure sensors (< 10 kPa) remains a challenge. In the present study, we have demonstrated the possibility to play on the injection of charge carrier at the Gold/Rubrene interface of an air-gap transistor to detect ultra-low pressure close to 1 Pa. The pressure sensor is based on a structure made by casting polydimethylsiloxane (PDMS) on a pre-wafer<sup>(1)</sup>. Gold electrodes are evaporated on these PDMS stamps. A defect-free single crystal laminated as organic semiconductor<sup>(2)</sup>. The pressure is applied on the sensor by using a piezo-robot gently touching the middle of the crystal. The crystal deflection is measured by optical profilometry to extract the related strain. A significant increase of drain current is measured with applied strain. In order to quantify this variation, and determine the sensibility of our device, the Gauge factor (GF) is calculated to values above 1900 by dividing the relative variation of current by the strain applied on the crystal. This value represents a record highly sensitive sensor. To explore the origin of such sensitivity, the influence of an additional thin MoO<sub>3</sub> layer between gold and rubrene is studied. Favoring the injection of charge carriers enables to produce better performing transistors<sup>(3,4)</sup>. However, the measured GF were then equal to GF calculated by dividing the relative variation of capacitance by the strain, i.e. the sensitivity is then low and due only to capacitance variations. This experiment clearly highlights that the high GF (without MoO<sub>3</sub>) are related to enhanced injection under strain and can be explained by a work function dependence of rubrene under compression as recently reported by Frisbie *et al.*<sup>(5)</sup>.



interface of pressure on an air-gap transistor patterned on these rubrene is The a small suspended by optical

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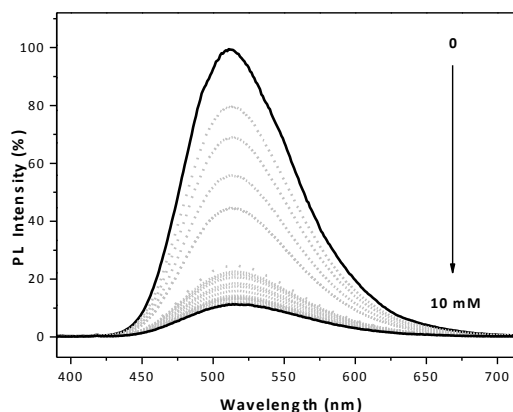
# Very high solid state Photoluminescence Quantum Yields of Poly(tetra-phenylethylene) Derivatives

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Aggregation-induced emission (AIE) has attracted much attention since it was first reported in 2001.<sup>[1]</sup> This young field of current materials research is developing fastly and recent reviews have summarized the state-of-the-art developments of AIE-type macromolecules, including their design, syntheses and applications.<sup>[2-3]</sup> The number of publications is growing exponentially, and great progress has been made so far. The widely accepted mechanism of AIE is through a restriction of intramolecular motions, including rotations and vibrations, as extensively discussed in the literature.<sup>[4]</sup> Typical, low molecular weight AIE chromophores possess a propeller-shaped structure with rotatable peripheral phenyl rings (rotors), with tetraphenylethylene (TPE) as the most prominent example. Many TPE-based AIEgens show a broad and very promising application potential in materials science and biology.<sup>[4-6]</sup>

In this study, we report the AIE properties of a series of five different poly(arylene-diarylvinylene)s (poly-TPEs) have been synthesized by reductive polyolefination starting from the corresponding bis( $\alpha,\alpha$ -dichlorobenzyl)-substituted monomers and dicobalt-octacarbonyl as reducing agent. The resulting polymers all contain main chain tetraphenylethylene units. Thanks to the aggregation-induced emission effect, the corresponding polymer films show remarkably high photoluminescence quantum yields (PLQYs) of 32%–73%. The polymer with the highest PLQY was as solid state sensing material for the PL-quenching-based detection of nitroaromatic analytes (1,3,5-trinitrobenzene as prototypical analyte).<sup>[7]</sup>



(a) PL spectra of P4 in CHCl<sub>3</sub>/ethanol (1:9) containing different amounts of TNB (polymer concentration: 10<sup>-5</sup> M;

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The tested

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# Polaron states in Fullerene adducts by Coarse Grain Molecular Dynamics and Tight Binding

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Charge transport mobility in organic semiconductors is relatively low. This is mainly due to the disordered and amorphous nature of these materials. Such low performance limits the efficiency and technological utility of organic electronics. The disorder introduces challenges in calculating the underlying electronic structure and simulating charge transport. Here we study fullerene adducts, solution processable derivatives of C<sub>60</sub>. We generate assemblies (1000 molecules) of different fullerene adducts using a coarse-grained empirical force field [1]. We construct a tight binding model of the electronic structure of the assembly using a separation dependent intermolecular coupling term that has been parameterised against quantum chemical calculations. We use this approach to calculate the electronic structure of coarse-grained molecular assemblies and to construct densities of states for different fullerene derivatives. We include self-consistent polaron formation by solving the tight-binding Hamiltonian for the system with the site energies perturbed by the response of the lattice to the charge density. This allows us to study the effect of the polaron on the density of states, the spatial delocalisation of the charged state and the nature of charge transport in these large assemblies.

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# New Challenges for Charge Transport: Isotropy

Audrey RICHARD<sup>1</sup>, Yves H. GEERTS<sup>1</sup>, Alejandro BRISEÑO<sup>2</sup>

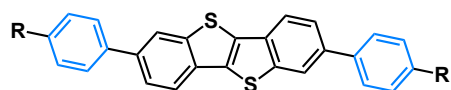
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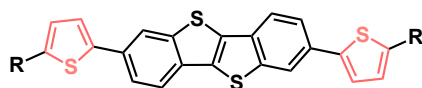
Organic electronics, based on the use of  $\pi$ -conjugated molecules and semiconducting polymers in various electronic devices, has grown considerably over the last two decades. The synthesis of new molecular structures is an important step for the development of more efficient organic semiconductors, but also to understand physicochemical processes inherent to charge carrier. The charge carrier mobility ( $\mu$ ) is a key parameter that determines the performances of semiconductors. In 2009, the group of Bao showed that it was possible to modify the charge transport properties of oligothiophenes *via* tuning of their packing by adding bulky groups (4TTMS). They obtained an in-plane isotropic mobility of  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>[1]</sup> Recently, G. Schweicher *et al* demonstrated an isotropic mobility of by adding bulky groups on the [1]Benzothieno[3,2-b]benzothiophene (BTBT).

This work is based on modulation of packing of BTBT by adding aromatic and bulky groups to improve the charge transport properties.



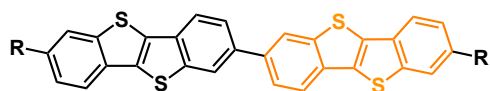
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Ph-BTBT-b R = tBu



T-BTBT-a R = H

T-BTBT-b R = tBu



Bi-BTBT-a R = H

Bi-BTBT-b R = tBu

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# Hybrid Field Effect Transistors (HFET), first example of a fully covalent transistor with a $\pi$ -conjugated organosilica material

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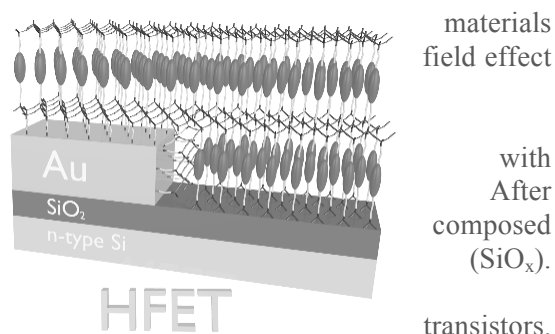
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Here we demonstrate the use of novel organosilica embedding  $\pi$ -conjugated moieties as semiconductor into transistors. The  $\pi$ -conjugated core chosen is [1]benzothieno[3,2-b][1]benzothiophene (BTBT)<sup>1</sup>, first functionalized with hydroxyl groups<sup>2</sup> and then modified with hydrolysable and cross-linkable triethoxysilyl moieties. polycondensation, this compound forms a hybrid material of charge transport pathways as well as insulating layers. However, overall, the material is found to be a semiconductor and can be incorporated into field effect transistors. These precursors, like in our previous report<sup>3</sup> showed J-Type aggregation that evolves towards H-type aggregates during the sol-gel process, which is optimal for charge transport. Taking advantage of the sol-gel chemistry involved here, we built Hybrid Field Effect Transistors that are fully cross-linked with covalent bonds. Molecules are cross-linked to each other, covalently bonded to the silicon oxide dielectric and also covalently bonded to the gold electrode thanks to the use of an appropriate self-assembled monolayer in between. This is the first report of fully covalent transistors. Those devices with modest mobilities show impressive resilience against polar, aliphatic and aromatic solvents (even under sonication). This study opens the route towards a new class of hybrid materials to create highly robust electronic applications.



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# Pinning and Polarization Effects in Molecular Junctions

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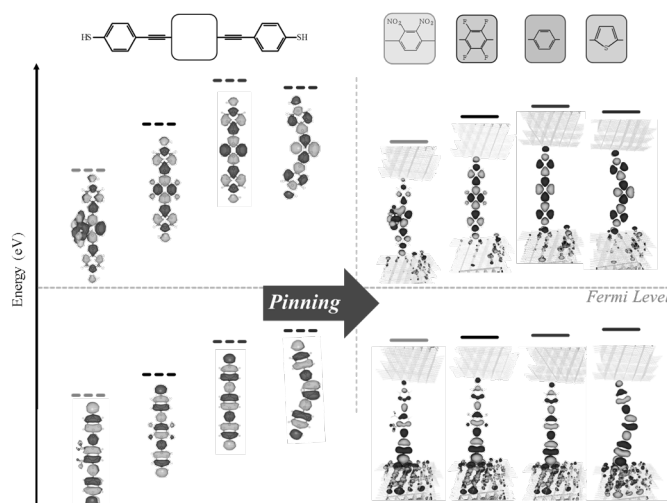
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The conductance of electrical charge through and across molecular entities is of crucial importance for the development of molecular electronics, organic electronics, nano-electronics, and other interface-related optoelectronic devices. The final electronic transport properties in functional devices, rather than being a simple property of the molecule itself, are dominated for the nature of the interface energetic in molecular junctions, more precisely by the electronic coupling strength of the frontier molecular orbitals to extended states in the electrode and the alignment of these orbitals relative to the contact Fermi level.

On one side, Fermi level pinning regime is promoted for a strong electronic coupling, pointing a similar alignment of the molecular levels responsible of the conductance, with the Fermi level of the electrodes.<sup>[1,2]</sup> On the other hand, a poor hybridization removes the pinning phenomena, limiting the extent of polarization effects.<sup>[3]</sup>

To analyze how controlled changes in the electronic structure of isolated compounds impacts on the I/V characteristics and the robustness of the pinning effect, we report a combined Non-Equilibrium Green's Function- Density Functional Theory study of molecular junctions,<sup>[4]</sup> related to the electronic properties of isolated systems. We evaluate an (OPE)-type oligomer, as straight bridge basic structure, and structural changes (nature of cycles, introduction of electro-active substituents, etc.) have been considered in order to modulate the gap and the absolute energies of the electronic levels.



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# Nanoscale C<sub>70</sub>-aggregates on pentacene for investigating the relation of charge carrier separation efficiency and crystallinity

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Crystallinity of fullerene domains is expected to play an important role for charge separation at organic donor/acceptor interfaces. An experimental investigation of the influence of crystallinity is difficult, since it requires a model system with well defined interfaces and tunable fullerene crystallinity, as well as an appropriate quantification of these characteristics. We use molecular beam deposition to create nanoscale interfaces by self-assembly of C<sub>70</sub>-aggregates on pentacene thin films (Figure 1). Size and distribution of these fullerene islands can be tuned in the range of a few 10 nm by proper choice of evaporation rate and sample temperature.

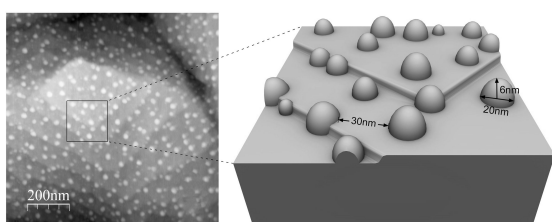


Figure 1: AFM height profile and idealized 3d picture of C<sub>70</sub>-aggregates on a pentacene layer.

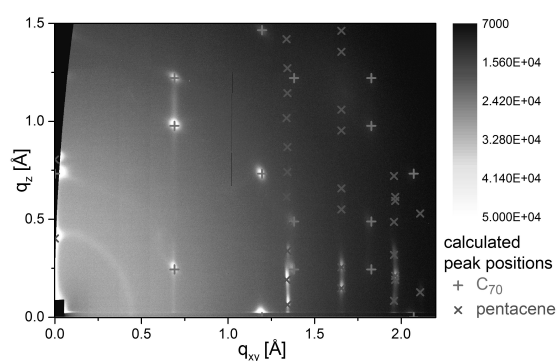


Figure 2: Grazing incidence wide angle X-ray scattering data of a pentacene/C<sub>70</sub> bilayer.

The same deposition parameters can be used to tailor the crystallinity of C<sub>70</sub>. X-ray Bragg scattering in reflection and grazing incidence geometry (Figure 2) reveals that the growth temperature affects the degree of order of the fullerene films strongly, allowing us to identify the temperature window which favors high crystallinity.

Combining these results with planned photoresponse measurements [1] constitutes an experimental approach to the relation of fullerene crystallinity and charge carrier separation efficiency at the donor/acceptor interface. Additional in situ measurements of thin film transistor characteristics during growth of the active layer, give insight into electronic effects, such as charging phenomena at the interface [2].

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# The Gated van der Pauw Approach to Mobility: Taking The Contacts Out of the Equation

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and Cedric Rolin*

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In this poster, we propose the gated van der Pauw method to determine the intrinsic charge carrier mobility and the threshold voltage of thin semiconducting films in the high charge density regime that is representative of transistor operation. The method delivers consistent and precise mobility values, thanks to the unequivocal data interpretation, independent of contact resistance and of geometrical dimensions. The device structure is easy to fabricate and the measurement procedure is straightforward to implement. We demonstrate this method with seven different organic semiconductors and thereby show its usefulness in the unambiguous extraction of crucial charge transport parameters of thin semic.

# Impact of Conjugated Polymer Chain Conformation on the Density of States and Charge Transport

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Charge transport in molecular electronic materials is known to be limited by the presence of defects and disorder in the charge carrier energy levels. Moreover, this disorder is believed to relate to the physical organisation of molecules and the resulting film microstructure. However, whilst molecular conformation can be expected to influence the density of states (DoS) hence the electronic properties, until now there has been no direct and quantitative demonstration of the relationship between a particular conformational defect in a conjugated polymer and the observed bulk charge transport properties.

Here, we combine time- and frequency-resolved probes to investigate the impact of a photophysically identifiable conformational defect, known as the  $\beta$ -phase<sup>[1]</sup>, on bulk hole transport through amorphous poly(9,9-dioctylfluorene) (PFO) films. We use a drift-diffusion model<sup>[2]</sup> that incorporates energetic disorder via an arbitrary DoS function which allows for charge carrier relaxation within, to simulate the effect of changes in the DoS on hole transport. We are able to reproduce the effect of the  $\beta$ -phase conformer on hole transport behaviour quantitatively by modifying the DoS according to information gained from spectroscopic measurements and experimentally estimated sub-gap DoS profiles of the conformational defect. We further show how apparently contradictory transport phenomena probed by different experimental techniques can be reconciled. Our estimated DoS profiles for glassy phase PFO with and without  $\beta$ -phase are supported by other complementary DoS mapping techniques, e.g. energy-resolved electrochemical impedance spectroscopy (ER-EIS)<sup>[3]</sup>.

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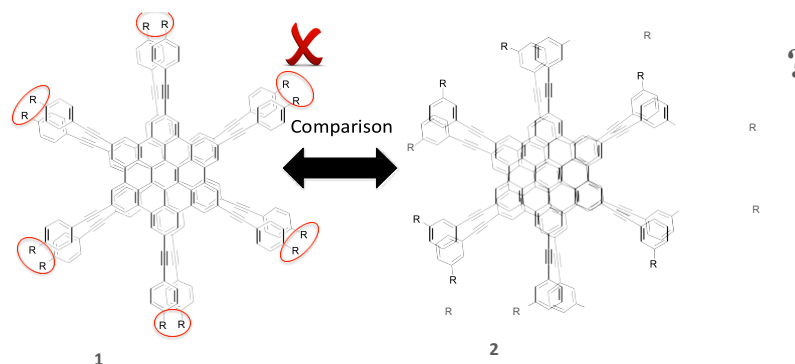
# RELATION BETWEEN SUPRAMOLECULAR STRUCTURE AND THE CHARGE AND EXCITED STATE DYNAMICS IN ORGANIC MATERIALS

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**Figure 1.** Steric hindrance effect by specific side chains

This study aims to achieve control over charge and excited state dynamics by engineering the optoelectronic properties of new organic semiconductor molecules and the way they organize in the solid state. HBCs have been studied extensively in the past and soluble alkyl-substituted derivatives of HBC exhibit some of the highest

intrinsic charge carrier mobilities.<sup>1,2</sup> Due to the steric hindrance of the side chains, there is typically a substantial

rotation of neighboring molecules with respect to each other which is 30 degrees for HBCs. Interestingly, when the charge transfer integral between neighboring molecules is considered by density functional theory calculations, it becomes clear that this is the least favorable conformation for charge and exciton transport.<sup>3,4</sup> In this work, we aim to reduce the steric hindrance by specific side chains where the aliphatic solubilizing substituents are placed in a meta configuration as shown in Figure 1. This leads to considerable differences in the supramolecular

organization, as shown by XRD and solid state NMR. It is shown that this changed supramolecular organization results in interesting changes in the electronic properties, for instance the mobility of charges.

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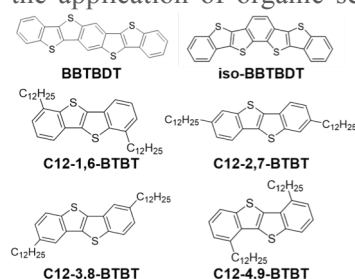
# Structure-Property Relationship of Thienoacenes Using Time-Resolved Microwave Conductivity

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Hundreds of newly synthesized organic semiconductors with unique properties have been reported day by day. Flash-Photolysis Time-Resolved Microwave Conductivity (FP-TRMC) enables direct observation of microscopic motion of charge carriers in the bulk without any electrodes or long range carrier transport. From the point of most electronic devices, charge carriers are transported at various interfaces. For the rapid evaluation of intrinsic carrier properties at interfaces, we have recently developed TRMC@Interfaces: Field-Induced Time Resolved Microwave Conductivity (FI-TRMC).

Thienoacene family is one of the fascinating candidates for the application of organic semiconductor because of its high chemical stability and exciting hole mobility. Their structural and electrical property have been studied by many researchers, but the understanding of their relation and the such high mobility is still limited. These challenging tasks reason for us to carry out comprehensive study of thienoacene series with TRMC techniques. In the present work, bis[1]benzothieno[2,3-*d'*]benzo[1,2-*b*;4,5-*b'*]dithiophene (BBTBDT) derivatives and didodecyl[1]benzothieno[3,2-*b*][1]benzothiophene (BTBT) were studied as shown in Figure. our *d*;2',3'- isomers



**Figure.** Chemical structures of thienoacenes studied by TRMC.

Metal-Insulator-Semiconductor (MIS) devices were fabricated with the configuration of Au/SiO<sub>2</sub>/PMMA/Semiconductor/Au for each BBTBDT derivatives for FI-TRMC measurement. The device was loaded in the microwave cavity with the resonant frequency of ca. 9 GHz and 10 Hz square gate voltages with various negative signs were applied to inject the holes into BBTBDT layer. The increase of the conductivity  $\Delta\sigma$  was monitored by the change of the reflected microwave power  $\Delta P_r$  from the cavity with the following relation:  $\Delta\sigma = A\Delta P_r$ , where  $A$  is the correlation factor depending on the microwave setup. Hole mobility of BBTBDT at PMMA interface was estimated as 4.5 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> from the dependence of  $\Delta\sigma$  upon the gate voltage, whereas iso-BBTBDT was resulted in the hole mobility of 0.6 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. These difference could be attributed as the stronger intermolecular interaction in BBTBDT from the absorption spectra and theoretical calculation<sup>[1]</sup>.

The structural, electronic, and conductive properties of four BTBT derivatives with two dodecyl chains at different positions (1,6-, 2,7-, 3,8-, and 4,9-positions) have also been studied<sup>[2]</sup>. From single crystal X-ray diffraction, 2,7-isomer adopts standard herringbone structure whereas the others stack in one dimensionally. Upon exposure to the laser, dropcasted samples loaded in a microwave cavity showed the prompt increase in photoconductivity  $\phi\Sigma\mu$ , where  $\phi$  and  $\Sigma\mu$  are quantum efficiency and sum of the electron and hole mobilities. Among these isomers, 2,7-isomer showed one order of magnitude higher photoconductivity  $(\phi\Sigma\mu)_{\max} = 1.4 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. FI-TRMC revealed that hole mobility of 2,7-isomer reached 170 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> on average at PMMA interface. We consider that the strikingly high performance in 2,7-isomer can be explained by the thermal motion of the BTBT core.

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# Role of grain boundaries for the electrical stability of organic n-channel transistors

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One of the main limiting factors for high charge carrier mobility of polycrystalline organic thin film transistors based on small molecules are grain boundaries. It is very well known, that they limit the charge carrier mobility. In our work, we show a series of experiments using perylene diimide based n-channel field effect transistors [1] that highlight the role of grain boundaries for the long-term and operational stability of organic TFTs. For example, we have utilized conductive atomic-force microscopy measurements to pinpoint that the resistance of grain boundaries increases during bias stress [2]. Furthermore, we show that grain boundaries are also responsible for the time-dependent degradation of organic thin film transistors during storage [3]. Finally, we have pinpointed the degradation mechanism in such thin films to stem from an electrochemical instability of the semiconducting in wet oxygen [4].

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# Modelling Charge Transport in Organic Molecular Materials

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Organic semiconductors (OS) are one of the most exciting materials that have been discovered in the last 50 years. Light-weight, flexible and relatively easy to produce from renewable resources, OS combine many desirable properties for thin film electronic devices. These materials have already profoundly impacted our daily lives. They form the active layers of organic light-emitting diodes (OLEDs) that are now routinely used in smart phones, flexible displays, and curved TV screens. A drawback of OS compared to inorganic semiconductors is their limited conductivity of electrical charges, which is one of the main physical processes underlying operation in the organic photovoltaics (OPVs). Radically improving charge mobility in OS while keeping the production costs sufficiently low is thus a key requirement for further advances in the field, in particular for OPVs. Yet, systematic development requires a sophisticated and experimentally-validated model that can guide materials and device design as a true predictive tool. My research work is aim to evaluate the performance of one such computational tool for the prediction of charge mobilities in organic crystals. The method is based on the assumption that the charge carrier is localized, i.e. forms a polaron that hops from one molecule to the next. Molecular dynamics simulation and quantum chemical calculations are used to calculate rate constants for each polaron hopping step and kinetic Monte Carlo simulations are carried out to compute the mobility from the set of hopping rate constants. The methodology has applied to electron hole hopping in pentacene, rubrene and C<sub>60</sub> single crystals. We find that our calculations reproduce very well the experimental mobility and anisotropy in pentacene and rubrene, suggesting that the methodology could be employed in future work for the simulation of more complex, disordered systems and for the investigation of structure-function relationships relevant to materials design.