



2<sup>nd</sup> International Conference on

# Interface Properties in Organic and Hybrid Electronics: Perspectives & Key Challenges

July 8-11, 2019  
Cergy-Pontoise University, France  
[www.ipoe-conference.com](http://www.ipoe-conference.com)

## Program and General Information



We would like to thank the following sponsors for their generous support:



## Welcome!

Dear IPOE-2019 Participant,

On behalf of the organizing committees, it is our great pleasure to welcome you at the 2<sup>nd</sup> International Conference on “Interface Properties in Organic Electronics: Perspectives & Key Challenges”.

In the continuation of the first edition (IPOE-2017, Cergy-Pontoise, France), IPOE-2019 will be entirely devoted to the physical phenomena occurring at organic/organic, organic/inorganic and organic/metallic interfaces, as motivated by their essential role in many (bio-)physico-chemical processes, ranging from solar energy conversion to biosensing. The conference will cover a large range of areas related to both experimental and theoretical aspects of these processes, covering the following topics (but not limited to):

- Charge separation mechanisms
- Charge generation mechanisms
- Energy transfer processes
- Energy landscape at interfaces
- Materials for interface engineering
- Interfacial versus bulk properties
- Hybrid organic/inorganic interfaces
- Metal/organic interfaces
- Solar energy conversion
- Organic sensors and bioelectronics
- Molecular spintronics
- OPVs, OLEDs, OFETs
- Experimental probes
- Molecular modelling and theoretical models

New insights are expected to emerge from this conference, providing additional design criteria for novel materials fulfilling optimized interfacial properties, along with key challenges for future research.

We would like to thank all members of the organizing committees, the Institute of Advanced Studies of the University of Cergy-Pontoise (IAS), the Laboratoire de Physico-chimie des Polymères et des Interfaces (LPPI).

We wish you to enjoy IPOE-2019 and your stay at Cergy-Pontoise.

**Gjergji Sini**  
Co-chair

**Jérôme Cornil**  
Co-chair

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\*Laboratoire de Physicochimie des Polymères et des Interfaces (LPPI)

**We are very grateful to the generous logistic and financial support from the University of Cergy-Pontoise, the Laboratoire de Physico-chimie des Polymères et des Interfaces (LPPI) the Institute of Advanced Studies (IAS) of Cergy-Pontoise University (France), and the University of Mons (Belgium).**



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## GENERAL INFORMATION

### Conference Site



Ecole Supérieure du Professorat et de l'Éducation (ESPE)  
Avenue Bernard-Hirsch  
95000 Cergy  
**GPS Coordinates: 49.032158, 2.07837**

### How to Reach the Conference Venue

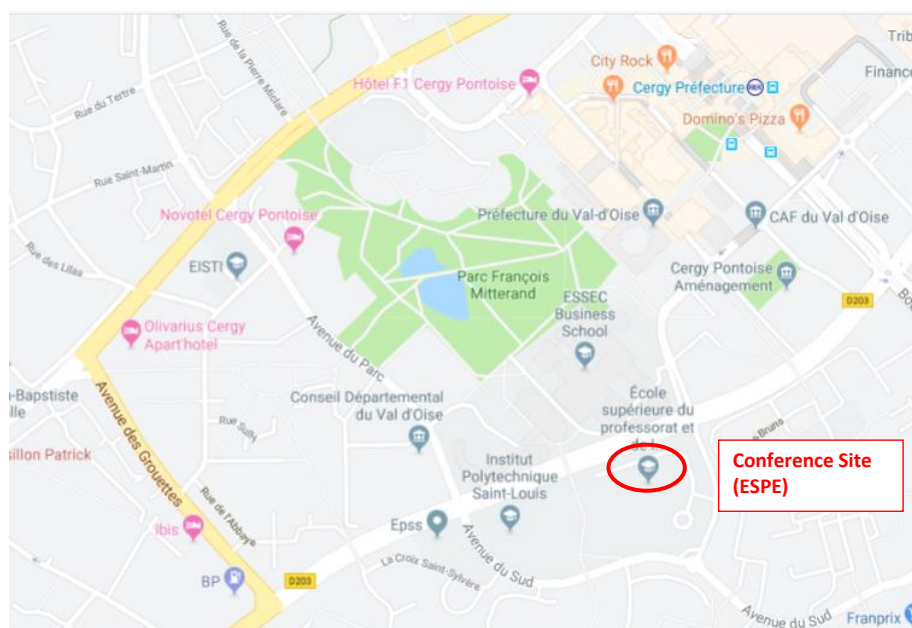
#### From the hotels at Cergy-Pontoise:

The conference venue is at **walking distance from the hotels**, and can be reached in approximately:

- 13 min from Novotel
- 17 min from Olivarius
- 19 min from Mercure
- 15 min from IBIS

#### From Paris:

Take the **RER A** bound for "Cergy le Haut", get off at "**Cergy-Préfecture**" (40 min approximately from center of Paris). From the station, the conference venue is at **walking distance**, and can be reached in approximately 11 min. Otherwise, you can take a taxi at the exit of the train station.



## Welcome Reception

The Welcome Reception will take place in the hall of **ESPE**, on Monday July 8<sup>th</sup>, 2019 at 11:30-13:00.

## Poster Sessions

The poster sessions will take place on **Tuesday (10:30-11:10; 16:00-16h40)** and on **Wednesday (10h30-11h10)**. Participants presenting posters are invited to expose their poster(s) on Monday either before the afternoon session, and leave them until Thursday (end of coffee break).

## Gala Dinner

The IPOE2019 gala evening will take place at **the Château (castle) d'Auvers-sur-Oise**, about ten kilometers from Cergy (conference venue). Château d'Auvers-sur-Oise offers the "Impressionist Vision" experience, plunging the visitor into the world of Impressionist painting. It is an immersive, emotional and sensory experience. The layout and scenography integrate innovative technology and lighting: projections, mappings, morphing, giant screens and much more. For a spectacular experience and an unforgettable visit.

Here are the highlights of this event:

- **Before the meal scheduled at 9pm, we offer you a visit to the Castle** (about 45 minutes) per group of up to 25 people
- The first group is programmed at 6.30pm, then the next ones every 15 minutes. The last group will start the visit at 7.30pm.
- During the waiting times, before or after the visit, you will have the opportunity to hydrate, walk in the gardens of the castle or go for a tour in the center of the village of Auvers-sur-Oise nearby (Maison du Docteur Gachet, Church and Cemetery (where Van Gogh lies) of Auvers-sur-Oise ....)
- **The appointment time for the cocktail is scheduled for 8.30pm** outdoors or indoors according to the weather conditions of the day, for a start of meals around 9pm.

## Special sites in Cergy to visit during July 2019

- **Port-Cergy** : Located 5 min from Olivarius or Ibis hotel, Port-Cergy is the first marinated built in the Ile-de-France (1989), giving this section of the Oise the feel of a seaside resort, with barges and small sailing craft. The terraces in front of the water will welcome you to relax in this pleasant setting.
- **Cergy-Neuville sports park**: This is one of the most popular places in France! The vast lakes occupy what used to be sand quarries located within a loop in the Oise. The result is a paradise for bathers, windsurfers and walkers. In the bird reserve, an observation hide makes it possible to observe herons, tufted ducks... who stop here. For more information, please visit: <https://cergy-pontoise.iledeloisirs.fr/>

## Special activities in Paris during July 2019

- **Le bal des pompiers/Firemen's ball:** The Paris Fire brigade organizes intramural "bal" (popular dance) on July 13 and / or July 14, from 9 pm to 4 am. There may be a fee for entrance, otherwise a traditional "barrel" will be installed to receive donations. The funds raised will be used to improve the condition of the firemen. On the program: good food, warm welcome, village atmosphere, popular "bal". The complete program is not available yet.
- **Le défilé militaire/Military Parade:** Since July 14<sup>th</sup> 1880, the show begins with its traditional military parade. Mounted, foot, motorized and aerial units will participate in the parade, that moves along the Champs-Élysées from Place de l'Étoile to Place de la Concorde, where the soldiers salute the President of the Republic, the government, the main authorities of the State, the diplomatic corps and foreign political personalities. The 14th of July parade on the Champs-Élysées is the highlight of the ceremonies of the national day. It takes place at 10 am on Champs-Elysées avenue.
- **Le grand concert du Champ-de-mars/The great concert of Champ-de-mars:** Following the success of the previous years, the Champ-de-Mars will once again host a big lyrical concert on the occasion of our National Day. The event will take place at the foot of the Eiffel Tower on Friday, July 14, 2019 from 9 pm. The biggest names of the classic will be gathered around the National Orchestra of France for the fifth edition.
- **Le Feu d'artifice/Fireworks:** The must-see show of the French National Holiday in Paris is the July 14<sup>th</sup> fireworks display. Like last year, the fireworks will be set off from the Eiffel Tower and the gardens of Trocadéro. This year promises another dazzling spectacle with choreographed multicoloured fireworks bursting open against the backdrop of the Parisian night sky. The public are invited to watch the show from the Champ de Mars. Starting time of the 14 July 2019 fireworks display: from 11pm, for a duration of 30 minutes (subject to conditions).
- **Les grandes eaux musicales du château de Versailles/ Great Musical Waters of Château de Versailles:** The garden of the castle of Versailles awakens and becomes the theater of a fairy-like animation. Ponds and waterfalls give a majestic spectacle in which the fountains bubble and entangled jets of water. Château de Versailles - Yvelines 78. For more information, please visit: <https://www.parisinfo.com/sortie-paris/136202/les-grandes-eaux-musicales-du-chateau-de-versailles>



# SCHEDULE

## Monday July 8<sup>th</sup>

10:00 - 12:00	Registration	
11:30 - 13:00	Cocktail - Lunch	
13:00 - 13:20	Welcome Address Gjergji Sini, Jérôme Cornil	
13:20 - 14:20	PL	<b>Rudolph A. Marcus - Nobel Prize in Chemistry 1992</b> California Institute of Technology, USA <i>Electron Transfer Theory and its Application to Molecular Conductance</i>
<b>Session 1</b> <b>Discussion leader : Jérôme Cornil - University of Mons, Belgium</b>		
14:20 - 15:20	K1	<b>Jean-Luc Brédas - Georgia Institute of Technology, USA</b> <i>Assessing the Nature of the Charge-Transfer Electronic States In Organic Solar Cells</i>
15:20 - 15:40	OC1	<b>Bernd Engels - University of Würzburg, Germany</b> <i>Simulation of Photo-Induced Processes at Organic-Organic Interfaces</i>
15:40 - 16:10	Coffee Break	
16:10 - 16:50	I1	<b>Claudine Katan - University of Rennes, France</b> <i>Versatility of Halide Perovskites: Insight From Atomic Scale Modelling</i>
16:50 - 17:10	OC2	<b>Kyung-Geun Lim - Korea Research Institution for Standard Science, Republic of Korea</b> <i>Energy Level Alignment of Decoupled Dipolar Interface Layers in Organic Solar Cells and Organic-Inorganic Hybrid Perovskite Solar Cells</i>
17:10 - 17:30	OC3	<b>Rowan Macqueen - Helmholtz-Zentrum Berlin, Germany</b> <i>Hybrid Lead Halide Perovskite As A Non-Excitonic Triplet Sensitiser For Triplet Fusion Upconversion</i>
17:30 - 17:50	OC4	<b>Steffen Duhm - Soochow University, P.R. China</b> <i>Energy-Level Alignment at Hybrid Organic-Inorganic Interfaces</i>
17:50 - 18:10	OC5	<b>Ren Wiscons - University of Michigan, USA</b> <i>Ferroelectric Charge-Transfer Solid Solutions With Tunable Curie Temperatures</i>
18:10 - 18:30	OC6	<b>Jan Dreiser - Paul Scherrer Institut, Switzerland</b> <i>Interface Engineering for the Stabilization of Single-Molecule Magnetic Bits</i>

## Tuesday July 9<sup>th</sup>

<b>Session 2</b>		
<b>Discussion leader : David Beljonne - University of Mons, Belgium</b>		
08:30 - 09:30	K2	<b>Seth R. Marder - Georgia Institute of Technology, USA</b> <i>Development of Redox Dopants for Organic Semiconductors and Interface Modification</i>
09:30 - 09:50	OC7	<b>Gregor Witte - Philipps-University Marburg, Germany</b> <i>Controlling the Work Function of Metals By Means of Phthalocyanine Thin Films</i>
09:50 - 10:10	OC8	<b>Martin Hantusch - IFW Dresden, Germany</b> <i>Electronic Configuration of Various F6tcnnq-Based Interfaces</i>
10:10 - 10:30	OC9	<b>Gabriele D'avino - Néel Institute of CNRS and Grenoble Alpes University, France</b> <i>Unveiling the Mechanism for Molecular Doping in Organic Semiconductors: Excitonic Effects and Host-Dependent Acceptor Levels</i>
10:30 - 11:10	<b>Coffee Break &amp; POSTER SESSION</b>	
11:10 - 11:50	I2	<b>Luisa Torsi - University of Bari Aldo Moro, Italy</b> <i>Single-Molecule Sensing of Biomarkers</i>
11:50 - 12:10	OC10	<b>Anne Charrier - University of Aix Marseille, France</b> <i>"When Bonding Makes You Stronger" Supported Lipid Monolayers as Sensing and Selective Layers for Isfet Sensors</i>
12:10 - 12:30	OC11	<b>Berta Gomez-Lor - Institute of Materials Science of Madrid, Spain</b> <i>High Mobility Columnar Self-Assembling Semiconductors: From Materials To Devices</i>
12:30 - 14:00	<b>Lunch</b>	
<b>Session 3</b>		
<b>Discussion leader : Norbert Koch - Hu Berlin, Institut für Physik, Germany</b>		
14:00 - 15:00	K3	<b>Antoine Kahn - Princeton University, USA</b> <i>Electronic Structure of Metal Halide Perovskite Surfaces: from 3D to 2D to 2D/3D</i>
15:00 - 15:20	OC12	<b>Colin Van Dyck - University of Alberta, Canada</b> <i>Charge Injection in 'Thick' Molecular Junctions</i>
15:20 - 15:40	OC13	<b>Pascal Martin - University of Paris-Diderot, France</b> <i>Charge Injection and Transport Properties of Large Area Organic Junctions with a Multilayer Graphene Electrode</i>
15:40 - 16:00	OC14	<b>Esther Barrena - Institute of Materials Science of Barcelona, Spain</b> <i>Chemical Endurance Versus On-Surface Defluorination Of C60f48 On Coinage Metals At Room Temperature: Structure And Electronic Properties</i>
16:00 - 16:40	<b>Coffee Break &amp; POSTER SESSION</b>	
16:40 - 17:20	I3	<b>Lionel Hirsch - University of Bordeaux, France</b> <i>Control of Hybride Perovskite Surface with Fluorinated Molecules</i>
17:20 - 17:40	OC15	<b>Christine Lartigau-Dagron - University of Pau and Pays de l'Adour, France</b> <i>The Role of Pedot:Pss On the Stability of Organic Solar Cells</i>
17:40 - 18:00	OC16	Anastasia Markina - Max Planck Institute for Polymer Research, Germany Molecular Design of Acceptors for Non-Fullerene Organic Solar Cells
18:00 - 18:20	OC17	Julien Gorenflot - KAUST Solar Center, Kingdom of Saudi Arabia Effect of Energy Offsets on Charge Generation in All-Small Molecule Non-Fullerene Acceptor Organic Solar Cells
18:20 - 18:40	OC18	<b>Cyril Poriel - University of Rennes, France</b> <i>C1-Linked Spirobifluorene Dimers: Pure Hydrocarbon Hosts For High Performance Blue Phosphorescent Oleds</i>

**Wednesday July 10<sup>th</sup>**

<b>Session 4</b> <b>Discussion leader : Denis Andrienko - Max Planck Institute for Polymer Research, Germany</b>		
08:30 - 09:30	K4	<b>Daniel Frisbie - University of Minnesota, USA</b> <i>Length Dependent Charge Transport in Molecular Junctions</i>
09:30 - 09:50	OC19	<b>Makoto Yoneya - National Institute of Advanced Industrial Science and Technology, Japan</b> <i>On the Monolayer Polymorph Crystal Structure of the Organic Semiconductor 7-Decyl-2-Phenyl[1]Benzothieno[3,2-B][1]Benzothiophene</i>
09:50 - 10:10	OC20	<b>Nada Mrkyvkova - Slovak Academy of Sciences, Slovakia</b> <i>Real-Time Study Of Diindenoperylene Thin-Film Structure On Mos2 Monolayer</i>
10:10 - 10:30	OC21	<b>Vincent Lemaur - University of Mons, Belgium</b> <i>Resilience to Conformational Fluctuations Rather Than Planar Backbones Drives Conjugated Polymer Materials with Low-Energy Disorder. Insights From Atomistic Simulations</i>
10:30 - 11:10	<b>Coffee Break &amp; POSTER SESSION</b>	
11:10 - 11:50	I4	<b>Concepcio Rovira - Institute of Materials Science of Barcelona, Spain</b> <i>Carbon Based Radicals On Surfaces</i>
11:50 - 12:10	OC22	<b>Damien Brunel - University of Aix Marseille, France</b> <i>Realization of a Ferrocenyl Triazole Molecular Diode in a Two Step Process</i>
12:10 - 12 : 30	OC23	<b>Jose Martinez - Institute of Materials Science of Madrid, Spain</b> <i>On-Surface Coupling Of P-Aminophenol: Synthesis Of Azine Derivatives With Strong Acceptor Behaviour</i>
12:30 - 14:00	<b>Lunch</b>	
<b>Session 5</b> <b>Discussion leader : Egbert Zojer - Graz University of Technology, Austria</b>		
14:00 - 15:00	K5	<b>Zhenan Bao - Stanford University, USA</b> <i>Skin-Inspired Organic Electronics</i>
15:00 - 15:20	OC24	<b>Olivier Dautel - Charles Gerhardt Institute of Montpellier, France</b> <i>Hybrid Field Effect Transistors (Hfet) a Fully Covalent Transistor with A Pi-Conjugated Organosilica Material</i>
15:20 - 15:40	OC25	<b>Simone Fratini - Néel Institute of CNRS and Grenoble Alpes University, France</b> <i>Prediction And Design Of Low Disorder, High Mobility Molecular Semiconductors: A Theoretical Perspective</i>
15:40 - 16:00	OC26	<b>Frank Ortmann - Technical University of Dresden, Germany</b> <i>Density of States of Doped Organic Films And its Impact On Charge Transport</i>
16:00 - 16:20	<b>Coffee Break</b>	
16:20 - 17:00	I5	<b>Natalie Stingelin - Georgia Institute of Technology, USA</b> <i>Designing Inorganic/Organic Photonic Light- and Heat-Management Structures For Solution-Processable and Printable Organic Optoelectronic Devices</i>
17:00 - 17:20	OC27	<b>Rocío Ponce Ortiz - University of Málaga, Spain</b> <i>Analyzing Thin Film Morphology By Resonance Raman Spectroscopy</i>
17:20 - 17:40	OC28	<b>Sergi Riera-Galindo - Linköping University, Sweden</b> <i>Tuning the Energetics of Molecular Dopants for Efficient N-Type Doping of Polymers</i>
<b>Gala Dinner at Château (castle) d'Auvers-sur-Oise</b>		

## Thursday July 11<sup>th</sup>

<b>Session 6</b> <b>Discussion leader : Veaceslav Coropceanu - Georgia Institute of Technology, USA</b>		
08:30 - 08:50	OC29	<b>Piotr De Silva - Technical University of Denmark, Denmark</b> <i>Simple Four-State Model of Efficient Thermally Activated Delayed Fluorescence</i>
08:50 - 09:10	OC30	<b>Sarah Hamdad - University of Sorbonne Paris Cité, France</b> <i>Nanoscale Interaction of Periodic Metallic Nanoparticle Arrays and Organic Emitters</i>
09:10 - 09:30	OC31	<b>Thanyarat Chawanpunyawat - Vidyasirimedhi Institute of Science and Technology, Thailand</b> <i>Molecular Design of Chrysenes-Based Deep Blue Emitters for Simple Structured Oleds</i>
09:30 - 09:50	OC32	<b>Ivan Kassal - University of Sydney, Australia</b> <i>How Energetic Disorder Determines Charge Generation in Organic Photovoltaics and How To Measure It</i>
09:50 - 10:30	I6	<b>Dieter Neher - University of Potsdam, Germany</b> <i>Interfaces Determine Charge Generation And Recombination In Organic Solar Cells</i>
10:30 - 11:00	<b>Coffee Break</b>	
11:00 - 11:20	OC33	<b>Heinz Baessler - University of Bayreuth, Germany</b> <i>What Is the Binding Energy of a Charge Transfer State In an Organic Solar Cell?</i>
11:20 - 11:40	OC34	<b>Alexei Chepelianskii - University of Paris Sud, France</b> <i>Spin Properties of Bi-Exciton State Formed Through Singlet Fission</i>
11:40 - 12:00	OC35	<b>Saghar Masoomi - University of Melbourne, Australia</b> <i>Liquid Crystallinity As a Self-Assembly Motif For Singlet Fission Materials</i>
12:00 - 13:00	K6	<b>Richard Friend - University of Cambridge, United Kingdom</b> <i>Management of the Coulomb Interaction In Organic Leds and Solar Cells</i>
13:00 - 13:15	<b>Conference Closure</b> <b>Gjergji Sini, Jérôme Cornil</b>	

## **ABSTRACTS**

## PLENARY SESSION

### ELECTRON TRANSFER THEORY AND ITS APPLICATION TO MOLECULAR CONDUCTANCE

**Rudolph A. Marcus**

Noyes Laboratory of Chemical Physics, California Institute of Technology, 1200 E. California Blvd.,  
Pasadena CA 91125-7200, USA

In the present talk some of the history of electron transfer theory, its developments and its applications to experiments will be described, including a very recent user friendly version by Jakub Sowa and the speaker (1) of a study (2) of molecular conductance that combines Landauer and Marcus theories, and a key role that lifetime broadening can play, particularly in “off-resonant” region.

#### REFERENCES

- (1) J. K. Sowa and R. A. Marcus (unpublished)
- (2) J.K. Sowa et al. J. Chem. Phys. 149, 154112 (2018)

## SESSION 1

K1

### ASSESSING THE NATURE OF THE CHARGE-TRANSFER ELECTRONIC STATES IN ORGANIC SOLAR CELLS

Jean-Luc Brédas

School of Chemistry and Biochemistry  
Center for Organic Photonics and Electronics  
Georgia Institute of Technology, Atlanta, GA 30332-0400, USA  
*jean-luc.bredas@chemistry.gatech.edu*

The charge-transfer electronic states appearing at the donor-acceptor interfaces in organic solar cells mediate exciton dissociation, charge generation, and charge recombination [1]. Assessing their nature is thus crucial to a thorough understanding of device operation and efficiency. To date, this characterization has been carried out, both theoretically and experimentally, on the basis of models that only involve the charge-transfer state and the ground state. Here, we show that it is essential to go beyond such a two-state model and to consider explicitly as well the electronic and vibrational couplings with the local absorbing state on the donor and/or acceptor.

We describe a three-state vibronic model that we have recently developed [2] and allows us:

- (i) to provide a reliable description of the optical absorption features related to the charge-transfer states;
- (ii) to underline the erroneous interpretations stemming from the application of the semi-classical two-state model; and
- (iii) to rationalize how the hybridization between the local-excitation state and charge-transfer state can lead to lower non-radiative voltage losses and higher power conversion efficiencies.

We show the application of our three-state approach to a number of organic photovoltaic blends and exploit it, in conjunction with detailed experimental characterizations, to establish design rules to minimize the energy/voltage losses [3].

In a final section, we discuss some of the characteristics shared by non-fullerene acceptors of the ITIC family, contrast them to those of the PCBM fullerene derivatives, and depict the role that isomerizations (on either the terminal groups or the core) can play on solar-cell performance.

**Acknowledgments:** We acknowledge funding of this work by the Department of the Navy, Office of Naval Research, under the MURI “Center for Advanced Organic Photovoltaics” (Awards Nos. N00014-14-1-0580 and N00014-16-1-2520) and under Award No. N00014-17-1-2208.

#### REFERENCES

- [1] Coropceanu, V., Chen, X.K., Wang, T., Zheng, Z. and & Bredas, J.L., Nature and role of the charge-transfer electronic states in organic solar cells, *Nature Reviews Materials*, in press (2019).
- [2] Chen, X.K., Coropceanu, V. & Bredas, J.L., Assessing the nature of the charge-transfer electronic states in organic solar cells, *Nature Communications* **9** (2018), doi.org/10.1038/s41467-018-07707-8.
- [3] Qian, D. *et al.*, Design rules for minimizing voltage losses in high-efficiency organic solar cells, *Nature Materials* **17**, 703-709 (2018).
- [4] Wang, T. and & Bredas, J.L., Nonfullerene small-molecule acceptors for organic photovoltaics: Understanding the impact of methoxy substitution position on molecular packing and electron-transfer properties, *Advanced Functional Materials*, 1806845 (2019).
- [5] Kupgan, G., Chen, X.K., Coropceanu, V., and & Bredas, J.L., Low energetic disorders in small-molecule non-fullerene electron acceptors, submitted (2019)

## OC1

## SIMULATION OF PHOTO-INDUCED PROCESSES AT ORGANIC-ORGANIC INTERFACES

Bernd Engels

Institute for Phys. & Theor. Chem., University of Würzburg, Würzburg, Germany.  
bernd.engels@uni-wuerzburg.de

In the present work we focus on investigations about photo-induced processes in thin organic films and at the organic-organic interfaces. Their accurate description and understanding is a prerequisite for the design opto-electronic devices such as organic solar cells or light emitting diodes. In organic solar cells, separation of optically excited electron-hole pairs and long-range charge transport play an important role for the efficiency. Both are largely influenced by the film structure and the molecular orientation at interfaces between electron donor (D) and acceptor (A) molecules. In our presentation we briefly mention the dimer approach which successfully delivered atomistic pictures for photo-induced relaxation effects in aggregates and allowed a correct description of the energy disorder in the vicinity of amorphous interfaces.[1,2] Furthermore, we focus on our simulations about the individual steps of the light to energy conversion process in the vicinity of the interfaces of organic solar cells [3] and describe recent works about the interpretation of femtosecond (fs) time-resolved second harmonic generation (TR-SHG) in DIP-PDIR-CN<sub>2</sub> interfaces.[4]

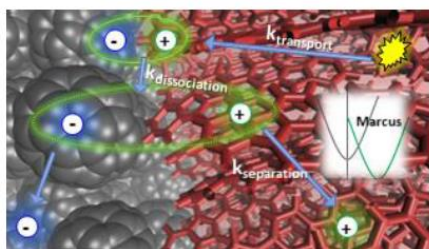


Figure 1: Various processes at organic-organic interfaces

## REFERENCES

- [1] B. Engels, V. Engel *PCCP* (2017), *19*, 12604  
 [2] C. Brueckner, M. Stolte, F. Wuerthner, J. Pflaum, B. Engels *J. Phys. Org.Chem.* (2017) *30*, c3740  
 [3] C. Brueckner, F. Wuerthner, K. Meerholz, B. Engels *J. Phys. Chem C* (2017), *121*, 4; *ibid J. Phys. Chem C* (2017), *121*, 26  
 [4] S. Wirsing, M. Hänsel, V. Belova, F. Maass, F. Schreiber, K. Broch, B. Engels, P. Tegeder in preparation

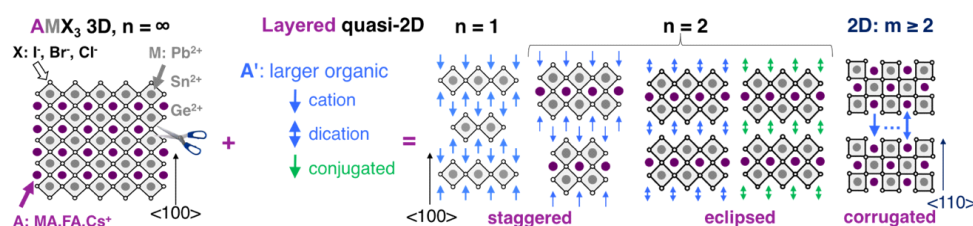


## VERSATILITY OF HALIDE PEROVSKITES: INSIGHT FROM ATOMIC SCALE MODELLING

Claudine Katan<sup>\*1</sup>, Boubacar Traore,<sup>2</sup> Joshua Leveillee,<sup>3</sup> Mikael Kepenekian,<sup>1</sup> André Schleife,<sup>3</sup>  
Amanda Neukirch,<sup>4</sup> Sergei Tretiak,<sup>4</sup> and Jacky Even<sup>2</sup>

<sup>1</sup> Univ Rennes, ENSCR, INSA Rennes, CNRS, ISCR, Rennes, France, *claudine.katan@univ-rennes1.fr*, *mikael.kepenekian@univ-rennes1.fr* - <sup>2</sup> Univ Rennes, INSA Rennes, CNRS, Institut FOTON, Rennes, France, *boubacar.traore@insa-rennes.fr*, *laurent.pedesseau@insa-rennes.fr*, *jacky.even@insa-rennes.fr* - <sup>3</sup> Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, USA. *joshua.levillee@gmail.com*, *schleife@illinois.edu* <sup>4</sup> Los Alamos National Laboratory, Los Alamos, USA. *ajneukirch@lanl.gov*, *serg@lanl.gov*

Both all inorganic and hybrid halide perovskites have recently demonstrated undeniably remarkable characteristics for a wide range of optoelectronic applications. The perovskite fever began with 3D halide perovskites of chemical formula  $AMX_3$  with A a small organic (e.g. methylammonium, formamidinium) or an inorganic cation (e.g.  $Cs^+$ ), M a metal ( $Pb^{2+}$ ,  $Sn^{2+}$ ,  $Ge^{2+}$ ), and X a halogen (I, Br, Cl), which have opened a route toward low-cost manufacture of solar cells while offering currently certified conversion efficiencies over 24%, at the level of the best known thin film technologies and not far from monocrystalline silicon (25%).<sup>[1]</sup> Since the initial breakthrough mid-2012,<sup>[2]</sup> halide perovskites have attracted worldwide efforts from the scientific community<sup>[3]</sup> leading to an extensive exploration of their structural versatility and an ever-growing diversity of structures.<sup>[4]</sup> Prior to the perovskite fever, especially in the 80's and 90's, most experimental efforts on halide perovskites were focused on chemistry and optical characterizations of monolayered halide perovskites of chemical formula  $A'MX_4$ , with A' a larger organic cation (e.g. alkylammonium).<sup>[5]</sup>



**Figure 1.** Layered metal-halide structures conceptually derived from the mother 3D perovskite network.

Currently, many different perovskite -with corner-sharing octahedra- as well as non-perovskite metal-halide networks are synthesized and their optoelectronic properties deserve to be unraveled (Figure). Among others, new compositions such as  $A'_2A_{n-1}M_nX_{3n+1}$  afford layered structures with a controlled number ( $n$ ) of octahedra in the perovskite layer and thus offer an ideal platform for fundamental understanding.<sup>[6]</sup> Here, through a couple of recent examples including newly discovered halide perovskite phases as well as experimental data from the early 90's, we will discuss their optoelectronic properties based on first-principles calculations, semi-empirical and empirical modelling. Impact of composition and structural pattern on properties will be inspected, with particular emphasis on the effect of quantum and dielectric confinements on charge carriers and excitons.<sup>[6,7]</sup> Theoretical inspection of low energy states associated with electronic states localized on the edges of the perovskite layers will also be shown to provide guidance for the design of new synthetic targets<sup>[8]</sup> taking advantage of experimentally determined elastic constants.<sup>[9]</sup> Opportunities to engineer halide perovskite properties by considering dication or conjugated molecules in the interlayer will also be discussed.<sup>[10]</sup>

## REFERENCES

- [1] <https://www.nrel.gov/pv/cell-efficiency.html>.
- [2] Lee, M. M. et al. *J. Am. Chem. Soc.* 2012, 134, 17396; Kim, H.-Set al. *Sci. Rep.* 2012, 2, 591.
- [3] Perovskites special issue, *Chemical Reviews* 2019, 119 (5), 3033-3452.
- [4] Katan, C et al. *Chemical Reviews* 2019, 119, 3140.
- [5] Papavassiliou, G. C. *Prog. Solid State Chem.* 1997, 25, 125; Mitzi, D. B. *Prog. Inorg. Chem.*; Karlin, K. D., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1999, 1.
- [6] Soe, C. M. M. et al. *Proc. Natl. Acad. Sci. U. S. A.* 2019, 116, 58.
- [7] Traore, B. et al. *ACS Nano* 2018, 12, 3321; Blancon, J.-C. et al. *Nature Com.* 2018, 9, 2254.
- [8] Blancon, J.-C. et al. *Science* 2017, 355, 1288; Kepenekian, M. et al. *Nano Lett.* 2018, 18, 5603.
- [9] Ferreira, A. C. et al. *Phys. Rev. Lett.* 2018, 121, 085502.
- [10] Leveillee, J. et al. *Phys. Rev. Materials* 2018, 2, 105406; Leveillee, J. et al. unpublished.

OC2

## ENERGY LEVEL ALIGNMENT OF DECOUPLED DIPOLAR INTERFACE LAYERS IN ORGANIC SOLAR CELLS AND ORGANIC-INORGANIC HYBRID PEROVSKITE SOLAR CELLS

**Kyung-Geun Lim<sup>\*1</sup>, Soyeong Ahn<sup>2</sup> and Tae-Woo Lee<sup>\*3</sup>**

<sup>1</sup> Korea Research Institution for Standard Science (KRISS), 267 Gajeong-ro, Yuseong-gu, Daejeon 34113, Republic of Korea, kglim@kriss.re.kr

<sup>2</sup> Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), San 31 Hyoja-dong, Nam-gu, Pohang,

<sup>3</sup> Department of Materials Science and Engineering, Research Institute of Advanced Materials, BK21 PLUS SNU Materials Division for Educating Creative Global Leaders, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea, twlees@snu.ac.kr

The dipole moment of interface materials has played the key role in efficient charge extraction in organic and hybrid perovskite solar cells, but the mechanisms of the interaction at the interface and of the resulting energy level alignment have not been well established. In this research, the decoupled dipole moments at the interface are investigated and clarified by using both the theoretical and experimental findings, with particular focus on dipolar interface materials and the consequent energy level alignment in organic and hybrid perovskite solar cells. The mechanisms of interface dipole moments in the interface layer are evaluated by using spontaneously and nonspontaneously aligned dipolar molecules, thereby the energy-level adjustment of the dipolar interface layer in the devices are elucidated. The diverse dipolar interface materials (e.g., self-assembled monolayers, conjugated or nonconjugated polymer, neutral molecules or electrolytes, zwitterion based molecules, electrolyte grafted copolymer) are introduced and classified according to their working mechanisms of decoupled dipole moments at the interface. We conclude that an efficient interface material and its particular treatment can be designed and developed by exploring the underlying mechanisms of the decoupled dipole moments.

## OC3

## HYBRID LEAD HALIDE PEROVSKITE AS A NON-EXCITONIC TRIPLET SENSITISER FOR TRIPLET FUSION UPCONVERSION

Frederik Eistrup<sup>1</sup>, Klaus Schwarzburg<sup>2</sup>, Sergiu Levenco<sup>3</sup>, Dennis Friedrich<sup>4</sup>, Thomas Unold<sup>3</sup>, Klaus Lips<sup>1</sup>, Eva L. Unger<sup>5,6</sup>, Rowan W. MacQueen\*<sup>1</sup>

<sup>1</sup> Institute for Nanospectroscopy, Helmholtz-Zentrum Berlin, Berlin, Germany, *frederik.eistrup@helmholtz-berlin.de*, *lips@helmholtz-berlin.de*, *rowan.macqueen@helmholtz-berlin.de*

<sup>2</sup> Department Nanoscale Structures and Microscopic Analysis, Helmholtz-Zentrum Berlin, Berlin, Germany, *schwarzburg@helmholtz-berlin.de*

<sup>3</sup> Department Structure and Dynamics of Energy Materials, Helmholtz-Zentrum Berlin, Berlin, GERM Germany, *sergiu.levenco@helmholtz-berlin.de*, *unold@helmholtz-berlin.de*

<sup>4</sup> Institute for Solar Fuels, Helmholtz-Zentrum Berlin, Berlin, Germany, *friedrich@helmholtz-berlin.de*

<sup>5</sup> Young Investigator Group Hybrid Materials Formation and Scaling, Helmholtz-Zentrum Berlin, Berlin, Germany

<sup>6</sup> Chemical Physics and NanoLund, Lund University, Lund, Sweden, *eva.unger@helmholtz-berlin.de*

Sensitised triplet fusion upconverters are photonic systems based on organic chromophores, which output significantly anti-Stokes shifted photoluminescence at potentially mild excitation densities. Triplet fusion occurs upon the encounter of two triplet excitons diffusing within the upconverting medium, which is usually a dense film or solution of polycyclic aromatic hydrocarbon derivatives [1]. Populating the triplet manifold of the system is the task of the triplet sensitiser. This is invariably a nanomaterial, such as a metal-organic complex or a metal chalcogenide nanocrystal, in which the excited state photophysics are exciton-dominated. Exciton mobility is thus a central concern in sensitised triplet fusion upconversion. The low exciton mobility of many organic materials can be an impediment to producing efficient systems [2].

In a new approach for photonic upconversion, we found that photoexcited carriers in thin film methylammonium lead iodide perovskite (MAPI) could generate triplet excitons in a surface coating of rubrene, a common triplet fusion upconverter. The triplet sensitisation mechanism does not rely on the existence of an exciton in the sensitiser material, proceeding instead by the interface transfer of nongeminate charge carriers. The result is that highly mobile photoexcited charge carriers in MAPI are harnessed to drive the exciton-reliant process of triplet fusion upconversion in rubrene.

Thin film MAPI samples were prepared using solution processing, then treated with spin-coated layers of small molecule organic semiconductors, including rubrene. After encapsulation in nitrogen, samples were characterised using time-resolved photoluminescence. Pumping MAPI resulted in delayed fluorescence emanating from the molecular layer, with a pump power dependence indicative of triplet fusion upconversion modified by density-dependent carrier diffusion in the MAPI film.

The described mechanism for triplet sensitization enables an energy-funneling effect, sidestepping the exciton mobility problems endemic to nanomaterial triplet sensitisers. Optimised versions of the MAPI-organic dye upconverters reported here should therefore permit efficient upconversion conditions to be obtained at very low irradiance. The efficient interconversion of excitons and charges at the MAPI-organic dye interface is also of potential interest for other optoelectronic applications, such as lasing [3].

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## REFERENCES

- [1] Schulze, T.F.; Schmidt, T.W. Photochemical upconversion: present status and prospects for its application to solar energy conversion. *Energy Environ. Sci.*, **2015**, *8*, 103-125.
- [2] Sripathy, K; MacQueen, R.W.; Cheng, Y.Y.; Dvorak, M; McCamey, D.R.; Treat, N.D.; Stingelin, N.; Schmidt, T.W. Highly efficient photochemical upconversion in a quasi-solid organogel. *Journal Mat. Chem. C*, **2014**, *3*, 616-622.
- [3] Mathies, F; Brenner, P; Hernandez-Sosa, G; Howard, I.A.; Paetzold, U.W.; Lemmer, U. Inkjet-printed perovskite distributed feedback lasers, *Optics Express*, **2018**, *26*, A144-A152.

OC4

## ENERGY-LEVEL ALIGNMENT AT HYBRID ORGANIC-INORGANIC INTERFACES

Steffen Duhm

Institute of Functional Nano &amp; Soft Materials (FUNSOM), Soochow University, Suzhou, P.R. CHINA.

duhm@suda.edu.cn

Contact formation at hybrid organic-inorganic interfaces is of utmost importance for the performance of electronic devices. We access interface energetics and chemical reactions by ultraviolet- and X-ray photoelectron spectroscopy (UPS and XPS) [1]. Work functions are an important parameter for energy-level alignment and we show how molecular monolayers can be used to lower the work function of TiO<sub>2</sub> down to 3.4 eV [2]. In contrast, by careful preparation the work function of VO<sub>2</sub> can reach up to 6.7 eV [3]. These materials can thus be used as versatile charge injection layers for organic electronics applications [4]. Likewise, the work function of organic-inorganic perovskite thin films depends critically on the surface CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> to CH<sub>3</sub><sup>+</sup> ratio [5] and we show how beneficial energy-alignment for photovoltaic applications can be achieved for both, solution processed and vacuum-sublimed, perovskite films [6]. Moreover, deposition of MoO<sub>x</sub> on hybrid perovskite leads to p–n junctions induced by local electronic doping [7]. In a similar way, an inversion layer can be induced in n-Si and consequently a dopant-free p-n junction is formed [8]. In organic solar cells the donor-acceptor interface is often ill-defined. However, we show by photon-energy dependent UPS experiments that the electronic-band dispersion of a  $\pi$ -stacked acceptor layer is largely maintained upon bulk heterojunction formation [9].

## REFERENCES

- [1] S. Kera, T. Hosokai and S. Duhm, *J. Phys. Soc. Jpn.* **87**, 061008 (2018).
- [2] S. Winkler, Q. Xin, C. Li, S. Kera, K. Müllen, N. Ueno, N. Koch and S. Duhm, *Electron. Struct.* **1**, 015007 (2019).
- [3] R.-B. Wang, T. Katase, K.-K. Fu, T.-S. Zhai, J.-C. Yang, Q.-K. Wang, H. Ohta, N. Koch and S. Duhm, *Adv. Mater. Interfaces* **5**, 1801033 (2018).
- [4] K.-K. Fu, R.-B. Wang, T. Katase, H. Ohta, N. Koch, S. Duhm, *ACS Appl. Mater. Interfaces* **10**, 10552 (2018).
- [5] R.-B. Wang, M.-P. Zhuo, J.-T. Li, T.-S. Zhai, J.-C. Yang, K.-K. Fu, L.-S. Liao, L.-J. Liu and S. Duhm, *Adv. Mater. Interfaces*, **in press**, DOI: 10.1002/admi.201801827
- [6] R.-B. Wang, C. Wu, Y. Hu, J.-T. Li, P.-F. Shen, Q. Wang, L.-S. Liao, L.-J. Liu, S. Duhm, *ACS Appl. Mater. Interfaces* **9**, 7859 (2017).
- [7] Q.-D. Ou, Y.-P. Zhang, Z.-Y. Wang, J. A. Yuwono, R.-B. Wang, Z.-G. Dai, W. Li, C.-X. Zheng, Z.-Q. Xu, X. Qi, S. Duhm, N. V. Medhekar, H. Zhang and Q.-L. Bao, *Adv. Mater.* **30**, 1705792 (2018).
- [8] T. Sun, R.-B. Wang, R.-Y. Liu, C. Wu, Y.-N. Zhong, Y.-Q. Liu, Y.-S. Wang, Y.-J. Han, Z.-H. Xia, Y.-T. Zou, T. Song, N. Koch, S. Duhm and B.-Q. Sun, *Phys. Status Solidi RRL*, **11**, 1700107 (2017).
- [9] N. Aghdassi, Q. Wang, R.-R. Ji, B. Wang, J. Fan and S. Duhm, *Nanotechnology* **29**, 194002 (2018).

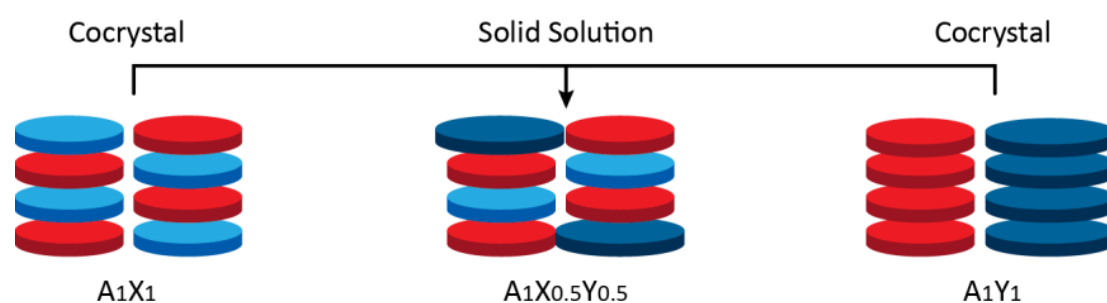
## FERROELECTRIC CHARGE-TRANSFER SOLID SOLUTIONS WITH TUNABLE CURIE TEMPERATURES

Ren A. Wiscons\*, Chris Swendris and Adam J. Matzger

Department of Chemistry and the Macromolecular Science and Engineering Program, University of Michigan, Ann Arbor, United States - [renwis@umich.edu](mailto:renwis@umich.edu), [caswe@umich.edu](mailto:caswe@umich.edu), [matzger@umich.edu](mailto:matzger@umich.edu)

With improved flexibility, modular chemical tunability, and solution processability, organic charge-transfer (CT) cocrystals are promising alternatives to silicon-based technologies. Despite the processability advantages offered by organic electronics, an area where CT cocrystals have struggled to compete with inorganics is ferroelectrics. Ferroelectric materials can act as thermal and mechanical sensors that can detect temperature and pressure fluctuations as electrical responses, making them excellent candidates for inexpensive miniaturized printable biotechnologies, such as wearable thermometers and heart-rate monitors. Ferroelectrics also show spontaneous polarization, which can be manipulated by an external electronic field for data storage. Unfortunately, most CT ferroelectrics are only active below room temperature, limiting their practical application. By combining conventional design strategies towards charge-transfer ferroelectric cocrystals with concepts underlying solid-state order-disorder transitions, we have developed a CT ferroelectric cocrystal between acenaphthene (AN) and 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F<sub>4</sub>TCNQ) that remains active up to 68 °C.<sup>1</sup> However, the challenge remains to further improve electrical performance.

The properties of a given CT cocrystal arise, in part, from the inherent electronic character of the complementary  $\pi$ -electron donor and acceptor coformers; however, due to the dependence of electronic coupling on crystal packing, engineering CT materials for specific application remains a challenge. This tendency to produce CT cocrystals with different packing motifs is particularly challenging for ferroelectric materials due to the stringent symmetry requirements for ferroelectricity. Historically, performance of inorganic electronics is improved through substitutional doping and the formation of solid solutions, which modifies the band structure through site substitution without changes to long-range packing. Unfortunately, analogous organic solid solutions are rare because the functional groups responsible for tuning molecular electronic properties tend to exhibit unique interaction modes in the solid state. Molecular doping in CT complexes has a higher chance of success relative to neutral molecular crystals because the dominant charge transfer interactions remain conserved. Here we explore the effects of solid solution formation on the working temperature range and polarization hysteresis behavior of the parent ferroelectric material AN-F<sub>4</sub>TCNQ. We have found that the working temperature range and polarization behavior can be independently tailored by partial substitution of one or both parent compounds.



**Figure 1.** The combination of two structurally dissimilar charge-transfer cocrystals (AX and AY) to form a solid solution containing molecules A, X, and Y. The red and blue discs represent charge-transfer donor and acceptor molecules, respectively.

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## REFERENCES

[1] Wiscons, R. A.; Goud, R. N.; Damron, J. T.; Matzger, A. J. Room-Temperature Ferroelectricity in an Organic Cocrystal. *Angew. Chem. Int. Ed.* **2018**, *57*, 9044-9047.

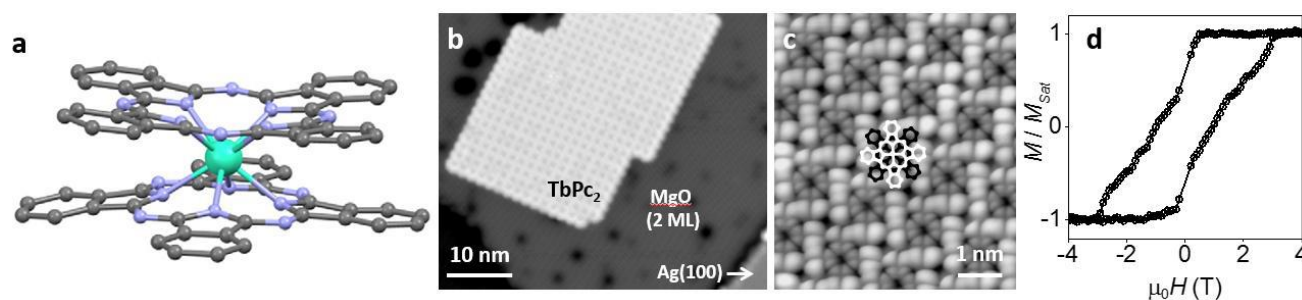
OC6

## INTERFACE ENGINEERING FOR THE STABILIZATION OF SINGLE-MOLECULE MAGNETIC BITS

Jan Dreiser\*

Swiss Light Source, Paul Scherrer Institut, Villigen PSI, Switzerland - [jan.dreiser@psi.ch](mailto:jan.dreiser@psi.ch)

Surface-adsorbed single-molecule magnets (SMMs)<sup>1–3</sup> containing transition metal or lanthanide ions are attracting a great deal of interest because of potential applications in ultra-high density storage and in quantum information processing devices. In a SMM the relaxation of the magnetic moment is blocked by a magnetic anisotropy barrier, and the magnetic relaxation times can reach up to days and months at low temperatures.<sup>4</sup> Until a few years ago the blocking temperature, which describes the critical temperature at which the magnetic information is retained, was limited to a few Kelvin. As a recent breakthrough, magnetic blocking in a SMM was reported beyond the liquid nitrogen temperature.<sup>5</sup> Despite these advances in bulk systems, the properties of SMMs when in contact with metallic and semiconducting surfaces are often destroyed, which is problematic for the electrical contacting of SMMs in devices. In this talk I will present our recent efforts in promoting the magnetic stability of TbPc<sub>2</sub> and DyPc<sub>2</sub> SMMs by introducing a few monolayer-thin film of magnesium oxide grown epitaxially on a Ag(100) surface.<sup>6</sup> By X-ray absorption spectroscopy and X-ray magnetic circular dichroism we demonstrate that for both SMMs the magnetic relaxation times increase drastically with the magnesium oxide film as compared to the adsorption on the bare Ag(100) substrate. We use scanning tunneling microscopy, X-ray photoelectron spectroscopy and density-functional calculations in order to get deep insight into this intriguing metal-insulator-organic interface. I will further highlight our findings on the mechanisms responsible for the magnetic relaxation and their differences between the metallic and the insulating substrates.<sup>7</sup>



**Figure 1.** (a) Ball-and-stick model of the LnPc<sub>2</sub> SMM. (b,c) Scanning tunneling microscopy images [(b) overview; (c) zoom] revealing self-assembled arrays of TbPc<sub>2</sub> on 2 monolayers (ML) of MgO. (d) Magnetic hysteresis loops of Tb in TbPc<sub>2</sub> obtained with X-ray magnetic circular dichroism at 3 K for 0.6 ML TbPc<sub>2</sub> on 5 ML MgO.

## REFERENCES

- [1] Cornia, A.; Mannini, M. Single-Molecule Magnets on Surfaces. In *Molecular Nanomagnets and Related Phenomena*; Gao, S., Ed.; Structure and Bonding; Springer Berlin Heidelberg, 2014; pp. 293–330.
- [2] Komeda, T.; Katoh, K.; Yamashita, M. Double-Decker Phthalocyanine Complex: Scanning Tunneling Microscopy Study of Film Formation and Spin Properties. *Prog. Surf. Sci.* **2014**, *89*, 127–160.
- [3] Dreiser, J. Molecular Lanthanide Single-Ion Magnets: From Bulk to Submonolayers. *J. Phys. Condens. Matter* **2015**, *27*, 183203.
- [4] Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. Magnetic Bistability in a Metal-Ion Cluster. *Nature* **1993**, *365*, 141–143.
- [5] Guo, F.-S.; Day, B. M.; Chen, Y.-C.; Tong, M.-L.; Mansikkamäki, A.; Layfield, R. A. Magnetic Hysteresis up to 80 Kelvin in a Dysprosium Metallocene Single-Molecule Magnet. *Science* **2018**, *362*, 1400–1403.
- [6] Wäckerlin, C.; Donati, F.; Singha, A.; Baltic, R.; Rusponi, S.; Diller, K.; Patthey, F.; Pivetta, M.; Lan, Y.; Klyatskaya, S.; Ruben, M.; Brune, H.; Dreiser, J. Giant Hysteresis of Single-Molecule Magnets Adsorbed on a Nonmagnetic Insulator. *Adv. Mater.* **2016**, *28*, 5195–5199.
- [7] Studniarek, M.; Wäckerlin, C.; Singha, A.; Baltic, R.; Diller, K.; Donati, Rusponi, S.; Brune, H.; Lan, Y.; Klyatskaya, S.; Ruben, M.; Ari P. Seitsonen, Dreiser, J., to be submitted.

## SESSION 2

K2

### DEVELOPMENT OF REDOX DOPANTS FOR ORGANIC SEMICONDUCTORS AND INTERFACE MODIFICATION

**Seth R. Marder\***

School of Chemistry and Biochemistry, School of Materials Science and Engineering, and  
Center for Organic Photonics and Electronics, Georgia Institute of Technology, Atlanta, USA.  
*seth.marder@chemistry.gatech.edu*

Organic semiconductors and hybrid/organic materials have attracted interest for electronic applications due to their potential for use in low-cost, large-area, flexible electronic devices. Here we will report on recent developments pertaining to both n- and p-dopants that could impact the charge injection/collection processes in organic light emitting diodes, organic field effect transistors, and organic photovoltaic and hybrid organic/inorganic perovskite devices, as well as on the bulk conductivity of doped semiconductors. We will consider the synthesis of new dopants and studies to illustrate the mechanisms by which the dopants react with organic semiconductors. The development of organic and metallo-organic-based dimers as n-dopants will also be discussed. We will highlight the application of n-dopants for reaction with polymers that lead to exceptionally high conductivities for n-doped systems and may have interesting thermoelectric performance.

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#### REFERENCES

- [1] "n-Doping of Organic Electronic Materials using Air-Stable Organometallics," *Adv. Mater.* **24** (5), 699-703 (2012). DOI: 10.1002/adma.201103238
- [2] "Modification of the fluorinated tin oxide/electron-transporting material interface by a strong reductant and its effect on perovskite solar cell efficiency." *Mol. Syst. Des. Eng.* **3**, 741-747 (2018). DOI: 10.1039/C8ME00031J
- [3] "Controllable, Wide-Ranging n-Doping and p-Doping of Monolayer Group 6 Transition-Metal Disulfides and Diselenides." *Adv. Mater.* **30**, 1802991 (2018). DOI: 10.1002/adma.201802991
- [4] "Beating the thermodynamic limit with photo-activation of n-doping in organic semiconductors." *Nat. Mater.* **16**, 1209/1-9 (2017). DOI: 10.1038/nmat5027

OC7

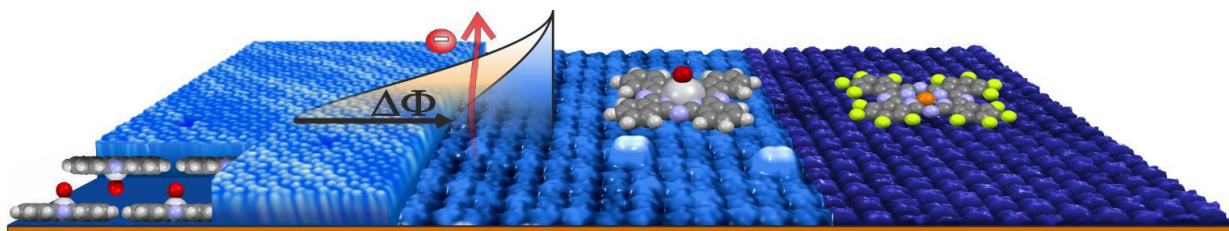
## CONTROLLING THE WORK FUNCTION OF METALS BY MEANS OF PHTHALOCYANINE THIN FILMS

Felix Widdascheck, Alrun Aline Hauke and Gregor Witte\*

Faculty of Physics, Molecular Solids, Philipps-University Marburg, Marburg, Germany  
gregor.witte@physik.uni-marburg.de

Efficient charge transfer at the interface between organic semiconductors and the respective device electrodes is of key importance for the advancement of organic electronics. It depends crucially on the energy level alignment and the reduction of potential injection barriers at such interfaces. A promising approach to effectively tune work functions and therefore optimize interface energetics are monolayers of flat lying molecules as contact primers. Compared to self-assembled monolayers they promise lower contact resistance due to shorter tunneling distances. Due to their chemical diversity and flat absorption geometry, phthalocyanines are an ideal model system [1] to identify important parameters for this process.

In the present study, we combined Scanning Tunneling Microscopy and Kelvin Probe measurements to compare the effect of highly ordered thin films of different phthalocyanines on the work function of noble metals and their possible use as contact primers. First, we investigated how polar as well as non-polar phthalocyanines modify the work functions of clean Au(111) and Ag(111) surfaces as a function of their coverage which enables a quantitative control of the metal work functions. The coverage dependence of the work function can be described empirically well in the frame of a Topping model, but may also serve as bench mark system for more refined theoretical modelling because the microstructure is known quite accurately. In a second step the behavior is successfully replicated for polycrystalline metal surfaces and it is found that full monolayers can even withstand air exposure when protected by sacrificial multilayers which are afterwards removed by thermal desorption [2]. This comparison allows on the one hand the transfer of results from single crystal model studies to electrodes as they occur in real devices and on the other hand validates the robustness of this contact primer approach under real fabrication conditions.



**Figure 1.** Exemplary STM images of highly ordered phthalocyanine thin films studied as contact primer on noble metal surfaces.

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## REFERENCES

- [1] J. M. Gottfried, *Surf. Sci. Rep.* **2015**, *70*, 259.  
[2] F. Widdascheck, A. A. Hauke, G. Witte, *Adv. Funct. Mater.* **2019**, DOI: 10.1002/adfm.201808385



OC8

## ELECTRONIC CONFIGURATION OF VARIOUS F6TCNNQ-BASED INTERFACES

M. Hantusch\*<sup>1</sup>, R. Kuhrt<sup>1</sup>, V. Bessergenev<sup>2</sup>, M. Knupfer<sup>1</sup><sup>1</sup> IFW Dresden, Helmholtzstraße 20, D-01069 Dresden, Germany

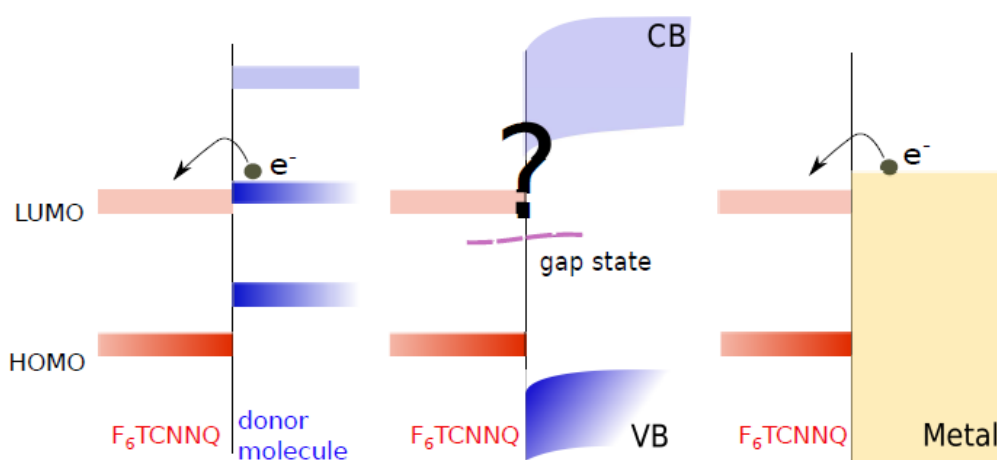
m.hantusch@ifw-dresden.de

<sup>2</sup> Universidade do Algarve, FCT and Centre of Marine Sciences (CCMAR), Campus de Gambelas, 8005-117 Faro, Portugal

Hexafluorotetracyanonaphthoquinodimethane (F6TCNNQ) is a widely used molecular p-dopant material in organic semiconductors as well as in inorganic semiconductors because of its strong electron acceptor properties [1, 2]. It is known that the electronic structure of F6TCNNQ can change significantly for different host materials [3]. While doping affects a bulk system, examining the physical processes at different F6TCNNQ-based interfaces in detail could lead to a deeper understanding of the charge transfer mechanisms depending on the substrate material. This work investigates the electronic configuration of various charge transfer interfaces which include F6TCNNQ.

We compare the results for thin film systems such as 'F6TCNNQ on an organic donor', 'F6TCNNQ on an inorganic (TiO<sub>2</sub>) substrate' and 'F6TCNNQ on a metal substrate' determined by X-ray photoelectron (XPS) and Ultra-Violet photoelectron spectroscopy (UPS).

Significant changes are observed in the nitrogen and the carbon core levels of the acceptor material depending on the host substrate. These changes indicating the presence of F6TCNNQ<sup>-</sup> ions and they are directly correlated with a full charge transfer across the interface. Furthermore, the analysis of the valence spectra of the F6TCNNQ-based interfaces reveals the presence of occupied electron states above the initial F6TCNNQ-HOMO-level (figure 1). The origin of these energy levels and their correlation with the charge transfer is discussed.



**Figure 1:** scheme of the energy levels of different F6TCNNQ-based interfaces according to the analysed valence spectra

**Acknowledgement:** Financial support by the DFG (KN393/25; KN393/26) is gratefully acknowledged.

## REFERENCES

- [1] Björn Lüsser, Max L Tietze, Hans Kleemann, Christoph Hoßbach, Johann W Bartha, Alexander Zakhidov, and Karl Leo. Doped organic transistors operating in the inversion and depletion regime. *Nature communications*, 4:2775, 2013.
- [2] Wei Chen, Yecheng Zhou, Linjing Wang, Yinghui Wu, Bao Tu, Binbin Yu, Fangzhou Liu, Ho-Won Tam, Gan Wang, Aleksandra B Djurišić, et al. Molecule-doped nickel oxide: Verified charge transfer and planar inverted mixed cation perovskite solar cell. *Advanced Materials*, 30(20):1800515, 2018.
- [3] Jing Li, Ivan Duchemin, Otello Maria Roscioni, Pascal Friederich, Marie Anderson, Enrico Da Como, Gabriele Kociok-Köhne, Wolfgang Wenzel, Claudio Zannoni, David Beljonne, et al. Host dependence of the electron affinity of molecular dopants. *Materials Horizons*, 6(1):107–114, 2019.

OC9

**UNVEILING THE MECHANISM FOR MOLECULAR DOPING IN ORGANIC SEMICONDUCTORS:  
EXCITONIC EFFECTS AND HOST-DEPENDENT ACCEPTOR LEVELS**

**Jing Li<sup>1</sup>, Ivan Duchemin<sup>2</sup>, David Beljonne<sup>3</sup>, Xavier Blase<sup>1</sup> and Gabriele D'Avino\*<sup>1</sup>**

<sup>1</sup> Institut Néel, CNRS and Grenoble Alpes University, F-38042 Grenoble, (France)  
*gabriele.davino@neel.cnrs.fr*

<sup>2</sup> INAC, MEM, L\_Sim, CEA and Grenoble Alpes University, Grenoble (France)

<sup>3</sup> Laboratory for the Chemistry of Novel Materials, University of Mons, Mons (Belgium)

Molecular doping is a key strategy for the tuning of the electrical properties of organic semiconductors that is at the core of the functioning of organic optoelectronic devices. We will report on our recent theoretical investigations on molecular doping shedding light on the fundamentals of its elusive mechanism. We take advantage of the quantitative accuracy of our novel embedded many-body electronic structure techniques (GW and Bethe-Salpeter formalisms coupled to atomistic polarizable models) [1,2] to show that in typical molecular p-type semiconductors (e.g, pentacene or NPD) the dopant acceptor levels lies very deep into the gap, also for strongly electron withdrawing dopants such as F4TCNQ or F6TCNNQ.[3,4] This is the result of a pronounced dependence of the dopant acceptor level (up to 1 eV) on the host semiconductor, resulting from intermolecular electrostatic interactions in the solid state.[4] The ionization of dopant impurities is rationalized upon including the excitonic electron-hole interaction that, together with structural relaxation (polaronic) effects, strongly stabilizes dopant-semiconductor charge transfer states.

Our findings question the pertinence of the electron affinity measured for pure dopants in order to predict the doping efficiency in a specific host, and reconcile conflicting experimental evidences regarding the partial vs. full charge transfer scenario discussed in the literature.[3,4] The role of the electron-hole interaction for the dopant-to-semiconductor charge transfer and for the release of doping-induced charges will be discussed, suggesting rational design rules for performances optimization.

**Acknowledgments:** This research received funding from the EU H2020 research and innovation programme under Grant agreement No. 646176 (EXTMOS).

#### REFERENCES

- [1] J. Li, G. D'Avino, I. Duchemin, D. Beljonne, X. Blase, *J. Phys. Chem. Lett.* **7**, 2814 (2018).
- [2] J. Li, G. D'Avino, I. Duchemin, D. Beljonne, X. Blase, *Phys. Rev. B* **97**, 035108 (2018).
- [3] J. Li, G. D'Avino, A. Pershin, D. Jacquemin, I. Duchemin, D. Beljonne, X. Blase, *Phys. Rev. Mater.* **1**, 025602 (2017).
- [4] J. Li, I. Duchemin, O. M. Roscioni, P. Friederich, M. Anderson, E. Da Como, G. Kociok-Köhn, W. Wenzel, C. Zannoni, D. Beljonne, X. Blase and G. D'Avino, *Mater. Horiz.* **6**, 107 (2019).

## SINGLE-MOLECULE SENSING OF BIOMARKERS

**Luisa Torsi**

Dipartimento di Chimica - Università degli Studi di Bari "Aldo Moro" - Bari (I)

CSGI (Centre for Colloid and Surface Science) - Bari (I)

Center for Functional materials, The Faculty of Science and Engineering - Åbo Akademi University - Turku (FI) -

*luisa.torsi@uniba.it*

Digitization is a major driver in biomarkers assay and can enable precision medicine to enter into the everyday clinical practice. Among the single-molecule detection methods proposed so far, only few are, however, exploitable for clinical assays.

The selective sensing platforms assessed in this lecture encompass low-background-noise fluorescent microscopies, plasmonic and electrical nano-transducers, all inherently unfit to sense a single-molecule in a bulk milieu. Recently commercialized label-based technologies relying on micro-beads that can find and detect few biomarkers in the bulk of real biofluids, have paved the way to a revolution in early-diagnostic. Lately, label-free, mass-manufacturable, bioelectronic capacity-coupled large electrolyte-gated transistors have been proven capable to detect a biomarker at the physical-limit in real bovine-serum.<sup>[1-5]</sup>

This lecture aims at discussing the material-science and devices-operational aspects underpinning the sensing-principles of the assessed technologies critically prioritizing them according to scrutinized figures-of-merit such as limit-of-detection, need for a labelling-step and feasibility to assay biofluids.

### REFERENCES

- [1]. Macchia, E.; Manoli, K.; Holzer, B.; Di Franco, C.; Ghittorelli, M.; Torricelli, F.; Alberga, D.; Mangiatordi, G.F.; Palazzo, G.; Scamarcio, G.; Torsi, L. Single-molecule detection with a millimetre-sized transistor. *Nature Communications* 2018, 9, 3223.
- [2]. Nature highlights - A sensor detects the light touch of a single molecule. *Nature* 2018, 560, 412.
- [3]. Macchia, E.; Romele, P.; Manoli, K.; Ghittorelli, M.; Magliulo, M.; Kovács-Vajna, Z.; Torricelli, F.; L. Torsi, L. Ultra-sensitive protein detection with organic electrochemical transistors printed on plastic substrates. *IOP Flexible and Printed Electronics*. 2018, 3, 034002.
- [4]. Macchia, E.; Tiwari, A.; Manoli, K.; Holzer, B.; Ditaranto, N.; Picca, R.A.; Cioffi, N.; Di Franco, C.; Scamarcio, G.; Palazzo, G.; Torsi, L. Label-free and selective single-molecule bioelectronic sensing with a millimeter-wide self-assembled monolayer of anti-immunoglobulins. *Chemistry of Materials* in press (2019).
- [5]. Macchia, E.; Manoli, K.; Holzer, B.; Di Franco, C.; Picca, R.A.; Cioffi, N.; Scamarcio, G.; Palazzo, G.; Torsi, L. Selective Single-Molecule Analytical Detection of C-Reactive Protein in Saliva with an Organic Transistor. *Analytical and Bioanalytical Chemistry* in press (2019).
- [6] Manning, R. *Super Organics*. *Wired*, May 2004, pp 176-181.
- [7] Peacock-Lopez, E. Exact Solutions of the Quantum Double Square-Well Potential. *Chem. Ed. [Online]* **2007**, 11, 383-393 <http://chemeducator.org/bibs/0011006/11060380lb.htm> (accessed Aug 23, 2007).

OC10

**"WHEN BONDING MAKES YOU STRONGER"**  
**SUPPORTED LIPID MONOLAYERS AS SENSING AND SELECTIVE LAYERS FOR ISFET SENSORS**

**V. Kilinc<sup>1</sup>, T. Nguy<sup>2</sup>, A. Kenaan<sup>3</sup>, S. Lamant<sup>4</sup>, C. Henry-de-Villeneuve<sup>5</sup>, G. Monier<sup>6</sup>,  
M. Petit<sup>7</sup>, Y. Wakayama<sup>8</sup>, J. M. Raimundo<sup>9</sup>, A. Charrier\*<sup>10</sup>**

<sup>1,3-4,7,9-10</sup> CINA<sup>M</sup>, Aix Marseille Université, CNRS, Marseille, France

<sup>5</sup> PMC, Ecole Polytechnique, Palaiseau, France

<sup>6</sup> Institut Pascal, Aubière, France

<sup>2,8</sup> NIMS, Tsukuba, Japan

*anne.charrier@univ-amu.fr*

We present an original platform constituted of an engineered lipid monolayer which is used as the active sensitive layer and as ultra-thin gate dielectric in field effect transistor sensors. Supported lipid layers, with thicknesses of a few nanometers indeed constitute good candidates. In living cells lipid membranes are known to constitute natural insulators which play an efficient role as barrier to both ionic and electronic transport across the membrane, associated with an electrical resistance of the order of several giga-Ohms in magnitude. However, despite excellent insulating properties, lipid bilayers and even more lipid monolayers have been poorly exploited in devices due to their inherent instability under application of an electric field, leading to damages caused mainly by an electroporation process occurring at low electric field. Furthermore a lack of mechanical stability is often observed.

We show that the mechanical and chemical stability of lipid layers as well as their dielectric performances can be improved by changing the molecular structure of the lipids and by achieving intra-chain reticulations within the layer, and that surprisingly both these properties are correlated. In fact such reticulated layers with a thickness of 2.5 nm only present low leakage current even at high electric field, and a direct dielectric breakdown occurring at  $\sim 30$  MV/cm, i.e. much higher than for a silicon oxide layer of similar thickness or other high- $\kappa$  dielectrics.

We show that once the lipid monolayer on the transistor channel the specificity of the sensor given by the grafting of probes to the lipids can be tuned using simple procedure making our sensor extremely versatile.

As a proof of concept, we present here different sensors that were developed for the detection of Fe<sup>3+</sup>, Cu<sup>2+</sup> and Cs<sup>+</sup> ions using different materials, inorganic transistors with silicon channel and organic transistors with a Poly(3-hethyl)thiophen as channel, and different types of probes.

Our sensors present good specificities with exceptional low limit of detection down to the sub-femtomolar range, high sensitivity and a linear response over several decades.

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## REFERENCES

- [1] Charrier A. et al., Langmuir 26, 2538 (2010)
- [2] Charrier at al., Patent: FR2983637/WO2013083490A1 (2013)
- [3] Dumas C. Et al., Langmuir 27, 13643 (2011)
- [4] Nguyen T.D. et al., J. Phys. Chem. B 116, 7190 (2012)
- [5] El Zein R. et al., J. Mat. Chem. B 1, 443 (2013)
- [6] Nguyen T.D. et al., Biosens. Bioelect. 54, 571 (2014)
- [7] Kenaan A. Et al., Anal. Chem.(88) 3804 (2016)
- [8] Charrier A. et al., Patent: PCT/EP2016/074569 (2016)
- [9] Kenaan et al., Adv. Func. Mat. 1801024 (2018)

OC11

## HIGH MOBILITY COLUMNAR SELF-ASSEMBLING SEMICONDUCTORS: FROM MATERIALS TO DEVICES

Berta Gómez-Lor \* and Angela Benito-Hernández

Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid, Spain.

bgl@icmm.csic.es, angela.benito@csic.es

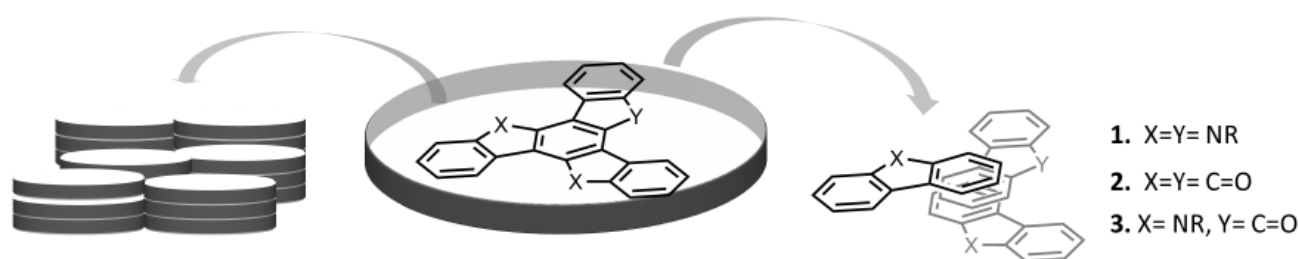
Charge carrier mobility in organic semiconductors has reached values already acceptable for many of the intended applications, however the implementation of high mobility organic semiconductors in the fabrication of devices shows still serious processability limitations. In the search of the necessary trade-off between processing and mobility values columnar self-assemblies of discotic liquid crystalline materials have been envisaged as promising candidates.<sup>1</sup>

In this context, we have introduced heptacyclic triindole **1** as a favorable disk-like core for the construction of semiconducting columnar mesogens. This molecule can be considered as three carbazole units that share a fused aromatic ring and has been demonstrated to be a high performance hole mobility semiconducting scaffold.<sup>2</sup> In fact, triindole-based columnar mesophases present mobility values that may compete with those of the best polycrystalline organic semiconductors reaching values up to  $2.8 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ .<sup>3</sup>

Truxenone **2** is structurally related to triindole. Using the same analogy as above, this molecule can be considered as three fluorenone units sharing a fused aromatic ring. The three ketone groups render this molecule electron deficient. Actually, attaching three peripheral chains to the truxenone core give rise to columnar superstructures presenting electron mobility values above  $1 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ .<sup>4</sup>

We have recently developed a new molecular scaffold (diazatruxenone, **3**)<sup>5</sup> that presents the same geometry and shares molecular characteristics of triindole and truxenone. The combination of electron rich and electron deficient segments in the same aromatic platform renders this molecule a promising candidate for ambipolar transport.

In this communication, we present how through an adequate functionalization we can modulate both the electronic and self-assembling properties of these three disk-like heptacyclic semiconducting scaffolds and optimize their performance and processability towards their incorporation in devices.



**Figure 1.** Structures of discotic scaffolds: triindole **1**, truxenone **2** and diazatruxene **3**.

## REFERENCES

- [1] Sergeyev, S.; Pisula, W.; Geerts, Y. H. Discotic liquid crystals: a new generation of organic semiconductors. *Chem. Soc. Rev.* 2007, 36, 1902-1929
- [2] García-Frutos, E. M.; Pandey, U. K.; Termine, R.; Omenat, A.; Barberá, J.; Serrano, J. L.; Golemme, A.; Gómez-Lor, B., High Charge Mobility in Discotic Liquid-Crystalline Triindoles: Just a Core Business? *Angew. Chem. Int. Ed.* 2011, 50, 7399-7402.
- [3] Benito-Hernández, A.; Pandey, U. K.; Cavero, E.; Termine, R.; García-Frutos, E. M.; Serrano, J. L.; Golemme, A.; Gómez-Lor, B. High Hole Mobility in Triindole-Based Columnar phases: Removing the Bottleneck of Homogeneous Macroscopic Orientation, *Chem. Mater.* 2013, 25, 117
- [4] Gómez-Esteban, S.; Benito-Hernandez, A.; Termine, R.; Hennrich, G.; Navarrete, J. T. L.; Ruiz Delgado, M. C.; Golemme, A.; Gómez-Lor, B., High-Mobility Self-Assembling Truxenone-Based n-Type Organic Semiconductors. *Chem. Eur. J.* 2018, 24, 3576-3583
- [5] Benito-Hernández, A.; El-Sayed, M. T.; López Navarrete, J. T.; Ruiz Delgado, M. C.; Gómez-Lor, B., Fused donor-acceptor  $\pi$ -conjugated diazatruxenones: synthesis and electronic properties. *Org. Chem. Front.* 2018, 5, 1748-1755.

## SESSION 3

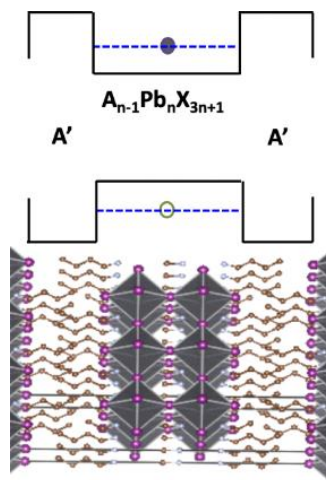
K3

## ELECTRONIC STRUCTURE OF METAL HALIDE PEROVSKITE SURFACES: FROM 3D TO 2D TO 2D/3D

Antoine Kahn

Department of Electrical Engineering, Princeton University, Princeton, NJ 08544, USA

Metal halide perovskites (MHP), which have generated so much world-wide attention over the past few years, come in many flavors, from all inorganic to hybrids, from single to mixed cations and halides, and from 3D to various shades of 2D structures. The vast parameter space that characterizes these materials makes them challenging, but also very promising, for electronic structure design. In this talk, we first review our investigations of 3D MHPs surfaces and interfaces with organic hole and electron transport layers via direct and inverse photoemission spectroscopy.[1,2] We emphasize the challenge posed by the determination of some electronic parameters, in particular the low density of states at the valence band edge in 3D lead halide perovskites  $APbX_3$  ( $A = MA$  or  $Cs$ ;  $X = I$  or  $Br$ ).[3] We then turn to 2D MHPs, perceived as interesting photovoltaic materials in their own right, and also as potentially efficient capping materials to improve the long-term stability of 3D MHP solar cells. Energy level alignment at 2D/3D heterojunctions and stability of the 2D materials are therefore of considerable interest. We focus here on the electronic structure and surface potential of films of the 2D Ruddlesden-Popper (RP) and Dion-Jacobson (DJ) phases of metal halides  $A'_{2n-1}A_nM_nX_{3n+1}$ , namely the butylammonium RP phase  $BA_2PbI_4$  ( $n=1$ ) and  $BA_2CsPb_2I_7$  ( $n=2$ ),[4,5], and the DJ phase  $A'PbI_4$  with  $A' =$  ethane-1,2-diammonium (EDA), butane-1,4-diammonium (BDA), and N,N-dimethylpropane-1,3-diammonium iodide (DMPD). In each case, the single particle gap of the quantum well structure corresponding to the inorganic  $PbX$  sheet (Fig. 1) is quantitatively determined and the exciton binding energy is evaluated. Finally, we turn to the direct measurement of the electronic structure of a 2D/3D perovskite heterojunction fabricated by exposing a film of 3D  $MAPbI_3$  to a butylammonium (BA) solution, resulting in the growth of an ultra-thin film of  $BA_2PbI_4$  on top of the 3D material. The energy diagram points to a heterojunction with little charge transfer between the two layers, but where the  $BA_2PbI_4$  layer introduces barriers to the extraction of both electrons and holes.



## REFERENCES

- [1] *Interface energetics in organo-metal halide perovskite-based photovoltaic cells*, Philip Schulz, Eran Edri, Saar Kirmayer, Gary Hodes, David Cahen and Antoine Kahn, *Energ. & Envir. Sci.* **7**, 1377 (2014)
- [2] *Electronic Level Alignment in Inverted Organometal Perovskite Solar Cells*, Philip Schulz, Luisa L. Whittaker-Brooks, Bradley A. MacLeod, Dana C. Olson, Yueh-Lin Loo and Antoine Kahn, *Adv. Mat. Int.* **2**, 1400532 (2015)
- [3] *Valence and conduction band densities of states of metal halide perovskites: a combined experimental - theoretical study*, James Endres, David A. Egger, Michael Kulbak, Ross A. Kerner, Lianfeng Zhao, Scott H. Silver, Gary Hodes, Barry P. Rand, David Cahen, Leeor Kronik, and Antoine Kahn, *J. Phys. Chem. Lett.* **7**, 2722 (2016)
- [4] *Characterization of the Valence and Conduction Band Levels of  $n=1$  Two-Dimensional Perovskites: A Combined Experimental and Theoretical Investigation*, Scott Silver, Jun Yin, Hong Li, Jean-Luc Brédas, Antoine Kahn, *Adv. Energ. Mat.* 1703468 (2018)
- [5] *Combined experimental and theoretical investigation of the quantum well energetics in  $n=2$  Ruddlesden Popper phase perovskites*, Scott Silver, Qingqing Dai, Hong Li, Jean-Luc Brédas, Antoine Kahn, *Adv. Energ. Mat.* (published online 5/25) (2019)

## CHARGE INJECTION IN 'THICK' MOLECULAR JUNCTIONS

Colin Van Dyck\*, Adam Bergren

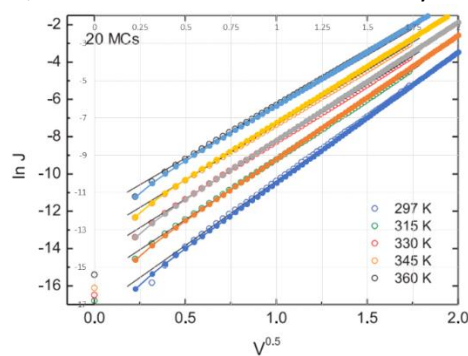
NRC Nanotechnology Research Center, University of Alberta, Edmonton, AB CANADA.

colin.vandyck@nrc.ca, Adam.Bergren@nrc-cnrc.gc.ca

Molecular electronics usually focuses on thin organic layers (thinner than 5 nm) contacted to electrodes, which transport properties are now well understood in terms of quantum tunnelling and the Landauer picture of conductance. In few interesting cases, organic layers thicker than 5 nm has been realized and characterized. Those evidenced a transition in the transport characteristics to a mechanism that is different from quantum tunnelling. In those layers, the charge carriers reside in the device, which translates into coherence and energy losses.[1-2] To some extent, thick molecular junctions bridge the gap between *molecular* and *organic* electronics. Those thick devices can be made very robust and exhibit many interesting features such as photocurrent generation under illumination or light emission, at the nanoscale.[3-4]

The transport mechanism in thick junctions is not well understood, and currently no consensus has been made across the variety of observed behaviours. The Frisbie group observed a thermally activated transport pointing to a well-characterized Marcus-like hopping transport mechanism, and suggested a nuclear tunnelling enhancement.[1][5] On the other hand, the McCreery group observed an activationless transport mechanism and several behaviours across layers from 5 to 22 nm.[6] Interestingly, the Von Wrochem group suggested a classical Schottky emission mechanism in 15 to 30 nm thick devices.[7]

In this contribution, we discuss the possibility of an injection limited mechanism in thick large area molecular junctions. We introduce a simple model of the injection mechanism and show that it reproduces well the transport characteristics observed in the Von Wrochem and McCreery groups. Importantly, it allows to extract physically meaningful transport parameters, controlled by the device structure, and ascribe the origin of differences observed in the conductance of different molecular structures. The model points to the important role played by disorder and defects in the molecular layer, strongly affecting the temperature dependence of current-voltage characteristics. Finally, it directly suggests a temperature dependent concentration of free charge carriers in thick molecular junctions, which origin can be rationalized in terms of mobile ions and/or thermal carriers within the layer.



**Figure 1.** Superimposition of predicted and measured current-voltage characteristics for thick (20 nm) organic layers, taken from reference [7]. The whole transport characteristics at different biases and temperatures can be reproduced using the same model parameters clearly pointing toward an injection limited transport process.

## REFERENCES

- [1] Choi, Kim and Frisbie, "Electrical resistance of long conjugated molecular wires", *Science*, 320, 1482-1486, **2008**
- [2] Ivashenko, Bergren and McCreery, "Light emission as a probe of energy losses in molecular junctions", *JACS*, 138, 722, **2016**
- [3] Morteza Najarian, Bayat and McCreery, "Orbital Control of Photocurrents in Large Area All-Carbon Molecular Junctions", *JACS*, 140, 1900-1909, **2018**
- [4] Tefashe, Nguyen, Lafolet, Lacroix and McCreery, "Robust Bipolar Light Emission and Charge Transport in Symmetric Molecular Junctions", *JACS*, 139, 7436-7439, **2017**
- [5] Taherinia and Frisbie, "Charge Transport in 4 nm Molecular Wires with Interrupted Conjugation: Combined Experimental and Computational Evidence for Thermally Assisted Polaron Tunneling", *ACS Nano*, 10, 4372-4383, **2016**
- [6] Yan, Bergren, McCreery et al, "Activationless charge transport across 4.5 to 22 nm in molecular electronic junctions", *PNAS*, 110, 5326-5330, **2013**
- [7] Karipidou and von Wrochem, "Ultrarobust Thin-Film Devices from Self-Assembled Metal-Terpyridine Oligomers", *Advanced Materials*, 28, 3473-3480, **2016**

OC13

## CHARGE INJECTION AND TRANSPORT PROPERTIES OF LARGE AREA ORGANIC JUNCTIONS WITH A MULTILAYER GRAPHENE ELECTRODE

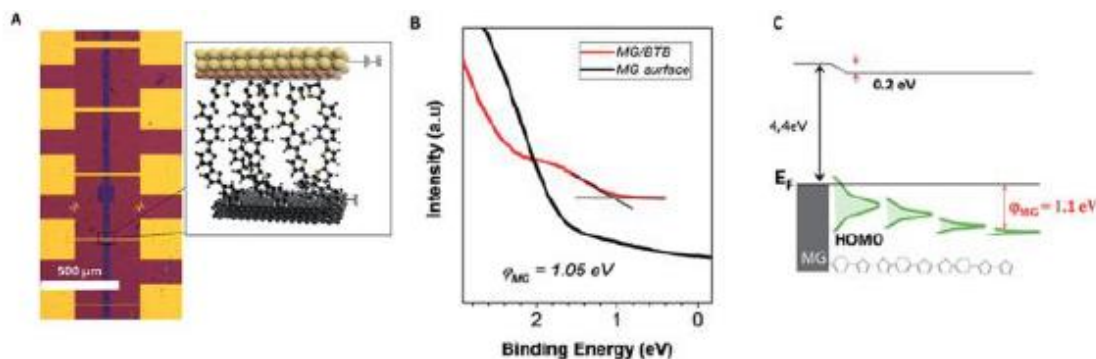
C. Barraud<sup>1</sup>, M. Lemaitre<sup>1</sup>, R. Bonnet<sup>2</sup>, J. Rastikian<sup>1</sup>, C. Salhani<sup>1</sup>, S. Lau<sup>2</sup>, Q. Van Nguyen<sup>2</sup>, P. Decorse<sup>2</sup>, J.-C. Lacroix<sup>2</sup>, M. L. Della Rocca<sup>1</sup>, P. Lafarge<sup>1</sup> and P. Martin\*<sup>2</sup>

<sup>1</sup>MPQ UMR 7162, Université de Paris, CNRS, F-75013 Paris, France

<sup>2</sup>ITODYS UMR 7086, Université de Paris, CNRS, F-75013 Paris, France

*pascal.martin@univ-paris-diderot.fr*

The quantum interaction between molecules and electrode materials at molecule/electrode interfaces is a major ingredient in the electron transport properties of organic junctions[1]. Driven by the coupling strength between the two materials, it results mainly in the broadening and energy shift of the interacting molecular orbitals. Using new electrode materials, such as the recently developed semiconducting two-dimensional nanomaterials[2], has become a significant advancement in the field of molecular/organic electronics that opens new possibilities for controlling the interfacial electronic properties and thus the charge injection properties. Here, we report the use of atomically thin two-dimensional multilayer graphene films as the base electrode in organic junctions[3] with a vertical architecture (figure 1). The interfacial electronic structure dominated by the covalent bonding between bis-thienyl benzene diazonium-based molecules and the multilayer graphene electrode has been probed by ultraviolet photoelectron spectroscopy and the results are compared with those obtained on junctions with standard Au electrodes. Room temperature injection properties of such interfaces have also been explored by electron transport measurements. We find that, despite strong variations of the density of states, the Fermi energy and the injection barriers, both organic junctions with Au base electrodes and multilayer graphene base electrodes show similar electronic responses. We explain this observation by the strong orbital coupling occurring at the bottom electrode/bis-thienyl benzene molecule interface and by the pinning of the hybridized molecular orbitals.



**Figure 1.** a) Optical image of MG–BTB//Ti/Au junctions with various dimensions of junctions. b) UPS spectra acquired on a bare MG surface (black line) and on a MG/BTB surface (red line). c) Schematic of the interfacial electronic structure with the reported values of dipoles and barrier.

**Acknowledgments:** This work is supported by the 2DSPIN project from the “Ville de Paris” Emergence program. ANR (Agence Nationale de la Recherche) and CGI (Commissariat à l’Investissement d’Avenir) are gratefully acknowledged for their financial support of this work through Labex SEAM (Science and Engineering for Advanced Materials and devices) ANR 11 LABX086, ANR 11IDEX 05 02. This work has also been supported by the Region Ile-de-France in the framework of DIM Nano-K (SMS project).

## REFERENCES

- [1] R.M. Metzger, Chem. Rev. 115, 5056 (2015).
- [2] J.S. Bunch, S.S. Verbridge, J.S. Alden, A.M. van der Zande, J.M. Parpia, H.G. Craighead, and P.L. McEuen, Nano Lett. 8, 2458 (2008).
- [3] C. Barraud, M. Lemaitre, R. Bonnet, J. Rastikian, C. Salhani, S. Lau, Q. van Nguyen, P. Decorse, J.-C. Lacroix, M.L. Della Rocca, P. Lafarge, and P. Martin, Nanoscale Adv. 1, 414 (2019).



OC14

## CHEMICAL ENDURANCE VERSUS ON-SURFACE DEFLUORINATION OF C<sub>60</sub>F<sub>48</sub> ON COINAGE METALS AT ROOM TEMPERATURE: STRUCTURE AND ELECTRONIC PROPERTIES

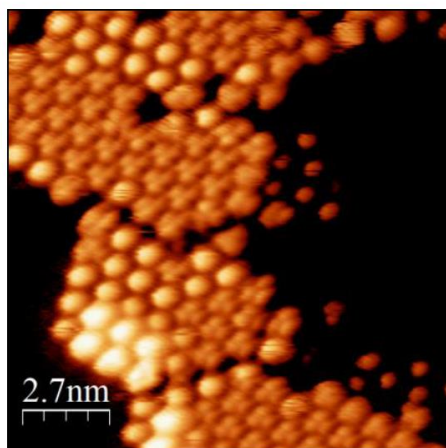
R. Palacios-Rivera<sup>1</sup>, D. C. Malaspina<sup>1</sup>, J. Faraudo<sup>1</sup>, O. Solomeshch<sup>2</sup>, N. Tessler<sup>2</sup>, E. Barrena<sup>1\*</sup> and C. Ocal<sup>1</sup>

<sup>1</sup>(ICMAB-CSIC), Campus UAB, Bellaterra, E-08193, (Spain) \*ebarrena@icmab.es

<sup>2</sup>Electrical Engineering Department, Nanoelectronic Center, Technion, Haifa 32000, Israel

Understanding the interactions of molecules on surfaces is important in the ongoing effort to optimize the interface properties in electronic organic devices. One aspect of key importance is to assure the chemical stability of the organic compound on the surface. In this work, we unveil the role that the organic-metal interactions have on the chemical stability of the fluorinated fullerene C<sub>60</sub>F<sub>48</sub> on coinage metals at room temperature. Fluorinated fullerenes have particular interest as p-type dopant due to its large electron affinity and high thermal stability [1-2].

We present a comparative study of the structural and electronic properties of C<sub>60</sub>F<sub>48</sub> on Au(111), Cu(111) and Ni(111) by scanning tunneling microscopy (STM) and X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS). We will demonstrate that despite the assumed stability of C<sub>60</sub>F<sub>48</sub>, its chemical integrity at room temperature depends on the particular molecule-metal interaction. Whereas on Au(111) the molecule preserves its molecular structure, on more reactive surfaces such as Cu(111) and Ni(111), it transforms into C<sub>60</sub>. By molecular dynamics simulations with reactive force fields we elucidate the mechanisms of the surface-induced catalytic defluorination of C<sub>60</sub>F<sub>48</sub> molecules.



**Figure 1.** STM image of C<sub>60</sub>F<sub>48</sub> deposited at room temperature on Cu(111)

### REFERENCES

- [1] R. Mitsumoto et al. Electronic Structures and Chemical Bonding of Fluorinated Fullerenes Studied by NEXAFS, UPS, and Vacuum-UV Absorption Spectroscopies *J. Phys. Chem. A* 1998, 102, 552-560
- [2] J. Li et al. Measurement of Small Molecular Dopant F4TCNQ and C60F36 Diffusion in Organic Bilayer Architectures *ACS Appl. Mater. Interfaces* 2015, 7, 28420-28428

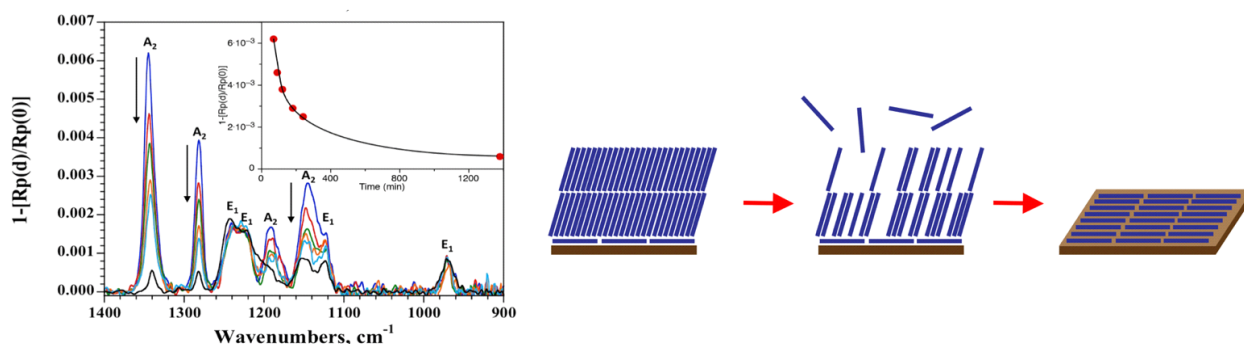
## CONTROL OF HYBRIDE PEROVSKITE SURFACE WITH FLUORINATED MOLECULES

Subha Sadhu<sup>1,2</sup>, Thierry Buffeteau<sup>2</sup>, Dario M. Bassani<sup>2</sup> and Lionel Hirsch\*<sup>1</sup><sup>1</sup> Univ. Bordeaux, IMS, CNRS UMR 5218, Bordeaux INP, ENSCBP, F-33405 Talence.<sup>2</sup> Univ. Bordeaux, ISM, CNRS UMR 5255, F-33405 Talence.

lionel.hirsch@ims-bordeaux.fr

In recent years, hybrid organic-inorganic perovskites (HOIP) have emerged as a novel material for applications in photovoltaics and photoelectric applications such as photo-detectors and lasers. This class of semiconductor is very attractive because it combines the advantages of the inorganic semiconductors, such as the direct bandgap, high charge carrier mobility and broad density of states, and the advantages of organic semiconductors, such as wet deposition at low temperature and resilience to defects.

Like other ionic crystals, perovskites possess under-coordinated ions and dangling bonds at the surface, causing defects and trap sites. For this reason, numerous groups have investigated passivation of the perovskite surface with the aim of improving photovoltaic performance by decreasing recombination and increasing charge injection to the electrode. In this presentation, we will demonstrate that fluorocarbons interact with the HOIP surface thanks to the polarization-modulation infrared reflection absorption spectroscopy (PM-IRRAS). Whereas this interaction is clearly counterintuitive considering the difference in hydrophobicity between the HOIP surface and fluorocarbons, we used it to modify the surface potential of the HOIP as well as to enhance the passivation to moisture.



**Figure 1.** Time dependent PM-IRRAS spectra of perfluorooctane (PFO) on methylammoniumleadtriiodide. Inset shows time evolution of the intensity at  $1360\text{ cm}^{-1}$ , evidencing the decrease of the  $A_2$  signals associated with a vertical arrangement of the PFO. On the right, we present a schematic of the monolayer of figure.

**Acknowledgments:** We are grateful to financial support from the LabEx AMADEus (ANR-10-LABX-0042-AMADEUS through grant ANR-10-IDEX-0003-02) and the ANR HYPEROL project (ANR-18-CE05-0021). We thank Dr. A. Lecoudre (CESAMO center for structural analysis) for assistance with the X-ray structure determination and B. Plano (IMS) for the SEM pictures.

## REFERENCES

- [1] J.-P. Correa-Baena, A. Abate, M. Saliba, W. Tress, T. Jesper Jacobsson, M. Gratzel and A. Hagfeldt, *Energy Environ. Sci.*, **2017**, 10, 710-727.
- [2] M. Crespo-Quesada, L. M. Pazos-Outón, J. Warnan, M. F. Kuehnel, R. H. Friend and E. Reisner, *Nature Communications*, **2016**, 12555.
- [3] N. K. Noel, A. Abate, S. D. Stranks, E. S. Parrott, V. M. Burlakov, A. Goriely and H. J. Snaith, *ACS Nano*, **2014**, 8, 9815-9821.
- [4] S. Sadhu, K. Aqueche, T. Buffeteau, J.-M. Vincent, L. Hirsch and D. M. Bassani, *Materials Horizons*. **2019**, 6 (1), 192-197.

OC15

## THE ROLE OF PEDOT:PSS ON THE STABILITY OF ORGANIC SOLAR CELLS

A. Gregori<sup>1</sup>, H. Awada<sup>1</sup>, A. Tournebize<sup>2,4</sup>, G. Mattana<sup>4</sup>, L. Rodriguez<sup>1</sup>, S. Schumann<sup>3</sup>, H. Peisert<sup>2</sup>, R. C. Hiorns<sup>1</sup>, T. Chassé<sup>2</sup>, D. Flahaut<sup>1</sup>, L. Vellutini<sup>1</sup>, L. Billon<sup>1</sup>, A. Allal<sup>1</sup>, A. Bousquet<sup>1</sup>, S. Chambon<sup>4</sup>, C. Lartigau-Dagron\*<sup>1</sup>

<sup>1</sup>CNRS/UNIV PAU & PAYS ADOUR/E2S UPPA, Institut des Sciences Analytiques et de Physico-chimie pour l'Environnement et les Matériaux, UMR 5254, 64000 Pau, France. *christine.lartigau-dagron@univ-pau.fr*

<sup>2</sup>Eberhard Karls Universität Tübingen, Institut für Physikalische und Theoretische Chemie, 72076 Tübingen, Germany.

<sup>3</sup>Heraeus Deutschland GmbH & Co. KG, Heraeus New Businesses, Chempark Leverkusen/Gebäude B 202, D-51368 Leverkusen, Germany.

<sup>4</sup>Université de Bordeaux, CNRS, Bordeaux INP, IMS, UMR 5218, F-33405 Talence, France

<sup>5</sup>Université de Bordeaux, CNRS, ISM, UMR 5255, F-33405 Talence, France

Organic solar cells are a multi-layer stack, due to the necessity to integrate interfacial layers to optimise the transport of charge carriers. In direct and inverted architectures, a layer of PEDOT-PSS (poly(ethylene dioxythiophene) doped with poly(styrene sulfonate)) is often used mainly to help the collection of holes.

In direct devices, it is well known that the acidic character of PEDOT-PSS tends to promote the degradation of layers in contact, in particular the ITO (Indium Tin Oxide) electrode. The strategy presented here is to avoid this degradation by replacing the layer of PEDOT-PSS by a thin layer of P3HT (poly(3-hexylthiophene) grafted on ITO. We developed an efficient method to graft P3HT on various surfaces, including ITO, confirmed by XPS measurements [1]. This modified electrode was used to prepare direct solar cells and compared to the one with PEDOT-PSS. Devices stored in air without encapsulation with the grafted P3HT as hole transporting layer exhibited the highest stability.

In inverted solar cells, the problem of chemical degradation of ITO is no longer observed as PEDOT-PSS is deposited on the active layer, on the rear side. While the electrical failure mechanisms in such devices have been thoroughly investigated, little is known about their mechanical stability, which is as important and critical to ensure long term reliability [2]. The characteristic thin films stresses of each layer provide the mechanical driving force for delamination of weak interfaces, leading to a loss of device integrity and performance [3]. In this study [4], we developed a technique to probe weak layers or interfaces in thin multilayer devices, establishing a new set-up for the so-called probe tack making it similar to a pull-off test [5]. The technique has been extended varying both active layers, using different p-type low bandgap polymers for the active layer in combination with two different PEDOT:PSS formulations (Clevios™ HTL Solar and HTL Solar 2). After mechanical tests, the upper and lower surfaces have been characterized by contact angle and XPS to locate the fracture point, which is dependent on the active layer and PEDOT-PSS formulations.

**Acknowledgments:** Part of the results were funded in the framework of the European Union Seventh Programme (FP7/2011 under grant agreement ESTABLIS n° 290022) and of ANR-13-JS09-0014-01 INSTEP.

## REFERENCES

- [1] H. Awada, G. Mattana, A. Tournebize, L. Rodriguez, D. Flahaut, L. Vellutini, C. Lartigau-Dagron, L. Billon, A. Bousquet, S. Chambon, *Org. Electronics* **2018**, 57, 186
- [2] M. Jorgensen, K. Norrman, S. A. Gevorgyan, T. Tromholt, B. Andreasen, F. C. Krebs, *Adv. Mater.* **2012**, 24, 5
- [3] S. R. Dupont, M. Oliver, F. C. Krebs, R. H. Dauskardt, *Sol. En. Mat. & Sol. Cells* **2012**, 97, 171
- [4] A. Gregori, A. Tournebize, S. Schumann, H. Peisert, R. C. Hiorns, T. Chassé, C. Lartigau-Dagron, A. Allal, *Sol. En. Mat. & Sol. Cells* **2018**, 25, 174
- [5] ASTM D4541-0

OC16

## MOLECULAR DESIGN OF ACCEPTORS FOR NON-FULLERENE ORGANIC SOLAR CELLS

Anastasia Markina\*<sup>1</sup>, Frédéric Laquai <sup>2</sup> and Denis Andrienko <sup>1</sup>

<sup>1</sup> Max Planck Institute for Polymer Research, Mainz, Germany Department, Institute, City, COUNTRY.  
*markina@mpip-mainz.mpg.de, andrienk@mpip-mainz.mpg.de*

<sup>2</sup> King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Physical Sciences and Engineering Division (PSE), Material Science and Engineering Program (MSE), Thuwal 23955-6900, Kingdom of Saudi.  
*frederic.laquai@kaust.edu.sa*

One promising method to achieve higher solar cell efficiencies is to replace fullerenes with strongly-absorbing dye molecules, namely, non-fullerene acceptors (NFAs). Combination of different building blocks (donor, acceptor, bridge blocks) of NFA allows one to get electrically active molecules with strong static quadrupole moments. Tuning of quadrupole moments can be used to control the photophysical properties of solar cells. However, the systematic design of acceptor molecules with tailored properties has yet to be demonstrated.

The ratio between quadrupole moments of donor /acceptor materials can be expressed in terms of electrostatic bias potential. By exploring the long-range electrostatic interaction at the interface, we demonstrate that, for a set of recently developed NFAs, the electrostatic bias potential can be directly related to the stabilization (or destabilization) of charge-transfer (CT) states as well as changes of the photovoltaic gap.

We find that the correlation between quadrupole moments, charge separation efficiency, and CT-state energy predicted by our model, is experimentally reproduced for several different donor /acceptor combinations [1-3]. This allows us to predict new NFA structures using combinations of readily available molecular building blocks that can potentially reach even higher performances than those currently achieved in state-of-the-art NFA devices.

### REFERENCES

- [1] M. Alamoudi, J. Khan, Y. Firdaus, K. Wang, D. Andrienko, P. Beaujuge, F. Laquai, ACS Energy Letters, 3, 802, 2018.
- [2] F. Hinkel, Y. Kim, Y. Zagraniarsky, F. Schluetter, D. Andrienko, K. Muellen, F. Laquai, J. Chem. Phys., 148, 044703, 2018.
- [3] A. Markina, A. Mondal, F. Laquai, D. Andrienko, in preparation, 2019.

OC17

## EFFECT OF ENERGY OFFSETS ON CHARGE GENERATION IN ALL-SMALL MOLECULE NON-FULLERENE ACCEPTOR ORGANIC SOLAR CELLS

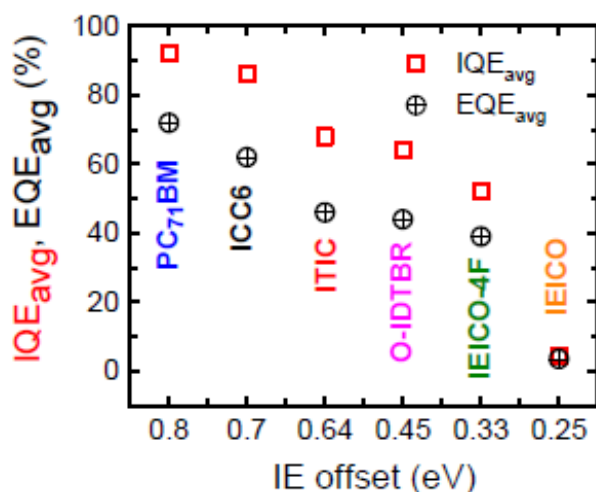
Julien Gorenflot,<sup>1</sup> Safakath Karuthedath,<sup>2</sup> Anastasia Markina,<sup>3</sup> Yuliar Firdaus,<sup>4</sup> George Harrison,<sup>5</sup> Weimin Zhang,<sup>6</sup> Iain McCulloch,<sup>7</sup> Thomas Anthopoulos,<sup>8</sup> Denis Andrienko,<sup>9</sup> Frédéric Laquai<sup>10</sup>

<sup>1,2,4,5,6,7,8,9,10</sup> King Abdullah University of Science and Technology (KAUST), KAUST Solar Center (KSC), Physical Sciences and Engineering Division (PSE), Material Science and Engineering Program (MSE), Thuwal 23955-6900, Kingdom of Saudi Arabia

*julien.gorenflot@kaust.edu.sa, safakath.karuthedath@kaust.edu.sa, frederic.laquai@kaust.edu.sa*

<sup>3,9</sup> Max Planck Institute for Polymer Research (MPIP), Ackermannweg 10, D-55128 Mainz, Germany.  
*denis.andrienko@mpip-mainz.mpg.de*

While ultrafast charge transfer driven by large differences in electron affinity and ionization energy is well understood in fullerene-based solar cells, the effect of (vanishing) energy offsets on photocurrent generation in novel donor : non-fullerene acceptor (NFA) blends is currently debated controversially. Here, we study hole transfer to a small molecule electron donor (DR3TBDDT) in a series of blends that use different non-fullerene electron acceptors. The solar cell characterization shows that for these all small molecule blends, the quantum efficiency is related to the difference in ionization energy (Figure 1), suggesting that a minimal driving force is required for hole transfer to occur. This is especially critical in case of blends that use low-bandgap acceptors, where energy transfer from the donor to the acceptor can occur prior to charge transfer, as shown by ultrafast transient absorption spectroscopy. We additionally, use transient absorption spectroscopy to investigate the relation between the ionization energy offset and hole transfer rate that could put hole transfer in kinetic competition with exciton decay.



**Figure 1.** Average solar cell internal- and external quantum efficiency as function of the ionization energy offset between between the donor DR3TBDDT and the respective non-fullerene acceptors.

### REFERENCES

[1] Karuthedath, S; Liang, R.-Z.; Markina, A.; Firdaus, Y.; Harrison, G.; Zhang, W.; Gorenflot, J.; Alarousu, E; Amassian, A; Anthopoulos, T.; Andrienko, D.; Beaujuge, P. M.; Laquai, F. Ionization energy offset determines charge generation efficiency in small molecule non-fullerene organic solar cells. *in preparation*.

OC18

## C1-LINKED SPIROBIFLUORENE DIMERS: PURE HYDROCARBON HOSTS FOR HIGH PERFORMANCE BLUE PHOSPHORESCENT OLEDs

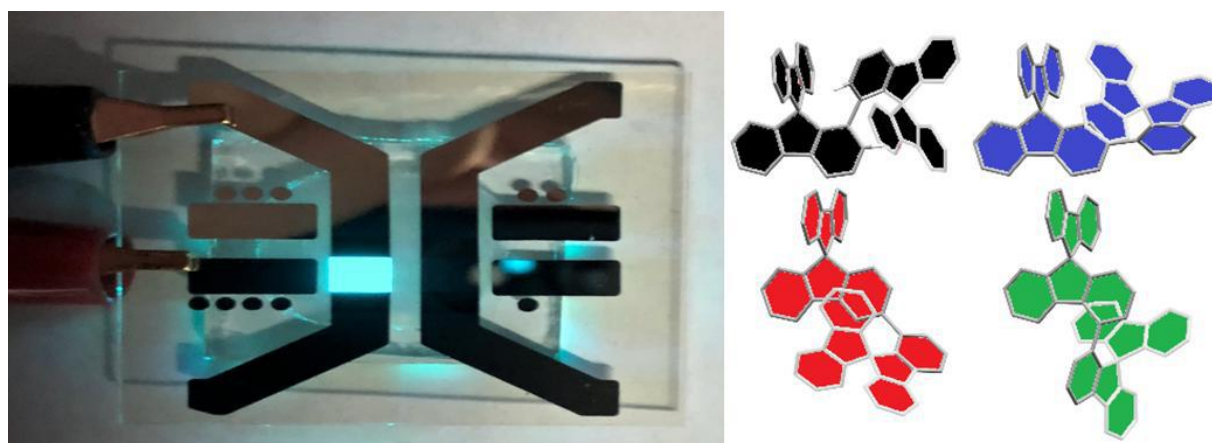
Cyril Poriel,<sup>\*a</sup> Joelle Rault-Berthelot,<sup>a</sup> Lambert Sicard,<sup>a</sup> Hong Cheng Li,<sup>b</sup> Qiang Wang,<sup>b</sup> Xiang-Yang Liu,<sup>b</sup> Liang-Sheng Liao,<sup>b</sup> Zuo-Quan Jiang<sup>b</sup>

<sup>a</sup> Univ Rennes, CNRS, ISCR- UMR 6226, F-35000 Rennes, France <sup>b</sup> LPICM, CNRS, Ecole Polytechnique, Université Paris Saclay, 91128, Palaiseau, France; <sup>c</sup>LICSEN, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA Saclay 91191 Gif-sur-Yvette Cedex, France.

cyril.poriel@univ-rennes1.fr

<sup>b</sup> Institute of Functional Nano & Soft Materials, Soochow University, Suzhou 215123, P.R. China.

Regioisomerism is an important concept in organic chemistry which can have remarkable consequences on the properties of molecules.[1-4] Indeed, a simple structural modification can drastically influence the electronic and physical properties of an organic semi-conductor (OSC), which in turn strongly modifies the performance and stability of the corresponding electronic device.[5-7] In this work, we show the impact of regioisomerism to tune the singlet and triplet energies of a key class of materials widely used in organic electronics, ie spirobifluorene regioisomers.[4, 8, 9] This work reports a structure-properties relationship study of the four positional isomers of spirobifluorene and highlights the influence of the bridge rigidification and of the linkages on the electronic properties. Incorporation of C1 linked Spirobifluorene dimers as pure hydrocarbon host in blue emitting Phosphorescent Organic Light-Emitting Diodes have led to high performance devices (External Quantum Efficiency over 23%).[9]



### REFERENCES

- [1]C. Poriel, J. Rault-Berthelot, *Acc. Chem. Res.* **2018**, *51*, 1818-1830.
- [2]M. Romain, S. Thiery, A. Shirinskaya, C. Declairieux, D. Tondelier, B. Geffroy, O. Jeannin, J. Rault-Berthelot, R. Métivier, C. Poriel, *Angew. Chem. Int. Ed.* **2015**, *54*, 1176-1180.
- [3]M. Romain, D. Tondelier, J.-C. Vanel, B. Geffroy, O. Jeannin, J. Rault-Berthelot, R. Métivier, C. Poriel, *Angew. Chem. Int. Ed.* **2013**, *52*, 14147-14151.
- [4]L. Sicard, C. Quinton, J.-D. Peltier, D. Tondelier, B. Geffroy, U. Biapo, R. Métivier, O. Jeannin, J. Rault-Berthelot, C. Poriel, *Chem. Eur. J.* **2017**, *23*, 7719-7723.
- [5]S. Thiery, D. Tondelier, C. Declairieux, B. Geffroy, O. Jeannin, R. Métivier, J. Rault-Berthelot, C. Poriel, *J. Phys. Chem. C* **2015**, *119*, 5790–5805.
- [6]M. Romain, M. Chevrier, S. Bebiche, T. Mohammed-Brahim, J. Rault-Berthelot, E. Jacques, C. Poriel, *J. Mater. Chem. C* **2015**, *3*, 5742-5753.
- [7]J.-D. Peltier, B. Heinrich, B. Donnio, E. Jacques, J. Rault-Berthelot, C. Poriel, *ACS Appl. Mater. Interfaces* **2017**, *9*, 8219-8232.
- [8]C. Poriel, J. Rault-Berthelot, *J. Mater. Chem. C* **2017**, *5*, 3869-3897
- [9]L. Sicard, H.-C. Li, Q. Wang, X.-Y. Liu, O. Jeannin, J. Rault-Berthelot, L.-S. Liao, Z.-Q. Jiang, C. Poriel, *Angew. Chem. Int. Ed.* **2019**, DOI: 10.1002/anie.201813604.

## SESSION 4

K4

## LENGTH DEPENDENT CHARGE TRANSPORT IN MOLECULAR JUNCTIONS

C. Daniel Frisbie

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN (USA)  
 frisbie@umn.edu

Charge transport can occur through long,  $\pi$ -conjugated molecules, and the term “molecular wire” is often used to describe conjugated molecules in which conduction is efficient over long distances. This talk will describe two experiments designed to probe the length dependence of transport in bundles of molecules connected in parallel between two metal contacts. In the first experiment, conjugated molecular wires up to 10 nm in length are grown on metal substrates using stepwise aryl amine-aryl aldehyde condensation reactions;<sup>1,2,3,4</sup> using this chemistry, the length and backbone architecture of the wires can be controlled precisely. Electrical conduction of ~80 parallel wires is measured using metal coated AFM tips to make the second contact. Both the temperature and length dependence of the wire resistance indicate a transition from tunneling to hopping transport at approximately 4 nm in wire length. A positive kinetic isotope effect on the resistance is also observed for longer wires and not for shorter wires, in support of the tunneling to hopping transition as wire length increases. Interesting outstanding questions include the number of hops per unit wire length and the nature of the transition states. In the second experiment, relatively short aliphatic and aromatic thiols (1-3 nm in length) bonded to gold are stretched by applying a force to the top metal contact (an AFM tip) and the tunneling resistance is measured simultaneously.<sup>5</sup> The resistance versus stretched length behavior is markedly different for the two cases. The results are explained by considering the difference in the localization and delocalization of the primary orbitals assisting tunneling. Such experiments help develop the physical picture of tunneling through simple self-assembled monolayers (SAMs) and resolve confusion in the literature regarding tunneling in aliphatic thiol SAMs in particular.

**Acknowledgments:** We acknowledge funding by the US National Science Foundation.

## REFERENCES

- [1] *Electrical resistance of long conjugated molecular wires*. Choi, S.H.; Kim, B.; Frisbie, C.D. *Science*, **2008**, *320*, 1482-1486. DOI: 10.1126/science.1156538.
- [2] *Transition from Tunneling to Hopping Transport in Long, Conjugated Oligo-imine Wires Connected to Metals*. Choi, S.H.; Risko, C.; Delgado, M.C.R.; Kim, B.; Bredas, J.-L.; Frisbie, C.D. *J. Am. Chem. Soc.*, **2010**, *132*, 4358–4368. DOI: 10.1021/ja910547c.
- [3] *Growth of Thin, Anisotropic, Pi-Conjugated Molecular Films by Stepwise "Click" Assembly of Molecular Building Blocks: Characterizing Reaction Yield, Surface Coverage, and Film Thickness versus Addition Step Number*. Demissie, AT; Haugstad, G; Frisbie, CD. *J. Am. Chem. Soc.*, **2015**, *137*(27), 8819-8828. DOI: 10.1021/jacs.5b04512.
- [4] *Charge Transport in 4 nm Molecular Wires with Interrupted Conjugation: Combined Experimental and Computational Evidence for Thermally Assisted Polaron Tunneling*. Taherinia, D; Smith, CE; Ghosh, S; Odoh, SO; Balhorn, L; Gagliardi, L; Cramer, CJ; Frisbie, CD. *ACS Nano*, **2016**, *10*(4), 4372-4383. DOI: 10.1021/acsnano.5b08126.
- [5] *Mechanical Deformation Distinguishes Tunneling Pathways in Molecular Junctions*. Xie, Z.; Baldea, I.; Haugstad, G.; Frisbie, C.D., *J. Am. Chem. Soc.* **2019**, *141*, 497-504. DOI: 10.1021/jacs.8b11248.

OC19

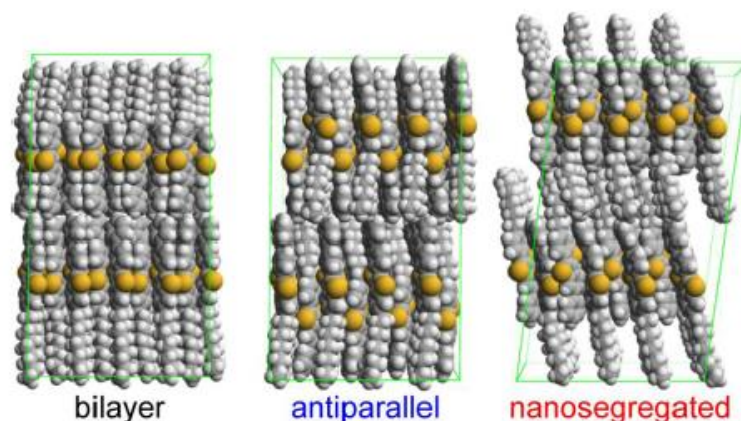
## ON THE MONOLAYER POLYMORPH CRYSTAL STRUCTURE OF THE ORGANIC SEMICONDUCTOR 7-DECYL-2-PHENYL[1]BENZOTHIENO[3,2-B][1]BENZOTHIOPHENE

Makoto Yoneya

National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan  
 makoto-yoneya@aist.go.jp

Recently, an asymmetric mono-alkylated material with a phenyl-benzothieno-benzothiophene (PhBTBT) core, 7-decyl-2-phenyl[1]benzothieno[3,2-*b*][1]benzothiophene (PhBTBT10) [1], has been reported to show a high carrier mobility over  $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  in solution processed OTFTs. However, thermal annealing of the as-deposited polycrystalline thin-films should be required to obtain a high carrier mobility for PhBTBT10. Extensive investigation has revealed that a monolayer-bilayer structural transition takes place during the annealing process and that a high carrier mobility over  $10 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  is only realized in the bilayer crystal of PhBTBT10 [1].

In this paper, the monolayer crystal phase structure of PhBTBT10 was theoretically investigated. Based on a transition model from the bilayer crystal structure obtained by X-ray diffraction [2] to possible monolayer crystal structures, two model structures for the monolayer crystal, i.e., antiparallel and core-chain nanosegregated structures were proposed (Fig. 1). The carrier mobilities of these two monolayer crystal models were compared through combined molecular dynamics, density functional theory and kinetic Monte Carlo simulations to obtain insight into the probable model for the monolayer crystal structure. The results show that the antiparallel monolayer crystal structure model is more probable than the nanosegregated model [3].



**Figure 1.** Investigated crystal structures.

**Acknowledgments:** I thank Dr. Hiromi Minemawari of AIST, Dr. Satoru Inoue of Nippon Kayaku Co., Ltd and Prof. Tatsuo Hasegawa of the University of Tokyo for valuable discussions. I also thank Ms. Ayano Miyamoto of AIST, Prof. Akira Oono of the Tokyo Institute of Technology, Dr. Anirban Mondal and Dr. Denis Andrienko of Max Plank Institute for Polymer Research for their help with the VOTCA-CTP package.

### REFERENCES

- [1] Iino, H.; Usui, T.; Hanna, J.-i. Liquid Crystals for Organic Thin-film Transistors. *Nat. Commun.* 2015, 6, 6828-6835.
- [2] Minemawari, H.; Tsutsumi, J.; Inoue, S.; Yamada, T.; Kumai, R.; Hasegawa, T. Crystal Structure of Asymmetric Organic Semiconductor 7-Decyl-2-Phenyl[1]Benzothieno[3, 2-*b*][1]Benzothiophene. *Appl. Phys. Express* 2014, 7, 091601.
- [3] Yoneya, M. Monolayer Crystal Structure of the Organic Semiconductor 7-Decyl-2-Phenyl[1]Benzothieno[3,2-*b*][1]Benzothiophene. *J. Phys. Chem. C* 2018, 122, 22225-22231.



OC20

REAL-TIME STUDY OF DIINDENOPERYLENE THIN-FILM STRUCTURE ON  $\text{MoS}_2$  MONOLAYER

N. Mrkyvkova<sup>\*1,2</sup>, M. Hodas<sup>3</sup>, J. Hagara<sup>1</sup>, P. Nadazdy<sup>1</sup>, Y. Halahovets<sup>1</sup>, M. Bodik<sup>1</sup>, K. Tokar<sup>1</sup>, J.W. Chai<sup>4</sup>, S.J. Wang<sup>4</sup>, D.Z. Chi<sup>4</sup>, A. Chumakov<sup>5</sup>, O. Konovalov<sup>5</sup>, A. Hinderhofer<sup>3</sup>, M. Jergel<sup>1</sup>, E. Majkova<sup>1,2</sup>, P. Siffalovic<sup>1,2</sup> and F. Schreiber<sup>3</sup>

<sup>1</sup>Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, Bratislava 84511, Slovakia

\*nada.mrkyvkova@savba.sk

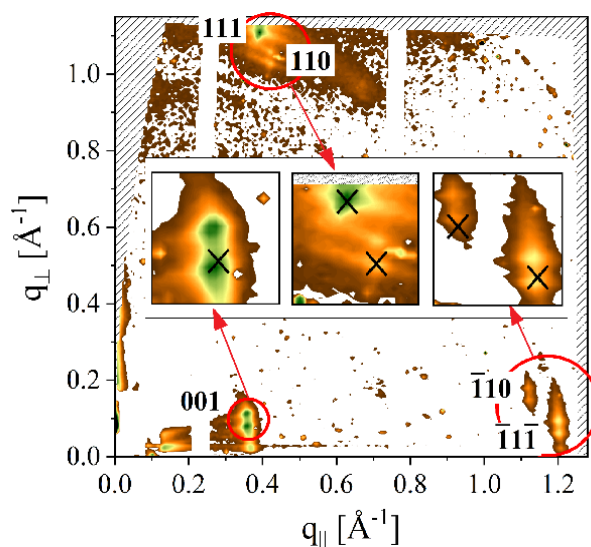
<sup>2</sup>Center of Excellence for Advanced Materials Application, Dúbravská cesta 9, Bratislava 84511, Slovakia

<sup>3</sup>Institut für Angewandte Physik, Universität Tübingen, Auf der Morgenstelle 10, 72076 Tübingen, Germany

<sup>4</sup>Institute of Materials Research & Engineering (IMRE), A\*STAR (Agency for Science, Technology and Research), 2 Fusionopolis Way, Innovis, Singapore 138634

<sup>5</sup>European Synchrotron Radiation Facility, 71 avenue des Martyrs, Grenoble 38000, France

Research on two-dimensional (2D) atomic crystals is one of the highly progressive topic in (opto)electronics. Van der Waals (vdW) interactions enable integration of 2D crystals with a broad range of materials to form so called vdW heterostructures [1]. Moreover, it was found that in case of organic molecules, 2D substrates change the molecular orientation, which in turn enhances the overall optoelectronic properties [2]. Here, we present the molecular orientation study of diindenoperylene (DIP), a representative of organic semiconductors, on 2D  $\text{MoS}_2$  monolayer. Our investigation shows that DIP forms separate islands on the top of  $\text{MoS}_2$  substrate with the *lying-down* orientation of the molecules. We combine the grazing-incidence wide-angle X-ray scattering (GIWAXS) technique with the atomistic simulations to reveal the exact molecular arrangement and the time-evolution of DIP thin film unit cell during the growth. We also show that the in-situ GIWAXS technique can serve as a suitable method to investigate the morphology of the deposited organic layer.



**Figure 1.** The  $q$  – space map of 12 nm thick DIP layer on 2D  $\text{MoS}_2$  film. The diffraction peaks are doubled along  $q_{\perp}$  where the upper peak is a spurious effect, caused by the total reflection from the  $\text{MoS}_2$  layer. The theoretical positions of the diffractions, given by the determined lattice parameters, are indicated by crosses. The calculated diffraction positions are magnified for a better resolution.

**Acknowledgments:** We acknowledge the support of APVV-17-0352, APVV-15-0641, APVV SK-CN-RD-18-0006, DAAD/PPP 57448506 and SERC Grant No. 152-70-00012.

## REFERENCES

- [1] M. Gobbi, E. Orgiu, and P. Samorì, *Adv. Mater.* **30**, 1 (2018).  
 [2] S.B. Jo, H.H. Kim, H. Lee, B. Kang, S. Lee, M. Sim, M. Kim, W.H. Lee, and K. Cho, *ACS Nano* **9**, 8206 (2015).

OC21

**RESILIENCE TO CONFORMATIONAL FLUCTUATIONS RATHER THAN PLANAR BACKBONES DRIVES CONJUGATED  
POLYMER MATERIALS WITH LOW-ENERGY DISORDER.  
INSIGHTS FROM ATOMISTIC SIMULATIONS**

**Vincent Lemaur\*<sup>1</sup>, Jérôme Cornil<sup>1</sup>, Roberto Lazzaroni<sup>1</sup>, David Beljonne<sup>1</sup>, Henning Sirringhaus<sup>2</sup> and Yoann Olivier<sup>1</sup>**

<sup>1</sup> Laboratory for Chemistry of Novel Materials, University of Mons, Mons, Belgium

*vincent.lemaur@umons.ac.be, jerome.cornil@umons.ac.be, roberto.lazzaroni@umons.ac.be,*

*david.beljonne@umons.ac.be, yoann.olivier@umons.ac.be*

<sup>2</sup> Optoelectronics Group, Cavendish Laboratory, University of Cambridge, Cambridge, UK. *hs220@cam.ac.uk*

The use of organic semiconductors in field-effect transistors has raised growing interest and efforts in the last decades, which led to outstanding improvements in their performances. It is now common to find organic conjugated materials with room-temperature charge carrier mobility exceeding 1cm<sup>2</sup>/Vs. Throughout the years, the highest values of the mobility were always reported for single crystals of organic small molecules.

Increasing the crystallinity of conjugated polymer thin films in concert with the planarization of the conjugated backbones has therefore been considered as the key for success in the design of polymer materials with optimized charge transport properties. Recently, this general belief had to be revisited with the emergence of a new class of disordered or even seemingly amorphous donor-acceptor conjugated polymers that exhibit charge mobilities larger than 1 cm<sup>2</sup>/Vs.

In this contribution, we will review our recent theoretical works addressing the structural packing of working horse p- and n-type conjugated polymer chains (PBTTT, NDITT, IDTBT, TIFBT, DPPs, ...) <sup>1-5</sup> in the crystalline, disordered, and amorphous states by means of molecular dynamics simulations performed with properly parameterized force fields and the resulting electronic properties at a quantum-chemical level.

Our results show that crystallinity of the materials and planarity of the polymer chains are not mandatory to get low-energetic-disorder polymers that promote high charge mobilities. A key factor governing charge transport is the resilience of the equilibrium torsion angle between ordered and disordered phases whatever its absolute value, thus implying that twisted chains can efficiently transport charges. Whereas planar systems always promote efficient charge transport in crystalline domains, a dramatic drop of charge mobility is observed if the chains are no longer planar in disordered phases. Finally, we also demonstrated that the bulkiness of the monomer unit strongly modifies the nature of the intermolecular interactions between the chains and therefore plays a significant role in the resulting opto-electronic properties of films.

## REFERENCES

- [1] Lemaur, V.; Muccioli, L.; Zannoni, C.; Beljonne, D.; Lazzaroni, R.; Cornil, J. and Olivier, Y. On the Supramolecular Packing of High Electron Mobility Naphtalene Diimide Copolymers: The Perfect Registry of Asymmetric Branched Alkyl Side Chains. *Macromolecules* **2013**, *46*, 8171-8178.
- [2] Olivier, Y.; Niedzalek, D.; Lemaur, V.; Pisula, W.; Müllen, K.; Koldemir, U.; Reynolds, J.; Lazzaroni, R.; Cornil, J. and Beljonne, D. High-Mobility Hole and Electron Transport Conjugated Polymers: How Structure Defines Function. *Advanced Materials* **2014**, *26*, 2119-2136.
- [3] Venkateshvaran, R.; Nikolta, M.; Sadhanala, A.; Lemaur, V.; Zelazny, M.; Kepa, M.; Hurhangee, M.; Kronemeijer, A.J.; Pecunia, V.; Nasrallah, I.; Romanov, I.; Broch, K.; McCulloch, I.; Emin, D.; Olivier, Y.; Cornil, J.; Beljonne, D. and Sirringhaus, H. Approaching disorder-free transport in high-mobility conjugated polymers. *Nature* **2014**, *515*, 384-388.
- [4] Chaudhari, S.R.; Griffin, J.M.; Broch, K.; Lesage, A.; Lemaur, V.; Dudenko, D.; Olivier, Y.; Sirringhaus, H.; Emsley, L. and Grey, C.P. Donor-Acceptor Stacking Arrangements in Bulk and Thin-Film High-Mobility Conjugated Polymers Characterized Using Molecular Modelling and MAS and Surface-Enhanced Solid-State NMR Spectroscopy. *Chemical Science* **2017**, *8*, 3126-3136.
- [5] Thomas, T.H.; Harkin, D.J.; Gillett, A.J.; Lemaur, V.; Nikolka, M.; Sadhanala, A.; Richter, J.M.; Armitage, J.; Chen, H.; McCulloch, I.; Menke, S.M.; Olivier, Y.; Beljonne, D. and Sirringhaus H. Short contacts between chains enhancing luminescence quantum yields and carrier mobilities in donor-acceptor conjugated copolymers. *Nat Commun*, **2019**, accepted.

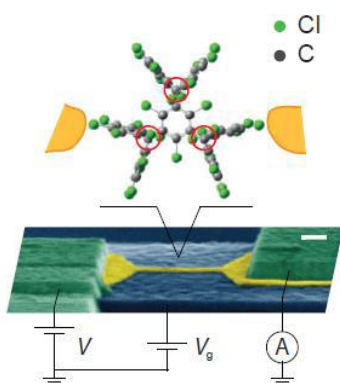
## CARBON BASED RADICALS ON SURFACES

Concepció Rovira

Institut de Ciència de Materials de Barcelona (ICMAB-CSIC)/CIBER-BBN, Campus de la UAB, 08193, Bellaterra, Spain.  
 cun@icmab.es

Stable organic radicals have been used in the last decades to develop very interesting materials ranging from polymers and dendrimers to crystals and nanoparticles. Those materials show a multitude of properties that goes from ferromagnets, magnetic sponges, energy storage, 2D photon absorption, to MRI contrast agents etc. We have used Ppchlorotriphenylmethyl (PTM) based radicals to construct a number of stable multi-functional materials and devices. PTM is a paramagnetic and electronically switchable compound that has attracted a great deal of attention in the field of molecular electronics and spintronics with many derivatives studied in solution, crystals, under the form of Self-Assembled Monolayers (SAMs) or in molecular junctions.[1-4] These radical systems exhibit a high chemical and thermal stability and present very different electronic, optical, and magnetic properties compared to the corresponding closed-shell forms.

This talk will be centred in surfaces modified with PTM derivatives, focusing the attention on the switchable properties and on the effect of the unpaired electron on the electronic/spintronic properties and on the different ways to link the molecules to electrodes and surfaces.



**Figure 1.** Molecular junction of a PTM triradical

### REFERENCES

- [1] Crystalline Materials: D. Maspoch, et al., *Nature Mater.*, **2003**, 2,190; D. Maspoch et al., *J. Am. Chem. Soc.*, **2004**, 126,730; N. Roques et al., *J. Mater. Chem.*, **2008**, 98; F. Vera et al. *Chem. Sci.*, **2012**, 3, 1958; M. Souto et al., *J. Am. Chem. Soc.*, **2016**,138, 11517; M. Souto et al., *Chemistry. Eur. J.*, **2018**, 24, 5500.
- [2] Studies of electron transfer in solution: C Sporer et al., *Angew. Chem. Int. Ed.* **2004**, 43, 5266; V. Lloveras, et al., *J. Am. Chem. Soc.*, **2011**, 133, 5818; J. Guasch et al. *J. Am. Chem. Soc.* **2013**,135, 6958; C. Franco et al., *J. Am. Chem. Soc.* **2017**, 139, 686; P. Mayorga et al. *Chem. Eur. J.* **2018**, 24, 3776.
- [3] Surfaces: N. Crivillers et al., *J. Am. Chem. Soc.* **2008**,130, 5499; N. Crivillers et al., *Adv. Mater.*, **2009**, 21,1177; N. Crivillers et al., *J. Am. Chem. Soc.*, **2009**,131, 6246; R. Gaudenzi et al., *Nano Letters*, **2011**,11, 4382; C. Simão, et al., *Nature Chemistry* **2011**, 3, 359; C. Simão et al., *Nano Letters*, **2011**, 11, 4382 ; L. Yuan et al., *Nature Commun* , **2016**, 7, 12066., G. Seber et al. *Chem. Eur. J.* **2017**, 23, 1415; V. Diez-Cabanesa, et al. *J. Mater. Chem. C* **2019** in press.
- [4] Single molecule devices: R. Frisenda et al., *Nano Lett.*, **2015**, 15, 3109; R. Gaudenzi et al., *Nano Lett.* **2016**, 16, 2066; R. Gaudenzi, et al. *ACS Nano*, **2017**, 11, 5879; F. Bejarano et al., *J. Am. Chem. Soc.*, **2018**, 140, 1691

OC22

## REALIZATION OF A FERROCENYL TRIAZOLE MOLECULAR DIODE IN A TWO STEP PROCESS

D.Brunel\*<sup>1</sup>, C.Reynaud<sup>2</sup>, V.Jangid<sup>3</sup>, D.Duchéz, C.Lebouins, R.M. Sauvage<sup>4</sup>, JJ.Simon<sup>2</sup>, L.Escoubas<sup>2</sup>, D.Gigmes<sup>1</sup>,  
F.Dumur<sup>1</sup>

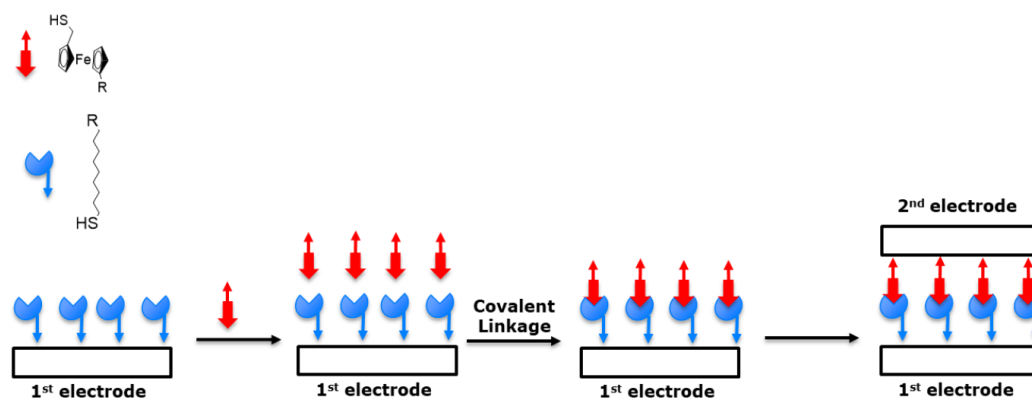
<sup>1</sup>Aix Marseille Univ, CNRS, Institut de Chimie Radicalaire, UMR 7273, F-13397, Marseille, France  
*damien.brunel@univ-amu.fr, frederic.dumur@univ-amu.fr*

<sup>2</sup>Aix Marseille Univ, CNRS, Institut Nanomatériaux Microélectronique Nanosciences de Provence, UMR 7334, F-13397, Marseille, France

<sup>3</sup>Aix Marseille Univ, CNRS, Matériaux Divisés, Interfaces, Réactivité, Electrochimie, UMR 7246, F-13397, Marseille, France

<sup>4</sup>DGA/DS/MRIS, Paris, France

Rectification of current by molecules is a subject that attracts many attentions nowadays because it would permit to reduce the size of the electronic devices. Theorized by Aviram and Ratner, the rectification can be achieved by an asymmetric molecule, enabling the electrons to be transferred in a preferential direction through the molecule. The state of the art of the organic molecular rectifiers shows rectification ratios up to 105 [1]. Such rectification ratios were obtained with molecules composed of a ferrocene, which is the key of the rectification process, linked to an insulating alkyl chain. At present, few studies have been devoted to control the orientation of the molecular rectifiers, relative to the electrode [2]. More precisely, the possibility to anchor the molecular rectifier to the two electrodes while controlling the orientation has only been scarcely investigated. In our case, such a control of the molecular orientation has been obtained by developing a two-step process based on Click Chemistry. Here, we present unprecedented works on the synthesis of new ferrocene derivatives designed as molecular rectifiers. Especially, a special effort is devoted : firstly, to allow the molecule to be covalently linked to two metal electrodes and secondly to definitely control the orientation of the molecular rectifier relative to the electrodes.



**Figure 1.** Two-step process described for new molecular rectifier.

**Acknowledgments:** I wish to acknowledge DGA and Aix Marseille University for the fund.

## REFERENCES

[1] L. Yuan, R. Breuer, L. Jiang, M. Schmittl and C. A. Nijhuis, *Nano Lett.*, **2015**, *15*, 5506–5512.

[2] L. Yuan, N. Nerngchamng, L. Cao, H. Hamoudi, E. del Barco, M. Roemer, R. K. Sriramula, D. Thompson and C. A. Nijhuis, *Nat. Commun.*, **2015**, *6*, 6324.

OC23

**ON-SURFACE COUPLING OF P-AMINOPHENOL: SYNTHESIS OF AZINE DERIVATIVES  
WITH STRONG ACCEPTOR BEHAVIOUR**

**José I. Martínez\*<sup>1</sup>, N. Ruiz del Árbol<sup>1</sup>, I. Palacio<sup>1</sup>, G. Otero-Irurueta<sup>2</sup>, P. L. de Andrés<sup>1</sup>, O. Stetsovych<sup>3</sup>, M. Moro<sup>3</sup>, P. Mutombo<sup>3</sup>, M. Svec<sup>3</sup>, P. Jelinek<sup>3</sup>, L. Floreano<sup>4</sup>, G. J. Ellis<sup>5</sup>, M. F. López<sup>1</sup>, J.A. Martín-Gago<sup>1</sup>**

<sup>1</sup> ESISNA Group, Institute of Materials Science of Madrid (ICMM-CSIC), 28049 Madrid, Spain.

*joseignacio.martinez@icmm.csic.es*

<sup>2</sup> Center for Mechanical Technology and Automation (TEMA), University of Aveiro, 3810-193 Aveiro, Portugal.

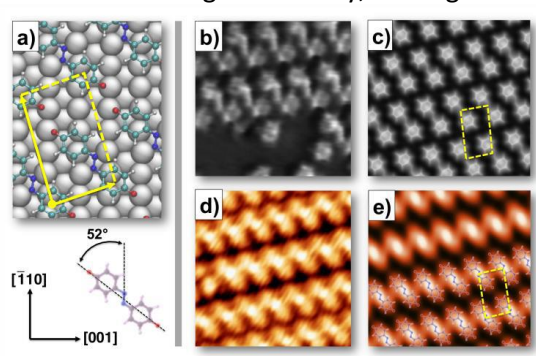
<sup>3</sup> Institute of Physics, Academy of Sciences of the Czech Republic Cukrovarnicka 10, 1862 53 Prague, Czech Republic.

<sup>4</sup> Laboratorio TASC, CNR-IOM, Basovizza SS-14, Km 163.5, 34149 Trieste, Italy.

<sup>5</sup> Polymer Physics Group, Institute of Polymer Science and Technology (ICTP-CSIC), 28006 Madrid, Spain.

Organic heterostructures based on acceptor-donor molecules on surfaces have become strategic materials due to their huge technological impact in fields such as organic light-emitting diodes (OLEDs), organic field effect transistors (OFETs), or solar cell devices, amongst others. In particular, the charge transfer process promoted by donor/acceptor molecules at the interface with metal electrodes may induce a realignment of the energy levels that can be exploited to tune the transport properties of the system.[1]

In the present work, we use on-surface chemistry to synthesize a strong electron acceptor organic molecule directly on a Cu(110) surface.[2] By a thermal annealing process, p-aminophenol (p-Ap) molecules deposited on Cu(110) undergo an azine-coupling reaction. Both, the chemical reaction mechanism and the charge transfer process induced by the substrate were followed by complementary surface techniques (nc-AFM/STM, XPS, NEXAFS and LEED) as well as by theoretical calculations (see Figure 1). We observe that Cu(110) catalyses a chemical reaction between two p-Ap molecules giving rise to a quinoneazine (QAz) molecule. The resulting molecule accepts 1.2 e<sup>-</sup> from the substrate, which induces a charge redistribution with recovering aromaticity, leading to an azo compound behaviour.



**Figure 1.** (a) Molecular self-assembly of QAz on Cu(110) optimized by theoretical methods. (b) Nc-AFM frequency shift image of QAz on Cu(110). (c) AFM image simulation obtained using the Probe Particle AFM model. (d) STM experimental image of QAz on Cu(110).  $V_s = +1350$  mV and  $I_{\text{tunnel}} = 0.031$  nA. (e) Computed Keldish-Green STM image obtained under the same experimental conditions as for the optimized QAz/Cu(110) configuration.

**Acknowledgments:** Graphene Flagship Core2 (785219), ERC-synergy program (ERC-2013-SYG-610256 Nanocosmos), CTI-CSIC and Spanish MINECO (grants MAT2017-85089-C2-1-R and RYC-2015-17730).

## REFERENCES

- [1] R. Otero, A. L. Vázquez de Parga, J. M. Gallego. Electronic, Structural and Chemical Effects of Charge-transfer at Organic/Inorganic Interfaces. *Surf. Sci. Rep.* **2017**; Vol. 72; pp 105-145.
- [2] N. Ruiz del Árbol, I. Palacio, G. Otero-Irurueta, et al. On-surface Bottom-up Synthesis of Azine Derivatives Displaying Strong Acceptor Behaviour. *Angew. Chem. Int. Ed.* **2018**; Vol. 57; pp 8582-8586.

## SESSION 5

K5

### SKIN-INSPIRED ORGANIC ELECTRONICS

**Zhenan Bao**  
Stanford University, USA

Skin is the body's largest organ, and is responsible for the transduction of a vast amount of information. This conformable, stretchable, self-healable and biodegradable material simultaneously collects signals from external stimuli that translate into information such as pressure, pain, and temperature. The development of electronic materials, inspired by the complexity of this organ is a tremendous, unrealized materials challenge. However, the advent of organic-based electronic materials may offer a potential solution to this longstanding problem. In this talk, I will describe the design of organic electronic materials to mimic skin functions. These new materials and new devices enabled arrange of new applications in medical devices, robotics and wearable electronics.

OC24

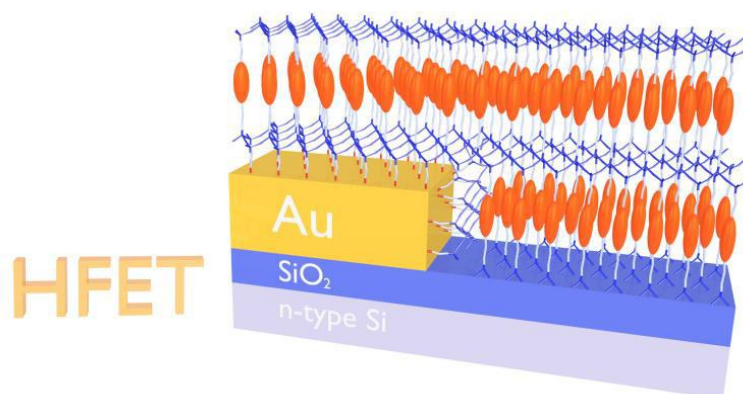
## HYBRID FIELD EFFECT TRANSISTORS (HFET) A FULLY COVALENT TRANSISTOR WITH A $\pi$ -CONJUGATED ORGANOSILICA MATERIAL

**G. Wantz<sup>1</sup>, G. H. ROCHE<sup>2</sup>, J. J. E. Moreau<sup>2</sup> and O. J. J. Dautel\*<sup>2</sup>**

<sup>1</sup>Laboratoire IMS, UMR 5218, Université de Bordeaux, Pessac, France  
*guillaume.wantz@ims-bordeaux.fr*

<sup>2</sup>AM2N, UMR 5253, Institut Charles Gerhardt de Montpellier, Montpellier, France  
*gilles.roche@enscm.fr, joel.moreau@enscm.fr, olivier.dautel@enscm.fr*

The use of novel organosilica materials embedding  $\pi$ -conjugated moieties as semiconductor into field effect transistors will be presented. For that purpose, the [1]benzothieno[3,2-b] [1]benzothiophene (BTBT),<sup>1</sup> has been chosen as  $\pi$ -conjugated core, first functionalized with hydroxyl groups<sup>2</sup> and then modified with hydrolysable and cross-linkable triethoxysilyl moieties. After polycondensation, this compound forms a hybrid material composed of charge transport pathways as well as insulating layers (SiO<sub>x</sub>). However, overall, the material is found to be a semiconductor and can be incorporated into field effect transistors. Taking advantage of the sol-gel chemistry<sup>3</sup> involved here, we built Hybrid Field Effect Transistors that are fully cross-linked with covalent bonds.<sup>4</sup> 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 additional interfacial monolayer in between. This is the first report of fully covalent transistors. Those devices show impressive resilience against polar, aliphatic and aromatics solvents (even under sonication). This study opens the route towards a new class of hybrid materials to create highly robust electronic applications.



**Figure 1.** Hybrid Field Effect Transistors (HFET), First example of a field effect transistor based on an entirely reticulated organosilica active layer.

### REFERENCES

- [1] Izawa, T.; Miyazaki, E.; Takimiya, K. Molecular Ordering of High-Performance Soluble Molecular Semiconductors and Re-evaluation of Their Field-Effect Transistor Characteristics. *Adv. Mater.* **2008**, *20*, 3388-3392.
- [2] Roche, G. H.; Tsai, Y.-T.; Clevers, S.; Thuau, D.; Castet, F.; Geerts, Y. H.; Moreau, J. J. E.; Wantz, G.; Dautel, O. J. The Role of H-bonds in the Solid State Organization of [1]Benzothieno[3,2-b][1]benzothiophene (BTBT) Structures : Bis(hydroxy-hexyl)-BTBT, as a Functional Derivative Offering Efficient Air Stable Organic Field Effect Transistors (OFETs). *J. Mat. Chem. C*, **2016**, 6742-6749.
- [3] Dautel, O. J.; Wantz, G.; Almairac, R.; Flot, D.; Hirsch, L.; Lere-Porte, J.-P.; Parneix, J.-P.; Serein-Spirau, F.; Vignau, L.; Moreau, J. J. E. Nanostructuring of Phenylenevinylene-di-Imide-Bridged Silsesquioxane: From Electroluminescent Molecular J-Aggregates to Photoresponsive Polymeric H-Aggregates. *J. Am. Chem. Soc.*, **2006**, *128*, 4892-4901.
- [4] Roche, G. H.; Thuau, D.; Valvin, P.; Clevers, S.; Tjoutis, T.; Chambon, S.; Flot, D.; Geerts, Y. H.; Moreau, J. J. E.; Wantz G.; Dautel, O. J.  $\pi$ -Conjugated Organosilica Semiconductors: Toward Robust Organic Electronics. *Adv. Electron. Mater.* **2017**, 1700218.

OC25

**PREDICTION AND DESIGN OF LOW DISORDER, HIGH MOBILITY MOLECULAR SEMICONDUCTORS:  
A THEORETICAL PERSPECTIVE**

**Gabriele D'Avino<sup>1</sup>, Michael T. Ruggiero<sup>2</sup>, Guillaume Schweicher<sup>3</sup>, Henning Sirringhaus<sup>3</sup>, Sergio Ciuchi<sup>4</sup>,  
Simone Fratini<sup>1\*</sup>**

<sup>1</sup> Institut Néel-CNRS and Université Grenoble Alpes, BP 166, F-38042 Grenoble Cedex 9, France,  
*simone.fratini@neel.cnrs.fr*

<sup>2</sup> Department of Chemical Engineering and Biotechnology, University of Cambridge, Philippa Fawcett Drive,  
Cambridge, CB3 0AS, United-Kingdom and Department of Chemistry, Materials Science and Computational  
Chemistry, University of Vermont

<sup>3</sup> Optoelectronics Group, Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE,  
United-Kingdom

<sup>4</sup> Dipartimento di Scienze Fisiche e Chimiche Università dell'Aquila, CNISM and Istituto Sistemi Complessi CNR, via  
Vetoio, I-67010 Coppito-L'Aquila, Italy

Large thermal molecular vibrations are believed to be the main factor that limits the charge mobility in weakly van der Waals bonded organic semiconductors. Little is known however to which extent one can influence such intrinsic source of dynamical disorder via molecular design. In this talk I shall present our current understanding of this issue based on the transient localization scenario, indicating two main routes that can be followed in order to efficiently improve the performances of organic materials: (i) tailoring the inter-molecular transfer integrals to obtain isotropic band structures with a reduced sensitivity to disorder [1] and (ii) suppressing the slow energetic fluctuations brought by the molecular motions, which are the most detrimental for charge transport. Regarding the latter, I will show how, in most organic materials, specific 'killer' phonon modes can be identified, which can contribute up to 80% of the total molecular disorder [2]; removing such killer modes should be a key target of design strategies in the quest for higher mobility organic compounds. If such strategies turn out to be successful, future organic compounds will arguably surpass the performances of rubrene and progressively move towards the band transport regime. I shall present a novel theoretical framework that encompasses both transient localization and Bloch-Boltzmann band transport theory [3], and is therefore suitable for the description of such future compounds. The conditions required for localization effects to vanish in organic semiconductors will be precisely assessed.

**REFERENCES**

- [1] S. Fratini, S. Ciuchi, D. Mayou, G. T. De Laissardière & A. Troisi, A map of high-mobility molecular semiconductors. *Nat. Mater.* **16**, 998–1002 (2017)
- [2] G. Schweicher et al., Chasing the 'killer' phonon mode for the rational design of low disorder, high mobility molecular semiconductors, *submitted*
- [3] S. Fratini, S. Ciuchi, From transient localization to band transport: on quantum corrections and lack thereof, *in preparation*



OC26

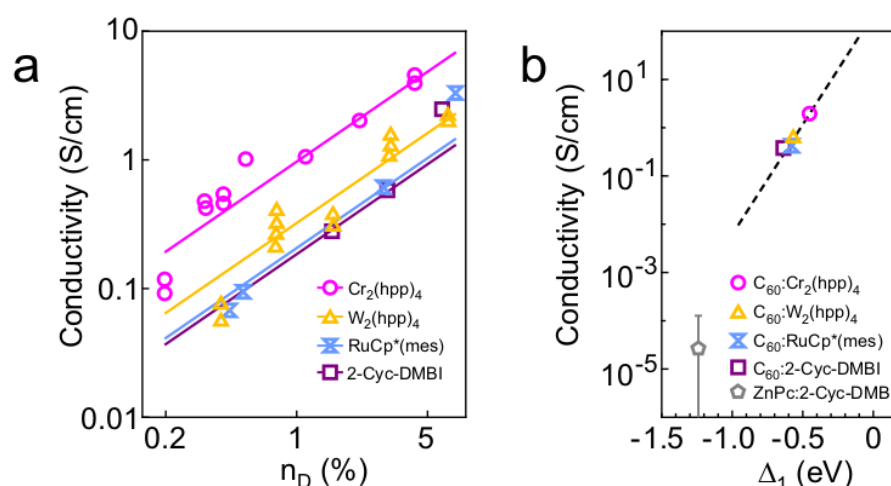
## DENSITY OF STATES OF DOPED ORGANIC FILMS AND ITS IMPACT ON CHARGE TRANSPORT

Christopher Gaul<sup>1</sup>, Martin Schwarze<sup>2</sup>, Sebastian Hutsch<sup>1</sup>, Karl Sebastian Schellhammer<sup>1</sup>, Karl Leo<sup>2</sup>,  
Frank Ortmann\*<sup>1</sup>

<sup>1</sup>Center for Advancing Electronics Dresden, Technische Universität Dresden, Dresden, Germany.  
*frank.ortmann@tu-dresden.de*

<sup>2</sup>Dresden Integrated Center for Applied Physics and Photonic Materials, Technische Universität Dresden, Dresden, Germany.

Doping plays a crucial role in semiconductor physics where *n*-doping is controlled by the ionization energy of the impurity relative to the conduction band edge. In organic semiconductors, efficient doping may be dominated by various effects, which are presently not well understood. We first discuss *n*-doping of prototypical organic materials with dopants from different classes to understand their efficiency for generating free carriers. [1] We provide molecular design rules for new efficient host-dopant combinations emphasizing that both species are relevant. We further correlate these results with measured conductivities and thus demonstrate the predictive power of our model in engineering charge transport. A larger set of host-dopant systems has been studied regarding charge transport and its connection to the molecular parameters relevant in this context, [2] which will be further discussed. An outlook for interfacial doping will be provided.



**Figure 1.** Conductivity and doping. (a) Doping concentration dependent conductivities for  $\text{C}_{60}$  host material and varying dopant: 2-Cyc-DMBI (this work),  $\text{Cr}_2(\text{hpp})_4$  and  $\text{W}_2(\text{hpp})_4$  and  $\text{RuCp}^*(\text{mes})$ . Solid lines approximate the conductivities in the doping regime between 0.5% and  $\leq 5\%$  by fitting. (b) Conductivities in *n*-doped  $\text{C}_{60}$  at 2% extracted from fits in (a) versus binding energy  $\Delta_1$ . The dotted line is a guide to the eye for the  $\text{C}_{60}$  host material. Error bar for ZnPc reflects the scatter in the conductivity data.

## REFERENCES

- [1] C. Gaul et al. Nat. Mater. 17, 439 (2018).  
[2] M. Schwarze et al. Nat. Mater. 18, 242 (2019).

**DESIGNING INORGANIC/ORGANIC PHOTONIC LIGHT- AND HEAT-MANAGEMENT STRUCTURES FOR SOLUTION-PROCESSABLE AND PRINTABLE ORGANIC OPTOELECTRONIC DEVICES**

**Natalie Stingelin**

School of Materials Science & Engineering and School of Chemical & Biomolecular Engineering  
Georgia Institute of Technology, Atlanta, USA.

*natalie.stingelin@gatech.edu*

An ever increasing interest in the development and application of innovative optical and optoelectronic devices places greater emphasis for the advancement of new smart and functional materials that are readily processable. Significant progress has already been realized in the fields of organic light-emitting diodes (OLEDs) and photovoltaic cells (OPVs) through development of novel semiconducting materials. Here we discuss developments and advancements in materials design towards inorganic/organic photonic structures that aid and improve light management in organic and inorganic/organic hybrid devices, with focus on solar cells. We cover systems targeted for use in light in-coupling structures, anti-reflection coatings, and beyond. Extension to architectures for heat management, important for a broad range of photovoltaic device platforms, including inorganic, inorganic/organic hybrid and organic devices, will also be presented.

## ANALYZING THIN FILM MORPHOLOGY BY RESONANCE RAMAN SPECTROSCOPY

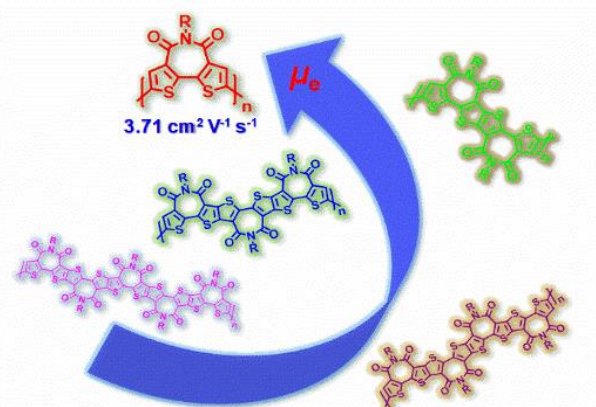
Rocío Ponce Ortiz\*<sup>1</sup>, Alexandra Harbuzaru<sup>1</sup>, Sergio Gámez Valenzuela<sup>1</sup>, María del Carmen Ruiz Delgado<sup>1</sup>, Yingfeng Wang<sup>2</sup> and Xugang Guo<sup>2</sup>

<sup>1</sup>Department of Physical Chemistry, University of Málaga, Málaga, Spain.  
 rocioponce@uma.es, harbuzaru@uma.es, sergiogamez@uma.es, carmenrd@uma.es

<sup>2</sup>Department of Materials Science and Engineering, SUSTech, Shenzhen, China.  
 wangyf@sustc.edu.cn, guo.xg@sustc.edu.cn

Polymeric organic thin film transistors (OFETs) and all-polymer bulk heterojunction solar cells (all-PCS), which are composed of a polymer donor and a polymer acceptor, have attracted considerable attention in the last years.[1] The interest of these polymeric materials present various advantages versus small molecular counterparts, including strong light absorption, excellent mechanical flexibility and durability, and great potential in printing applications due to their great processability.[2]

In OFETs and bulk heterojunction solar cells, the morphology and crystallinity control of the neat polymer or blended donor-acceptor polymer films is essential in order to improve device performance. In this communication, we present a Resonance Raman spectroscopy [3] study directed to disentangle the film morphology of a series of all-acceptor and donor acceptor polymers for OFETs and all-PCS applications.[4]



**Figure 1.** Chemical structures of selected polymers materials under study. The arrow indicates the electron mobility increase with monomer building block length.

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## REFERENCES

- [1] (a) Benten, H.; Mori, D.; Ohkita, H.; Ito, S. *J. Mater. Chem A* **2016**, *4*, 5340-5365. (b) Fan, B.; Ying, L.; Zhu, P.; Pan, F.; Liu, F.; Chen, J.; Huang, F.; Cao, Y. *Adv. Mater.* **2017**, *29*, 1703906.
- [2](a) Kim, T.; Kim, J.-H.; Kang, T. E.; Lee, C.; Kang, H.; Shin, M.; Wang, C.; Ma, B.; Jeong, U.; Kim, T.-S.; Kim, B. J. *Nat. Commun.* **2015**, *6*, 8547. (b) Chen, S.; Jung, S.; Cho, H. J.; Kim, N.-H.; Jung, S.; Xu, J.; Oh, J.; Cho, Y.; Kim, H.; Lee, B.; An, Y.; Zhang, C.; Xiao, M.; Ki, H.; Zhang, Z.-G.; Kim, J.-Y.; Li, Y.; Park, H.; Yang, C. *Angew. Chem. Int. Ed.* **2018**, *57*, 13277-13282.
- [3] (a) Tsoi, W. C.; James, D. T.; Buchaca Domingo, E.; Kim, J. S.; Al-Hashimi, M.; Murphy, C. E.; Stingelin, N.; Heeney, M.; Kim, J.-S. *ACS Nano* **2012**, *6*, 9646-9656. (b) Kim, J.-H.; Wood, S.; Park, J. B.; Wade, J.; Song, M.; Yoon, S. C.; Jung, I. H.; Kim, J.-S.; Hwang, D.-H. *Adv. Funct. Mater.* **2016**, *26*, 1517-1525. (c) Razzell-Hollis, J.; Fleischli, F.; Jahnke, A. A.; Stingelin, N.; Seferos, D. S.; Kim, J.-S. *J. Phys. Chem. C* **2017**, *121*, 2088-2098.
- [4] Wang, Y.; Guo, H.; Harbuzaru, A.; Udin, M.A.; Arrechea-Marcos, I.; Ling, S.; Yu, J.; Tang, Y.; Sun, H.; López Navarrete, J. T.; Ponce Ortiz, R.; Young Woo, H.; Guo, X. *J. Am. Chem. Soc.* **2018**, *140*, 6095-6108.

OC28

## TUNING THE ENERGETICS OF MOLECULAR DOPANTS FOR EFFICIENT N-TYPE DOPING OF POLYMERS

**Sergi Riera-Galindo\***,<sup>1</sup> **Suhao Wang**,<sup>1</sup> **Alessandra Forni**,<sup>2</sup> **Eleni Pavlopoulou**,<sup>3</sup> **Martijn Kemerink**,<sup>4</sup> **Magnus Berggren**,<sup>1</sup>  
**Gabriele di Carlo**,<sup>2</sup> **Simone Fabiano**<sup>1</sup>

<sup>1</sup>Laboratory of Organic Electronics, Department of Science and Technology, Linköping University SE-601 74  
Norrköping, Sweden.  
*simone.fabiano@liu.se*

<sup>2</sup>Department of Chemistry, University of Milan, INSTM Research Unit, Via C. Golgi 19, 20133 Milano, Italy.

<sup>3</sup>Laboratoire de Chimie des Polymères Organiques (LCPO - UMR 5629), Bordeaux INP, Université de Bordeaux, CNRS,  
16 Av. Pey-Berland, 33607, Pessac, France.

<sup>4</sup>Complex Materials and Devices, Department of Physics, Chemistry and Biology (IFM), Linköping University,  
Linköping, Sweden.

Conjugated polymers are emerging materials for energy and storage applications, due to their easily tuneable optoelectronic properties, mechanical flexibility, and solution processability. The increasing interest in organic thermoelectrics for harvesting waste-heat energy has intensified the attention on doping as a way to achieve high electrical conductivity. However, unlike their p-type counterpart, the conductivity of n-doped conjugated polymers still lags behind, and very few of them are stable in air. The n-doping of organic materials can be achieved either by reduction of the host material by direct electron transfer from the dopant or either by decomposition of a stable dopant precursor to an intermediate that can reduce the host. Here, we report the impact of the energetics of newly synthesized molecular dopant on the thermoelectric properties of a donor-acceptor n-type conjugated polymer. We characterized the system by using a plethora of techniques such as Density Functional Theory, Monte Carlo simulation, conductivity and Seebeck coefficient measurements, as well as atomic force microscopy and grazing incidence wide angle X-ray scattering.

## SESSION 6

OC29

## SIMPLE FOUR-STATE MODEL OF EFFICIENT THERMALLY ACTIVATED DELAYED FLUORESCENCE

Piotr de Silva\*<sup>1</sup>, Changhae Andrew Kim<sup>2</sup>, Tianyu Zhu<sup>2</sup> and Troy Van Voorhis<sup>2</sup><sup>1</sup> Department of Energy Conversion and Storage, Technical University of Denmark, Kgs. Lyngby, Denmark.  
*pdes@dtu.dk*<sup>2</sup> Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, USA.  
*tvan@mit.edu*

Organic molecules exhibiting thermally activated delayed fluorescence (TADF) are currently the most promising class of materials to improve the efficiency of organic light-emitting diodes (OLED). The emission of light from a bright singlet excited state is preceded by a thermally-activated up-conversion of triplet excitons. This reverse intersystem crossing proceeds efficiently thanks to a small singlet-triplet energy gap and non-vanishing spin-orbit coupling. The detailed mechanism of TADF is still a subject of a debate, as within the simplest model, efficient reverse intersystem crossing and high quantum yields appear to be competing properties. The role of both, charge transfer (CT) and locally excited (LE) states, as well as non-adiabatic effects has been recently extensively studied to explain the phenomenon. In this contribution we propose a simple quantum-mechanical model for TADF, which is based on representation of a Hamiltonian in the basis of four spin-mixed diabatic states representing pure CT and LE excitations. The model can explain the coexistence of fast  $T_1 \rightarrow S_1$  intersystem crossing and  $S_1 \rightarrow S_0$  radiative decay. We show that the parameter space of the model can be largely explored through conformational fluctuations. The analysis enables to formulate new guidelines for optimization of TADF emitters.

## NANOSCALE INTERACTION OF PERIODIC METALLIC NANOPARTICLE ARRAYS AND ORGANIC EMITTERS

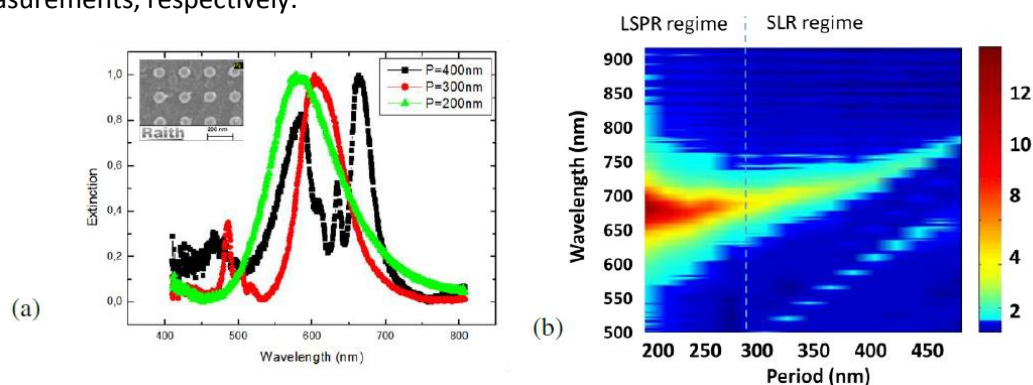
S. Hamdad\*, A.T. Diallo, M. Chakaroun and A. Boudrioua

Laboratoire de Physique des Lasers CNRS UMR 7538, Université Paris 13, Sorbonne Paris Cité, Villetaneuse, France

Sarah.hamdad@univ-paris13.fr

Interactions between organic emitters and metallic nanoparticles offer several interest in the field of nanophotonics [1]. In particular, periodic metallic nanoparticles structures allow a precise control of the interaction between organic molecules and the metallic NPs. At the nanoscale, they can allow two different phenomena: localized surface plasmon resonances (LSPR) and Surface Lattice Resonance (SLR). In fact, the contribution of a large number of ordered metallic nanoparticles with a long period allows obtaining collective modes with very narrow bandwidths (SLR) due to a strong coupling between the localized plasmonic and delocalized photonic modes. This phenomenon appears when particular grating wavelengths, known as Rayleigh anomalies [2], approach the well-defined LSPR of an isolated metallic nanoparticle, and strongly depend on the period of the considered array. Therefore, the grating parameters offer an efficient tool to select collective hybrid modes at wavelengths of interest In order to enhance organic emitter's spontaneous emission rated, directivity and coherence.

In this work, we report the investigation of interactions between organic emitter and metallic nanoparticle arrays throughout the evaluation of the plasmon resonance peaks of periodic metallic NPs structures. For our experiments, we used samples of periodic Ag nanoparticles covered by organic molecules (Alq3). The study concerns Ag arrays of periods ( $p$ ) ranging from 190nm to 480nm by a step of 20nm. The ordered structures are regular square nanocylinders of 100nm diameters fabricated by using the e-beam lithography technique (inset fig 1.a). The obtained structures have been, numerically and experimentally, studied by using finite difference time domain method and performing extinction measurements, respectively.



**Figure 1.** a. Examples of extinction spectra and an SEM image of periodic arrays (inset). b. Extinction map of the Ag arrays as a function of the period and wavelength.

For instance, fig. 1.a shows the measured extinction spectra of  $p = 200\text{nm}$ ,  $300\text{nm}$  and  $400\text{nm}$  and fig.1.b draws the experimental map of the extinction intensity as vs the period and wavelength. Two gratings types can be distinguished: the so-called short period gratings for periods  $< 240\text{nm}$ , showing a near field coupling effect which exhibits an LSPR plasmonic response effect, and the so called long-period gratings that correspond to the excitation of hybrid resonances (SLR) showing a dominant far-field coupling effect. Thus, tuning the array parameters offers the possibility to select a specific optical response: near or far field coupling effect. The excitation of collective lattice modes allows confining an intense field at the emitter location that modify its spontaneous emission rate and provide additional desexcitation channels. Therefore, periodic metallic structures can be used as a nano-integrated chip that provides a tool to modify the emission properties of organic emitters.

**Acknowledgments:** This project has received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 665850.

### REFERENCES

- [1] M. A. Garcia, "Surface plasmon in metallic nanoparticles: fundamentals and applications," J. Phys. D: Appl. Phys. 44, 283001 (2011).
- [2] D. Khlopin *et al.*, "Lattice modes and plasmonic linewidth engineering in gold and aluminum nanoparticle arrays," JOSA B, 34 (3), 691 (2017).

OC31

## MOLECULAR DESIGN OF CHRYSENE-BASED DEEP BLUE EMITTERS FOR SIMPLE STRUCTURED OLEDs

Thanyarat Chawanpunyawat<sup>1\*</sup>, Pongsakorn Chasing<sup>2</sup>, Thaweesak Sudyodsuk<sup>3</sup>, Vinich Promarak<sup>4</sup><sup>1, 2, 3, 4</sup> Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong, Thailand.

s15\_thanyarat.c@vistec.ac.th, pongsakorn.c\_s16@vistec.ac.th, thaweesak.s@vistec.ac.th, vinich.p@vistec.ac.th

In this work, we designed deep blue emitters with hole-transporting property based on chrysene core end-capped with triphenylamine. To realize a deep blue emission, phenyl -spacer with different substitution position was placed in between the two moieties. Four emitters including 4,4'-(chrysene-6,12-diyl)-bis-(N,N-diphenylaniline) (TC) with no -space, 4',4'''-(Chrysene-6,12-diyl)-bis-(N,N-diphenyl-[1,1'-biphenyl]-4-amine) (TPC) with having 1,4-phenylene - spacer, 4',4'''-(chrysene-6,12-diyl)-bis-(2',5'-dimethyl-N,N-diphenyl-[1,1'-biphenyl]-4-amine) (TdMPC) with having 2,5-dimethyl-1,4-phenylene -spacer and 3',3'''-(chrysene-6,12-diyl)-bis-(N,N-diphenyl-[1,1'-biphenyl]-4-amine) (TmPC) with having 1,3-phenylene -spacer, were synthesized and characterized. In thin film, they showed emission spectra in blue region with the maximum emission ( $\lambda_{em}$ ) less than 450 nm and the most hypsochromic (blue) shift was found from TmPC with  $\lambda_{em}$  of 406 nm and CIE coordinates at (0.172, 0.091). The hole-transporting layer free OLED devices were fabricated with simple configuration of ITO/PEDOT:PSS or PEDOT:PSS:PFI/ emitter/TPBi/LiF:Al. The turn-on voltages were found around 3-4 V for all devices. Among these, TdMPC showed the deepest blue emission color with  $\lambda_{em}$  at 415 nm and CIE coordinates of (0.161, 0.070). Luminescence of TdMPC was increased up to 1,607 cd/m<sup>2</sup> and reached EQE of 1.31% using PEDOT:PSS:PFI. However, the highest luminescence achieved from TPC emitter was 8,032 cd/m<sup>2</sup> with high EQE of 2.07%.

**Acknowledgments:** This research was supported by Vidyasirimedhi Instituted of Science and Technology (VISTEC). All instruments were supported from Frontier Research Center (FRC), VISTEC.

OC32

**HOW ENERGETIC DISORDER DETERMINES CHARGE GENERATION IN ORGANIC PHOTOVOLTAICS AND HOW TO MEASURE IT****Ivan Kassal**School of Chemistry, University of Sydney, Sydney, AUSTRALIA  
*ivan.kassal@sydney.edu.au*

Energetic disorder is a defining feature of organic semiconductors, exerting a significant impact on device physics. Although disorder diminishes some aspects of device performance (such as the mobility), it enhances charge generation in organic solar cells. Combined with entropy, it suffices to explain how the interfacial charges are able to overcome their strong Coulomb interaction [1]. Indeed, when entropy and disorder are included in charge separation models, the barrier to separation is dramatically reduced or absent altogether [1]. This conclusion holds even if charge delocalisation is included in the model [2]. Furthermore, kinetic simulations show that, when it comes to predicting the efficiency of charge separation, disorder is a fundamental parameter, which cannot be encapsulated using an effective measure like the bulk mobility [3].

The influence of disorder on charge generation can also be used to measure the disorder, which has proven difficult to determine unambiguously in the past. In particular, energetic disorder can be measured in a robust way from the dependence of the internal quantum efficiency of charge generation on the frequency of the incident light [4]. Experimental results for several systems suggest that disorder in organic semiconductors is likely larger than previously reported. The measured values are consistent with the disorder that is predicted to result in efficient charge separation.

**REFERENCES**

- [1] S. Hood and I. Kassal, "Entropy and Disorder Enable Charge Separation in Organic Solar Cells", *J. Phys. Chem. Lett.* **7**, 4495 (2016).
- [2] A. Gluchowski, K. Gray, S. Hood, and I. Kassal, "Increases in the Charge Separation Barrier in Organic Solar Cells Due to Delocalization", *J. Phys. Chem. Lett.* **9**, 1359 (2018).
- [3] J. Zhou, L. Jiang, C. Birch, and I. Kassal, "Bulk Charge-Carrier Mobility is an Imperfect Predictor of Charge-Generation Efficiency in Organic Photovoltaics", submitted (2019).
- [4] S. Hood, N. Zarrabi, P. Meredith, I. Kassal, and A. Armin, "Measuring energetic disorder in organic semiconductors using the photo-generated charge-separation efficiency", submitted (2019).



## INTERFACES DETERMINE CHARGE GENERATION AND RECOMBINATION IN ORGANIC SOLAR CELLS

**Dieter Neher**

University of Potsdam, Institute of Physics and Astronomy, Karl-Liebknecht-Str. 24-25, 14776 Potsdam, Germany  
*neher@uni-potsdam.de*

The invention of new materials combined with an improved knowledge of structure-property relationships of organic donor-acceptor solar cells led to an impressive improvement in their energy conversion efficiency (PCE) to more than 16 % [1]. This success triggered the search for the efficiency-limiting process in these multicomponent devices. Recently, vibronic coupling involving C-C bond stretching was identified as the main pathway of non-radiative recombination, thereby limiting the attainable  $V_{oc}$  [2].

In this talk, we will present experimental results regarding the generation and recombination of free charges in selected bulk heterojunction solar cells. We show that the efficiency of these processes is strongly linked to the energetics and excitation dynamics at the internal donor-acceptor interfaces. For fullerene-based solar cells with a low donor content, we find that the efficiency of charge generation is limited by the same mechanism that limits the  $V_{oc}$ , namely non-radiative recombination of the CT states via vibronic coupling [3]. Notably, the rate of this recombination process obeys the classical energy gap law, implying that donor-acceptor blends benefit from a higher CT energy through longer CT lifetimes and more efficient charge generation. Consistent with this result, we observe that devices suffer from inefficient CT dissociation also through a higher rate of non-geminate recombination [4]. As a consequence, it's only the systems with very efficient charge generation and very fast CT dissociation that the free carrier recombination is strongly suppressed, irrespective of the details of the spin statistics. We, finally, present recent results on a highly efficient polymer:NFA blend, where we find a surprisingly low activation energy for free charge generation, despite a low energy offset at the heterojunction. This results highlights the importance of a comprehensive understanding of the energy landscape, and how it affects the pathway from the bound CT exciton to the spatially separated electron-hole pair [5,6].

### REFERENCES

- [1] Xu, X.; Feng, K.; Bi, Z.; Ma, W.; Zhang, G.; Peng, Q. Single-Junction Polymer Solar Cells with 16.35% Efficiency Enabled by a Platinum(II) Complexation Strategy. *Adv. Mater.* **2019**, 1901872
- [2] Benduhn, J.; Tvingstedt, K.; Piersimoni, F.; Ullbrich, S.; Fan, Y.; Tropiano, M.; McGarry, K. A.; Zeika, O.; Riede, M. K.; Douglas, C. J.; et al. Intrinsic Non-Radiative Voltage Losses in Fullerene-Based Organic Solar Cells. *Nat. Energy* **2017**, 2, 17053.
- [3] Collado-Fregoso, E.; Pugliese, S. N.; Wojcik, M.; Benduhn, J.; Bar-Or, E.; Perdigón Toro, L.; Hörmann, U.; Spoltore, D.; Vandewal, K.; Hodgkiss, J. M.; et al. Energy-Gap Law for Photocurrent Generation in Fullerene-Based Organic Solar Cells: The Case of Low-Donor-Content Blends. *J. Am. Chem. Soc.* **2019**, 141, 2329–2341.
- [4] Shoaee, S.; Armin, A.; Stolterfoht, M.; Hosseini, S.M.; Kurpiers, J.; Neher, D. Decoding charge recombination through charge generation, submitted
- [5] Kurpiers, J.; Ferron, T.; Roland, S.; Jakoby, M.; Thiede, T.; Jaiser, F.; Albrecht, S.; Janietz, S.; Collins, B. A.; Howard, I. A.; et al. Probing the Pathways of Free Charge Generation in Organic Bulk Heterojunction Solar Cells. *Nat. Commun.* **2018**, 9, 2038.
- [6] Sini, G.; Schubert, M.; Risko, C.; Roland, S.; Lee, O. P.; Chen, Z.; Richter, T. V.; Dolfen, D.; Coropceanu, V.; Ludwigs, S.; et al. On the Molecular Origin of Charge Separation at the Donor-Acceptor Interface. *Adv. Energy Mater.* **2018**, 8, 1702232.

OC33

### WHAT IS THE BINDING ENERGY OF A CHARGE TRANSFER STATE IN AN ORGANIC SOLAR CELL?

**Stavros Athanasopoulos<sup>1</sup>, Franz Schauer,<sup>2</sup> Vojtech Nádaždy<sup>3</sup>, Mareike Weiß,<sup>4</sup> Frank-Julian Kahle,<sup>4</sup> Anna Köhler,<sup>4,6</sup> Heinz Bäessler<sup>6</sup> \***

1 Departamento de Física, Universidad Carlos III de Madrid, Madrid, Spain  
*astavros@fis.uc3m.es*

2 Faculty of Applied Informatics, Tomas Bata University in Zlín, Czech Republic  
*fschauer@volny.cz*

3 Institute of Physics of the Slovak Academy of Sciences, Bratislava, Slovak Republic, *vojtech.nadazdy@savba.sk*

4 Soft Matter Optoelectronics, University of Bayreuth, Bayreuth, Germany  
*s1meweis@uni-bayreuth.de, Frank-Julian.kahle@uni-bayreuth.de, anna.koehler@uni-bayreuth.de*

6 Bayreuth Institute of Macromolecular Research (BIMF), University of Bayreuth, Bayreuth, Germany  
*Heinz.baessler@uni-bayreuth.de*

The high efficiencies reported for organic solar cells, and reports on an almost negligible thermal activation for the photogeneration of charge carriers have called into question whether photoinduced interfacial charge transfer states are bound by a significant coulomb attraction, and how this can be reconciled with very low activation energies. We have addressed this question here in a combined experimental and theoretical approach. We determined the interfacial binding energy of a charge-transfer state in a blend of MeLPPP:PCBM, using energy resolved electrochemical impedance spectroscopy and find it to be about 0.5 eV. Temperature-dependent photocurrent measurements on the same films, however, give an activation energy that is about one order of magnitude lower. Using analytical calculations and MC simulation we illustrate how (i) interfacial energetics and (ii) topology of transport reduce the activation energy required to separate the interfacial electron-hole pair, with about equal contributions.

OC34

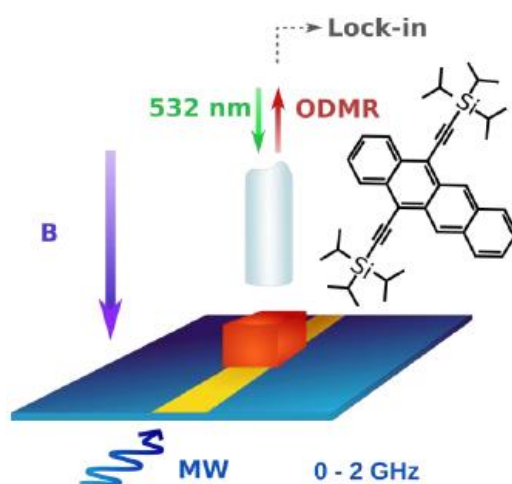
### SPIN PROPERTIES OF BI-EXCITON STATE FORMED THROUGH SINGLET FISSION

A.D. Chepelianskii<sup>1\*</sup>, K. Yunusova<sup>1</sup>, S. Bayliss<sup>1</sup>, and L. Weiss<sup>2</sup>

<sup>1</sup>Laboratoire de physique des solides, Université Paris Sud, France

<sup>2</sup>Optoelectronics Group, Cavendish Laboratory, Cambridge University, UK

From organic electronics to biological systems, understanding the role of intermolecular interactions between spin pairs is a key challenge. Here we show how such pairs can be selectively addressed with combined spin and optical sensitivity. We demonstrate this for bound pairs of spin-triplet excitations formed by singlet fission, with direct applicability across a wide range of synthetic and biological systems. We show that the site-sensitivity of exchange coupling allows distinct triplet pairs to be resonantly addressed at different magnetic fields, tuning them between optically bright singlet ( $S=0$ ) and dark triplet, quintet ( $S=1,2$ ) configurations: this induces narrow holes in a broad optical emission spectrum, uncovering exchange-specific luminescence. Using fields up to 60 T, we identify three distinct triplet-pair sites, with exchange couplings varying over an order of magnitude (0.3-5 meV), each with its own luminescence spectrum, coexisting in a single material. Our results reveal how site-selectivity can be achieved for organic spin pairs in a broad range of systems. We then show how broadband optically detected magnetic resonance can allow to find the microscopic positions of the triplet exciton that for a strongly bound quintet state within the crystal structure of TIPS-Tetracene.



#### REFERENCES

- [1] Sam L Bayliss, Leah R Weiss, Anatol Mitioglu, Krzysztof Galkowski, Zhuo Yang, Kamila Yunusova, Alessandro Surrente, Karl J Thorley, Jan Behrends, Robert Bittl, John E Anthony, Akshay Rao, Richard H Friend, Paulina Plochocka, PCM Christianen, Neil C Greenham, Alexei D Chepelianskii, Site-selective measurement of coupled spin pairs in an organic semiconductor, *PNAS* **115**, 5077 (2018).
- [2] Sam L. Bayliss, Alexei D. Chepelianskii, Alessandro Sepe, Brian J. Walker, Bruno Ehrler, Matthew J. Bruzek, John E. Anthony, and Neil C. Greenham, *Phys. Rev. Lett.* **112**, 238701 (2014).

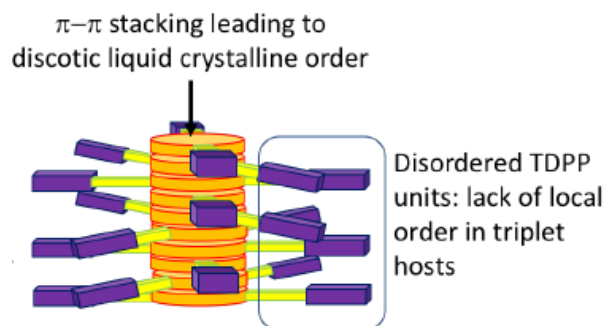
OC35

## LIQUID CRYSTALLINITY AS A SELF-ASSEMBLY MOTIF FOR SINGLET FISSION MATERIALS

Saghar Masoomi-Godarzi\*<sup>1</sup>, Trevor A. Smith<sup>2</sup> and David J. Jones<sup>1</sup><sup>1</sup> Bio21 Institute and <sup>2</sup> School of Chemistry, University of Melbourne, Parkville, Victoria 3010, Australia

The major loss mechanism in single-junction PVs is due to the higher energy photons which lose the excess energy above the bandgap as heat (thermalisation losses), leading to a maximum theoretical efficiency of 32% for a single-junction PV, the Shockley-Queisser limit.<sup>1</sup> A process that has the potential to increase this limit to 45% is to use high energy photons to produce two electron-hole pairs. In organic materials, such a photophysical process is called as singlet fission (SF), the spin allowed conversion of a singlet excited state into two triplets by an assembly of two or more chromophores. SF has been reported and extensively studied in crystalline acenes, and more recently acene dimers to better understand the fundamental photophysics and materials requirements for this process. Incorporation of these SF materials into functional solar cells, although demonstrating modest efficiency enhancements, have had limited success. In our efforts to produce higher efficiency printed organic solar cells we had the desire to incorporate solution processible SF materials in printed organic solar cells, however most of the reported SF materials are highly crystalline and either do not promote SF in the amorphous solid state or controlling crystallisation is difficult.

We aimed to develop a new class of SF materials that are more amenable to inclusion into solar cell devices, and remove the “local-order constraint”. In this study, we investigate the use of hexa-peri-hexabenzocoronene (HBC) as a self-organizing core to promote singlet fission in amorphous films. Using design criteria outlined by Busby et al.<sup>2</sup>, suggesting an Acceptor-Donor-Acceptor (A-D-A) structure may support SF, we have used strong  $\pi$ - $\pi$  interactions of a fluorenyl-substituted hexabenzocoronene (FHBC) donor to promote strong self-assembly, coupled with thienyl-substituted diketopyrrolopyrrole (TDPP) as the triplet host. To design this system, we consider different SF requirement including i) energy level requirement for SF that is  $E(S1) \geq 2E(T1)$ , ii) strong self-association through the core, and iii) solution processability. Thin films of the discotic liquid crystalline FHBC(TDPP)<sub>2</sub> material forms hexagonally packed columns<sup>3</sup> (Figure 1). SF studies on FHBC(TDPP)<sub>2</sub> demonstrate a triplet yield of 150% in amorphous thin films, increasing to 170% in thermally annealed films. This constitutes a new class of singlet fission materials.



**Figure 1.** A schematic representation of self-association in FHBC(TDPP)<sub>2</sub>. hexabenzocoronene (HBC, core D) provides strong promoting discotic liquid crystalline order. The TDPP units act as triplet hosts which remain disordered removing any local order for the dithienyldiketopyrrolopyrrole (TDPP, A) acceptor units.

## REFERENCES

- [1] Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells *J. Appl. Phys.* 1961, 32, 510-519.
- [2] Busby, E.; Xia, J.; Wu, Q.; Low, J. Z.; Song, R.; Miller, J. R.; Zhu, X. Y.; Campos, L. M.; Sfeir, M. Y. A design strategy for intramolecular singlet fission mediated by charge-transfer states in donor-acceptor organic materials *Nat. Mater.* 2015, 14, 426-33.
- [3] Wong, W. W. H.; Subbiah, J.; Puniredd, S. R.; Purushothaman, B.; Pisula, W.; Kirby, N.; Muellen, K.; Jones, D. J.; Holmes, A. B. Liquid Crystalline hexa-peri-hexabenzocoronene-diketopyrrolopyrrole organic dyes for photovoltaic applications *J. Mater. Chem.* 2012 22, 39, 21131-21137.

K6

**MANAGEMENT OF THE COULOMB INTERACTION IN ORGANIC LEDS AND SOLAR CELLS****Richard Friend***Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK*

The physics of organic semiconductors is often controlled by large electron-hole Coulomb interactions and by large spin exchange energies. I will discuss recent strategies that allow these interactions to be harnessed for efficient device operation. For LEDs, 3:1 statistical formation of triplet:singlet excitons through electron-hole recombination limits efficiency if the triplet state is non-emissive, but is recovered for systems with reduced exchange energy and strong spin-orbit coupling in organo-metallic systems or for system where triplet-triplet collisions produce singlet excitons efficiently [1]. We have recently demonstrated that  $\pi$ -conjugated radical materials with doublet ground states can operate with high efficiency in the doublet manifold. For organic PV systems, long-range charge separation from the donor-acceptor heterojunction must overcome a substantial Coulomb barrier, which we find always sets up a measurable optical Stark shift that we measure to be 200 meV or more. Whether this separation is ultrafast (sub-picosecond) or slow (>10 psec) depends on the 'excess' energy provided by the photogenerated exciton to the separating electron-hole pair, both for fullerene acceptor systems and those with non-fullerene acceptors [2]. Longer time bimolecular recombination should show similar spin statistics to LED operation, causing significant non-radiative recombination for triplet formation where there is easy access to a low-lying localized triplet states. I will present evidence that though fullerene systems generally show rapid bimolecular triplet formation, this can process can be very strongly reduced in some non-fullerene acceptor systems.

**REFERENCES**

- [1] Ai, X.; Evans, E. W.; Dong, S.; Gillett, A. J.; Guo, H.; Chen, Y.; Hele, T. J. H.; Friend, R. H.; Li, F., Efficient radical-based light-emitting diodes with doublet emission. *Nature* **2018**, *563*, 540.
- [2] Menke, S. M.; Cheminal, A.; Conaghan, P.; Ran, N. A.; Greehnam, N. C.; Bazan, G. C.; Nguyen, T.-Q.; Rao, A.; Friend, R. H., Order enables efficient electron-hole separation at an organic heterojunction with a small energy loss. *Nature Communications* **2018**, *9* (1), 277.

## **POSTER COMMUNICATIONS**

**Best Poster Award granted by  
Materials Horizons  
(Royal Society of Chemistry)**

P1

## IMPACT OF CONTACT IN MOLECULAR JUNCTIONS: WHEN PHYSICS DICTATES THE CHEMICAL PROPERTIES

Colin Van Dyck\*, Adam Bergren

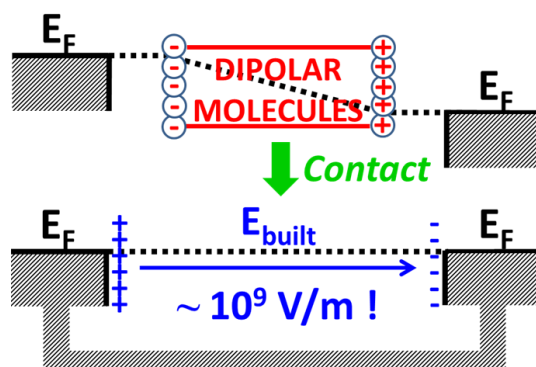
NRC Nanotechnology Research Center, University of Alberta, Edmonton, AB Canada

colin.vandyck@nrc.ca, Adam.Bergren@nrc-cnrc.gc.ca

Molecular junctions are nanomaterials made of one molecule, or a thin organic layer, sandwiched between two metallic electrodes. These systems are now widely and intensively studied due to a high potential for nanoelectronic applications. If these devices can now be reliably made and characterized, this field of research is facing a clear issue: the modification of the molecular structure offers a poor control over the device characteristics.

The basic idea of the design in Molecular Electronics is that the molecular level landscape in the junction will affect the electron transport, offering control over the current/voltage characteristics. Driven by chemical intuition, the usual design of molecular junctions relies on electron donating or accepting building blocks. In this presentation, we show and explain that this approach which focuses on the isolated molecule properties provides a very limited picture as the contact of a molecule to two metal electrodes leads to a completely different entity.

Using first principle DFT calculations, we demonstrate that the contact of an asymmetric organic layer to metal electrodes comes with the creation of spontaneous and very intense electric fields in the junction. This field completely modifies the energy landscape in the junction. We show that only a design that takes into account such large contact renormalization effects could finally lead to the control of the electronic structure of molecular junctions and then move the molecular electronics effort in the intelligent design era.



**Figure 1.** We will describe the emergence of large built-in fields arising upon asymmetric contact of molecular layers to metal electrodes. We will further explain how it renormalizes energy levels and the role of molecular parameters (interface dipoles, permanent dipoles and dielectric response) will be emphasized.

### REFERENCES

- [1] Aviram and Ratner, "Molecular rectifiers", *Chemical Physics Letters*, 29, 277-283, **1974**
- [2] Van Dyck and Ratner, "Molecular rectifiers: a new design based on asymmetric anchoring moieties" *Nano Letters*, 15, 1577-1584, **2015**
- [3] Van Dyck and Ratner, "Molecular junctions: Control of the energy gap achieved by a pinning effect" *J. Phys. Chem. C*, 121, 3013-3024, **2017**
- [4] Van Dyck and Bergren, "Large Built-in Fields Control the Electronic Properties of Nanoscale Molecular Devices with Dipolar Structures", *Advanced Electronic Materials*, 8, 1802439, **2018**

## SEQUENTIAL PROCESSING OF 2D COVALENT NETWORKS ON METAL SUBSTRATES

Frederic Dumur\*<sup>1</sup>, Thomas Faury<sup>1,2</sup>, Sylvain Clair<sup>2</sup> and Didier Gigmes<sup>1</sup>

<sup>1</sup> Aix Marseille Univ, CNRS, ICR, UMR 7273, F-13397 Marseille, France  
 frederic.dumur@univ-amu.fr

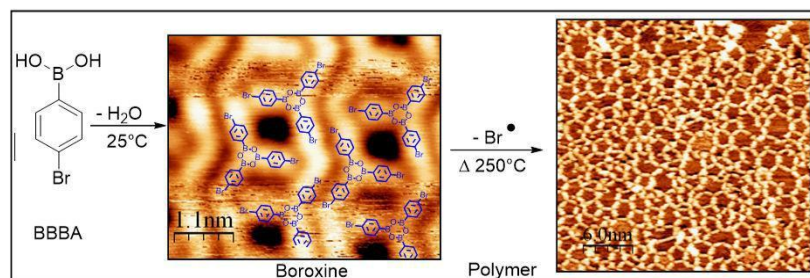
<sup>2</sup> Aix Marseille Univ, University Toulon, CNRS, IM2NP, Marseille, France

The chemistry of boronic acids is currently one of the ways used for the formation of covalent organic 3D networks (COF). Our goal is to apply this concept to the formation of two-dimensional organic nanostructures on metal surfaces to prepare organic nanoporous masks of various sizes.

Previous work carried out in our laboratory on the molecule of 1,4-Benzene DiBoronic Acid (BDBA) led to the STM observation of 2D covalent honeycomb-like nanoporous networks with 15 Å pores.<sup>1</sup> However due to the irreversibility of the covalent bond formation, defects are present in the polymer film.

To improve the regularity of the 2D network, a promising approach consists in controlling the kinetics of formation by use of two successive reactions. In this aim, we recently combined two reactions that significantly varied by their mechanisms, each reaction being activated in a specific range of temperature i.e. formation of the boroxine rings by dehydration at room temperature followed by C-C bond formation via an Ullmann coupling at temperature higher than 200°C (Fig. 1).

Herein, we present our results obtained during the sequential polymerization of 1-Bromo Benzene 4-Boronic Acid (BBBA) on Au(111) surface (Fig. 1).<sup>2</sup> Using the above-mentioned stepwise approach, a polymer network of higher quality with 23 Å hexagonal pores was thus obtained.



**Figure 1.** Polymerization mechanism and BBBA network, STM images of the boroxine and polymer phases on Au (111).

**Acknowledgments:** The authors thanks Aix Marseille University and the CNRS for financial support.

### REFERENCES

1. Zwaneveld N. A. A.; Pawlak R.; Abel M.; Catalin D.; Gigmes D.; Bertin D.; Porte L. *Journal of the American Chemical Society* **2008**, *130*, 6678-6679
2. Faury, T.; Clair, S.; Abel, M.; Dumur, F.; Gigmes, D.; Porte, L.; *J. Phy. Chem. C* **2012**, *116*, 4819-4823



P3

## UNDERSTANDING THE STRUCTURE-PROPERTY CORRELATIONS OF N-TYPE ORGANIC SEMICONDUCTORS IN OFETS

Alexandra Harbuzaru\*<sup>1</sup>, I. Arrechea Marcos<sup>2</sup>, J.T. López Navarrete<sup>3</sup>, Rocío Ponce Ortiz<sup>4</sup>, M.C. Ruiz Delgado<sup>5 1-5</sup>

Department of Physical Chemistry, Malaga University, Malaga, Spain.

harbuzaru@uma.es

In the organic electronic research field, the development of high-performance unipolar n-type semiconductors is still challenging. Here we present an in-depth study of a series of ladder-type semiconductors, which due to their all-acceptor backbones, exhibit unipolar n-type transport in OTFTs.

It is well known that the performance of organic semiconductors is governed not only by their molecular structures but also by their intermolecular assembly in the solid state. Thus, highly planar backbones are beneficial for a good molecular packing and film ordering leading to good charge transport characteristics. In this contribution, we study a series of BTI small molecules and polymers, both from a molecular and from a supramolecular point of view, in order to establish useful structure-property relationships that may guide the rational synthesis of new and improved materials.

To carry out this study, we make use of different spectroscopic techniques, supported by quantum theoretical calculations at the DFT level.



**Figure 1.** Optimized minimum-energy geometry (B3LYP/6-31G\*\*) for one of the studied BTI-based semiconductors.

## REFERENCES

- [1] Y. Yang, H. Guo, S. Ling, I. Arrechea-Marcos, Y. Wang, J. T. López Navarrete, R. Ponce Ortiz, X. Guo, *Angew. Chem. Int. Ed.* 2017, 56, 9924-9929.
- [2] Y. Wang, H. Guo, A. Harbuzaru, M. A. Uddin, I. Arrechea-Marcos, S. Ling, J. Yu, Y. Tang, H. Sun, J. T. López Navarrete, R. Ponce Ortiz, H. Y. Woo, X. Guo, *J. Am. Chem. Soc.* 2018, 140, 6095-6108.
- [3] J. Mei, Y. Diao, A. L. Appleton, L. Fang, Z. Bao, *JACS* 2013, 135 (18), 6724-6746.

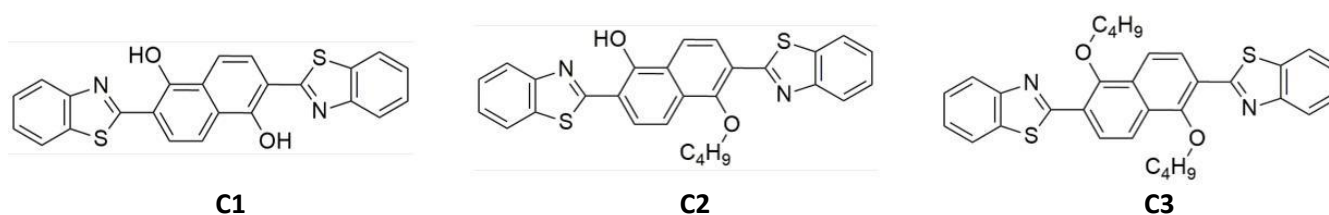
## INSPIRED EXCITED-STATE PROTON TRANSFER (ESPT) OF 2-(2'-HYDROXYPHENYL)BENZOTHAZOLE FOR FLUORESCENCE MATERIALS: COMBINED EXPERIMENTAL AND THEORETICAL STUDY

Komsun Chaihan<sup>1</sup>, Thanh-Tuân Bui\*<sup>2</sup>, Nawee Kungwan\*<sup>1</sup>,  
Fabrice Goubard\*<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand  
Komsun.nchai@gmail.com, naweekung@gmail.com

<sup>2</sup>Laboratoire de Physicochimie des Polymères et des Interfaces, Université de Cergy-Pontoise, 5 Gay Lussac, Neuville-sur-Oise 95000, France  
tbui@u-cergy.fr, fabrice.goubard@u-cergy.fr

Organic molecules having excited-state proton transfer (ESPT) play important roles in various applications especially luminescence materials and fluorescence sensors [1-2]. In this work, we have designed molecules in the series of 2-(2'-hydroxyphenyl) benzothiazole (HBT) and studied their photophysical properties driven by ESPT process. For our syntheses, three new molecules are synthesized using 1,5-dihydroxynaphthlene as a core depicted in Figure 1. Their photophysical properties are experimentally observed by means of steady state absorption and emission spectra found that absorption and emission spectra bands of C1 and C2, which are double and single ESPT molecules respectively, exhibit a large of red-shift compared to C3 without ESPT. The ESPT molecules provide fluorescence from the transient keto tautomer in which double ESPT is longer wavelength than single ESPT. Thus, Stokes shift is largely as a function of number of ESPT coordinate. Moreover, we use theoretical calculations based on density functional theory (DFT) and time-dependent density functional theory (TD-DFT) approaches [3-6] to support experimental results. These calculations reveal that single emission peak of C1 could be a combined-fluorescence from two emissive species which are monoketo (via single ESPT) and diketo (via double ESPT) forms. For C2, only one fluorescence peak associating with keto emission is observed whereas for C3 with fully protecting on ESPT, only emission of the original form not the keto form is shown.



**Figure 1.** Synthesized molecules based on ESPT of HBT series; **C1**: double ESPT, **C2**: single ESPT, and **C3**: without ESPT

### REFERENCES

- [1] Lou, Z.; Li, P.; Han, K., Redox-Responsive Fluorescent Probes with Different Design Strategies. *Accounts of Chemical Research* **2015**, *48*, 1358-1368.
- [2] Wu, J.; Liu, W.; Ge, J.; Zhang, H.; Wang, P., New Sensing Mechanisms for Design of Fluorescent Chemosensors Emerging in Recent Years. *Chemical Society Reviews* **2011**, *40*, 3483-3495.
- [3] Becke, A. D., Density-Functional Thermochemistry. III. The Role of Exact Exchange. *The Journal of chemical physics* **1993**, *98*, 5648-5652.
- [4] Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Physical review B* **1988**, *37*, 785.
- [5] Feller, D., The Role of Databases in Support of Computational Chemistry Calculations. *Journal of Computational Chemistry* **1996**, *17*, 1571-1586.
- [6] Schäfer, A.; Horn, H.; Ahlrichs, R., Fully Optimized Contracted Gaussian Basis Sets for Atoms Li to Kr. *The Journal of Chemical Physics* **1992**, *97*, 2571-2577.

## FIRST-PRINCIPLES INVESTIGATION OF THE ADSORPTION OF CARBON DIOXIDE, CARBON MONOXIDE AND OXYGEN ON CSPBX<sub>3</sub> (X= CL, BR, I) SURFACES

Arpit Mishra<sup>1,2</sup>, Philippe Baranek<sup>1,2</sup>, and Andrei Postnikov<sup>3</sup>

<sup>1</sup>EDF R&D, Department EFESE, EDF Lab – Paris Saclay, 7 Boulevard Gaspard Monge, F-91120 Palaiseau, France

<sup>2</sup>Institut Photovoltaïque d'Ile de France (IPVF), 30 Route départementale 128, F-91120 Palaiseau,

<sup>3</sup>Institut Jean Barriol, Laboratoire de Chimie et Physique–Approche Multi-échelle des Milieux Complexes (LCP-A2MC), Université de Lorraine, 1 Bd Arago, F-57078 Metz, France

In the field of photovoltaics, perovskites are steadily attracting interest because of their low cost and high efficiency (22.7% for methylammonium lead iodide). Hence, organic-inorganic halide perovskites might be seen as a promising alternative to current Si-based systems or as constituents of the tandem cells. However, their poor stability in the presence of moisture, oxygen, carbon monoxide and carbon dioxide remains a major challenge for their commercial applications. In this work, we focus on inorganic CsPbX<sub>3</sub> (X= Cl, Br, I) perovskites. The adsorption of CO<sub>2</sub>, CO and O<sub>2</sub> on their (100) surface has been investigated from first principles, using hybrid functionals. The adsorption was simulated on both types of surface terminations, PbX<sub>2</sub> and CsX. The effect of supercell size on the equilibrium octahedral tilting was studied. The results were interpreted in terms of Mulliken population analysis, density of states, vibration spectra and adsorption energy. So far, the physisorption of all the molecules on the CsPbX<sub>3</sub> (X= Cl, Br, I) surfaces were confirmed. The affinity of CO<sub>2</sub>, CO and O<sub>2</sub> towards CsPbI<sub>3</sub> surface is higher than that towards CsPbBr<sub>3</sub> and CsPbCl<sub>3</sub>. For CsPbI<sub>3</sub>, the PbI<sub>2</sub> termination is more reactive than the CsI one. On the contrary, in both CsPbBr<sub>3</sub> and CsPbCl<sub>3</sub>, the surfaces with CsX termination turn out to be more reactive.

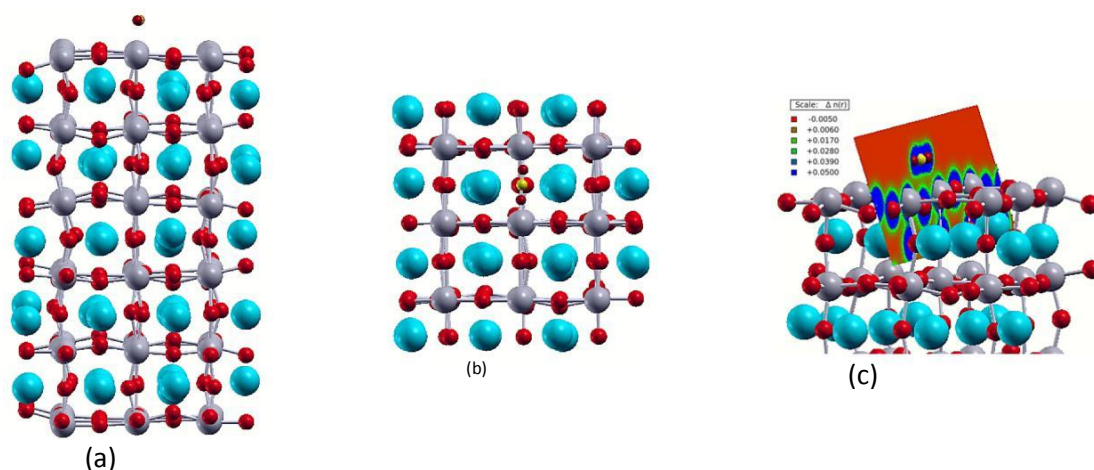


Figure: Cs (cyan) is encapsulated in PbX<sub>6</sub> (Pb=grey, halide=red) octahedra. CO<sub>2</sub> adsorbed on CsPbX<sub>3</sub> surface. a) side view along the (100) plane ; b) top view of the (001) surface plane ; c) difference of the total and isolated atomic charges density maps which indicates the physisorption of CO<sub>2</sub>.

## ON-SURFACE SYNTHESIS OF ALIGNED FUNCTIONAL NANORIBBONS MONITORED BY SCANNING TUNNELLING MICROSCOPY AND VIBRATIONAL SPECTROSCOPY

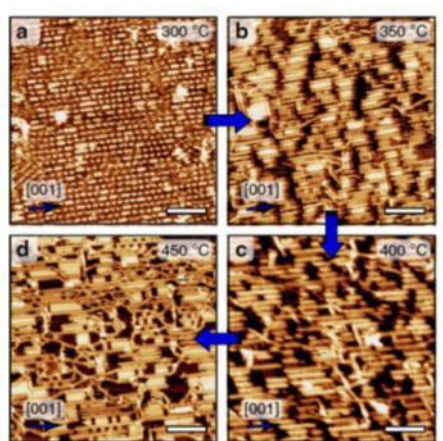
Corentin Pigot,<sup>1,\*</sup> Frédéric Dumur,<sup>1</sup> Nataliya Kalashnyk,<sup>2</sup> Eric Salomon,<sup>3</sup> Didier Gigmes,<sup>1</sup> Sylvain Clair<sup>2</sup>

<sup>1</sup>Aix Marseille Univ, CNRS, ICR, Marseille, France  
corentin.PIGOT@univ-amu.fr, Frederic.dumur@univ-amu.fr,

<sup>2</sup>Aix Marseille Univ, University Toulon, CNRS, IM2NP, Marseille, France

<sup>3</sup>Aix Marseille Univ, CNRS, PIIM, Marseille, France

In the blooming field of on-surface synthesis, molecular building blocks are designed to self-assemble and covalently couple directly on a well-defined surface, thus allowing the exploration of unusual reaction pathways and the production of specific compounds in mild conditions. Up to now, most of the single-layered surface covalent organic frameworks (SCOFs) have been prepared by Ullmann dehalogenation reactions of brominated aromatic compounds or trimerization of diboronic acids. Here we present our results concerning the creation of functionalized organic nanoribbons on the Ag(110) surface by mean of an oxidative coupling unprecedented in the literature<sup>1</sup>. Interestingly, length of the resulting nanoribbons could be efficiently controlled by mean of the temperature deposition whereas the anisotropic substrate could act as an efficient template fostering the alignment of the nanoribbons, up to the full monolayer regime. <sup>[1]</sup>



**Figure 1.** Nanoribbon formation and their evolution upon further annealing

### REFERENCES

[1] Kalashnyk, N.; Mouhat, K.; Oh, J.; Jung, J.; Xie, Y.; Salomon, E.; Angot, T.; Dumur, F.; Gigmes, D.; Clair, S. On-surface synthesis of aligned functional nanoribbons monitored by scanning tunnelling microscopy and vibrational spectroscopy *Nat. Commun.* **2017**, *8*, 14735.

## DESIGN OF SWITCHABLE INTERFACES: TOWARDS A NEW GENERATION OF RESPONSIVE OPTO-ELECTRONIC DEVICES

V. Diez-Cabanes\*<sup>1</sup>, A. Galanti<sup>2</sup>, M. Souto<sup>3</sup>, Q. Wang<sup>4</sup>, I. Ratera<sup>3</sup>, N. Koch<sup>4</sup>, J. Veciana<sup>3</sup>, P. Samori<sup>2</sup>, J. Cornil<sup>1</sup>

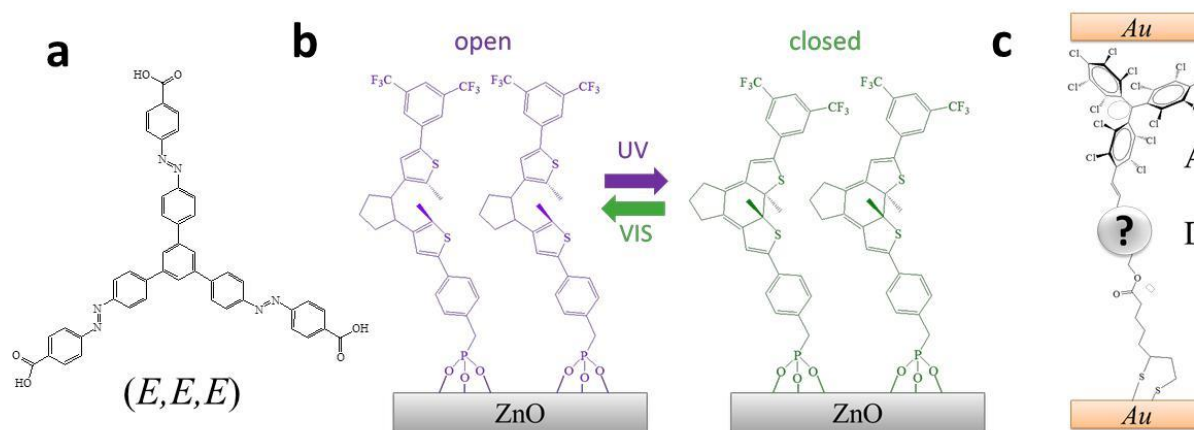
<sup>1</sup>Laboratory for Chemistry of Novel Materials, University of Mons, Place du Parc 20, B-7000 Mons, Belgium  
valentin.diezcabanes@umons.ac.be, jerome.cornil@umons.ac.be

<sup>2</sup>Université de Strasbourg, CNRS, ISIS UMR 7006, 8 allée Gaspard Monge, 67000 Strasbourg, France  
galanti@unistra.fr, samori@unistra.fr

<sup>3</sup>Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Spain  
manuel.souto@uv.es, iratera@icmab.es, vecianaj@icmab.es

<sup>4</sup>Institut für Physik & IRIS Adlershof Humboldt-Universität zu Berlin Brook-Taylor-Str. 6, 12489 Berlin, Germany  
qiankun@physik.hu-berlin.de, norbert.koch@physik.hu-berlin.de

Molecular switches have attracted a great attention in the field of Nanotechnology due to their ability to reversibly switch between several states by means of external stimuli (such as light or electrical current), and thus to display several functions and mixing electronic with optical, magnetic or sensing properties. In order to achieve such multifunctionality, we can introduce molecular switches as building blocks in order to form responsive components and interfaces to be integrated into electronic devices to gain a dynamic control of their properties. The efficiency and performance of such opto-electronic devices can be improved by a deeper understanding of switchable assembled systems. The efficiency and performance of such opto-electronic devices can be improved by a deeper understanding of switchable assembled systems. In our work, several theoretical approaches and characterization methods were employed to characterize various switchable architectures. In a first stage, Molecular Mechanics and Dynamics (MM/MD) simulations were used to evaluate the different forces driving the self-assembled patterns obtained with a multi-state compound formed by three azobenzene groups (see Figure 1-a), which could be employed as building blocks of responsive host-guest systems or organic frameworks. Ultraviolet Photoemission Spectroscopy (UPS) measurements were then confronted to Density Functional Theory (DFT) calculations performed with Periodic Boundary Conditions (PBC) to shed light on the change in the electrode surface properties upon adsorption of switchable Self-Assembled Monolayers (SAMs) based on diarylethene (DAE) molecules (see Figure 1-b), which can be exploited to dynamically tune the amount of current injected in devices such as organic field-effect transistors (OFETs) and light-emitting diodes (OLEDs). Finally, the transmission through Donor-Acceptor (D-A) dyad based switchable junctions, where the perchlorotriphenylmethyl (PTM) radical acts as electron acceptor (A) (see Figure 1-c), was analyzed with the Non-Equilibrium Green Function method coupled to DFT (NEGF-DFT) calculations in order to develop new functional rectifiers.



**Figure 1.** Chemical structures of the compounds under study: (a) multi-azobenzene compound in the full *trans* (*E,E,E*) isomer, (b) DAE-based SAMs adsorbed on ZnO substrate; and (c) D-A SAMs sandwiched between two Au electrodes.

**Acknowledgments:** this work was supported by the EC through the Marie Skłodowska-Curie ITN project iSwitch (GA-642196).

## ZINC-PORPHYRIN BASED DYES AS SENSITIZERS FOR DYE-SENSITIZED SOLAR CELLS

Tinnagon Keawin<sup>1</sup>, Kanokkorn Sirithip<sup>2</sup>, Taweesak Sudyoadsuk<sup>3,4</sup>, Siriporn Jungsuttiwong<sup>1</sup> and Vinich Promarak<sup>3,4</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Ubon Ratchathani University, Ubon Ratchathani, Thailand

<sup>2</sup>Department of Science and Technology, Faculty of Liberal Arts and Sciences, Roi Et Rajabhat University, Roi Et, Thailand

<sup>3</sup>School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong, Thailand

<sup>4</sup>Research Network of NANOTEC-VISTEC on Nanotechnology for Energy, Vidyasirimedhi Institute of Science and Technology, Wangchan, Rayong, Thailand

Dye-sensitized solar cell (DSSC), another type of bio-inspired solar cell development, has emerged as one of the most attractive photovoltaic devices because it offers the possibility of low-cost conversion of photoenergy. Ruthenium complex is currently the most efficient dye. This dye, however, is costly and hard to prepare in high yield. Organic dyes exhibit not only higher extinction coefficient, but simple preparation, structure modification and purification procedure with a low cost. In this presentation, a series of zinc-porphyrin dyes that contain different *meso* substituents (phenyl, carbazole phenyl, triphenylamine and carbazole thiophenyl groups), different numbers of anchoring group (1-3) and different types of  $\pi$ -conjugated anchoring moiety at the *meso*-positions of porphyrin ring were designed, synthesized, characterized and applied as sensitizers for dye-sensitized solar cells (DSSCs). The effects of these modifications on the properties of the porphyrin dyes were theoretically and experimentally investigated. The relationships between structures and properties and cell performances of these dyes will be drawn and discussed. Among these dyes, Zn-FA dye made of triphenylamine as *meso* substituent and ethynylbenzoic acid as  $\pi$ -conjugated anchoring group gave rise to the highest conversion efficiency ( $\eta$ ) of 8.36% ( $J_{sc} = 16.25 \text{ mA/cm}^2$ ,  $V_{oc} = 0.73 \text{ V}$ , and  $FF = 0.69$ ).

**Acknowledgments:** This work was financially supported by the TRF (RTA6080005) and NANOTEC, NSTDA, Ministry of Science and Technology, Thailand, through its program of Research Network NANOTEC.

## REFERENCES

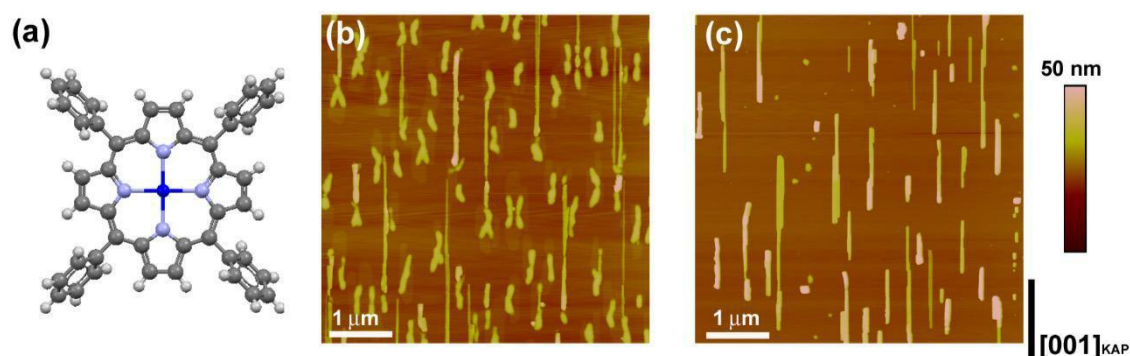
- [1] T. Keawin, R. Tarsang, K. Sirithip, N. Prachumrak, T. Sudyoadsuk, S. Namuangruk, J. Roncali, N. Kungwan, V. Promarak, S. Jungsuttiwong, *Dyes and Pigments*, 2017, 136, 697-706.
- [2] K. Sirithip, N. Prachumrak, R. Rattanawan, T. Keawin, T. Sudyoadsuk, S. Namuangruk, S. Jungsuttiwong, V. Promarak, *Chemistry-An Asian Journal*, 2015, 10, 882-893.
- [3] K. Sirithip, N. Prachumrak, T. Sudyoadsuk, S. Jungsuttiwong, V. Promarak, Unpublished results

## SELECTIVE GROWTH OF METALLO-TETRAPHENYLPORPHYRIN NANOWIRES BY POST-GROWTH PROCESSES

L. Raimondo, S. Trabattoni and A. Sassella

Department of Materials Science, University of Milano - Bicocca, Milan, Italy  
*luisa.raimondo@unimib.it, silvia.trabattoni@unimib.it, adele.sassella@unimib.it*

Controlling self-organization of small organic molecules in nanostructures with the desired shape and size is one of the main challenges in organic nanoelectronics. Here, a strategy for selectively growing uniaxially aligned nanowires of meso-tetraphenyl porphyrin-Zn(II) (ZnTPP, Fig. 1a) is presented, based on post-growth processes. ZnTPP is deposited by Organic Molecular Beam Epitaxy on potassium hydrogen phthalate (KAP), an organic salt easily giving cm-sized single crystals, demonstrated to be particularly suitable as substrate for organic epitaxy. The as-grown films typically display a rather rich surface morphology, characterized by the presence of nanowires and other nm-sized aggregates (see Fig. 1b). Properly tuned aging processes in vacuum and in air are demonstrated to be a tool for the selection of crystalline ZnTPP nanowires, with controlled crystal structure, shape and size, and with uniaxial orientation (see Fig. 1c), at the expenses of the other phases via quasi-Ostwald ripening. This phenomenon is driven by organic epitaxy between the matching crystal surfaces of ZnTPP and KAP. The ability of growing ZnTPP nanowires with a unique crystal structure and precise orientation gives the chance to study the intrinsic properties of the triclinic polymorph of ZnTPP, such as the role of intermolecular interactions in driving its optical response.



**Figure 1.** a) Molecular structure of ZnTPP: H atoms in white, C atoms in grey, N atoms in light purple, Zn atom in blue; AFM height ( $5 \times 5 \mu\text{m}^2$ ) images of a ZnTPP sample grown on KAP, one (b) collected immediately after growth and the other one (c) collected after applying a proper post-growth aging protocol, aimed at selecting the nanowires. The color scale and the orientation of the  $[001]_{\text{KAP}}$  axis on the right apply to both panels.

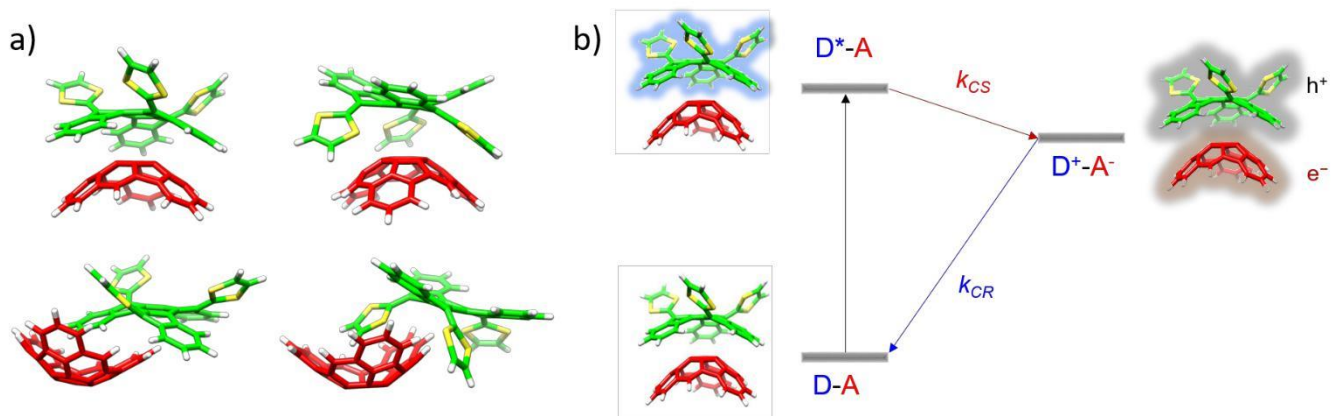
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## INFLUENCE OF THE SUPRAMOLECULAR STRUCTURE ON THE CHARGE-SEPARATION AND -RECOMBINATION RATE CONSTANTS IN THE DONOR–ACCEPTOR truxTTF-C<sub>30</sub>H<sub>12</sub> COMPLEX

Jesus Cerda<sup>1</sup>, Joaquin Calbo<sup>1</sup>, Juan Aragó<sup>1</sup> and Enrique Ortí<sup>1</sup>

<sup>1</sup>Instituto de Ciencia Molecular (ICMol), Universitat de València, Valencia, Spain  
jesus.cerda@uv.es

Fullerenes and their derivatives are one of the most important electron-acceptor (A) compounds in organic electronics.<sup>1</sup> In particular, fullerene and fullerene fragments (buckybowls) in combination with the electron-donor (D) truxene-tetrathiafulvalene (truxTTF) form donor–acceptor supramolecular complexes that undergo an efficient photoinduced electron-transfer process (Figure 1a).<sup>2,3</sup> In this contribution, we present a detailed analysis of how the supramolecular structure of the truxTTF-C<sub>30</sub>H<sub>12</sub> complex determines the charge-separation and -recombination rate constants (Figure 1b) computed by using a Marcus–Levitch–Jortner rate-type expression<sup>4,5</sup> and Density Functional Theory (DFT) and time-dependent DFT (TDDFT) calculations. In particular, this analysis is focused on the influence of the supramolecular structure on the most relevant parameters that determine the final rate constants (electronic coupling, reorganization energy and energy difference between the electronic states involved in the electron-transfer process).



**Figure 1.** a) Minimum energy geometries of the truxTTF-C<sub>30</sub>H<sub>12</sub> supramolecular complex. b) Diagram of the supramolecular organization between truxTTF and C<sub>30</sub>H<sub>12</sub> and the photoinduced electron transfer events.

### REFERENCES

- [1] D. M. Guldi, B. M. Illescas, C. M<sup>a</sup> Atienza, M. Wielopolski and N. Martín, *Chem. Soc. Rev.*, **2009**, *38*, 1587–1597
- [2] E. M. Pérez, M. Sierra, L. Sánchez, M. R. Torres, R. Viruela, P. M. Viruela, E. Ortí and N. Martín, *Angew. Chem. Int. Ed.* **2007**, *46*, 1847–1851
- [3] M. Gallego, J. Calbo, J. Aragó, R. M. Krick Calderon, F. H. Liquido, T. Iwamoto, A. K. Greene, E. A. Jackson, E. M. Pérez, E. Ortí, D. M. Guldi, L. T. Scott, and N. Martín, *Angew. Chem. Int. Ed.* **2014**, *53*, 2170–2175
- [4] J. Jortner, *J. Chem. Phys.* **1976**, *64*, 4860
- [5] R. P. Fornari, J. Aragó, A. Troisi, *J. Chem. Phys.* **2015**, *142*, 184105.

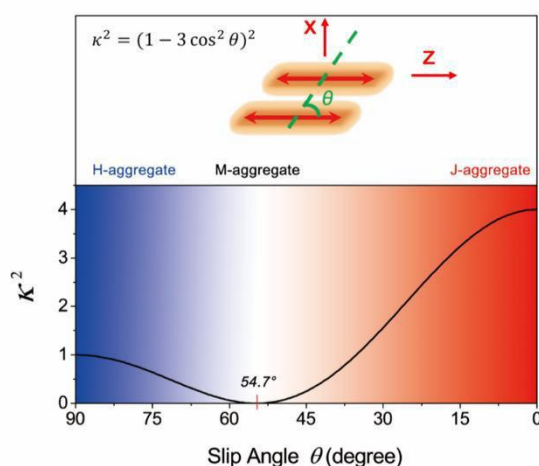


## REVISIT THE MAGIC-ANGLE STACKING OF PERYLENE AGGREGATES WITH HIGH LEVEL AB INITIO CALCULATIONS

Wenlan Liu<sup>\*1,2</sup>, Jiadong Zhou<sup>3</sup>, Zengqi Xie<sup>3</sup> and Andreas Köhn<sup>#2</sup><sup>1</sup>Polymer Theory Department, Max Planck Institute for Polymer Research, D-55128 Mainz, Germany. <sup>2</sup>Institute of Theoretical Chemistry, University of Stuttgart, D-70569 Stuttgart, Germany.<sup>3</sup>Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, 510640 Guangzhou, People's Republic of China\* [liuwenlan@mpip-mainz.mpg.de](mailto:liuwenlan@mpip-mainz.mpg.de)# [koehn@theochem.uni-stuttgart.de](mailto:koehn@theochem.uni-stuttgart.de)

Other than its well-known usage in the fields of nuclear magnetic resonance (NMR) spectroscopy and electron energy-loss spectroscopy (EELS), the term “magic angle” is also used in the field of material design to determine the relative position of the neighbored dye molecules. At the magic angle orientation, the material will show attractive optoelectronic functions such as efficient NIR emission and high electron mobility. Recently, a novel single crystal of N,N'-bis(4-methoxybenzyl)perylene-3,4,9,10-bis-(dicarboximide) (mb-PBI) has been grown through physical vapor transport (PVT) method by Zhou and Xie etc.[1]. The micro structure of the crystal possesses magic-angle stacking (M-type stacking) and retains strong intermolecular  $\pi$ - $\pi$  interaction. However, the ideal magic-angle ( $54.7^\circ$ ) was predicted using the classical orientation factor ( $\kappa^2$ ) model[2], and this value is quite different from the ab initio result ( $30.0^\circ$ ) in our previous research[3].

In this contribution, we scan the lowest lying electronically excited states surfaces of perylene based dimers in different translational directions (see Figure 1 for more details) at the SCS-ADC(2)/SVP level. For each specific dimer, the calculated stacking pattern, in terms of H-, J-, and M-type stacking, has been carefully compared with the ones that evaluated by using the classical orientation factor ( $\kappa^2$ ) model. The difference and relation will be discussed in details.



**Figure 1.** Upper: the relation between the orientation factor ( $\kappa^2$ ) and the slip angle ( $\theta$ ), where the two molecular planes are parallel to each other. “x” and “z” are the moving directions of a perylene molecule, while we are scanning different dimer structures; Lower:  $\kappa^2$  and the corresponding stacking patterns, where the H-, J-, and M-type stackings are colored in blue, red and white respectively, in respect to  $\theta$ .

## REFERENCES

- [1] J. Zhou, etc., *J. Phys. Chem. Lett.* **2018**, *9*, 596–600  
 [2] R. E. Dale, and J. Eisinger, *Biopolymers*, **1974**, *13*, 1573-1605  
 [3] W. Liu, etc., *J. Comput. Chem.* **2018**, *39*, 1979-1989

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## INORGANIC METAL HALIDES FOR OPTOELECTRONICS APPLICATIONS

**Paz Sebastia-Luna, Francisco Palazon, Michele Sessolo\* and Henk J. Bolink**

Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, C/ Catedrático José Beltrán, 2, Paterna, Spain  
*paz.sebastia@uv.es, francisco.palazon@uv.es, michele.sessolo@uv.es, henk.bolink@uv.es*

Lead-based perovskites show outstanding properties in applications such as solar cells and light-emitting devices, however, their instability in air and high toxicity might be a bottleneck in the commercialization of perovskite optoelectronic devices. This is why the search towards alternative materials with similar properties has become one of the focus of the actual research. Manganese and bismuth have emerged as a non-toxic alternatives for this purpose, displaying showing in particular intense photoluminescence (PL). Here, we report the synthesis of a series of fully-inorganic manganese and bismuth halides (X=Cl, Br, I) and their characterization. Dry ball milling at room temperature of the different precursors is used as the synthesis technique, with short development times. The as-prepared powders were analysed by X-ray diffraction, confirming the formation of the different halide salts. In addition, optical characterization including absorption and PL, both in steady state and time-resolved, was performed.

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## IMPROVEMENT OF HYBRID VAPOR-SOLUTION PEROVSKITE SOLAR CELLS VIA METHYLAMINE GAS POST-TREATMENT

**Isidora Susic, Michele Sessolo\*, Francisco Palazón and Henk J. Bolink**

Instituto de Ciencia Molecular (ICMol), Universidad de Valencia, C/ Catedrático José Beltrán, 2, Paterna, Spain  
*susic@uv.es, michele.sessolo@uv.es, francisco.palazon@uv.es, henk.bolink@uv.es*

Metal halide perovskites have proven to be excellent semiconductors, with tuneable band gap, high absorption coefficients, large charge diffusion length, and for these reasons are widely studied as absorbers in photovoltaics devices. One the biggest challenge in order to achieve high-performance perovskite solar cells is the control over the film morphology. High crystallinity, low defect density, together with the formation of uniform films are important requirements in order to ensure efficient charge collection and minimize non-radiative recombination. Here, we introduce the methylamine gas post-treatment to tune the film morphology. We have used thermal vacuum deposition to prepare methylammonium lead iodide thin films, which are typically homogeneous and flat, composed by fine (< 100 nm) grains. Upon controlled exposure to methylamine, the perovskite film is partially recrystallized, obtaining films with different and enhanced crystallinity. In particular, by tuning the temperature and gas concentration, we are able to substantially increase the average grain size. We will present extensive morphological and structural characterization, as well as preliminary results on the implementation of the recrystallized films in thin-film solar cells.

## OPTO-ELECTRONIC CHARACTERISATION OF VACUUM-DEPOSITED PEROVSKITE SOLAR CELLS

Chris L. Dreeßen\*<sup>1</sup>, Ana M. Igual Muñoz<sup>1</sup>, Lidón Gil-Escrig<sup>2</sup>, Wiria Soltanpoor<sup>3</sup>, Pablo P. Boix<sup>1</sup> and Henk J. Bolink<sup>1</sup>

<sup>1</sup>Instituto de Ciencia Molecular, Universidad de Valencia, Paterna, SPAIN.

*chris.dreessen@uv.es, ana.i.munoz@uv.es, Pablo.P.Boix@uv.es, henk.bolink@uv.es*

<sup>2</sup>Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Young Investigator Group for Perovskite Tandem Solar Cells, Berlin, Germany

*Lidon.Gil@uv.es*

<sup>3</sup>Department of Micro and Nanotechnology, METU, Ankara, TURKEY.

*wiriasr@gmail.com*

Vacuum-deposition of halide perovskites and charge-selective materials enables a wide range of variations in the device architecture [1]. This technique permits an accurate control on the layer thickness and stacking sequence, which is particularly suitable for applications such as tandem devices. Here, we use the intrinsically additive nature of vapor-based processes to carry out a detailed study of the opto-electronic properties of different perovskites and their solar cell interfaces. The use of optical and opto-electronic measurements allows us to determine the loss sources of fully vacuum-processed narrow- and wide-bandgap as well as hybrid-vapor-solution-based perovskite devices.

### REFERENCES

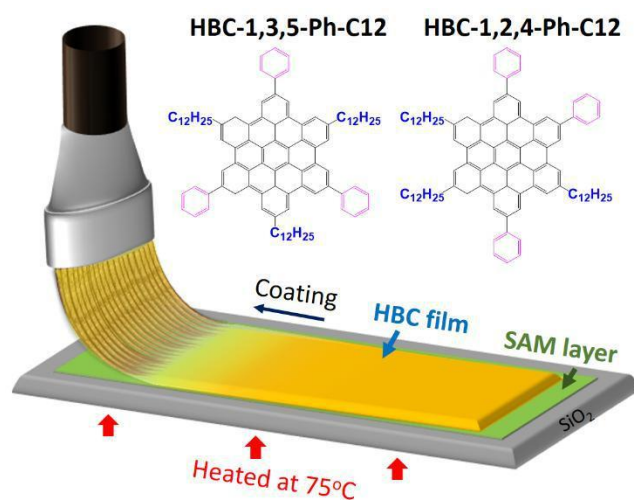
[1] Jorge Avila, Christina Momblona, Pablo P. Boix, Michele Sessolo, and Henk J. Bolink, "Vapor-Deposited Perovskites: The Route to High-Performance Solar Cell Production, *Joule*. (2017), 1(3), pp. 431–442.

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## MOLECULARLY ALIGNED HEXA-PERI-HEXABENZOCORONENE FILMS BY BRUSH-COATING AND THEIR APPLICATION IN THIN FILM TRANSISTORS

Fang-Ju Lin,<sup>1</sup> Hsiu-Hui Chen,<sup>\*,2</sup> Yu-Tai Tao<sup>\*,1</sup> <sup>1</sup>Institute of Chemistry, Academia Sinica, 115 Taipei, Taiwan *fangju.lin6@gmail.com, ytt@gate.sinica.edu.tw* <sup>2</sup>Department of Chemistry, National Kaohsiung Normal University, 824 Kaohsiung, Taiwan *t3836@nknu.edu.tw*

The facile Chinese brush-coating method was used to prepare oriented thin films of hexa-*peri*-hexabenzocoronene derivatives on silicon substrate. As a result of the directional solution-coating, the  $D_{3h}$ -symmetry (HBC-1,3,5-Ph-C12) and the  $C_1$ -symmetry (HBC-1,2,4-Ph-C12) derivatives displayed anisotropic alignment, with mostly edge-on orientation on SiO<sub>2</sub> surfaces modified with various silane-based monolayers. On these silane-modified surfaces, the higher symmetry molecule HBC-1,3,5-Ph-C12 developed a hexagonally packed superstructure, which provided greater  $\pi$  orbital overlap and presumably the electronic coupling between neighboring molecules. In particular, the use of octyltrichlorosilane(OTS)-modified surface enabled brush-coated thin films to have higher anisotropic orientation, crystallinity and favorable molecular arrangement. In contrast, the growth of the hexagonal packing of low symmetry derivative HBC-1,2,4-Ph-C12 were only achieved on the PTS and OTS surfaces. Thin film transistors based on these brush-coated films gave a maximum mobility of  $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and  $0.056 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  respectively, which are two orders of magnitude improvement over the devices with un-oriented films prepared by spin-coating. The results indicate that molecular packing of discotic liquid crystals on silane-modified surface is sensitively influenced by the molecular symmetry which affects intermolecular interactions as well as molecule/surface interactions. This study provides a simple way to fabricate aligned films for HBC derivatives for transistor application.



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### REFERENCES

[1] Lin, F.-J.; Guo, C.; Chuang, W.-T.; Wang, C.-L.; Wang, Q.; Liu, H.; Hsu, C.-S.; Jiang, L. Directional Solution Coating by the Chinese Brush: A Facile Approach to Improving Molecular Alignment for High Performance Polymer TFTs, *Adv. Mater., Communication*, **2017**, *29*, 1606987.

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## WHAT MAKES A LAYER SELECTIVE? CHARGE SELECTIVITY AS A FUNCTION OF CHARGE TRANSPORT LAYER PROPERTIES FOR PEROVSKITE SOLAR CELLS

Christian Ahläng\*<sup>1</sup>, Syeda Qudsia<sup>2</sup>, Oskar Sandberg<sup>3</sup>, Mathias Nyman<sup>1</sup>, Jan-Henrik Smått<sup>2</sup>, Ronald Österbacka<sup>1</sup>

<sup>1</sup>Physics, Faculty of Science and Engineering and Center for Functional Materials,  
Åbo Akademi University, Porthaninkatu 3, 20500 Turku, Finland  
\*cahlang@abo.fi

<sup>2</sup>Physical Chemistry, Faculty of Science and Engineering and Center for Functional Materials,  
Åbo Akademi University, Porthaninkatu 3, 20500 Turku, Finland

<sup>3</sup>Department of Physics, Swansea University, Singleton Park, Swansea SA2 8PP Wales, United Kingdom

As the efficiency of perovskite solar cells is approaching the Shockley–Queisser limit, increasing efforts are put into finding more suitable charge transport layers. Charge transport layers ensure that majority charge carriers; holes for the hole transport layer and electrons for the electron transport layer, are extracted at the desired electrodes. A good charge transport layer will also minimize the surface recombination velocity for minority charge carriers; electrons at the hole transport layer and vice versa. Designing good charge transport layers is especially difficult if one wants to fabricate devices with long-term stability, using environmentally friendly techniques and therefore have to make do with rather thick layers that are not highly doped.

Charge transport layers are, ideally, charge selective, which is often taken to mean that majority charge carriers can pass through it, while minority charge carriers cannot. This criterion can be met, for example by choosing materials with appropriate energy levels, but minority charge carriers will still be able to recombine via interface trap states at the perovskite interface, and in some cases, this will be the dominating recombination mechanism of the device<sup>1</sup>. The role of charge transport layers for various thin-film solar cells has been investigated using effective parameters describing charge extraction, such as surface recombination velocity<sup>1-4</sup>. In general, no obvious connections can be made relating the material parameters of the selective layer to the effective parameters, but in some cases, such connections have been made between interfacial trap states and the surface recombination velocity<sup>3,4</sup>. In the case of perovskites solar cells, our understanding of recombination via interface trap states is still lacking and therefore it is unclear how different charge transport layers affect the surface recombination of minority charge carriers<sup>1</sup>.

In this study, we investigate how material properties of charge transport layers affect the charge selectivity of the contacts in the device and its solar cell performance. Utilizing one- and two-dimensional drift-diffusion simulations, we investigate how the energy levels, mobilities, doping concentration and morphology of a charge transport layer affect the recombination rate for minority charge carriers, as well as the extraction of majority charge carriers. Building upon this, we will provide numerical guidelines on how to find optimal charge transport layers for a particular perovskite layer or device structure, which can be determined by considering the trade-off between good majority carrier extraction and minimal minority carrier recombination.

### REFERENCES

- [1] Kirchartz, T.; Krückermeier L.; Unger E. L. Research Update: Recombination and open-circuit voltage in lead-halide perovskites *APL Materials* **2018**, *6* 100702.
- [2] Sandberg, O. J.; Nyman, M.; Österbacka, R. Effect of Contacts in Organic Bulk Heterojunction Solar Cells *Phys. Rev. Applied* **2014**, *1*, 024003.
- [3] Mora-Seró, I.; Bisquert, J. Effect of reduced selectivity of contacts on the current-potential characteristics and conversion performance of solar cells. *Sol. Energ. Mat. Sol. Cell.* **2004**, *81*, 51-62.
- [4] Brandt, R. E.; Mangan, N. M.; Li, J. V.; Lee, Y. S.; Buonassisi T. Determining interface properties limiting open-circuit voltage in heterojunction solar cells *J. Appl. Phys.* **2018**, *121* 185301.

## DUAL PLASMONIC ENHANCED ORGANIC POLYMER SOLAR CELLS BY INCORPORATING SILVER NANODISKS INTO HOLE-TRANSPORT LAYER AND GRATING STRUCTURE ON TOP ELECTRODE

T. Putnin <sup>1,2</sup>, C. Lertvachirapaiboon <sup>1</sup>, R. Ishikawa <sup>1</sup>, K. Shinbo <sup>1</sup>, K. Kato <sup>1</sup>, F. Kaneko <sup>1</sup>,  
K. Ounnunkad <sup>\*2</sup> and A. Baba <sup>\*1</sup>

<sup>1</sup> Graduate School of Science and Technology, Niigata University, Niigata, Japan  
Thitirat.pt091@gmail.com, chutiparn.l@eng.niigata-u.ac.jp, ishikawa@eng.niigata-u.ac.jp, kshinbo@eng.niigata-u.ac.jp, keikato@eng.niigata-u.ac.jp,  
fkaneko@eng.niigata-u.ac.jp, ababa@eng.niigata-u.ac.jp

<sup>2</sup> Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand  
Thitirat.pt091@gmail.com, suriyacmu@yahoo.com

In this work, we designed the nanoengineering of metallic nanostructures to enhance light harvesting of organic polymer thin film solar cells (OPSCs) by dual surface plasmon resonance (SPR) phenomena originated from grating-coupled configuration with Blu-ray disc recordable (BD-R) grating of current collector and addition of silver nanodisks (Ag NDs) series. Different types and sizes of metallic nanoparticles (NPs), gold (Au) NPs, Ag nanospheres (NSs), and Ag NPs, were employed for our study and blended separately into a PEDOT:PSS hole transport layer (HTL). The best devices of grating-imprinted structure Al/P3HT:PCBM/Ag NDs:PEDOT:PSS/ITO were fabricated. The results from *J-V* curves indicated that the power conversion efficiency (PCE) of grating substrate Al/P3HT:PCBM/PEDOT:PSS/ITO was 3.10 % which was better than that of flat substrate for 1.55 times while devices with flat Al and addition of Au NPs, Ag NSs, or Ag NDs in a HTL performed with the PCEs in a range of 3.15-3.37. We further developed the OPSCs with Al grating substrate by incorporating Ag NDs series into a PEDOT:PSS layer. The PCEs of the devices were increased around 11-21% as compared to that of a pristine device. This indicated that the light absorption enhancement at the active layer is attributed to GSPR and LSPR excitation with strong near-field distributions penetrated into absorption polymer, which could lead to higher efficiencies, thus resulting in better current generation.

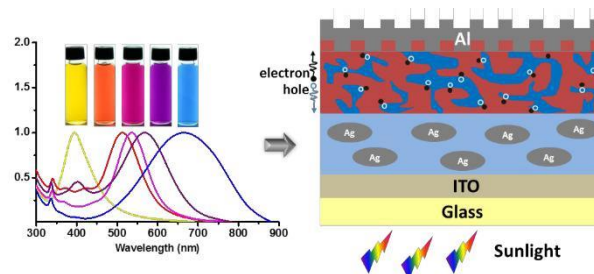


Figure 1. Schematic of organic polymer solar cell devices..

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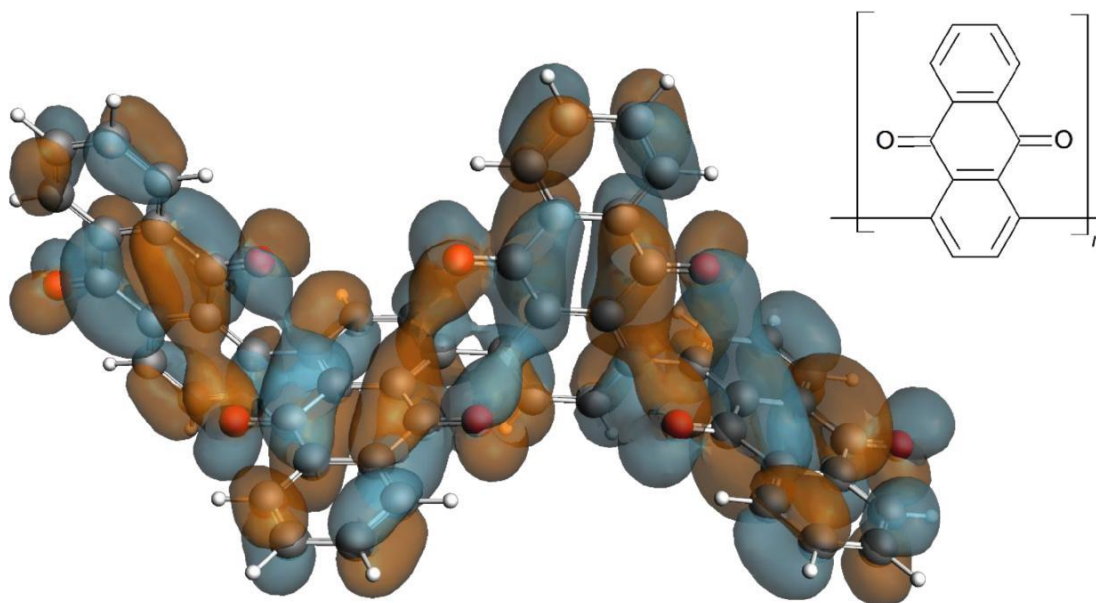
### REFERENCES

- [1] Nootchanat, S.; Pangdam, A.; Ishikawa, R.; Wongraveeb, K.; Shinbo, K.; Kato, K.; Kaneko, F.; Ekgasit, S.; Baba, A. Grating-Coupled Surface Plasmon Resonance Enhanced Organic Photovoltaic Devices Induced by Blu-ray Disc Recordable and Blu-ray disc Grating Structures, *Nanoscale* **2017**, *9*(15), 4963-4971.
- [2] Baba, A.; Aoki, N.; Shinbo, K.; Kato, K.; Kaneko, F. Grating-Coupled Surface Plasmon Enhanced Short-Circuit Current In Organic Thin-Film Photovoltaic Cells, *ACS Appl. Mater. Interfaces* **2011**, *3*(6), 2080-2084.

## UNEXPECTEDLY LARGE COUPLINGS BETWEEN ORTHOGONAL UNITS IN ANTHRAQUINONE POLYMERS

Rocco P. Fornari\*<sup>1</sup> and Piotr de Silva<sup>1</sup><sup>1</sup>Department of Energy Conversion and Storage, Technical University of Denmark, Kongens Lyngby, Denmark.  
rocfor@dtu.dk, pdes@dtu.dk

Organic materials offer a wide range of possible applications even in the field of energy storage where inorganic materials are prevalent. Polymers with quinone units in the main chain have the potential to be good redox-active electrode materials for batteries.[1,2] In particular, 1,4-polyanthraquinone (14PAQ) has been shown to have excellent redox behaviour and cycling stability both in Mg-ion [1] and Li-ion [2] batteries. Due to steric reasons, the monomers of 14PAQ are nearly orthogonal to each other.[3] However, its undoped conductivity has been reported to be comparable to that of semiconducting polymers.[4] In order to better explain this unexpected behaviour, we investigate with computational methods the charge transport and electrochemical properties of this class of polymers. Despite the large dihedral angle between monomers, which in principle should break the conjugation, electronic structure calculations show delocalization of electrons along the polymer chain (**Figure 1**). The couplings between frontier orbitals on neighbouring monomers are found to be larger than expected for such geometry but are not large enough to explain the good transport properties. Once the principles determining the unusual properties of this class of organic materials are understood, better performing polymers for energy storage and organic electronics can be designed.



**Figure 1.** LUMO of a 1,4-polyanthraquinone tetramer.

## REFERENCES

- [1] Pan, B.; Huang J.; Feng Z.; Zeng L.; He M.; Zhang L.; Vaughey J. T.; Bedzyk M. J.; Fenter P.; Zhang Z.; Burrell A. K.; Liao C. Polyanthraquinone-Based Organic Cathode for High-Performance Rechargeable Magnesium-Ion Batteries. *Adv. Energy Mater.* **2016**, *6*, 1600140.
- [2] Song, Z. ; Qian, Y. ; Gordin, M. L.; Tang, D. ; Xu, T. ; Otani, M. ; Zhan, H. ; Zhou, H. and Wang, D. Polyanthraquinone as a Reliable Organic Electrode for Stable and Fast Lithium Storage. *Angew. Chem. Int. Ed.* **2015**, *54*, 13947-13951.
- [3] Gautrot, J. E.; Hodge, P.; Cupertino, D.; Helliwell, M. Experimental evidence for carbonyl-p electron cloud interactions. *New J. Chem.* **2006**, *30*, 1801–1807.
- [4] Yamamoto, T.; Muramatsu, Y.; Lee, B.-L.; Kokubo, H.; Sasaki, S.; Hasegawa, M.; Yagi, T.; and Kubota, K. Preparation of New Main-Chain Type Polyanthraquinones. Chemical Reactivity, Packing Structure, Piezochromism, Conductivity, and Liquid Crystalline and Photonic Properties of the Polymers. *Chem. Mater.* **2003**, *15*, 4384-4393.



## ALTERNATIVE PRINTABLE INTERLAYERS FOR ORGANIC PHOTOVOLTAIC DEVICES

C. Carbonera\*<sup>1</sup>, A. Caneschi<sup>2</sup>, A. Cominetti<sup>3</sup>, A. Congiu<sup>4</sup>, M. Mannini<sup>5</sup>, S. Perucchini<sup>6</sup>, R. Po<sup>7</sup>, A. Savoini<sup>8</sup>,  
G. Serrano<sup>9</sup> and E. Trippodo<sup>10</sup>

<sup>1,3,4,6,7,8</sup> Solar Department, Decarbonization and Environmental R&D, Eni S.p.A., Novara, Italy  
*chiara.carbonera@eni.com, alessandra.cominetti@eni.com, annalisa.congiu@eni.com, sara.perucchini@eni.com,*  
*riccardo.po@eni.com, alberto.savoini@eni.com*

<sup>2,9</sup> Dipartimento di Ingegneria Industriale, Università degli Studi di Firenze and INSTM, Firenze, Italy.  
*andrea.caneschi@unifi.it, giulia.serrano@unifi.it*

<sup>5</sup> Dipartimento di Chimica "Ugo Schiff", Università degli Studi di Firenze and INSTM, Sesto Fiorentino (FI), Italy.  
*matteo.mannini@unifi.it*

<sup>10</sup> Dipartimento di Fisica e Astronomia, Università di Catania, Catania, Italy  
[elisa.trippodo@studium.unict.it](mailto:elisa.trippodo@studium.unict.it)

Polymer solar cells (PSCs) state-of-the art power conversion efficiencies (PCEs) have overpassed 13% [1-4] for what concerns laboratory scale devices and are attracting interest for potential large-area and large-scale applications. Indeed, there are still quite a number of issues that need to be addressed in order to be able to afford high throughput Roll-to-Roll production via printing techniques. Among these we can count not only technological limits but also materials related issues.

Now, one of the key layers in a PSC is the Hole Transporting Layer (HTL). On the small scale, this generally consists of a 10 nm thin MoOx layer, that is obtained via thermal evaporation methods. Both the material and the technique used at the small scale do not represent an option when thinking to a scaled production [5]. At the moment in printed OPV cells and modules various ink formulations of PEDOT:PSS are used but they seldom show a good wetting ability on any active layer. Actually, there are a few active layers that show to be compatible with them. Further investigation is needed to find out a good alternative to MoOx, printable, and "universal". In this work we focus on possible R2R printable layers able to replace the thermally evaporated top buffer layer. As mentioned above, PEDOT:PSS based inks work fine with P3HT and a few other polymers but they do not when combined with active layers based on several low band gap (LBG) polymers. Soluble transition metal derivatives have been suggested as possible alternative materials to PEDOT:PSS, but there are still drawbacks in their use [6]. We here describe alcoholic solutions of metallic polyoxometalate (M-POMs) as printable inks to be used as anodic interlayers in inverted PSCs, but also suited in conventional devices to replace PEDOT:PSS. These inks consist in solutions of a metal-based compound in alcohol such as ethanol. We here show that the results (PSC photovoltaic parameters) obtained by depositing this solution on the active layer of the devices by spin-coating are equal or better compared to the thermally evaporated MoOx layer. We also demonstrate the compatibility of this kind of inks with several active layers and show that the ink is compatible with printing techniques. Finally, we propose some hypothesis to explain the working mechanisms of the M-POMs based inks.

## REFERENCES

- [1] Zhao, W. ; Li, S. ; Yao, H. ; Zhang, S. ; Zhang, Y. ; Yang, B. and Hou, J. Molecular Optimization Enables over 13% Efficiency in Organic Solar Cells. *J. Am. Chem. Soc.* **2017**, *139*, 7148–7151.
- [2] Li, S. ; Ye, L. ; Zhao, W. ; Yan, H. ; Yang, B. ; Liu, D. ; Li, W. ; Ade, H. and Hou, J. A Wide Band Gap Polymer with a Deep Highest Occupied Molecular Orbital Level Enables 14.2% Efficiency in Polymer Solar Cells. *J. Am. Chem. Soc.* **2018**, *140*, 7159–7167.
- [3] Xiao, Z. ; Jia, X. and Ding, L. Ternary organic solar cells offer 14% power conversion efficiency. *Sci. Bull.* **2017**, *62*, 1562-1564.
- [4] Li, H. ; Xiao, Z. ; Ding, L. and Wang J. Thermostable single-junction organic solar cells with a power conversion efficiency of 14.62%. *Sci. Bull.* **2018**, *63*, 340-342.
- [5] Po', R. ; Bernardi, A. ; Calabrese, A. ; Carbonera, C. ; Corso, G. and Pellegrino, A. From lab to fab: how must the polymer solar cell materials design change?—an industrial perspective. *Energy Environ. Sci.* **2014**, *7*, 925-943.
- [6] Xu, M.-F. ; Cui, L.-S. ; Zhu, X.-Z. ; Gao, C.-H. ; Shi, X.-B. ; Jin, Z.-M. ; Wang, Z.-K. and Liao, L. S. Aqueous solution-processed MoO<sub>3</sub> as an effective interfacial layer in polymer/fullerene based organic solar cells. *Organic Electronics* **2013**, *14*, 657–664.

## DYE AND ELECTROACTIVE MONOMER CONJUGATES FOR SOLID-STATE DYE-SENSITIZED SOLAR CELLS

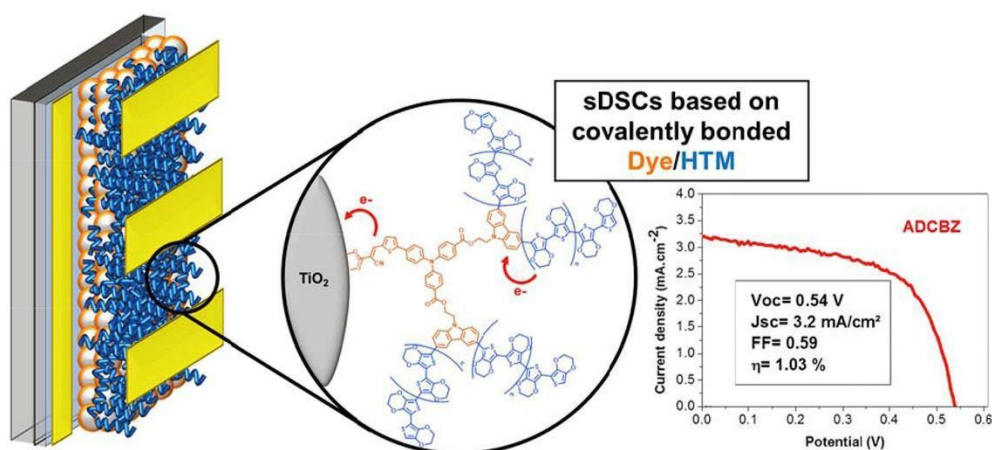
Zijun XU, Sébastien BELYNCK, Marie-Pierre SANTONI, Mohamed JOUINI, François MAUREL, and Chang-Zhi DONG

Department of Chemistry, ITODYS UMR 7086 CNRS, Paris, France  
zijun.xu@univ-paris-diderot.fr

Solar energy is the most abundant and represents the most promising energy supply for the future on a worldwide scale. Over the past decades, dye-sensitized solar cells (DSCs) have been investigated widely, since the emerging photovoltaic technology presents many attractive advantages, such as low cost, design opportunities (transparency, shape and color), and flexibility.

Our group has been focusing on the studies of solid-state DSCs by using conducting polymers (CP), produced by *in situ* copolymerization, as hole transport material (HTM) to replace the liquid  $I_3^-/I^-$  electrolyte, in order to prevent leakage and electrode corrosion which limits the commercialization of DSSCs<sup>[1]</sup>. Covalently linked dye and CP conjugates have been developed in our lab to improve the charge transfer by suppressing the physical contact between both components and the proof of concept has been validated by the promising results obtained<sup>[2]</sup>.

In this work, new types of metal-free triarylamine-based conjugates have been designed and prepared by using different bridging  $\pi$ -systems and linkers. Their physicochemical and electrochemical properties have been studied to understand the importance of the modified structure moieties. Their contribution to the performance, once they are integrated in solid-state DSCs, will be discussed.



**Figure 1.** Schematic representation of sDSCs based on covalently bonded Dye/HTM <sup>[2]</sup>

## REFERENCES

[1] Zhang, J.; Vlachopoulos, N.; Jouini, M.; Johansson, M. B.; Zhang, X.; Nazeeruddin, M. K.; Boschloo, G.; Johansson, E. M. J.; Hagfeldt, A. Efficient Solid-State Dye Sensitized Solar Cells: The Influence of Dye Molecular Structures for the In-Situ Photoelectrochemically Polymerized PEDOT as Hole Transporting Material. *Nano Energy* 2016, 19, 455–470

[2] Annette Delices, Jinbao Zhang, Marie-Pierre Santoni, Chang-Zhi Dong, François Maurel, Nick Vlachopoulos, Anders Hagfeldt and Mohamed Jouini. *Electrochimica Acta*, 2018, **269**, 163

## IMPACT OF SUBSTITUTIONAL GROUPS IN THE INTERFACIAL DOPING OF ORGANIC SEMICONDUCTORS

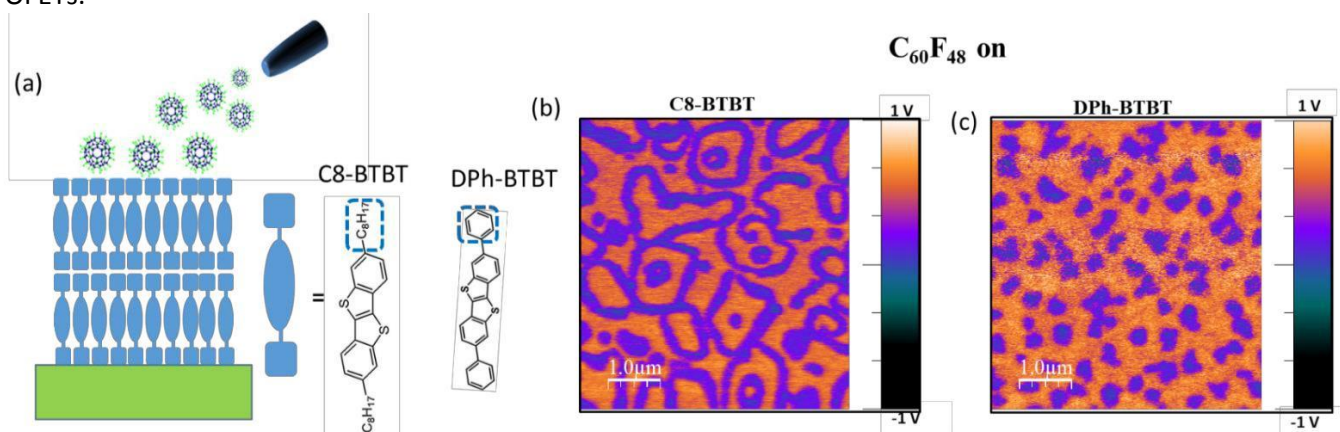
A. Babuji<sup>1</sup>, A. Pérez-Rodríguez<sup>1</sup>, F. Silvestri<sup>1</sup>, Y. H. Geerts<sup>2</sup>, N. Tessler<sup>3</sup>, O. Solomeshch<sup>3</sup>,  
B. C. Ocal<sup>1\*</sup> and E. Barrena<sup>1\*</sup><sup>1</sup>Instituto de Ciencia de Materiales de Barcelona, (ICMAB-CSIC), 08193 Bellaterra, Barcelona, Spain<sup>2</sup>Laboratoire de Chimie des Polymères, Faculté des Sciences, Université Libre de Bruxelles (ULB)  
CP206/1, Boulevard du Triomphe, 1050 Brussels, Belgium<sup>3</sup>Electrical Engineering Department, Nanoelectronic Center, Technion, Haifa 32000, Israel

\*cocal@icmab.es and \*ebarrena@icmab.es

Derivatives of BTBT([1]benzothieno[3,2- b][1]benzothiophene) are promising organic semiconductors(OSC) for organic field effect transistors(OFETs) due to its high intrinsic charge carrier mobility [1]. One critical issue in BTBT-based OFETs is the large injection barrier at gold electrodes. Contact doping (or surface transfer doping), where a thin injection layer is inserted between the organic film and electrode, has been successfully employed as a strategy to reduce the contact resistance in p-type organic field effect transistors(OFETs)[2]. The concept of contact doping relies on the charge transfer between OSC and dopant molecules across their interface. Still very little is known about how the doping efficiency depends on the specific structural and electronic properties of the interface. To address this issue, in this work, we focus on a comparative study of two BTBT derivatives, C8-BTBT and DPh-BTBT, substituted with alky chains and phenyl groups, respectively(Figure 1a).

As molecular p-dopant we have chosen the fluorinated fullerene, C<sub>60</sub>F<sub>48</sub> which shows low volatility, bulkier shape and

higher thermal stability than already established dopants[3]. In this work we investigate the structure, growth, thermal stability and electronic properties. We employ KPFM to follow the molecular organization of C<sub>60</sub>F<sub>48</sub> at the interface with increasing coverage and to quantify local changes in work function. The evolution of the crystallinity has been investigated by grazing Incidence Xray Diffraction(GIXD). To have a comprehensive picture, Photoelectron Spectroscopy (XPS and UPS) measurements have been performed as well to know more about the correlation between the structural and electronic properties at the diverse organic interfaces. The feasibility of the approach has been preliminary tested in OFETs.



**Figure 1.** (a) Scheme of the structure of C8-BTBT and DPh-BTBT molecules, (b), (c) Surface potential image of C<sub>60</sub>F<sub>48</sub> deposited on top of C8-BTBT and Ph-BTBT films (SiO<sub>2</sub>/Si substrate)

## REFERENCES

- [1] Takimiya, K.; Kunugi, Y.; Konda, Y.; Niihara, N.; Otsubo, T. 2,6-Diphenylbenzo[1,2-b:4,5-b']dichalcogenophenes: A New Class of High-Performance Semiconductors for Organic Field-Effect Transistors. *J. Am. Chem. Soc.* **2004**, *126*, 5084-5085.
- [2] Ante, F.; Kälblein, D.; Zschieschang, U.; Canzler, T. W.; Werner, A.; Takimiya, K.; Ikeda, M.; Sekitani, T.; Someya, T.; Klauk, H. Contact Doping and Ultrathin Gate Dielectrics for Nanoscale Organic Thin-Film Transistors. *Small.* **2011**, *7*, 1186-1191.
- [3] Kawasaki, S.; Aketa, T.; Touhara, H.; Okino, F.; Boltalina, O. V.; Gol'dt, I. V.; Troyanov, S. I.; Taylor, R. Crystal Structures of the Fluorinated Fullerenes C<sub>60</sub>F<sub>36</sub> and C<sub>60</sub>F<sub>48</sub>. *J. Phys. Chem. B.* **1999**, *103*, 1223-1225.

## ENERGY LEVEL ALIGNMENT OF BURIED METHYLAMMONIUM LEAD TRIIODIDE/TITANIUM DIOXIDE INTERFACE IN PEROVSKITE SOLAR CELLS

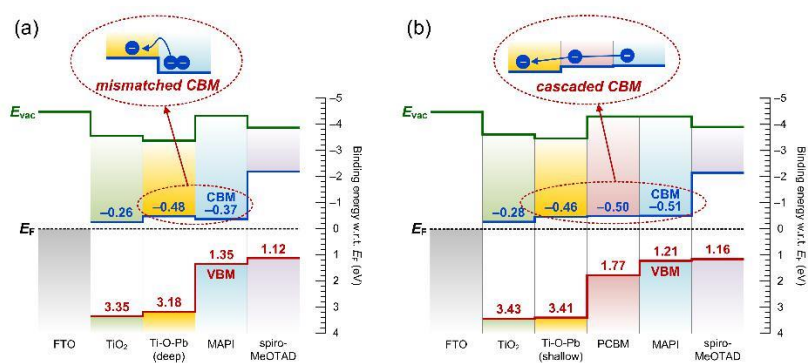
Junkyeong Jeong<sup>1,2</sup>, Hyunbok Lee<sup>\*3</sup> and Yeonjin Yi<sup>\*1,2</sup>

<sup>1</sup>Institute of Physics and Applied Physics, Yonsei University, Seoul, Republic of Korea

<sup>2</sup> Van der Waals Materials Research Center, Yonsei University, Seoul, Republic of Korea  
mylask@naver.com, yeonjin@yonsei.ac.kr

<sup>3</sup> Department of Physics, Kangwon National University, Chuncheon, Republic of Korea  
hyunbok@kangwon.ac.kr

Despite high power conversion efficiencies of perovskite solar cells (PSCs) using a TiO<sub>2</sub> electron transport layer, the MAPI/TiO<sub>2</sub> interface is believed as an electron accumulation position during device operation. To elucidate the cause of the electron accumulation, the energy level alignment of the MAPI/TiO<sub>2</sub> interface should be understood. However, the buried MAPI/TiO<sub>2</sub> interface forms after the thick MAPI layer deposition, and thus the electronic structure of the MAPI/TiO<sub>2</sub> interface cannot be measured using surface-sensitive photoelectron spectroscopy in a conventional stack-up manner. In this study, we investigated the electronic structure at the buried MAPI/TiO<sub>2</sub> interface via a removal of the MAPI and organic layers with solvent immersion. As a result, we reveal that the conduction band minimum (CBM) mismatch occurs owing to the Ti-O-Pb bonding on the TiO<sub>2</sub> surface. However, the [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM) layer was inserted, the CBM mismatch was removed owing to the high work function of PCBM, although the Ti-O-Pb bonding on the TiO<sub>2</sub> surface was not averted completely. Thus, the device performance of PSCs was significantly enhanced with the insertion of the PCBM layer.



**Figure 1.** Energy level diagram of spiro-MeOTAD/MAPI/ETL/FTO, where the ETL is (a) TiO<sub>2</sub> or (b) PCBM/TiO<sub>2</sub> (unit: eV).

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### REFERENCES

- [1] Fakharuddin, A.; Schmidt-Mende, L.; Garcia-Belmonte, G.; Jose, R.; Mora-Sero, I. Interfaces in Perovskite Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1700623.
- [2] Kim, H.-S.; Jang, I.-H.; Ahn, N.; Choi, M.; Guerrero, A.; Bisquert, J.; Park, N.-G. Control of I-V Hysteresis in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> Perovskite Solar Cells. *J. Phys. Chem. Lett.* **2015**, *6*, 4633-4639.
- [3] Kim, B. J.; Kim, D. H.; Kwon, S. L.; Park, S. Y.; Li, Z.; Jung, H. S. Selective Dissolution of Halide Perovskites as a Step Towards Recycling Solar Cells. *Nat. Commun.* **2016**, *7*, 11735.
- [4] Ip, A. H.; Quan, L. N.; Adachi, M. M.; McDowell, J. J.; Xu, J.; Kim, D. H.; Sargent, E. H. A Two-Step Route to Planar Perovskite Cells Exhibiting Reduced Hysteresis. *Appl. Phys. Lett.* **2015**, *106*, 143902.

## HOLE TRANSPORT LAYERS INFLUENCE ION MIGRATION IN PEROVSKITE SOLAR CELLS

**L. McGovern<sup>\*1</sup>, M. Futscher<sup>1</sup>, S. Sanchez<sup>2</sup> and B. Erhler<sup>1</sup>**

<sup>1</sup>Department, AMOLF, Amsterdam, the Netherlands  
*l.mcgovern@amolf.nl*

<sup>2</sup>LSPM, EPFL, Lausanne, Switzerland  
*sandy.sanchezalonso@epfl.ch*

Solar cells based on halide perovskites show efficiencies close to highly-optimized silicon solar cells. However, ions migrating in these perovskites lead to rapid device degradation which in turn impedes their growth towards a mature technology and rapid commercialisation. We recently showed that transient ion-drift is a powerful method to quantify activation energy, concentration, and diffusion coefficient of mobile ions in perovskite solar cells.

In this work, we look at the effect of the hole transport layer on the ion migration behaviour in mixed Cs<sub>0.05</sub>MA<sub>0.5</sub>FA<sub>0.45</sub>PbI<sub>1.5</sub>Br<sub>1.5</sub> perovskite devices. These devices are prepared in the “classic” n-i-p architecture comparing TiO<sub>2</sub> and SnO<sub>2</sub> as hole transport layers and in the “reverse” p-i-n architecture comparing NiO<sub>x</sub> and PTAA. We show a relation between the choice of hole transport layer and the concentration and diffusion coefficient of mobile ions. Our results shed light on the passivating behavior of transport layers such as NiO<sub>x</sub> and PTAA, a key to develop robust protocols for the fabrication of highly efficient perovskite devices.

## COMPREHENSIVE MODELLING STUDY OF SINGLET EXCITON DIFFUSION IN DONOR-ACCEPTOR DYADS: WHEN SHAPE MATTERS

Giacomo Londi\*<sup>1</sup>, Rishat Dilmurat<sup>1</sup>, Gabriele D'Avino<sup>2</sup>, Yoann Olivier<sup>1</sup> and David Beljonne<sup>1</sup>

<sup>1</sup> Laboratory for Chemistry of Novel Materials, University of Mons, Place du Parc, 20, 7000 Mons, Belgium  
Giacomo.LONDI@umons.ac.be, Rixiati.DILIMURATI@umons.ac.be, Yoann.OLIVIER@umons.ac.be,  
David.BELJONNE@umons.ac.be

<sup>2</sup> Institut Néel, CNRS and Grenoble Alpes University, 38042, Grenoble, France  
gabriele.davino@neel.cnrs.fr

Two small push-pull  $\pi$ -conjugated organic molecules (Figure 1) were studied in the context of their use as donors in bulk heterojunction (BHJ) organic photovoltaic devices. In vacuum-evaporated solar cells SA321 show a better power conversion efficiency (5.1%)<sup>1</sup> with respect to TV38 (2.2%)<sup>2</sup>. Along with their electron-acceptor counterpart, the SA321 molecule based solar cells have higher efficiency. It was suggested that this feature partly arises from an improved exciton diffusion.

Here, to achieve an in-depth microscopic picture for the relationships between primary chemical structure and excited-state properties, we adopted a fully atomistic modelling study of the energetics and dynamics of singlet electronic excitations in solid films of SA321 and TV38. More specifically, in order to gain access to the morphology of these materials, classical Force Field Molecular Dynamics simulations on the pristine molecules were performed. On the resulting morphologies, Time Dependent Density Functional Theory and MicroEletrostatic<sup>3</sup> calculations were carried out to assess the nature of the relevant electronic excitations and their energy landscape. Then, the internal and external reorganization energies were evaluated as well as the excitonic couplings between neighboring molecules that were injected into an energy transfer rate expression taken from the Marcus-Levich-Jortner formalism. Based on these rates, kinetic Monte Carlo simulations were performed in order to achieve the diffusion coefficient and the exciton diffusion length. Our results show that the exciton diffusion in these two small  $\pi$ -conjugated molecules is driven by their electronic properties and by their molecular shape.

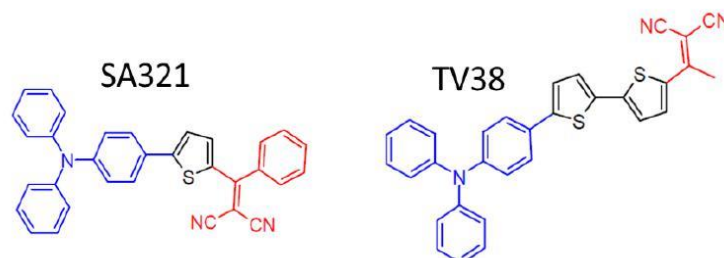


Figure 1: Chemical structures of SA321 and TV38

**Acknowledgments:** The work in Mons was supported by the European Union's Horizon 2020 research and innovation programme under Marie Skłodowska Curie Grant agreement No.722651 (SEPOMO). Computational resources were provided by the Consortium des Équipements de Calcul Intensif (CÉCI), funded by the Fonds de la Recherche Scientifiques de Belgique (F.R.S.-FNRS) under Grant No. 2.5020.11, as well as the Tier-1 supercomputer of the Fédération Wallonie-Bruxelles, infrastructure funded by the Walloon Region under Grant Agreement No. 1117545. D.B. is a FNRS Research Director.

### REFERENCES

1. Kozlov, O. V *et al.* Simple donor-acceptor molecule with long exciton diffusion length for organic photovoltaics. *Org. Electron.* **53**, 185–190 (2018).
2. Kozlov, O. V *et al.* Triphenylamine-Based Push–Pull Molecule for Photovoltaic Applications: From Synthesis to Ultrafast Device Photophysics. *J. Phys. Chem. C* **121**, 6424–6435 (2017).
3. D'Avino, G., Muccioli, L., Zannoni, C., Beljonne, D. & Soos, Z. G. Electronic polarization in organic crystals: A comparative study of induced dipoles and intramolecular charge redistribution schemes. *J. Chem. Theory Comput.* **10**, 4959–4971 (2014).

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## DESIGN AND INVESTIGATION OF LIGHT-EMITTING ELECTROCHEMICAL CELLS WITH INTERDIGITATED ELECTRODES UNDER PULSED ELECTRICAL EXCITATIONS

Lynda Dehbi, Mahmoud Chakaroun, Sarah Hamdad, Firas Hijazi and Azzedine Boudrioua

Laboratoire Physique des Lasers, Institut Galilée, Université Paris 13, Villetaneuse, France

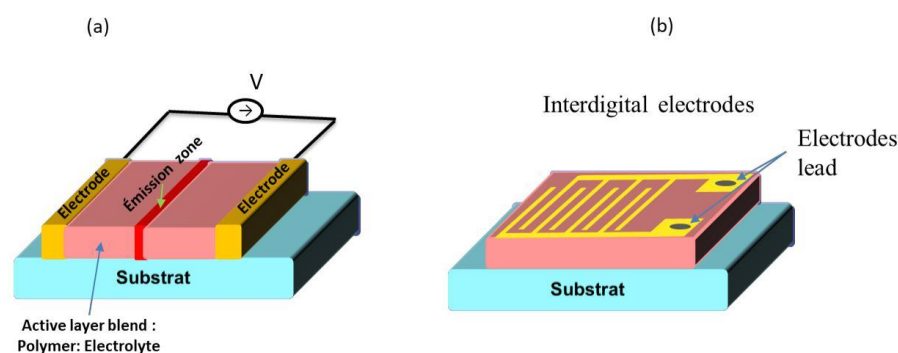
A. Mezeghrane, A. Belkhir and O. Lamrous

Laboratoire de Physique et Chimie Quantique, University of Tizi-Ouzou, BP 17 RP, 15000 Tizi-Ouzou, Algeria

dehbi.lynda@yahoo.fr

Light-emitting electrochemical cells (LECs) are one of the simplest and attractive candidates for low-cost light-emitting devices. In their simplest form, the basic LEC structure consists of an active organic layer that contains a luminescent polymer within an electrolyte of a mixed ionic/electronic conductor [1]. Under the application of an external electrical field, a p-n junction structure is formed which takes place near the anode and the cathode respectively. The light emission occurs in the bulk of the polymer film where the p and n doped regions coincide (figure1-a). They operate with low voltage, which allows high power efficiencies and air stable electrodes. However, despite their advantages, LEC devices suffer from low efficiency at high current densities. Since the discovery of the first LEC device in 1995 the impact of the different elements that the device contains (liquid electrolyte ions, polymer electronic states) on the device mechanism has thoughtfully been studied but there is no consensus about the device mechanism.

In this work, we report the study of a new design of light-emitting electrochemical cells by using interdigitated electrodes with different spacing ranging from  $4\mu\text{m}$  to  $1\text{mm}$  (figure1-b). The LEC device consists of ITO interdigital anode on top of a glass substrate covered by an emitting layer of a conjugated MEH-PPV polymer mixed with PEO polymer as an ionic conductor within an electrolyte solution. The various spacing configurations allow the study of different physical phenomena related to the operation of LECs. Besides, we designed and fabricated  $\mu$ -LEC devices in order to work under a pulsed electrical regime (1 -10 ns) and to have a strong timescales separation of the ionic and electronic phenomena [2]. The main objective is to study the mobility of each species and their contribution on the global operation mechanism of the LEC device.



**Figure 1:** Scheme of: (a) Light Electrochemical Cell (LEC), (b) interdigitated electrode device

### REFERENCES

- [1] E. Frestaab, R. D. Costa, J MATER. CHEM. C, "Light Emitting Electrochemical Cells", 5, (2017), 5643-5675
- [2] T. Sakanoue, J. Li, H. Tanaka, R. Ito, S. Ono, T. Takenobu, "High Current Injection into Dynamic p-n Homo Junction in Polymer Light-Emitting Electrochemical Cells", Adv. Mater., 29, (2017), 1606392 (1-7)

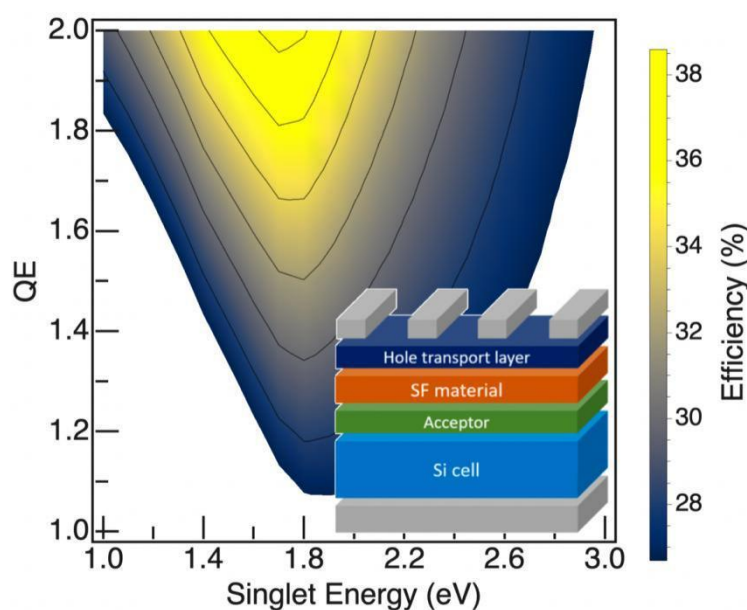
## EFFICIENCY POTENTIAL OF SINGLET FISSION ENHANCED SILICON SOLAR CELLS USING DIFFERENT ENERGY TRANSFER SCHEMES

Benjamin Daiber\*<sup>1</sup>, Koen v.d. Hoven<sup>1</sup>, Moritz H. Futscher<sup>1</sup> and Bruno Ehrler<sup>1</sup>

<sup>1</sup> Center for Nanophotonics, AMOLF, Amsterdam, The Netherlands  
*b.daiber@amolf.nl, ehrler@amolf.nl*

Silicon is the dominating solar cell material, therefore add-ons on the silicon solar cell that can improve the power conversion efficiency are urgently needed. In certain organic materials singlet fission generates two triplet (spin 1) excitons from one singlet (spin 0) exciton. If the triplet excitons are harvested in the silicon solar cell the efficiency could be dramatically increased, as we show. There are different transfer pathways between the organic singlet fission material and silicon. We have simulated the achievable efficiency for each transfer path with realistic assumptions such as a singlet fission quantum efficiency of 1.7 (1.7 e-h pairs per high energy photon), a transmission loss of 5%, and a 50 meV Stokes shift in case of optical transmission.

Even with these realistic assumptions, the efficiency of a silicon/singlet fission solar cell can be as high as 34% when combined with the current record silicon solar cell of 27%. We found that dissociating the triplet excitons at the interface leads to a large potential efficiency gain because a triplet energy lower than the silicon bandgap still leads to charge generation, and allows for high current generation. We also find that current singlet fission materials do not absorb light strongly enough, motivating sensitization schemes. Finally, we compare the singlet fission/silicon solar cells to the efficiency potential of perovskite/silicon tandem solar cells. We find that tandem cells are particularly beneficial for a silicon base cell with low efficiency, while a highly efficient silicon solar cells benefits less from the perovskite top cell. In contrast, the efficiency gain from the singlet fission layer is almost constant for all silicon base cells, and for highly efficient silicon cells would clearly outperform a high-efficiency perovskite top cell.



**Figure 1.** Efficiency of a direct charge transfer singlet fission-silicon solar cell, as function of singlet energy level and quantum efficiency of the singlet fission process



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## ENHANCEMENT OF ELECTRON INJECTION INTO AN OLED POLYMER TRANSPORT LAYER USING A DIMERIC DOPANT

Hannah L. Smith<sup>\*1</sup>, Stephen Barlow<sup>2</sup>, Seth Marder<sup>2</sup> and Antoine Kahn<sup>1</sup>

<sup>1</sup>Electrical Engineering, Princeton University, Princeton, NJ, USA.

*hannahsmith@princeton.edu*

<sup>2</sup>Center for Organic Photonics and Electronics and School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA, USA.

Improving electron injection into the emissive layer via doping of the electron transport layer (ETL) is one key method for increasing the efficiency of organic light emitting diodes (OLEDs). Incorporating an n-dopant into the ETL enables the increase in conductivity and shifts the Fermi level closer to the lowest unoccupied molecular orbital (LUMO), thus improving the injection of electrons. In this work, we investigate a new n-type dimeric dopant [RuCp\*TMDA]<sub>2</sub> of the same class of air-stable reducing agents introduced by Guo et al. [1]. The dopant is incorporated into the polymer F8BT [poly(9,9-dioctylfluorene-alt-benzothiadiazole)] via solution processing. F8BT films are spin-coated for characterization or device fabrication. Ultra-violet and inverse photoelectron spectroscopies (UPS, IPES) are used to determine the F8BT ionization energy (IE = 5.7 eV), electron affinity (EA = 2.7 eV), work function and Fermi level (E<sub>F</sub>) position. UPS shows a 300 meV shift of the Fermi level of the doped F8BT in comparison to the undoped F8BT, to ~ 0.5 eV below the LUMO of the polymer. This shift controlled by the n-dopant correlates with an increase in conductivity of over two orders of magnitude relative to the undoped material. Doping appears to follow the mechanism of dimer cleavage reported in previous work [2], which results from a photoactivation process achieved with photons with energy larger than the optical bandgap of F8BT. OLEDs fabricated using the doped F8BT layer as an ETL demonstrate a substantial improvement in luminance and external quantum efficiency (EQE) when compared to identical OLEDs fabricated with undoped F8BT.

### REFERENCES

- [1] Guo, S., Kim S. B., Mohapatra S., Qi Y., Sajoto T., Kahn A., Marder S.R., Barlow S. n-Doping of Organic Electronic Materials Using Air-Stable Organometallics. *Adv. Mat.* **2012**, 24, 699.
- [2] Lin, X., Wegner, B., Lee, K. M., Fusella, M. A., Zhang, F., Moudgil, K., Rand, B. P., Barlow, S., Marder, S. R., Koch, N., Kahn, A. Beating the thermodynamic limit with photoactivation of n-doping in organic semiconductors. *Nat. Mater.* **2017**, 16, 1209.

## THEORETICAL INVESTIGATION OF HEAT TRANSPORT IN BTBT DERIVATIVES

A. Vercouter\*<sup>1</sup>, D. Beljonne\*<sup>1</sup> and J. Cornil\*<sup>1</sup>

<sup>1</sup> Laboratory for Chemistry of Novel Materials, University of Mons, Place du Parc 20, B-7000 Mons, Belgium.  
*Alexandre.VERCOUTER@umons.ac.be, Jerome.CORNIL@umons.ac.be, David.Beljonne@umons.ac.be*

Thermoelectricity (TE) relies on the ability to convert heat into electricity or the inverse and show great potentials for applications in power generation as well as solid-state cooling and heating. Thermoelectric performances are defined by the dimensionless figure of merit  $ZT = \sigma\alpha^2T/(\kappa_e + \kappa_L)$  where  $\sigma$ ,  $\alpha$ ,  $\kappa_e$  and  $\kappa_L$  refer to the electrical conductivity ( $\text{cm}^2/\text{V.s}$ ), the Seebeck coefficient ( $\text{V/K}$ ), and electronic and lattice thermal conductivities ( $\text{W/m.K}$ ), respectively. Up to now, commercial modules are built with toxic and expensive inorganic materials; this has recently motivated the use of doped organic semiconductors. Whereas their charge transport properties have been widely studied in recent years, the design of thermoelectric modules based on organic semiconductors is still limited by the lack of data on thermal transport. In order to tackle this issue, this work has been dedicated to the theoretical characterization of the lattice thermal conductivity in single crystals of organic semiconductors widely used in (opto-) electronic devices.<sup>[1]</sup> More specifically, 2,7-dialkyl[1]benzothieno[3,2-b][1]benzothiophene ( $\text{C}_n$ -BTBTs) derivatives are promising candidates for the elaboration of efficient thermoelectric devices. They display quite decent field-effect transistor properties<sup>[2]</sup> and an earlier theoretical investigation revealed that certain  $\text{C}_{12}$ -BTBTs isomers show unprecedented hole mobility values.<sup>[3]</sup> Thus, their lattice thermal conductivity has been estimated by performing and comparing both out-of-equilibrium approaches<sup>[4,5]</sup> implemented in the LAMMPS package.

**Acknowledgments:** The research was supported by the National Fund for Scientific Research (F.R.S-FNRS) under Grant. Computational resources were provided by the Consortium des Equipements de Calcul Intensif (CECI). J. Cornil and D. Beljonne are FNRS research directors.

## REFERENCES

- [1] B. Russ et al., Organic thermoelectric materials for energy harvesting and temperature control, *Nat. Mat.* 16050, 1, 2016.
- [2] H. Minemawari et al., Inkjet printing of single-crystal films, *Nature*, 475, 2011.
- [3] Y. Tsutsui, G. Schweicher, et al., Unraveling Unprecedented Charge Carrier Mobility Through Structure Property Relationship of Four Isomers of Didodecyl[1]benzothieno[3,2-b][1]benzothiophene, *Adv. Mater.*, 28, 2016.
- [4] F. Müller-Plathe et al., Cause and effect reversed in non-equilibrium molecular dynamics: an easy route to transport coefficients, *Comput. Theor. Polym. Sci.*, 9, 203, 1999.
- [5] C. Melis et al., Calculating thermal conductivity in a transient conduction regime: theory and implementation, *Eur. Phys. J. B.*, 2014.

## ULTRA-FAST CRYSTALLIZATION DYNAMICS AT AN ORGANIC-INORGANIC INTERFACE REVEALED IN REAL TIME BY GRAZING INCIDENCE FAST ATOM DIFFRACTION

A. Momeni<sup>1</sup>, E. M. Staicu Casagrande<sup>1</sup> and H. Khemliche<sup>1</sup>

<sup>1</sup> Institut des Sciences Moléculaires d'Orsay, CNRS, Univ. Paris-Sud, Université Paris-Saclay, Bât.520, Université Paris-Sud, F-91405 Orsay cedex, France.

*anouchah.momeni@u-psud.fr, elena-magdalena.staicu-casagrande@u-psud.fr  
hocine.khemliche@u-psud.fr*

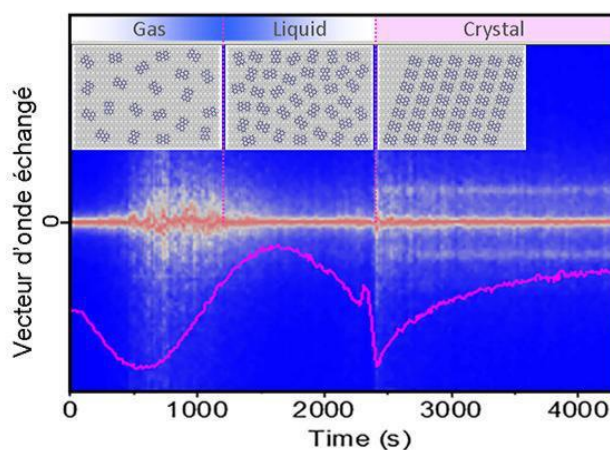
Organization modes of thin organic layers on inorganic substrates determine for a large part their optical and electronic properties. Being able to precisely describe and then gain control over the organization dynamics of these systems may provide a mean to select and optimize the final properties. This is an essential challenge in a context where a multitude of applications of these hybrid nanostructures are predicted. One could then be able to produce high quality organic layers in a reproducible manner.

From the experimental point of view, the breakthrough may come from a new analytical approach that is highly sensitivity to the last surface plane, non-invasive and able to characterize in real time the growth process [1].

Grazing Incidence Fast Atom Diffraction (GIFAD) seems to fulfill these requirements [2]. It relies on scattering of  $\sim 1$  keV He atoms at grazing incidence angles near  $1^\circ$ . The scattered particles are collected on a position sensitive detector; their intensity distribution provides a wealth of information of the surface properties.

Results on the growth of a monolayer perylene (C<sub>20</sub>H<sub>12</sub>) on Ag(110) reveal an unexpected and complex organization dynamics[3]. In particular, crystallization of the first layer into a very dense packing occurs quasi-instantaneously at a critical coverage reached by molecule incorporation from the second layer. Following this transition, the diffraction pattern is clearly resolved, indicating a long rang order in the crystalline monolayer.

The rich organization dynamics observed on this model organic/inorganic interface and its dependence on the growth rate should offer the possibility to produce very high quality organic layers.



**Figure 1.** Evolution of the GIFAD reflectivity during deposition of perylene on Ag(110), with the evolution of the diffraction pattern. An ultrafast transition to a dense crystalline phase appears at 2400s.

### REFERENCES

- [1] Atkinson, P et al In Dynamic grazing incidence fast atom diffraction during molecular beam epitaxial growth of GaAs Applied Physics Letters 105, 021602 (2014)
- [2] Khemliche, H. et al Grazing incidence fast atom diffraction: An innovative approach to surface structure analysis In Applied Physics Letters 95, 151901(2009).
- [3] Momeni, A et al. Ultrafast Crystallization Dynamics at an Organic–Inorganic Interface Revealed in Real Time by Grazing Incidence Fast Atom Diffraction In J. Phys. Chem. Lett. 2018, 9, 908–913

P30

## EXCITON DIFFUSION AND DISSOCIATION DYNAMICS IN PEROVSKITE NANOCRYSTAL-FULLERENE COMPOSITES

En-Ping Yao<sup>1,2</sup>, Bernhard J. Bohn<sup>1,2</sup>, Yu Tong<sup>1,2</sup>, He Huang<sup>1,2</sup>, Lakshminarayana Polavarapu<sup>1,2</sup>, Jochen Feldmann<sup>1,2</sup><sup>1</sup>Chair for Photonics and Optoelectronics, Nano-Institute Munich, Department of Physics, Department of Physics, Ludwig-Maximilians-Universität (LMU), Königinstr. 10, 80539 Munich, Germany.<sup>3</sup>Nanosystems Initiative Munich (NIM) and Center for NanoScience (CeNS), Schellingstr. 4, 80799 Munich, Germany  
*EnP.Yao@physik.uni-muechen.de*

Solution-processable perovskite nanocrystals (NCs) are gaining increasing interest in the field of photovoltaics because of their enhanced stability compared to their thin-film counterparts. However, charge transfer dynamics in perovskite NC based light-harvesting systems are not well understood. By applying femtosecond differential transmission (DT) spectroscopy we investigate the photoinduced charge transfer from inorganic perovskite CsPbBr<sub>3</sub> NCs to the fullerene derivative phenyl-C61-butyric acid methyl ester (PCBM) for two fundamentally different architectures, namely layer-by-layer heterostructures as well as blend structures. Varying the thickness of the NC layer on top of the PCBM in the layer-by-layer heterostructure, an exciton diffusion length of  $290 \pm 28$  nm for CsPbBr<sub>3</sub> NC is extracted. The diffusion process is followed by an ultrafast exciton dissociation (within 200 fs) at the CsPbBr<sub>3</sub> NC/PCBM interface. In blend structures an overall faster charge transfer process is observed. Furthermore, photoconductivity measurements on a blend structure-based photodetector reveal an effective charge extraction from the active layer resulting in a high photosensitivity. DT measurements on this blend structure including adjacent electron- or hole-transport layers give insight into the extraction process and suggest a certain degree of phase segregation, which assists the charge collection.

**Acknowledgments:** This research work was supported by the Bavarian State Ministry of Science, Research, and Arts through the grant “Solar Technologies go Hybrid (SolTech)”, by the German Research Foundation (DFG) through the Excellence Cluster “e-conversion”, and by the European Union’s Framework Programme for Research and Innovation Horizon 2020 (2014-2020) under the Marie Skłodowska-Curie Grant Agreement No. 754388 (E.-P. Yao) and from LMU Munich’s Institutional Strategy LMUexcellent within the framework of the German Excellence Initiative (No. ZUK22).

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## SURFACTANT-FREE MINIEMULSION FOR LOW BAND GAP ROD-COIL BLOCK COPOLYMER WATER-PROCESSABLE NANOPARTICLES: A NEW SUSTAINABLE APPROACH FOR ORGANIC SOLAR CELLS

Stefania Zappia<sup>1\*</sup>, Anna Maria Ferretti<sup>2</sup>, Guido Scavia<sup>1</sup>, Umberto Giovanella<sup>1</sup>, Varun Vohra<sup>3</sup>, Tersilla Virgili<sup>4</sup>, Lucia Ganzer<sup>4</sup>, Mattia Russo<sup>4</sup>, and Eduardo Arias,<sup>5</sup> Ivana Moggio,<sup>5</sup> and Silvia Destri<sup>1</sup>

<sup>1</sup>Istituto per lo Studio delle Macromolecole (ISMAC), Consiglio Nazionale delle Ricerche (CNR),  
via A. Corti 12, 20133 Milano, ITALY.

*s.zappia@ismac.cnr.it, g.scavia@ismac.cnr.it, u.giovanella@ismac.cnr.it, s.destri@ismac.cnr.it*

<sup>2</sup>Istituto di Scienze e Tecnologie Molecolari (ISTM), Consiglio Nazionale delle Ricerche (CNR), Lab. Nanotecnologie,  
via G. Fantoli 16/15, 20138 Milano, ITALY.

*anna.ferretti@istm.cnr.it*

<sup>3</sup>University of Electro-Communications 1-5-1 Chofugaoka, Chofu, Tokyo 182-858, JAPAN

*varun.vohra@uec.ac.jp*

<sup>4</sup>Istituto di Fotonica e Nanotecnologie (IFN), Consiglio Nazionale delle Ricerche (CNR),  
P.zza Leonardo Da Vinci 32, 20132 Milano, ITALY

*tersilla.virgili@polimi.it, lucia.ganzer@polimi.it, mattia.russo@polimi.it* <sup>5</sup>Centro de Investigación en Química Aplicada (CIQA), Blvd. Enrique Reyna Herosillo 140, 25294 Saltillo, MEXICO *ivana.moggio@ciqa.edu.mx, eduardo.arias@ciqa.edu.mx*

Water-processable organic nanoparticles (WPNPs) of semiconducting polymers are receiving wide attention for optoelectronic applications due to their simple fabrication and tunable properties. The WPNP-based approach could be appealing to control active layer morphology in optoelectronic devices, such as organic photovoltaics (OPVs), organic light-emitting diodes, and organic field-effect transistors.<sup>1</sup>

Here we will present a series of four amphiphilic low band gap (LBG) rod-coil block copolymers (BCPs), constituted by a LBG polymer, PCPDTBT, as electron donor material, and differing for the poly-4-vinylpyridine (P4VP)-based flexible blocks with different length and chemical composition.<sup>2,3</sup> We exploited a surfactant-free miniemulsion approach to prepare suspensions stabilized in aqueous medium by the coil block in the BCPs. In order to elucidate the coil block role on the WPNP morphology and stability, we performed a complete WPNP characterization with DLS, TEM, STEM-EDX, and AFM. This study revealed that the rod blocks assemble mainly into the WPNP inner part while the 4VP-based coil segments segregate at the WPNP edge, producing *core-shell like* nanostructures.<sup>4</sup>

Moreover, we prepared semiconducting blend WPNPs by combining the LBG rod-coil BCPs with [6,6]-phenyl-C61-butyric acid methyl ester (PC<sub>61</sub>BM), which can act as electron acceptor in OPVs. We achieved adequate morphologies in the blend WPNP aqueous suspensions, without non-conducting surfactant use. Pump-probe measurements were used to gain information on ultrafast phenomena, such as donor-acceptor charge generation rate into the blend WPNP casted films. Thus, we were able to prepare working OPV devices, exhibiting high short-circuit current density ( $J_{sc}=11.5 \text{ mA}\cdot\text{cm}^{-2}$ , PCE 2.5%), with a sustainable fabrication process, considerably reducing halogenated solvent use.<sup>5</sup>

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### REFERENCES

- [1] Organic Electronics: Emerging Concepts and Technologies, **2013**, Wiley-VCH.
- [2] Zappia, S.; Mendichi, R.; Battiato, S.; Scavia, G.; Mastria, R.; Samperi, F.; Destri, S. *Polymer* **2015**, *80*, 245.
- [3] Zappia, S.; Di Mauro, A.E.; Mastria, R.; Rizzo, A.; Curri, M.L.; Striccoli, M.; Destri, S. *Eur Pol. J.* **2016**, *78*, 352.
- [4] Ferretti, A.M.; Zappia, S.; Scavia, G.; Giovanella, U.; Villafiorita-Monteleone, F.; Destri, S. *Polymer* **2019**, *174*, 61.
- [5] Zappia, S.; Scavia, G.; Ferretti, A.M.; Giovanella, U.; Vohra, V.; Destri, S. *Adv. Sustainable Syst.* **2018**, *2*, 1700155.

**C-SI SOLAR CELLS WITH TETRACENE AS SINGLET FISSION SENSITIZER:  
ORGANIC INTERLAYERS AS HYBRID INTERFACE MODIFIERS**

**Jens Niederhausen\*<sup>1</sup>, Clemens Gersmann<sup>2</sup>, Rowan W. MacQueen<sup>3</sup>, Martin Liebhaber<sup>4</sup>, Moritz H. Futscher<sup>5</sup>,  
Benjamin Daiber<sup>6</sup>, Bruno Ehrler<sup>7</sup>, Klaus Lips<sup>8</sup>**

<sup>1,2,3,4,8</sup> Insitut für Nanospektroskopie and Energy Materials In-Situ Laboratory Berlin (EMIL), Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany.

*jens.niederhausen@helmholtz-berlin.de, cgersmann@gmail.com, rowan.macqueen@helmholtz-berlin.de,  
martin\_liebhaber@gmx.net, lips@helmholtz-berlin.de*

<sup>5,6,7</sup> AMOLF, Center for Nanophotonics, Science Park 104, 1098 XG Amsterdam, The Netherlands.  
*M.Futscher@amolf.nl, B.Daiber@amolf.nl, B.Ehrler@amolf.nl*

With conventional c-Si solar cells approaching their theoretical efficiency limit, large research efforts are currently devoted to addressing their fundamental loss mechanisms. One appealing strategy to reduce losses due to carrier thermalization is the implementation of organic layers that can split the energy of blue photons into two triplet excitons via singlet fission. [1] However, efficiently harvesting these excitons relies on favorable excited state dynamics at the hybrid organic/c-Si interface. [2] The introduction of suitable ultrathin organic interlayers can assist this process two ways: (i) they can be used to tune the interfacial energy-level alignment and thus promote exciton dissociation at the hybrid interface and (ii) they can act as charge acceptor, thereby shifting the exciton dissociation process to the organic/organic interface.

In this work, we employed tetracene (Tc) as singlet fission sensitizer and tested two different interlayer materials, Buckminsterfullerene (C<sub>60</sub>) and 2,2'-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6TCNNQ). C<sub>60</sub> has already been shown to facilitate efficient harvesting of singlet fission-generated excitons [1, 3, 4], whereas its effectivity to tune the interfacial energy-level alignment is only moderate. In contrast, F6TCNNQ has been found to be extremely potent in increasing the work functions of inorganic semiconductors [5]. F6TCNNQ and C<sub>60</sub> can therefore be expected to preferably induce schemes (i) and (ii), respectively.

We performed photoelectron spectroscopy to monitor the formation of the inorganic/organic and organic/organic interfaces and their effect on the energy-level alignment. By means of time-resolved photoluminescence and external quantum efficiency measurements we then evaluated the interlayers' effect on the exciton dynamics at the hybrid interfaces. Together with supplemental structural characterizations we were able to identify some pitfalls that thus far prevented us to successfully employ organic interlayers to improve the triplet exciton harvest yield.

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## REFERENCES

- [1] Pazos-Outón, Luis M. *et al.*, A Silicon–Singlet Fission Tandem Solar Cell Exceeding 100% External Quantum Efficiency with High Spectral Stability. *ACS Energy Lett.* **2017**, 2, 476–480.
- [2] MacQueen, R. W. *et al.*, Crystalline silicon solar cells with tetracene interlayers: the path to silicon-singlet fission heterojunction devices, *Mater. Horiz.* **2018**, 5, 1065-1075.
- [3] Wai-Lun Chan *et al.*, Observing the Multiexciton State in Singlet Fission and Ensuing Ultrafast Multielectron Transfer. *Science* **2011**, 334, 1541.
- [4] Daniel N. Congreve *et al.*, External Quantum Efficiency Above 100% in a Singlet-Exciton-Fission -Based Organic Photovoltaic Cell. *Science* **2013**, 340, 334.
- [5] T. Schultz *et al.*, Impact of surface states and bulk doping level on hybrid inorganic/organic semiconductor interface energy levels. *J. Appl. Phys.* **2018**, 123, 245501.

P33

### COMBINED STM AND DFT STUDY: THE PARTIAL ADSORPTION OF A NON-CONJUGATED DONOR-ACCEPTOR-DYAD ON Pt(111)

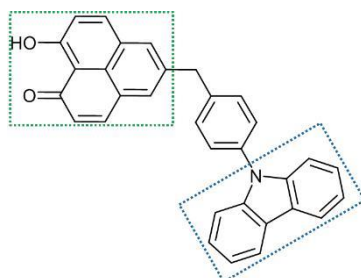
R. Ebeling<sup>\*1</sup>, N. P. Arasu<sup>2</sup>, L. Bensch<sup>3</sup>, T. J. J. Müller<sup>3</sup>, H. Vázquez<sup>2</sup> and S. Karthäuser<sup>1</sup>

<sup>1</sup>Forschungszentrum Jülich GmbH, Peter Grünberg Institut – Elektronische Materialien (PGI-7), Jülich, Germany  
r.ebeling@fz-juelich.de

<sup>2</sup>Institute of Physics, Academy of Sciences of the Czech Republic, Prague 6 CZ-162 00, Czech Republic

<sup>3</sup>Institut für Organische und Makromolekulare Chemie, Heinrich-Heine Universität Düsseldorf, Düsseldorf 40225, Germany

Single 5-[4-(9H-Carbazol-9-yl)benzyl]-9-hydroxy-1H-phenalen-1-on (CBHP) molecules, a new and promising kind of molecular switches, were analysed on a Pt(111) surface by low temperature ultra-high vacuum scanning tunneling microscopy (LT-UHV STM). These dyads are composed of a phenalenon (acceptor) derivative and a carbazol (donor) derivative, which are two delocalized  $\pi$ -systems separated by a methylene-linker and a phenyl group (see Figure 1). Their molecular arrangement on the substrate surface is essential for possible applications in nanoelectronics [1]. By detailed analysis of the spatially resolved electronic and topographic features of the molecule, we were able to distinguish three different on-surface states of CBHP with partial adsorption to the substrate. As the coupling at the molecule/metal interface plays a crucial role for the reversible or irreversible switching behaviour of the used molecule [2, 3], these orbital resolved STM results were compared to DFT calculations of single CBHP molecules on a metal surface. Supported by additional scanning tunneling spectroscopy (STS) measurements we were able to get detailed insight into the electronic states of the different configurations of CBHP on Pt(111). These results, in combination with the careful investigation of possible electronic triggers for on surface conformation changes identify CBHP as a switchable molecule with different partial adsorption states while adsorbed on a metallic surface.



**Figure 1.** Structural formula of the CBHP molecule with its donor (blue) and acceptor (green) part.

**Acknowledgments:** The authors gratefully acknowledge financial support from the Volkswagen Stiftung through the ‘Optically Controlled Spin Logic’ project.

#### REFERENCES

- [1] Morgenstern, K. Isomerization Reactions on Single Adsorbed Molecules. *Accounts of Chemical Research* **2009**, 42, 213-223.
- [2] McNellis, E. R.; Meyer, J.; Reuter, K. Azobenzene at Coinage Metal Surfaces: Role of Dispersive Van Der Waals Interactions. *Physical Review B* **2009**, 80, 205414.
- [3] Comstock, M. J.; Levy, N.; Kirakosian, A.; Cho, J.; Lauterwasser, F.; Harvey, J. H.; Strubbe, D. A.; Fréchet, J. M. J.; Trauner, D.; Louie, S. G.; Crommie, M. F. Reversible Photomechanical Switching of Individual Engineered Molecules at a Metallic Surface. *Phys. Rev. Lett.* **2007**, 99, 038301.

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**CHARGE-TRANSFER STATES AT ORGANIC INTERFACES:  
IMPACT OF STATIC AND DYNAMIC DISORDERS**

**Veaceslav Coropceanu,<sup>1</sup> Zilong Zheng,<sup>1</sup> and Jean-Luc Brédas<sup>1</sup>**

<sup>1</sup>School of Chemistry and Biochemistry and Center for Organic Photonics and Electronics Georgia Institute of Technology, Atlanta, Georgia 30332-0400 *coropceanu@gatech.edu*

The charge-transfer electronic states formed at donor-acceptor interfaces play a critical role in determining the performance of organic solar cells as they mediate exciton dissociation, charge separation, and charge recombination processes. In general, the charge-transfer states are characterized by an energy distribution that arises due to contributions related to dynamic disorder and static disorder. We have developed an approach that combines molecular dynamics simulations and density functional theory calculations with ensemble and time average procedures, and allows the evaluation of both static and dynamic disorder contributions. We show that each of these two disorder components can be partitioned into contributions related to the energetic disorder of the transport states and to the disorder associated with the hole-electron electrostatic interaction energies. We apply our methodology to evaluate the energy distributions of the CT states in representative bulk heterojunctions based on both fullerene and non-fullerene acceptors. The impact of static and dynamic disorders on radiative and non-radiative geminate recombination processes is also discussed.

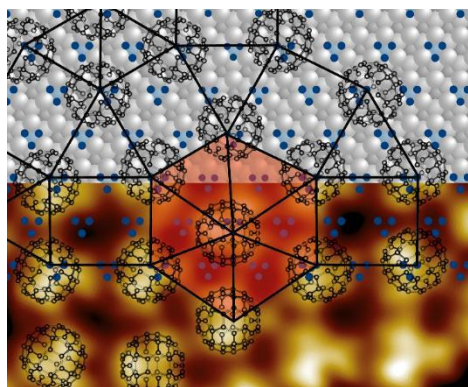


## WELL SEPARATED SWITCHING ELEMENTS IN A 2D-DODECAGONAL FULLERENE QUASICRYSTAL

Silvia Karthäuser\*<sup>1</sup>, Michael Paßens<sup>1</sup>, Michael Feuerbacher<sup>2</sup>, Vasile Caciuc<sup>3</sup> and Nicolae Atodiresei<sup>3</sup><sup>1</sup> Peter Grünberg Institut (PGI-7) and JARA-FIT, Forschungszentrum Jülich GmbH, Jülich, GERMANY.*s.karthaeuser@fz-juelich.de*<sup>2</sup> Peter Grünberg Institut (PGI-5) and Ernst Ruska-Centre, Forschungszentrum Jülich GmbH, Jülich, GERMANY.<sup>3</sup> Peter Grünberg Institut (PGI-1) and Institute for Advanced Simulation (IAS-1), Forschungszentrum Jülich GmbH, Jülich, GERMANY.

Close-packed monolayers of Buckminsterfullerenes ( $C_{60}$ ) on metallic substrates are very rich systems with respect to their rotational degrees of freedom and possible interactions with different adsorption sites or next neighbors. Moreover,  $C_{60}$  has the ability to form self-assembled monolayers that mirror impressively the electronic properties of the respective substrate. Most interestingly, in the case of a  $Pt_3Ti(111)$ -single crystal alloy [1] used as substrate the influence of subsurface Ti-atoms on the self-assembly behaviour of fullerenes leads to the formation of a 2-dimensional quasicrystalline structure [2]. Conventional crystals have a periodic structure whose elementary cells are repeated at regular intervals and can be joined together without gaps. Quasicrystals, in contrast, also enable other symmetries – for example fivefold symmetries or the here determined dodecagonal structure which is formed by triangular and quadrangular basic elements consisting of fullerenes.

Using low-temperature UHV-STM and STS and employing density functional theory calculations, we identify the complex adsorption energy landscape of the Pt-terminated  $Pt_3Ti$ -surface that is responsible for the quasicrystal formation [2]. The LT-STM images with highly resolved orbital structure allow a distinct assignment of the  $C_{60}$  adsorption orientation and geometry with respect to the underlying substrate (Figure 1) and thus, provide a detailed insight into an interface-driven formation mechanism of the dodecagonal quasicrystalline structure. In addition, fullerenes adsorbed on the  $3^6$  vertex configuration are identified to exhibit a distinctly increased mobility [3]. An analysis of the crystallographic and energetic constraints at the molecule/metal interface reveals an inequality of local potentials for different vertex sites that is responsible for the switching ability of distinct fullerenes.



**Figure 1.** Schematic showing the assignment of fullerenes to the energetically preferred bridge sites (dark blue spots) on the 2Pt- $Pt_3Ti(111)$  surface. A hexagon in the superimposed tiling representation is highlighted.

**Acknowledgments:** We gratefully acknowledge financial support from the Volkswagen-Stiftung through the “Optically Controlled Spin Logic” project.

## REFERENCES

- [1] Paßens, M.; Caciuc, V.; Atodiresei, N.; Moors, M.; Blügel, S.; Waser, R.; Karthäuser, S. Tuning the surface electronic structure of a  $Pt_3Ti(111)$  electro catalyst. *Nanoscale* **2016**, *8*, 13924 – 13933.
- [2] Paßens, M.; Caciuc, V.; Atodiresei, N.; Feuerbacher, M.; Moors, M.; Dunin-Borkowski, R. E.; Blügel, S.; Waser, R.; Karthäuser, S. Interface-driven formation of a two-dimensional dodecagonal fullerene quasicrystal. *Nat. Commun.* **2017**, *8*, 15367.
- [3] Paßens, M.; Karthäuser, S. Rotational switches in the two-dimensional fullerene quasicrystal. *Acta Cryst A* **2019**, *75*, 41-49.

## TOWARDS A UNIFIED PICTURE OF ELECTRICAL DOPING IN ORGANIC AND INORGANIC SEMICONDUCTORS

Massimiliano Comin<sup>1</sup>, Simone Fratini<sup>1</sup>, Xavier Blase<sup>1</sup>, Gabriele D'Avino<sup>1</sup>

<sup>1</sup> Institut Néel, CNRS and Grenoble Alpes University, F-38042 Grenoble, FRANCE.  
*massimiliano.comin@neel.cnrs.fr, simone.fratini@neel.cnrs.fr, xavier.blase@neel.cnrs.fr,*  
*gabriele.davino@neel.cnrs.fr*

The mechanism for molecular doping in organic semiconductors is believed to be qualitatively different from the textbook picture for inorganic semiconductors of shallow excitonic impurity levels, based on the hydrogenic model. In order to shed light onto the elusive mechanism of molecular doping and try to reconcile the two conflicting pictures of electrical doping, we consider an excitonic model for a dopant impurity into a molecular semiconductor that has been derived and validated by means of state-of-the-art ab initio calculations accounting for many-body correlations and solid-state embedding effects. [1,2]

Our model, which takes as inputs physically meaningful parameters such as molecular energy levels (IP, EA), intermolecular hoppings and the excitonic electron-hole interactions, is able to capture the crossover from a neutral inert impurity to a complete dopant ionization, passing through a fractional charge transfer regime. [2] Thanks to accurate first principles parameterization for the prototypical system F4CNQ-doped pentacene, we were able to show that the acceptor level lies very deep in the gap, but the dopant gets fully ionized because of the very strong excitonic interaction. [2,3]

We will further show that the very same model is able to recover the analytical results of the two-dimensional hydrogenic system in the limit of large hopping (wide bands). This demonstrates that the essential physics of doping in different semiconducting materials can be captured as two limiting cases of a unifying framework, i.e. excitonic binding leading over the kinetic energy in organic systems, while the opposite occurs in inorganic ones.

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## REFERENCES

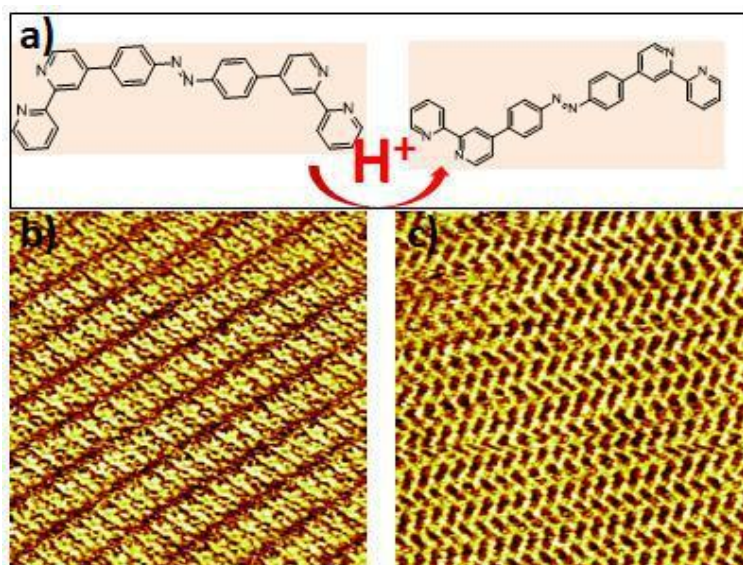
- [1] J. Li, G. D'Avino, I. Duchemin, D. Beljonne, X. Blase, *Phys. Rev.* **B 97**, 035108 (2018).
- [2] J. Li, G. D'Avino, A. Pershin, D. Jacquemin, I. Duchemin, D. Beljonne, X. Blase, *Phys. Rev. Mater.* **1**, 025602 (2017).
- [3] J. Li, I. Duchemin, O. M. Roscioni, P. Friederich, M. Anderson, E. Da Como, G. Kociok-Köhn, W. Wenzel, C. Zannoni, D. Beljonne, X. Blase and G. D'Avino, *Mater. Horiz.* **6**, 107 (2019).

## DOUBLE FUNCTIONAL SWITCHING FROM PHOTOCHROMIC MOLECULES ON SURFACE

Imen Hnid <sup>\*1</sup>, Xiaonan Sun<sup>1</sup>, Frédéric Lafalet<sup>1</sup>, Denis Frath<sup>1</sup>, Jean Christophe Lacroix<sup>1</sup><sup>1</sup>Laboratoire ITODYS-CNRS-UMR 7086, Université Paris Diderot, Paris, FRANCE.  
im.hnid@gmail.com, sun.xiaonan@univ-paris-diderot.fr, lacroix@univ-paris-diderot.fr

Molecules can be switched between different states by different stimuli, including heating, light, and pH. Among these molecules, aromatic azobenzenes are excellent candidates as photochromic molecular switches since they can exist in two forms, the AZO-cis and the AZO-trans isomers [1]. We introduce here two different molecules incorporating an azobenzene group as a central photochromic unit bridging two different terminal groups: bipyridine for the first [Bipy-Azo-Bipy] and terpyridine for the second [Tpy-Azo-Tpy]. The organizations of these molecules on a surface have been investigated by Scanning Tunneling Microscopy (STM). Both molecule self-assemble on surfaces and various supramolecular networks can be observed with a sub-molecular resolution, thanks to the intermolecular interactions of the terminals moieties.

Hence, we studied by STM the different phase transitions induced by the protonation of the bipyridine terminal moieties or by the photo-switching of the photochromic central bridge. Indeed, a multiscale irreversible phase transition upon protonation was already observed on similar molecules consisting of a central bifluorene bridge and bipyridine terminal groups [Bipy-FI-Bipy] [2]. Using [Bipy-Azo-Bipy], a similar, protonation induced, phase transition involving the switching from a cis-like to a trans like isomers is also observed as depicted in Figure 1. Next we studied the effect of irradiation on the system. The photo-switching transition from the Azo-trans bridge (the stable state) to the Azo-cis can be triggered by UV light and reversed back to its initial state by visible light [3]. The photo-effect on the central photochromes was firstly confirmed in solution by UV-visible absorption spectroscopy and the organisation the Azo-cis isomers on surfaces will be presented.



**Figure 1.** a) Transition cis to trans. b),c) STM images 25x25 nm<sup>2</sup> of b) cis Bipy -Azo-Bipy structure at 1-octanol/HOPG interface and c) trans Bipy -Azo-Bipy structure at acid/1-octanol/HOPG interface.

## REFERENCES

- [1] Merino, E.; Ribagorda, M. Beilstein J. Org. Chem. 2012, 8, pp 1071–1090.  
 [2] Sun, X.; Frath, D.; Lafalet, F.; Lacroix, J.C. J. Phys. Chem. C, 2018, 122 (39), pp 22760–22766.  
 [3] Garah, M.E.; Borré, E.; Ciesielski, A.; Dianat, A.; Gutierrez, R.; Cuniberti, G.; Bellemin-Laponnaz, S.; Mauro, M.; Samorì, P. Small, 2017, 13(40), pp 1701790.

## MOLECULAR ISOMERIZATION AND SELF-ASSEMBLIES FROM DITOPIC MOLECULES WITH VARIABLE CENTRAL BRIDGES

Xinlei Yao<sup>1</sup>, Xiaonan Sun<sup>1</sup>, Denis Frath<sup>1</sup>, Gilles Lemerrier<sup>2</sup>, Frédéric Lafalet 1, François Maurel<sup>1</sup>, Jean-Christophe Lacroix<sup>1</sup>

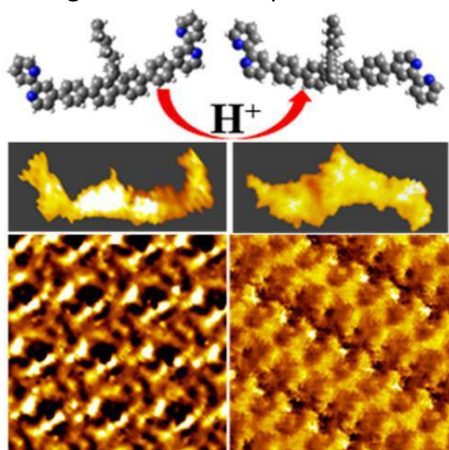
<sup>1</sup> Univ. Paris Diderot, ITODYS, CNRS UMR 7086-15, rue Jean-Antoine de Baïf, 75205 Paris Cedex 13, FRANCE  
Email:yxlei676@gmail.com

<sup>2</sup> Univ. de Reims, UMR 7312 CNRS, BP1039, 51687 Reims Cedex 2, FRANCE.

Series of molecules with a format of **Bpy-X-Bpy** (Bpy is presenting Bipyridine) are synthesized and are investigated by Scanning Tunneling Microscopy (STM) at the solid liquid interface. The bipyridine moiety is employed as molecular terminal groups due to its active capabilities to form selective hydrogen bonds. The central X bridges can vary so as to involve different molecular functionalities.

Molecules **Bpy-F-Bpy** (F is presenting a fluorecene center) are observed to form variable two dimensional (2D) supramolecular networks. Highly ordered gear chains organizations are observed at the none-acid/HOPG interface where Bpy-F-Bpy molecule shows a cis-like conformation. The organizations are stabilized with intermolecular CH-N hydrogen bonds. When involving acid solvents, the surface organizations turn into a 2D linear stripe organization with the Bpy-F-Bpy molecule in trans-like conformation. The intermolecular interaction has been modified to stronger NH-N hydrogen bonds simultaneously. The H<sup>+</sup> protonation induced Bpy-F-Bpy cis-to-trans isomerization is therefore a multi-scale switch which involves a change from weak to strong hydrogen bonds, and a structural phase transformation of gear chains into a stripe-like organization.

Molecules **Bpy-PE2P-Bpy** (where PE2P is presenting a biEDOT center) can self-assemble into various ordered organizations on surfaces. The molecule shows a same cis-to-trans isomerization behavior from the bipyridine protonation, whereas the biEDOT central bridge is always locked in its trans conformation thanks to the intramolecular sulfur-oxygen interactions. The cis-bpy-PE2P-bpy conformers form linear supramolecular stripe and herringbone structures. The trans-bpy-PE2P-bpy conformers form both a zigzag structure and supramolecular wires of variable width. In the various supramolecular organizations, the intermolecular hydrogen bonds between the bipyridine units vary, whereas the biEDOT moieties are always aligned with the same organization and the intermolecular biEDOT interactions remain identical as a dominating force for the supramolecular self-assembly.



**Figure 1** The cis to-trans isomerization in the supramolecular network of bpy-F-bpy molecules

### REFERENCES

- [1] X. Sun; F. Lafalet; G. Lemerrier; F. Maurel ; J. C. Lacroix, J. Phys. Chem. C 2017, 121, 20925–20930.  
[2] X. Sun; D. Frath ; F. Lafalet ; J. C. Lacroix, J. Phys. Chem. C 2018, 122, 22760–22766.

## COMPUTATIONAL DESIGN OF MOLECULAR SYSTEMS FOR NANO THERMOELECTRIC APPLICATIONS

V. Delmas<sup>\*1</sup>, E. Scheer<sup>2</sup>, A. Fihey<sup>1</sup>, J. Cornil<sup>3</sup> and K. Costuas<sup>1</sup>

<sup>1</sup>Université de Rennes 1, institut des sciences chimiques de Rennes, Rennes, FRANCE.

*vincent.delmas@univ-rennes1.fr, Karine.Costuas@univ-rennes1.fr, arnaud.fihey@univ-rennes1.fr*<sup>2</sup>

Universität Konstanz, Fachbereich physic - Mesoscopic systems, Konstanz, GERMANY.

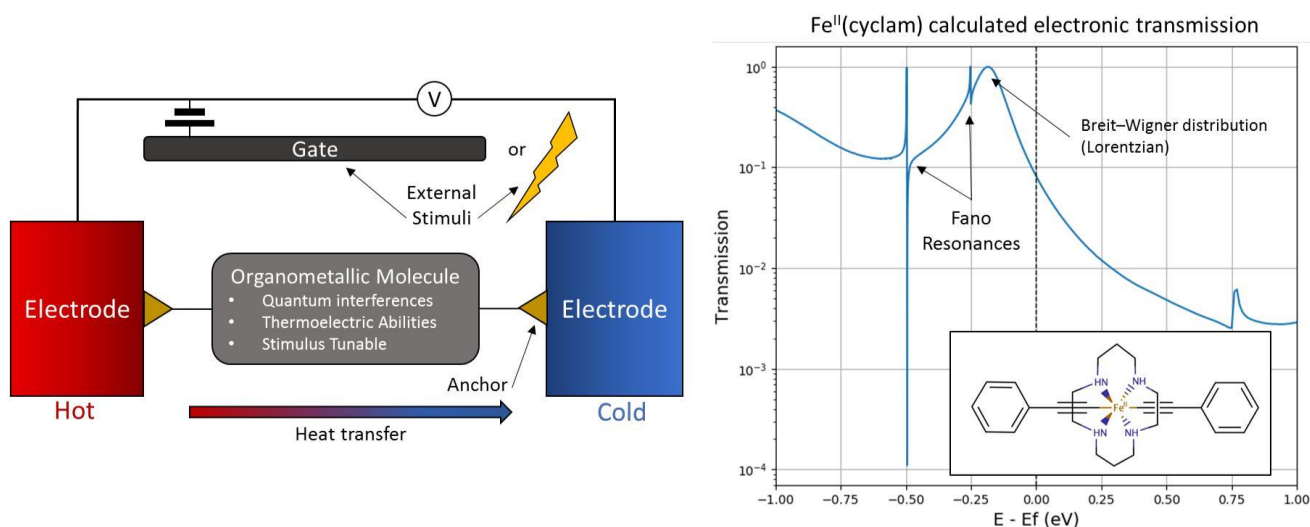
*elke.scheer@uni.kn*

<sup>3</sup>University of Mons, Laboratory for Chemistry of Novels Materials, Mons, BELGIUM.

*Jerome.Cornil@umons.ac.be*

Worldwide financial supports have been dedicated those last two decades to research developing technologies in molecular electronics for promising applications. Remarkably, even though thermoelectricity at the nanoscale can be a reliable solution for energy harvesting, activities research in this domain are very limited. Recent demonstrated the ability of molecular-based systems to convey thermoelectric properties (**Figure 1**).

The present research aims at using computational chemistry as a molecular screening tool to design performant molecular-based devices with thermoelectric properties when incorporated between electrodes. The main idea to achieve thermoelectric molecular junctions is to generate quantum interferences (QI), especially Fano interferences, in the electronic transmission. Some efforts have been focused on [1] junctions containing molecules with side groups (pendant groups) or modified fullerenes [2]. We are investigating here a new route using organometallic molecules, which have the benefits of possessing tuneable electronic properties and of combining numerous functionalities. We currently develop a computationally-assisted molecular design to obtain Seebeck coefficient larger than the best organic molecular systems known to date ( $S > 30 \mu\text{V/K}$ ).



**Figure 1.** Left: Scheme of an “electrode | molecule | electrode” system. Right: Fe<sup>II</sup>(cyclam) molecule and its electronic transmission (DFT-NEGF) calculated with sulfur anchor between gold electrodes.

### REFERENCES

- [1] Mishchenko, A.; Wandlowski, T. Single-Molecule Junctions Based on Nitrile-Terminated Biphenyls: A Promising New Anchoring Group. *JACS* **2011**, 133 (2), 184–187. doi.org/10.1021/ja107340t.
- [2] Rincón-García, L.; Lambert, C. J. Molecular Design and Control of Fullerene-Based Bi Thermoelectric Materials. *Nature Materials* **2016**, 15 (3), 289–293. doi.org/10.1038/nmat4487.

## SPECTROSCOPIC STUDY OF CHARGE TRANSFER BETWEEN Ag-In-S QUANTUM DOTS AND METHYL VIologen

Oleksandr Selyshchev<sup>1</sup>, Volodymyr Dzhagan<sup>2</sup>, Oleksandr Stroyuk<sup>1,3</sup>, Alexandra Raevskaya<sup>3</sup>,  
and Dietrich R. T. Zahn<sup>1</sup>

<sup>1</sup>*Semiconductor Physics, Chemnitz University of Technology, Chemnitz, GERMANY.  
oleksandr.selyshchev@physik.tu-chemnitz.de, zahn@physik.tu-chemnitz.de*

<sup>2</sup>*V.E. Lashkaryov Institute of Semiconductors Physics, Nat. Acad. of Science of Ukraine, Kyiv, UKRAINE.  
dzhagan@isp.kiev.ua*

<sup>3</sup>*L.V. Pysarzhevsky Institute of Physical Chemistry, Nat. Acad. of Science of Ukraine, Kyiv, UKRAINE.  
alstroyuk@ukr.net, alraevskaya@ukr.net*

Charge transfer between methyl viologen molecules ( $MV^{2+}$ ) and quantum dots (QDs) has been widely studied for binary cadmium chalcogenides  $CdX$  ( $X = S, Se, Te$ ) [1], while there is only a single report up to now for multinary alloyed QDs such as  $ZnS-AgInS_2$  [2]. Ag-In-S QDs (AIS) have the advantage that they are free of toxic metals, and in our recent studies we made them even more environmentally friendly by developing a method of synthesizing AIS QDs in aqueous solutions, with biocompatible glutathione as a stabilizing ligand [3]. The band gap of  $\approx 2.5$  eV makes these QDs promising as light absorbers for solar cells, while the broadband photoluminescence (PL), with a quantum yield up to 60% [3], make AIS QDs attractive also for applications in LEDs and as bio-labels.

The possibility of charge transfer to organic molecular mediators like  $MV^{2+}$  reveals their perspectives in light harvesting applications. For colloidal QDs the efficiency of charge transfer is controlled by ligands on their surface. The effect of glutathione on this process with AIS QDs is still unknown. Charge transfer is a process competitive to radiative recombination of excitons, and the study of photoluminescence (PL) quenching is a convenient tool of probing its efficiency. Moreover, investigating the charge transfer between  $MV^{2+}$  and AIS QDs via PL intensity and lifetime variations is especially interesting and new because the nature of the PL in this kind of QDs cannot be attributed to being purely excitonic or trap related [3]. Here we study the effect of two different native ligands, reduced glutathione (GSH) and thioglycolic acid (TGA), on the efficiency of PL quenching of AIS and AIS/ZnS core-shell QDs by  $MV^{2+}$ . We observe that neither GSH nor TGA ligands prevent PL quenching in AIS and AIS/ZnS QDs. The dependence on  $MV^{2+}$  concentration shows that the relative decrease in PL intensity is higher in the case of the TGA ligand, which correlates with its smaller size as compared to GSH. Most likely,  $MV^{2+}$  does not substitute the native ligands, but positively charged  $MV^{2+}$  species attach to negatively charged deprotonated carboxylic groups of the TGA and GSH ligands. Time-resolved PL shows that QD PL lifetimes do not change upon (partial) quenching. This behaviour is typical for a static quenching of PL, when the luminophore and quencher form a non-emissive complex. Unchanged UV-vis spectra of the QDs upon PL quenching exclude the degradation of the QDs. Raman spectra of the samples with strongly quenched PL allowed us to measure AIS and AIS/ZnS lattice phonon spectra. The latter give us the information about ZnS shell parameters, which are a very important tool in controlling the balance between desired suppression of non-radiative surface traps and unwanted additional barrier for electron transfer. A gradual alloying structure of the shell, inferred from the phonon Raman spectra, is supposed to be a prerequisite for such a balance. Vibrational Raman modes of methyl viologen in assemblies with AIS QDs show characteristic modes of the methyl viologen cation radical ( $MV^+$ ), which is a direct confirmation of the charge transfer process in the studied systems.

## REFERENCES

- [1] Zhu et al., Auger-Assisted Electron Transfer from Photoexcited Semiconductor Quantum Dots, *Nano Lett.* **2014**, *14*, 1263–1269.
- [2] Uematsu et. al., Photoinduced Electron Transfer of  $ZnS-AgInS_2$  Solid-Solution Semiconductor Nanoparticles: Emission Quenching and Photocatalytic Reactions Controlled by Electrostatic Forces, *J. Phys. Chem. C*, **2013**, *117*, 15667–15676.
- [3] Stroyuk et. al., Origin and Dynamics of Highly Efficient Broadband Photoluminescence of Aqueous Glutathione-Capped Size-Selected Ag-In-S Quantum Dots, *J. Phys. Chem. C*, **2018**, *122*, 13648–13658.

## CONTROL OF STABILITY OF HALIDE PEROVSKITE THIN FILMS BY FUNCTIONALIZATION OF INTERMEDIATE METAL OXIDE LAYERS WITH TAILORED SELF-ASSEMBLED MONOLAYERS

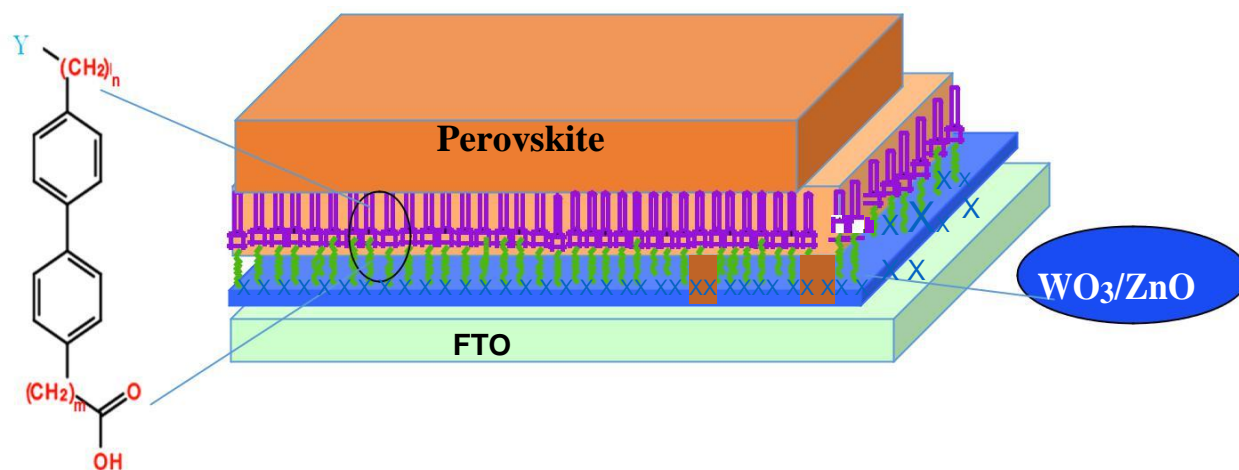
Hedi Kouki<sup>1,2</sup>, Asma Torkhani<sup>1,2</sup>, Faiza Mamèche<sup>1</sup>, Fayçal Kouki<sup>2</sup>, Philippe Lang<sup>1</sup>

<sup>1</sup> Laboratoire ITODYS-CNRS-UMR 7086, Université Paris Diderot, Paris, FRANCE.

<sup>2</sup> Laboratoire matériaux avancés et phénomènes quantiques, Université Tunis EL-MANAR, TUNISIE  
 koukimedhedhi02@gmail.com, Lang@univ-paris-diderot.fr

The insertion of Electron and Hole transport layers (ETL, HTL) metallic oxides between the conducting electrodes (FTO, metals) and the halide perovskite (HP) film are required in order to transport electrons and block holes or the opposite, i.e. blocking holes and transporting electrons respectively. However these MOx layers may have defects, surface states which limit the reproducibility and cell performances by favorizing the charge recombination. An elegant way to solve this issue consists to modify the MOx layers by adequate functionalized **Self-Assembled Monolayers (SAMs)**. SAM treatment is a convenient way to tailor the work function of the Mox interlayers and to control the growth, structure and stability of HP films.

In this context, we address the deposition of various self-assembled monolayers based on bi-functionalized molecules  $[(\text{COOH}-(\text{CH}_2)_n-\Phi-\text{CH}_2)_m-\text{Y}]$  ( $n, m=0,1$ ;  $\text{Y}=\text{CN}, \text{NH}_2, \text{NH}_3^+\text{Cl}^-$ ) on ZnO, WO<sub>3</sub>... layers. The organization and orientation of the SAMs have been analyzed by IR spectroscopy (PM-IRRAS). Then we study and compare the influence of such SAMs on the structure and stability of MAPbX<sub>3</sub> perovskite film ( $\text{X}=\text{Cl}, \text{I}$ ). HP films are characterized by UV-Vis spectroscopy, XR diffraction and MEB.



**Figure 1.** Architecture of perovskite solar cell thin films included SAM's.

## FUNCTIONALIZATION OF ETL AND HTL METALLIC OXIDE BY FORMAMIDINIUM (FA) BASED SELF-ASSEMBLED MONOLAYERS FOR FAPBX3 PEROVSKITE-BASED PHOTOVOLTAIC CELLS

A. Torkhani<sup>1,2</sup>, H.kouki<sup>1, 2</sup>, F.Mameche<sup>1</sup>, F. Kouki<sup>2</sup>, P. Lang<sup>1</sup>

1: ITODYS University of Paris Diderot, CNRS, 75205 Paris FRANCE

2: LMAPQ Faculty of Sciences of Tunis, University of Tunis El-Manar, 2092 Tunis TUNISIA

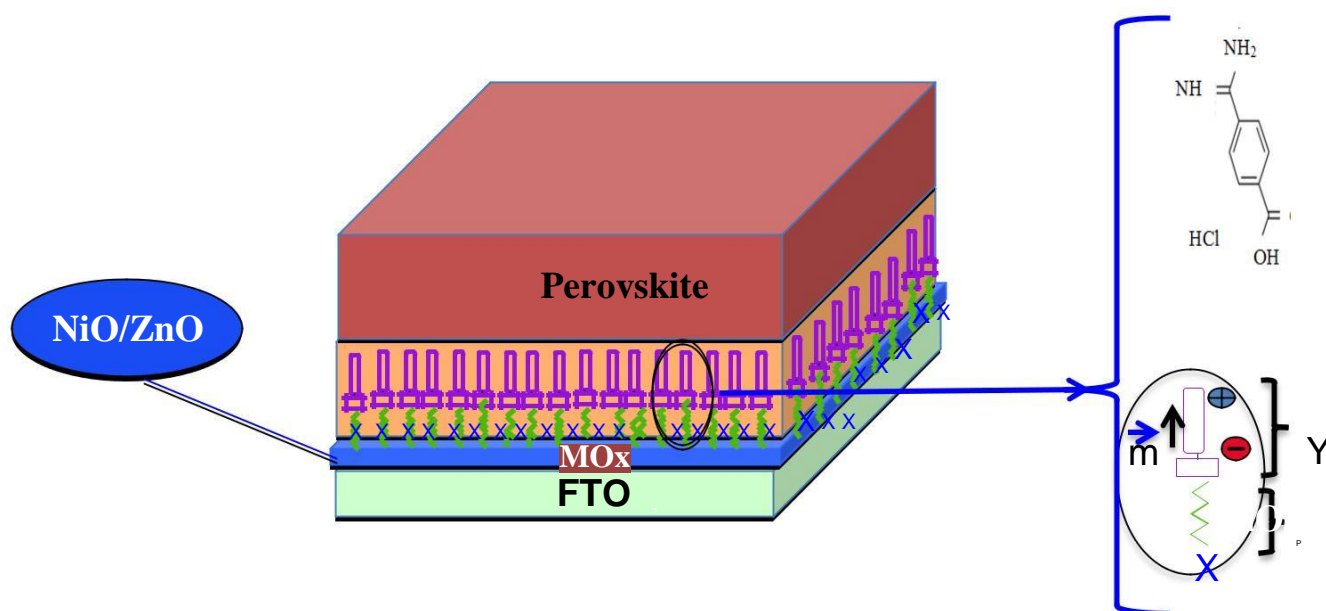
*torkhania92@gmail.com*

The performance of hybrid photovoltaic (OHPV) devices, particularly halogenated perovskite (HP) - based photovoltaic cells, is greatly improved by the insertion of Electron and Hole transport layers (ETL, HTL) metallic oxides between the conducting electrodes (FTO, metals) and the active layers.

The MO<sub>x</sub> layer present at electrodes should transport holes and block electrons or the opposite, i.e. blocking holes and transporting electrons.

The control of the interfaces should lead to the improvement of charge collection and the overall device performance.

Their role is to get a better control of MO<sub>x</sub> surface, notably by the suppressing of interfacial defects and charge trapping. An elegant way to solve this issue consists to graft adequate functionalized Self-Assembled Monolayers (SAMs). These monolayers aim i) to adjust the electronic levels of the MO<sub>x</sub> layers with those of the HP one, ii) to optimize the structure and global properties of the active film. We address here the grafting of Formamidinium terminated molecules (NH<sub>2</sub>NHPCOOH) on MO<sub>x</sub> layers such as ZnO (ETL) and NiO (HTL). The organization and orientation of the SAMs have been analyzed by IR spectroscopy (PM-IRRAS). Then we studied and compared the influence of such SAMs on the structure of APbX<sub>3</sub> perovskite film (A= MA, FA; X=Cl, I). HP films are characterized by UV-Vis spectroscopy, XR diffraction and Scanning Electron Microscopy SEM.





## ROLE OF POLYETHYLENIMINE ETHOXYLATED INTERLAYER IN PERFORMANCE OF RED-LIGHT SENSITIVE ORGANIC NONFULLERENE PHOTODETECTORS WITH REVERSE STRUCTURE

Tomasz Klab<sup>1</sup>, Beata Luszczynska<sup>1</sup>, Jacek Ulanski<sup>1</sup>,  
Qingya Wei<sup>2</sup>, Guohui Chen<sup>2</sup> and Yingping Zou<sup>2</sup>

<sup>1</sup>Department of Molecular Physics, Lodz University of Technology, 90-924 Lodz, POLAND  
163925@edu.p.lodz.pl, beata.luszczynska@p.lodz.pl, jacek.ulanski@p.lodz.pl

<sup>2</sup>College of Chemistry and Chemical Engineering, Central South University, Changsha 410083, P. R. CHINA  
2698864866@qq.com, 406513275@qq.com, yingpingzou@csu.edu.cn

Organic photodetectors sensitive for red or near infrared light require use of low band gap semiconductors; however such semiconductors exhibit usually relatively high conductivity in dark, what is undesirable from the point of view of detectivity of the photodetector [1]. The dark current can be reduced by applying the reversed photodiode structure, with properly modified ITO electrode [2, 3].

We have elaborated and studied red-light sensitive photodiodes with reverse structure based on donor-acceptor copolymer HFQx-T (where HFQx stands for hexafluoroquinoxaline acceptor units, and T for benzodithiophene derivative donor blocks) blended with acceptor ITIC (with indacenodithieno[3,2-b]thiophene as central donor unit and 2-(3-oxo-2,3-dihydroinden-1-ylidene) malononitrile as acceptor end groups) [4]. The ITO electrode was modified by interlayer of polyethylenimine ethoxylated (PEIE) of different thicknesses. It was found, that in such photodiodes the dark current is three orders of magnitude lower than the dark current measured in classical photodiode structure without PEIE, what, together with high photocurrent, results in remarkably high detectivity, exceeding  $2 \cdot 10^{13}$  Jones. On the other hand introduction of the PEIE interlayer affects considerably the dynamic performance of the photodetector. We conclude that construction of the red- or infrared-sensitive photodetectors requires trade-off between the detectivity and time response of the photodetector: reduction of the dark current by introduction of hole or electron blocking layers improves detectivity but may lead to lower responsivity and extended time response of the photodiode.

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### REFERENCES

- [1] Luszczynska, B., Akkuratov, A.V., Szymanski, M.Z., Susarova, D.K., Dupont, B.G.R., Babenko, S.D., Inasaridze, L.N., Bujak, P., Troshin, P.A., Ulanski, J., New copolymers with fluorinated and non-fluorinated benzothiadiazole units for efficient single layer near infra-red photodiodes with fast time response, *Synth. Met.* **2018**, *243*, 67–74 .
- [2] Kielar, M., Dhez, O., Pecastaings, G., Curutchet, A. and Hirsch, L., Long-Term Stable Organic Photodetectors with Ultra Low Dark Currents for High Detectivity Applications, *Sci. Rep.*, **2016**, *6*, 1–11.
- [3] Ping Li, P., Wang, G., Cai, L., Ding, B., Zhou, D., Hu, Y., Zhang, Y., Xiang, J., Wan, K., Chen, L., Alameh, K., Song, Q., High-efficiency inverted polymer solar cells controlled by the thickness of polyethylenimine ethoxylated (PEIE) interfacial layers, *Phys. Chem. Chem. Phys.*, **2014**, *16*, 23792–23799.
- [4] Xu, S., Feng, L., Yuan, J., Zhang, Z.-G., Li, Y., Peng, H. and Zou, Y., Hexafluoroquinoxaline Based Polymer for Nonfullerene Solar Cells Reaching 9.4% Efficiency, *ACS Appl. Mater. Interfaces*, **2017**, *9*, 18816–18825.

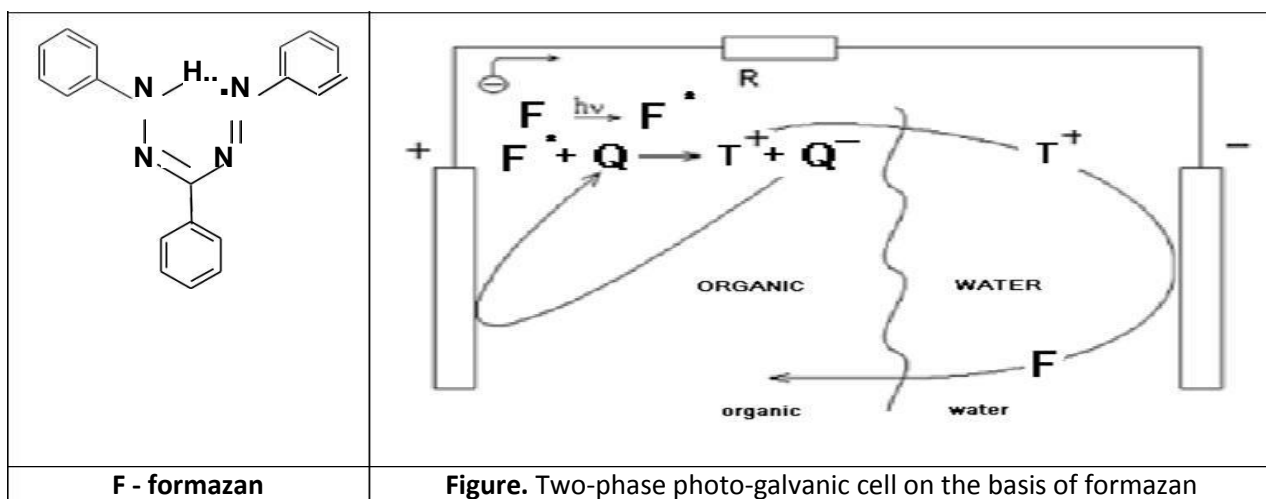
## TWO-PHASE PHOTO-GALVANIC CELL ON THE BASIS OF FORMAZAN PHOTOREDOX CONVERSIONS

Alexander I. Ponyaev\*<sup>1</sup>, Alexander B. Zhivich<sup>2</sup> and Yana S. Glukhova<sup>1</sup><sup>1</sup>Research Department, Saint-Petersburg State Institute of Technology (Technical University), Saint-Petersburg, RUSSIA.

ponyaev@technolog.edu.ru, jancha@mail.ru

<sup>2</sup>Department of Chemical Technology of Organic dyes and Phototropic compounds, Saint-Petersburg State Institute of Technology (Technical University), Saint-Petersburg, RUSSIA.

The presence of mobile  $\pi$ -electron system in formazans, the ease of redox processes, the ability to isomerization and prototropic tautomerism, increased basicity and acidity, especially hetarylformazans create prerequisites for using them to directly convert sunlight into electric current. The spectral-kinetic characteristics of triphenylformazan derivatives in the presence of an electron acceptor were studied by the method of stationary and flash photolysis. The photovoltaic effect was studied in a standard glass conductometric cell with two flat electrodes. An organic solvent (chloroform or toluene) - water containing chlorinearyl, triphenylformazan nitro derivative, 2,3,5-triphenyltetrazolium chloride and tetraethylammonium chloride as an electrically conductive additive, was used as the working solution of the cell. One electrode of the cell was completely immersed in the aqueous phase, and the other in the organic phase. The organic layer of the two-phase system was illuminated full light of incandescent lamp. Formazan (F) being in the organic phase, absorbs the quantum of light and goes into an excited state, in which it interacts with the quinone (Q). Without irradiation, there is no interaction, since the absorption spectrum of a mixture of formazan + chlorinearyl is additive. As a result of the interaction and subsequent transformations, the reduced form of quinone ( $Q^-$ ) and the tetrazolium salt ( $T^+$ ) are formed, which migrates into the water. Due to their different solubilities, reverse electron transfer is difficult and thus provides directional electron transfer in the system. Thus, the electron donor ( $Q^-$ ) accumulates in the organic phase, and the ( $T^+$ ) acceptor accumulates in the aqueous phase. As they accumulate, the discharge of anions at the anode in the organic phase and cations at the cathode in the water phase begins, resulting in an electrical current, the cycle closes and the system returns to its original state (figure).



Thus, the possibility of direct conversion of sunlight into electric current using derivatives of formazans in a two-phase photovoltaic cell is shown. Prospects for improving this kind of photovoltaic cells are very large, since sunlight is directly converted into electric current.

**Acknowledgments:** This work was supported by the Ministry of Science and Higher Education of the Russian Federation (4.4697.2017/6.7) and the Russian Foundation for Basic Research (19-08-01232).

## ADSORPTION AND ELECTRONIC PROPERTIES OF DIAZAPENTACENE AND ITS DERIVATIVE ON METAL SURFACE

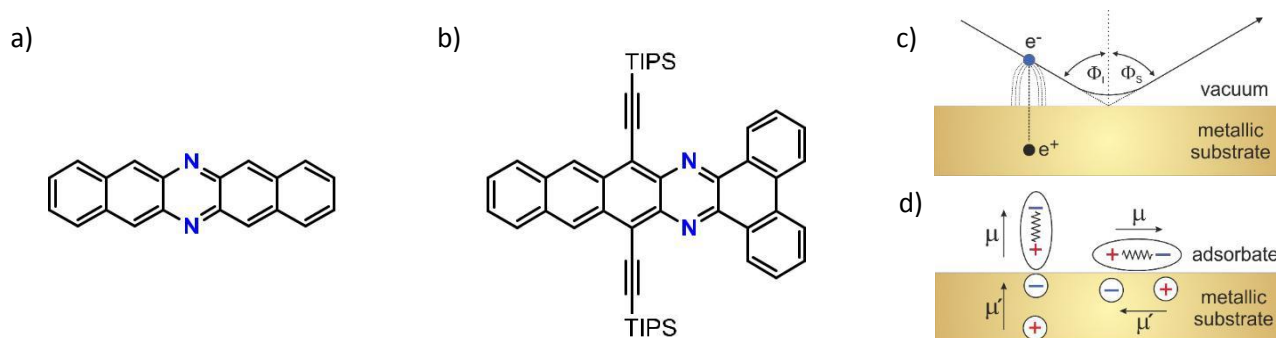
M. Ajdari\*<sup>1</sup>, M. Müller<sup>2</sup>, H. Reiss<sup>2</sup>, U. H. F. Bunz<sup>2</sup>, P. Tegeder<sup>1</sup>

<sup>1</sup> Physikalisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Heidelberg, GERMANY.  
*mohsen.ajdari@stud.uni-heidelberg.de*

<sup>2</sup> Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Heidelberg, GERMANY.

Diazapentacene and its derivative belong to N-heteropolycyclic aromatic compounds that are promising candidates for a variety of (opto) electronic applications. In these molecules, introduction of nitrogen in their aromatic backbone in its pyridine form decreases the energy of both HOMO and LUMO, resulting in an improved stability due to an increased ionization potential and electron affinity of organic semiconductor <sup>1, 2</sup>.

Understanding the adsorption and electronic properties of these molecules on inorganic substrates provides important insights into the charge transfer properties at organic/inorganic interface. High-resolution electron energy loss spectroscopy (HREELS) is a powerful tool for investigating both the adsorption geometry via vibrational excitations and electronic properties of the molecules by utilizing electrons with sufficient energy to excite electronic transitions. In this work, we employed HREELS to study the adsorption and electronic properties of diazapentacene and its derivative as a function of coverage on Au(111).



**Figure 1.** a) Schematic of diazapentacene molecule; b) diazapentacene derivative; c) basic principle of HREELS measurement; d) surface selection rule.

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### REFERENCES

- [1] Winkler M, Houk KN. Nitrogen-rich oligoacenes: candidates for n-channel organic semiconductors. *Journal of the American Chemical Society*. 2007 Feb 14;129(6):1805-15.
- [2] Hoff JJ, Zhu L, Dong Y, Albers T, Steel PJ, Cui X, Wen Y, Lebedyeva I, Miao S. Diazapentacene derivatives: synthesis, properties, and structures. *RSC Advances*. 2016;6(90):86824-8.

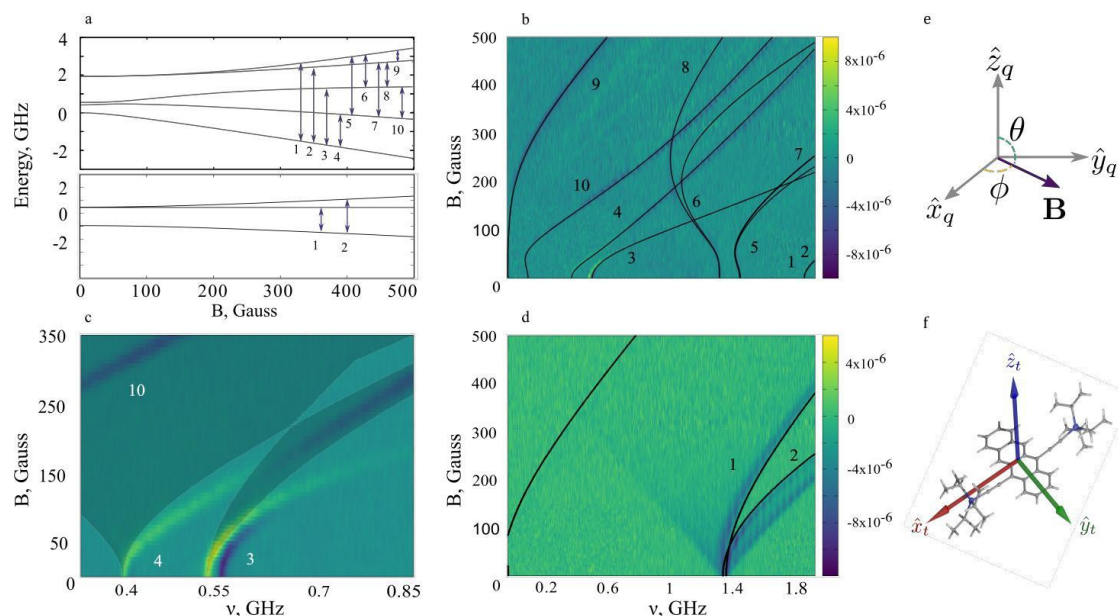
## MAGNETIC RESONANCE STUDIES BI-EXCITON FINE STRUCTURE AND TRIPLET-PAIR GEOMETRY IN A SINGLET FISSION MATERIAL

K.M. Yunusova\*<sup>1,2</sup>, L.R. Weiss<sup>3</sup> and A.D. Chepelianskii<sup>1</sup>

<sup>1</sup>LPS, Univ. Paris-Sud, CNRS, UMR 8502, F-91405, Orsay, France  
kamila.yunusova@u-psud.fr, alexei.chepelianskii@u-psud.fr

<sup>2</sup>Institute of Physics, Kazan Federal University, Kazan, 420008, Russian Federation  
<sup>3</sup>Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, United Kingdom

In organic semiconductors the bi-exciton state is a key intermediate in carrier-multiplication and annihilation. Of particular recent interest is the spin-2 (quintet) bi-exciton [1-3], which is comprised of two triplet excitons and can be formed by singlet fission, the formation of two triplet excitons from one singlet state, or by triplet-triplet annihilation, the reverse process [4]. Of interest for photovoltaics and photocatalysis, the wavefunction of bi-excitons are difficult to probe experimentally and predict theoretically [5-6]. However, the localization of the pair-state is imprinted in the fine structure of its spin Hamiltonian. To access the fine structure of the quintet-state we develop and deploy broadband optically detected magnetic resonance from zero-field to X-band (0-9 GHz) and extract its fine structure and local geometry in an organic crystal. We then correlate the experimentally extracted spin structure with the molecular crystal structure to identify the specific molecular sites on which the bound exciton-pair resides.



**Figure 1.** Optically detected magnetic resonance (ODMR) studies of quintet and triplet states dynamics. **a**, quintet and triplet energy levels and transitions. **b,c**, calculated quintet transitions overlaid on the ODMR map. **d**, calculated triplet transitions overlaid on the ODMR map. **e,f**, quintet and triplet states principle axes.

### REFERENCES

- [1] Bryant, G. W. (1990). Biexciton binding in quantum boxes. *Physical Review B*, 41(2), 1243.
- [2] Chen, G., Stievater, T. H., Batteh, E. T., Li, X., Steel, D. G., Gammon, D., ... & Sham, L. J. (2002). Biexciton quantum coherence in a single quantum dot. *Physical review letters*, 88(11), 117901.
- [3] Hu, Y. Z., Koch, S. W., Lindberg, M., Peyghambarian, N., Pollock, E. L., & Abraham, F. F. (1990). Biexcitons in semiconductor quantum dots. *Physical review letters*, 64(15), 1805.
- [4] Smith, M. B., & Michl, J. (2010). Singlet fission. *Chemical reviews*, 110(11), 6891-6936.
- [5] Tayebjee, M. J., Sanders, S. N., Kumarasamy, E., Campos, L. M., Sfeir, M. Y., & McCamey, D. R. (2017). Quintet multiexciton dynamics in singlet fission. *Nature Physics*, 13(2), 182.
- [6] Weiss, L. R., Bayliss, S. L., Kraffert, F., Thorley, K. J., Anthony, J. E., Bittl, R., ... & Behrends, J. (2017). Strongly exchange-coupled triplet pairs in an organic semiconductor. *Nature Physics*, 13(2), 176.

## ELECTRONIC PROPERTIES OF AZOBENZENE IN INTERACTION WITH THE Au SURFACE: IMPLICATIONS FOR UNDERSTANDING THE ISOMERIZATION PATHWAY OF A PROTOTYPICAL MOLECULAR SWITCH

**Gabriel F. Martins,<sup>1</sup> Christiane Nazareth Silva,<sup>2</sup> Nuno Galamba,<sup>1,3</sup> Demétrio A. da S. Filho,<sup>2</sup>  
Benedito J. C. Cabral<sup>1</sup>**

<sup>1</sup>Universidade de Lisboa, 1749-016 Lisboa, Portugal

<sup>2</sup>Instituto de Física-Universidade de Brasília, Campus Universitário Darcy Ribeiro, 70919-970 Brasília-DF

<sup>3</sup>Centre of Chemistry and Biochemistry of the University of Lisbon, C8, Campo Grande, 1749-016 Lisbon, Portugal.  
*christianenazarethsilva@gmail.com, gabriel\_ma21@hotmail.com, njgalamba@fc.ul.pt, dasf@unb.br, bjcabral@fc.ul.pt*

Several recent studies analysed the interactions between azobenzene (AB) and metallic surfaces [1,2,3]. These studies are of interest to the understanding of the cis-trans isomerization energetics and dynamics of molecular switches and reflect the importance of nanostructures where photoswitches are attached to metal surfaces, allowing designing sensors and molecular machines [1]. Another relevant issue concerns the cis-trans isomerization in the dark [4], which is associated to electron transfer (ET) induced isomerization, when AB is coupled to gold nanoparticles (AuNPs) [4]. The ET mechanism depends on the ionization and electron attachment to AB and although it has been recently investigated in the gas phase [5] much less is known when AB is coupled to metal surfaces. Thus, some fundamental issues concerning the interactions of AB with metallic surfaces remain elusive. Specifically, the electronic properties of AB in interaction with metal surfaces as well as the energetics of these interactions deserve further analysis. Moreover, in the case of AuNPs, it is crucial to investigate the dependence of the interaction of AB with AuNPs on the surface curvature of the nanoparticles. Recently, the loss of the switching function of AB near metallic surfaces due to a significant change of the conformational barriers has been pointed out

[6]. To further discuss these issues we are reporting Density Functional Theory results on the electronic properties and energetics of AB in interaction with the Au (111) surface. In the case of AuNPs, model Au systems with different curvatures are investigated. Concerning electronic properties, the emphasis is placed on the calculation of the HOMO-LUMO gap and its dependence on the cis-trans isomerization pathway, and the coupling strength to the metal surface. These results are of interest for a better understanding of the cis-trans isomerization mechanisms of AB in interaction with metallic and AuNPs surfaces.

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### REFERENCES

- [1] Russew, M.-M.; Hecht, S. Photoswitches: From Molecules to Materials, *Adv. Mater.* 2010, 22, 3348–3360.
- [2] , C.; Filinova, O.; Kubitschke, J.; Herges, R.; Magnussen, O. Photoswitching of Azobenzene-Functionalized Molecular Platforms on Au Surfaces, *J. Phys. Chem. C* 2012, 116, 25493-25948.
- [3] Fuchsel, G.; Klamroth, T.; Dokic, J.; Saalfrank, P. On the Electronic Structure of Neutral and Ionic Azobenzenes and Their Possible Role as Surface Mounted Molecular Switches, *J. Phys. Chem. B* 2006, 110, 16337-16345.
- [4] Hallett-Tapley, G. L.; D'Alcanta, C.; Pacioniza, N. L.; McTiernan, C. D.; González-Béjar, M.; Lanzalunga, O.; Alarcona, E. I.; Scaiano, J. C., Gold Nanoparticle Catalysis of the Cis–Trans Isomerization of Azobenzene, *Chem. Commun.*, 2013, 49, 10073-10075.
- [5] Martins, G. F.; Cabral, B. J. C. Electron Propagator Theory Approach to the Electron Binding Energies of a Prototypical Photo-Switch Molecular System: Azobenzene on Au(111). *J. Phys. Chem. C* 2019, 123, 2091–2099.
- [6] Maurer, R. J.; Reuter, K. Bistability Loss as a Key Feature in Azobenzene (Non-)Switching on Metal Surfaces, *Angew. Chem. Int. Ed.* 2012, 51, 12009 –12011.

## THE REACTIVITY AND SELECTIVITY OF NI(111) FOR PROPANE DEHYDROGENATION TO PRODUCE PROPYLENE

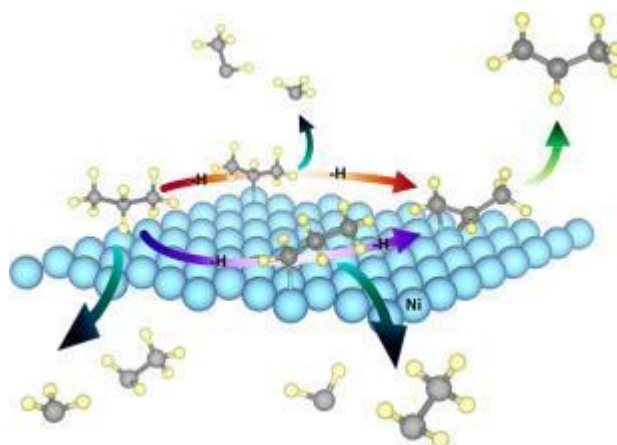
Nawee Kungwan\*<sup>1</sup>, Tinnakorn Saelee<sup>1</sup>, Supawadee Namuangruk<sup>2</sup> and Anchalee Junkaew<sup>2</sup>

<sup>1</sup> Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand. *naweekung@gmail.com, saelee.tinnakorn@gmail.com*

<sup>2</sup> National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency, Pathumthani, Thailand.

*supawadee@nanotec.or.th, anchalee@nanotec.or.th*

Propylene, the important raw material for a variety of products such as propylene oxide, acrylonitrile and alcohols, can be produced via propane dehydrogenation (PDH) using high effective catalyst. To date, platinum- (Pt-) based catalyst is widely used for PDH process. Due to the high reactivity of alkane reaction on Ni catalyst and good stability at high temperatures as well as lower price than Pt-based catalyst, the Ni is a promising candidate for PDH reaction. However, the reaction mechanism of PDH on Ni catalyst is still unclear. In this study, mechanisms of PDH and side reactions are theoretically investigated on Ni(111) surface. For PDH reaction, the dehydrogenation of propane to form 1-propyl intermediate before undergoing to propylene formation is more feasible than that of 2-propyl because of more kinetic favourable of PDH reaction and more thermodynamic stable of 1-propyl on Ni(111) surface. Moreover, the side reaction of C-C bond cracking cannot be taken place during PDH process. Understanding of the reaction mechanisms of PDH and side reactions on Ni(111) surface is useful for designing and developing the better selective Ni catalyst by increasing the reactivity of propylene desorption and inhibiting the side reaction of C-C bond cracking and deep dehydrogenation.



**Figure 1.** All proposed mechanisms of PDH and side reaction on Ni(111) surface.

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### REFERENCES

- [1] Yang, M.-L.; Zhu, Y.-A.; Fan, C.; Sui, Z.-J.; Chen, D.; Zhou, X.-G. Density Functional Study of the Chemisorption of C1, C2 and C3 Intermediates in Propane Dissociation on Pt(111). *Journal of Molecular Catalysis A: Chemical*. 2010, 321, 42– 49.
- [2] Saelee, T.; Namuangruk, S.; Kungwan, N., Junkaew, J. Theoretical Insight into Catalytic Propane Dehydrogenation on Ni(111), *Journal of Physical Chemistry C*. 2018, 122, 14678-14690.
- [3] M.-L. Yang, J. Zhu, Y.-A. Zhu, Z.-J. Sui, Y.-D. Yu, X.-G. Zhou, D. Chen, Tuning Selectivity and Stability in Propane Dehydrogenation by Shaping Pt Particles: A Combined Experimental and DFT Study. *Journal of Molecular Catalysis A: Chemical*. 2014, 395, 329-336.

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## CARBENE-METAL-AMIDE BOND DEFORMATION, RATHER THAN LIGAND ROTATION, DRIVES DELAYED FLUORESCENCE

Elliot J. Taffet\*<sup>1</sup>, Yoann Olivier<sup>2</sup>, Frankie Lam<sup>1</sup>, David Beljonne<sup>2</sup> and Gregory D. Scholes<sup>1</sup>

<sup>1</sup> Department of Chemistry, Princeton University, Princeton, USA.  
*etaffet@princeton.edu, slflam@princeton.edu, gscholes@princeton.edu*

<sup>2</sup> Department of Chemistry, University of Mons, Mons, BELGIUM.  
*yoann.OLIVIER@umons.ac.be, david.BELJONNE@umons.ac.be*

We report three characteristics of ideal thermally activated delayed fluorescence molecular systems apparent in carbene–metal–amides: (a) an exceptionally small singlet–triplet gap that effectively eliminates the thermal activation barrier to reverse intersystem crossing; (b) significant singlet oscillator strength promoting fluorescence in the region of this small barrier; and (c) enlarged spin–orbit coupling driving reverse intersystem crossing in this region. We carry out highly correlated quantum-chemical calculations to detail the relative energies of and spin–orbit couplings between the singlet and triplet states, finding that they fall closer together in energy and couple more strongly into the singlet ground-state to the triplet optimized geometry. This structural reorganization is defined not by rotation of the ligands but by a nontrivial bending of the carbene–metal–amide bond angle. This bending reduces carbene–metal–amide symmetry and enhances singlet–triplet interaction strength. We clarify that the reverse intersystem crossing triggering delayed fluorescence occurs around the coplanar triplet geometric optimum.

### REFERENCES

- [1] Taffet, E. J.; Olivier, Y.; Lam, F.; Beljonne, D.; Scholes, G. D. Carbene–Metal–Amide Bond Deformation, Rather Than Ligand Rotation, Drives Delayed Fluorescence. *J. Phys. Chem. Lett.* **2018**, *9*, 1620–1626.
- [2] Di, D.; Romanov, A. S.; Yang, L.; Richter, J. M.; Rivett, J. P. H.; Jones, S.; Thomas, T. H.; Abdi Jalebi, M.; Friend, R. H.; Linnolahti, M.; et al. High-Performance Light-Emitting Diodes Based on Carbene-Metal-Amides. *Science* **2017**, *356*, 159–163.
- [3] Föllner, J.; Marian, C. M. Rotationally Assisted Spin-State Inversion in Carbene–Metal–Amides Is an Artifact. *J. Phys. Chem. Lett.* **2017**, *8*, 5643–5647.

## NUCLEAR MOTION INVERTS THE ORDERING OF CAROTENOID LOWEST-LYING BRIGHT AND DARK STATES

Elliot J. Taffet\*<sup>1</sup>, Benjamin G. Lee<sup>2</sup>, Zi S.D. Toa<sup>1</sup>, Natalie Pace<sup>2</sup>, Garry Rumbles<sup>2</sup>, June Southall<sup>3</sup>, Richard J. Cogdell<sup>3</sup> and Gregory D. Scholes<sup>1</sup>

<sup>1</sup>Department of Chemistry, Princeton University, Princeton, USA.  
*etaffet@princeton.edu, ztoa@princeton.edu, gscholes@princeton.edu*

<sup>2</sup>Chemical and Materials Science Center, National Renewable Energy Laboratory, Golden, USA.  
*Benjamin.lee@nrel.gov, natalie.pace@nrel.gov, garry.rumbles@nrel.gov*

<sup>3</sup>Institute of Molecular, Cell and Systems Biology, University of Glasgow, Glasgow, UK.  
*June.southall@glasgow.ac.uk, richard.cogdell@glasgow.ac.uk*

We report quantum chemical calculations using density-matrix-renormalization-group (DMRG) with multireference perturbation theory (MRPT) and photothermal deflection spectroscopy measurements to investigate the manifold of carotenoid excited states and establish their energies relative to the bright state ( $S_2$ ) as a function of nuclear reorganization. We conclude that the primary photophysics and function of carotenoids are determined by interplay of only the bright ( $S_2$ ) and lowest-energy dark ( $S_1$ ) states. A key question we examine is whether the nuclear coordinate responsible for the displacement of the dark state ( $S_1$ ) equilibrium from  $S_2$  is quantum mechanical such that  $S_1$  could in principle be observed below  $S_2$  in the Franck-Condon region of the absorption spectrum. In contrast, our results suggest that the nuclear coordinate in this plot is classical, in the sense that it denotes physical reorganization of the molecule to re-order the state energies.



## THE NATURE OF NASCENT CORRELATED TRIPLET PAIRS

Elliot J. Taffet\*<sup>1</sup>, Leah R. Weiss<sup>2</sup>, Francesca D. Fassioli<sup>1</sup>, David Beljonne<sup>3</sup> and Gregory D. Scholes<sup>1</sup>

<sup>1</sup>Department of Chemistry, Princeton University, Princeton, USA.  
*etaffet@princeton.edu, folsen@princeton.edu, gscholes@princeton.edu*

<sup>2</sup> Cavendish Laboratory, University of Cambridge, Cambridge, UK  
*lrw35@cam.ac.uk*

<sup>3</sup>Department of Chemistry, University of Mons, Mons, Belgium  
 *david.BELJONNE@umons.ac.be*

We report spin-state-averaged density matrix renormalization group electronic-structure calculations across one-dimensional and two-dimensional molecular topologies and assert that the nature of nascent correlated triplet pairs (CTP) in singlet fission is defined by a single parameter: the exchange coupling  $J$ . The ladder of singlet, triplet and quintet eigenstates of the CTP is clearly delineated by exchange-split energy gaps of  $J$  and  $3J$  between singlet and triplet, and singlet and quintet, respectively. Moreover, we find an inverse correlation between  $J$  and intramolecular-singlet-fission efficiency in the molecular systems we study. For intermolecular singlet fission in tetracene crystals, we observe that the molecular orientation of dimer pairs in the unit cell determines the exchange coupling. We reconcile the language of spin decorrelation and spatial sequestration of CTP in singlet fission by quantifying the thermodynamics of the entropy-driven transition from the strongly- to the weakly-interacting CTP, revealing that a reduction in  $J$  is associated with realization of the spatially-diffused  $^1(T...T)$  CTP.

## CONTROLLING POLYMORPHISM IN OTFT OF BTBT DERIVATIVE BY BAR ASSISTED MENISCUS SHEARING SOLUTION BLEND

Tommaso Salzillo\*<sup>1,2</sup>, Campos Antonio<sup>1</sup>, Yves H. Geerts<sup>3</sup> and Marta Mas-Torrent<sup>1</sup>

<sup>1</sup> Department of Molecular Nanoscience and Organic Materials, Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) and (CIBER-BBN), Bellaterra, SPAIN.

*tsalzillo@icmab.es, acamposg@icmab.es, mmas@icmab.es*

<sup>2</sup> Universidad Autónoma de Barcelona, Bellaterra, SPAIN.

<sup>3</sup> Laboratoire de Chimie des Polymères - Faculté des Sciences, Université Libre de Bruxelles, Brussels, SPAIN.

*ygeerts@ulb.ac.be*

The understanding of crystal structure is a key issue in the design of the peculiar properties of molecular crystals in materials science, particularly for their application in organic electronics.

The control of polymorphism, the possibility for the same chemical compound to exhibit two or more crystalline modifications, represents a great challenge in organic electronics since it may produce serious problems to achieve device-to-device reproducibility. In fact, mobilities depend on the crystal structure and to match the ideal device with the most suitable polymorph it is crucial to realise a structural control during the preparation of the semiconductor active layer, which is highly sensitive to slight modifications of the deposition parameters.

The 2,7-dioctyloxy[1]benzothieno[3,2-b]benzothiophene (C<sub>8</sub>OBTBT) molecule, one of the most promising organic semiconductors, also presents two different crystalline phases: a co-facial structure (bulk phase) and a herringbone structure also defined surface-induced phase (SIP phase)<sup>[1]</sup>. It has been reported that the SIP phase with aging or after solvent vapor annealing transforms to the thermodynamically stable bulk structure<sup>[2]</sup>.

In this work we report the stabilization of the SIP phase by blending the (C<sub>8</sub>OBTBT) with an insulating polymer and preparing the thin film transistors (TFTs) by the bar assisted meniscus shearing (BAMS) technique<sup>[4]</sup>. All the TFTs based on C<sub>8</sub>OBTBT with polystyrene (PS) of low molecular weight (i.e., 3K) and high molecular weight (i.e., 100K) present the SIP structure and display good electrical properties with a field-effect mobility close to 1 cm<sup>2</sup>/V·s, a threshold voltage around 0 V and an on/off current ratio of 10<sup>7</sup>-10<sup>8</sup>. However, after 3 months in ambient conditions the C<sub>8</sub>OBTBT:PS100k film retain the same morphology, while the film based on the lower molecular weight PS presents the formation of different crystal domains on top of the pristine layer. The structural inhomogeneity of the C<sub>8</sub>OBTBT:PS3k was investigated by Lattice phonon Raman spectroscopy.

A different lattice phonon spectra was recorded for these two areas. In fact, the Raman spectrum of areas without changes in morphology confirm the SIP phase, whereas the spectrum of the new morphology grown on the pristine film reveals the transformation to the bulk phase. From this results it can be demonstrated that processing an organic semiconductor together with a blending polymer results not only in the improvement of the performance but also in the enhancement of the phase stability.

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### REFERENCES

- [1] Bedoya-Martínez, N.; Schrode, B.; Jones, A. O. F.; Salzillo, T.; Ruzié, C.; Demitri, N.; Geerts, Y. H.; Venuti, E.; Della Valle, R. G.; Zojer, E.; Resel, R. DFT-Assisted Polymorph Identification from Lattice Raman Fingerprinting *J. Phys. Chem. Lett.* **2017** *8*, 3690.
- [2] Jones, A. O. F.; Geerts, Y. H.; Karpinska, J.; Kennedy, A. R.; Resel, R.; Röthel, C.; Ruzié, C.; Werzer, O.; Sferrazza, M. Substrate-Induced Phase of a [1]Benzothieno[3,2-b]benzothiophene Derivative and Phase Evolution by Aging and Solvent Vapor Annealing *ACS Appl. Mater. Interfaces* **2015** *7*, 1868.
- [3] Schrode, B.; Jones, A. O. F.; Resel, R.; Bedoya, N.; Schennach, R.; Geerts, Y. H.; Ruzié, C.; Sferrazza, M.; Brillante, A.; Salzillo, T.; Venuti, E. Substrate-Induced Phase of a Benzothiophene Derivative Detected by Mid-Infrared and Lattice Phonon Raman Spectroscopy *ChemPhysChem* **2018** *19*, 993.
- [4] Temiño, I.; Del Pozo, F. G.; Ajayakumar, M. R.; Galindo, S.; Puigdollers, J.; Mas-Torrent, M. A Rapid, Low-Cost, and Scalable Technique for Printing State-of-the-Art Organic Field-Effect Transistors *Adv. Mater. Technol.* **2016** *1*, 1600090.

**SYNTHESIS, CRYSTAL STRUCTURE AND CHARACTERIZATION OF THE NEW ORGANIC–INORGANIC HYBRID  
[NH<sub>3</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>COOH] SnCl<sub>6</sub>. APPLICATION SOLAR CELL**

**M H. Geesi<sup>\*1</sup>, A. Kaiba<sup>2</sup>, Y A. Riadi<sup>3</sup>, P. Guionneau<sup>4</sup>, T. Aljohani<sup>5</sup>**

<sup>1</sup> Chemistry Department, College of science and humanity studies, Alkharj, KSA.  
*m.geesi@psau.edu.sa*

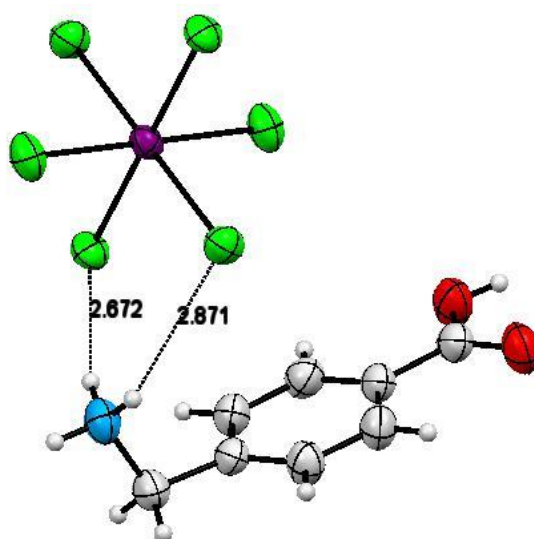
<sup>2</sup> Physics Department, College of science and humanity studies, Alkharj, KSA  
*a.kaiba@psau.edu.sa*

<sup>4</sup> college of pharmacy, Alkharj, KSA  
*y.riadi@psau.edu.sa*

<sup>4</sup> Switchable Molecules and Materials, ICMCB Institute, Bordeaux, France

<sup>5</sup> King Abdulaziz City for Science and Technology, Riyadh, KSA

The research into organic-inorganic hybrid solar cells has led to a highest conversion efficiency now exceeding 20% [1]. In this context, the new hybrid compound was prepared and characterized by single crystal X-ray diffraction, Spectroscopy measurement, thermal study and optical properties [2-3]. The single crystal X-ray diffraction studies revealed that the compound crystallizes in Triclinic system P-1 space group with cell parameters  $a = 6.8643(2) \text{ \AA}$ ,  $b = 6.9777(2) \text{ \AA}$ ,  $c = 14.0056(5) \text{ \AA}$ ,  $\alpha = 91.120(2)^\circ$ ,  $\beta = 118.476(2)^\circ$ ,  $\gamma = 118.476(2)^\circ$  and  $Z=1$ . The atomic arrangement shows an alternation of organic and inorganic entities. The cohesion between these entities is performed via N–H···Cl and C–O–H···O=C hydrogen bonding to form a three-dimensional network. The X-ray powder is in agreement with the X-ray structure. Scanning electronic microscopy (SEM) was carried out. Furthermore, the room temperature Raman spectroscopy spectrum was recorded and analyzed on the basis of data found in the literature. Besides, the thermal analysis studies were performed for stability study. The UV-visible measurement of the compound was investigated in the solid state at room temperature and Solid state exhibited one band at 325 nm



**Figure 1**

**REFERENCES**

- [1] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, Solar cell efficiency tables (Version 45), Prog. Photovoltaics 23, 1 (2015).  
 [2] M.S. Lassoued et al. Journal of Molecular Structure, 1155 (2018) 536-547  
 [3] Z.AlouiV.Ferrettib et al. Journal of Molecular Structure, 1087 (2015) 26-32

## LIGHT-INDUCED EPR STUDY OF INTRA- AND INTERLAYER CHARGE TRANSFER IN NARROW-BANDGAP COPOLYMER:FULLERENE COMPOSITES

**V. I. Krinichnyi\***, E. I. Yudanova, N. N. Denisov and V. R. Bogatyrenko Department of Kinetics and Catalysis, Institute of Problems of Chemical Physics, Chernogolovka, RUSSIA. *kivi@cat.icp.ac.ru, yudan@cat.icp.ac.ru, ndenisov@cat.icp.ac.ru, bvr@cat.icp.ac.ru*

Narrow-bandgap  $\pi$ -conjugated copolymers attract great interest due to their perspective utilization in novel molecular devices [1]. Outstanding properties of such devices can be explained by their bilayer "column-like" morphology and ambipolarity. This causes, e.g., ultrafast charge separation before localization of the primary excitations to form a bound excitons in bulk heterojunctions of their fullerene composites [2]. The type of the initial excitons should also determine functionality and efficiency of electronic devices. Milichko et al. showed [3], that irradiation of a bilayer ordered inorganic composite initiates intralayer excitons inside each layer and interlayer excitons, whose electrons and holes are formed on neighboring layers. Because some organic narrow-bandgap copolymers consist of the donor and acceptor subgroups (ambipolarity), one may expect the formation of the analogous excitons also in their bulk heterojunctions. So, the morphology and ambipolarity of such systems should predetermine their exciton state and electronic properties.

Both charge carriers possess spin. The lifetime of the intralayer excitations and the resultant spin pairs is shorter than that of the less mobile interlayer excitons. This allows one to obtain by the direct light-induced EPR method the correlations of electronic parameters of a composite with the photoinitiated exciton type and the main spin parameters of resulting charge carriers [4] which can be used in organic electronics, photovoltaics and spintronics. This method was used for the study of magnetic resonance, relaxation and dynamic parameters of polarons and methanfullerene radical anions, initiated by the near IR-Vis-UV photons in interfaces formed by narrow-bandgap [(9,9-dioctylfluorenyl-2,7-diyl)-co-(bithiophene)] (F8T2), poly[2,7-(9,9-dioctylfluorene)-alt-4,7-bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT) and poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) copolymers with [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) globules. The formation of spin traps in the copolymer matrix and the exchange interaction between different spin packets cause the extreme sensitivity of these parameters to the number and energy of the initiating photons. Compared to F8T2 and PFO-DBT, the structure of the PCDTBT composite was shown to be more organized, resulting in a decrease in the number of spin traps and a change in the order of the charge recombination process. The decay of free charge carriers is interpreted in terms of the trapping-detrapping spin diffusion in bulk heterojunctions. The recombination of both charge carriers in the F8T2:PC<sub>61</sub>BM and PFO-DBT:PC<sub>61</sub>BM can be described in terms of a bimolecular process of the second order, whereas charge decay in the PCDTBT:PC<sub>61</sub>BM interfaces follows the first order. This evidences the formation of different types of excitons in the compounds under study which controls their magnetic, relaxation and electronic properties.

### REFERENCES

- [1] Huang, F.; Yip, H.-L.; Cao, Y., *Polymer Photovoltaics: Materials, Physics, and Device Engineering*. The Royal Society of Chemistry: Cambridge, 2015.
- [2] Banerji, N.; Cowan, S.; Leclerc, M.; Vauthey, E.; Heeger, A. J., Exciton Formation, Relaxation, and Decay in PCDTBT. *J. Am. Chem. Soc.* **2010**, *132*, 17459-17470.
- [3] Milichko, V. A.; Makarov, S. V.; Alexey V. Yulin; Vinogradov, A. V.; Krasilin, A. A.; Ushakova, E.; Dzyuba, V. P.; Hey-Hawkins, E.; Pidko, E. A.; Belov, P. A., van der Waals Metal-Organic Framework as an Excitonic Material for Advanced Photonics. *Adv. Mater.* **2017**, *29*, 1606034.
- [4] Krinichnyi, V. I. EPR Spectroscopy of Polymer:Fullerene Nanocomposites. In *Spectroscopy of Polymer Nanocomposites*, 1 ed.; Thomas, S.; Rouxel, D.; Ponnamma, D., Eds.; Elsevier: Amsterdam, 2016; pp 202-275; Naveed, K.-u.-R.; Wang, L.; Yu, H.; Ullah, R. S.; Haroon, M.; Fahad, S.; Li, J.; Elshaarani, T.; Khan, R. U.; Nazir, A., Recent Progress in the Electron Paramagnetic Resonance Study of Polymers. *Pol. Chem.* **2018**, *9*, 3306-3335.

**QUANTUM DYNAMICAL STUDIES OF THE INTERFACIAL CHARGE SEPARATION MECHANISM:  
ROLE OF ELECTRON-LATTICE INTERACTIONS AND SPATIAL DISORDER**

**Kevin-Davis Richler\***<sup>1,2</sup> and **Didier Mayou**<sup>1,2</sup> <sup>1</sup>University Grenoble Alpes, Inst NEEL, F-38042 Grenoble, France.  
<sup>2</sup>CNRS, Inst NEEL, F-38042 Grenoble, France.  
*kevin.richler@gmail.com, didier.mayou@neel.cnrs.fr*

At present, the mechanism responsible for charge separation at the donor-acceptor interface in organic photovoltaic devices is not well understood and still actively debated [1-3]. An obvious question relates to the mutual interplay of electron-vibration interaction, spatial disorder (time-independent), and the interfacial Coulomb interaction between the electron and hole. A microscopic understanding of this process, though crucial, has not yet been achieved due to the many-body and the non-translational invariant nature of the problem.

To overcome these difficulties we present an inhomogeneous dynamical mean-field theory (I-DMFT) that is suitable to investigate electron-lattice interactions in non-translationally invariant systems [4]. The presented approach, whose only assumption is that of a local, site-dependent self-energy, provides an interpolation between the non-interacting case, in which it gives the exact solution of the problem and the strong electron-vibration coupling limit in which it also becomes exact. In particular, I-DMFT has been proven successful in treating strongly correlated, spatially inhomogeneous systems [5,6]. Working with a model Hamiltonian, whose parameters have clear physical meanings and where all parameters are chosen such, that they are for most fullerene derivatives in a realistic experimental range, we then provide microscopic evidence that the efficiency of electron transfer across interfaces is subtly impacted by electron-vibration interactions. In particular, we unveil, that the electron remains in the presence of weak-vibronic interactions fully delocalized. Upon increasing the vibronic interaction, the local density of states fragments into polaronic sub-bands (self-trapping). Self-trapping of the electron hinders, in this case, the interfacial electron transfer drastically as parts of the electron wave-function remain localized at the interface resulting in a poor charge transfer efficiency. Using Fermi's golden rule, we then quantify, as a function of the incoming electron energy, the quantum mechanical donor-acceptor interface transfer rate showing that the formation of polaronic bands hinders the range of incoming electron energies. Overall our results point toward, that the formation of polaronic bands, when compared to static disorder, is the main detrimental mechanism and thus organic molecules with moderate reorganization energies should be used preferentially in next-generation materials.

Finally, the presented approach and physics may be of general interest to a wider call of light harvesting systems. In particular, it has been highlighted recently, that the role of static and dynamic potentials may enhance the quantum efficiency in photosynthesis by creating additional transfer channels [7].

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#### REFERENCES

- [1] J. Lee et al., Am. Chem. Soc. 132, 11878 (2010)
- [2] K. Vandewal et al., Nat. Mater. 13, 63 (2014)
- [3] A. E. Jailaubekov et al., Nat. Mater. 12, 66 (2013)
- [4] Potthoff M and Nolring W 1999 Physical Review B 59 2549
- [5] Richler K D, Fratini S, Ciuchi S and Mayou D 2018 Journal of Physics: Condensed Matter 30 465902
- [6] Jacob D, Haule K and Kotliar G 2010 Physical Review B 82 195115
- [7] O'Reilly E J and Olaya-Castro A 2014 Nature communications 5 3012

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## EFFECT OF PERMANENT DIPOLE LAYERS IN THE ELECTRICAL CHARACTERISTICS OF ELECTRONIC DEVICES AND SOLAR CELLS

**Eloi Ros, Benjamin Pusay, Estefania Almache, Pablo Ortega, Cristobal Voz, Joaquim Puigdollers**

Departament Enginyeria Electronica, Universitat Politècnica Catalunya, Barcelona SPAIN.

*eloi.ros@upc.edu, benjamin.andres.pusay@upc.edu, rosa.estefania.almache@upc.edu, pablo.rafael.ortega@upc.edu, cristobal.voz@upc.edu, joaquim.puigdollers@upc.edu*

Conceptually speaking, the dipole of the molecule induces a build-in tension on the layer that can move the effective work function of the metallic electrode at the interface with the semiconductor.

This effect is strongly dependent on the dipole package and orientation, but also the on the individual molecular dipole moment.

Amino acids, are known for strong spatial charge splitting as amino group protonation yields a net positive charge and Carboxylate ionization yields a net negative charge. This accounts for many amino acids strong dipole moment. In this group we can find Glycine, as a stable and easy processable material with a very strong permanent dipole moment over 10Debyes, much greater than the already established n-type contact LiF, with a dipole moment of 6.2Debyes [1]. Furthermore, amino-acids can change the physical and chemical properties of surfaces. This functionalization performed on inorganic materials such as Silicon, can ultimately increase biocompatibility of the original material and open the field to new applications on biointerficies.

In a first approximation, we have studied the electric contact using Transfer Length Method (TLM) of n-type crystalline silicon with an Atomic Layer Deposited Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> stack, reaching a maximum contact resistance of 0.75 Ohms·cm<sup>2</sup>. Furthermore, the effect of the dipole layer has been confirmed on Thin-Film Transistors (TFTs) by depositing a glycine thin-film layer (20 and 5 nm thick) between the silicon dioxide and the semiconductor. The incorporation of the glycine interlayer results in a significant increase of the threshold voltage. Variation of the threshold voltage allows to estimate the dipole moment of the interlayer.

Finally, the influence of the incorporation of the glycine dipole was studied on final solar cells devices. In particular, low temperature dopant-free c-Si solar cells were fabricated using Glycine as a new Electron Transport Layers with the following structures ITO/V<sub>2</sub>O<sub>5</sub>/n-cSi/a-Si:H/Glycine/Al and ITO/V<sub>2</sub>O<sub>5</sub>/n-cSi/Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>/Glycine/Al.

### REFERENCES

[1] Dipole Moment Function of LiF and LiCl Obtained from the Herman–Wallis Analysis: A Comparative Study with the MBER Data Journal of Molecular Spectroscopy. Vol. 194, Issue 1, March 1999, Pages 17-21

## CHARACTERIZATION OF THE DIFFERENT INORGANIC LIGHT EMITTING DIODES (LEDs) AND THE PHOTOVOLTAIC EFFECT ON THESE LEDs

K. Remidi\*<sup>1</sup>, A. Cheknane<sup>2</sup>, M. Haddadi<sup>3</sup>

<sup>1</sup>Department of Physics Ecole Normale Supérieure (ENS), Algeria

\* remidikam@gmail.com

This paper describes an experimental work on the electrical characterization of commercial LED of different colors and their photoelectric effect.

This experiment was conducted at the IMS (Laboratory of the Material System Integration) Bordeaux has a test bench for the intrinsic characterization of various light-emitting diodes in direct and reverse polarization. This bench allows incidental to compare these experimental values with the theoretical values obtained with model results.

A second work of the ENP d'El Harrach has allowed us to develop measurement means to show that there is a photovoltaic effect on LEDs. For this, we measured the electrical characteristics of individual LEDs and studied their light intensities using a pyranometer EPLEY. This work was concerned LED red, green and yellow.

The basic principle is to measure the variation in the current according to the voltage applied across a LED regulated temperature. The bench of the block diagram is shown in spoke [1] temperature controlled by the bench, and the outside temperature of the assembly of the led.

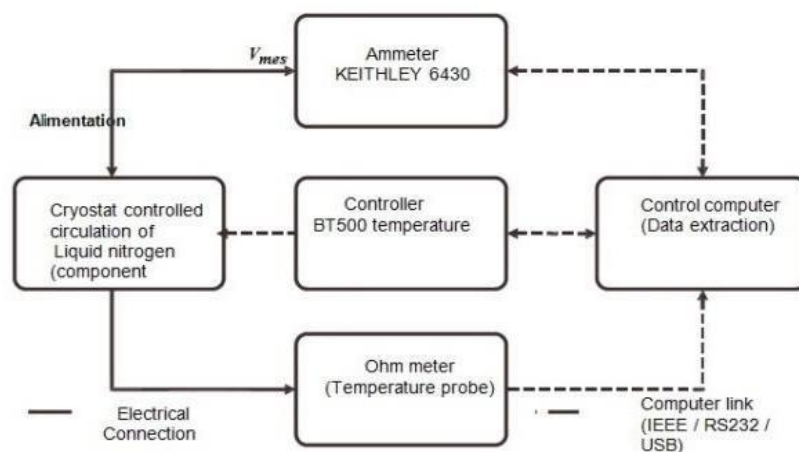


Fig.1: Schematic diagram of the bench  $I=f(V)$

### REFERENCES

- [1] Cha Sarasqueta, K. Roy Choudhury, D.Y. Kim and F. So, "Novel organic/inorganic nanocomposites for high dielectric constant materials", Appl. Phys. Lett. 93, 123305-123307 (2008)
- [2] Jaewon Lee, Neetu Chopra, Debasis Bera, Sergey Maslov, Sang-Hyun Eom, Ying Zheng, Edward Wrzesniewski, Paul Holloway, Jiangeng Xue and Franky So, "Down-conversion white organic light-emitting diodes using microcavity structure", Adv. Energy Mater. 1, 174-178 (2011) Journal Cover.
- [3] So, Franky; Adachi, Chihaya; "Organic Light-Emitting Materials and Devices", Journal of Photonics for Energy, DOI: 10.1117/1.JPE.2.021299, 2012.

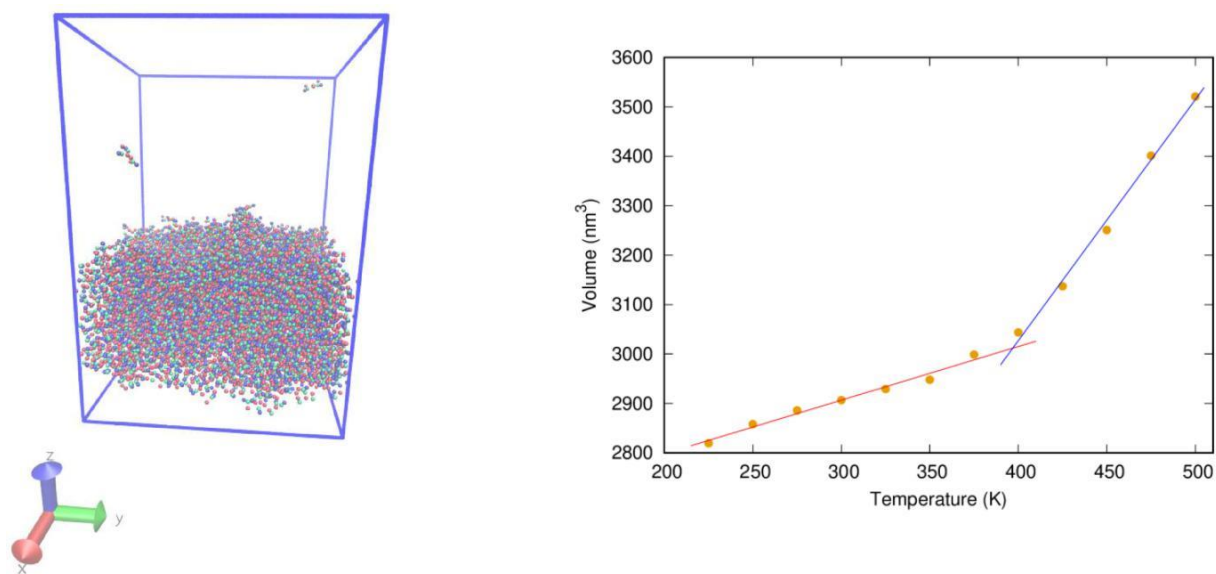
## ULTRASTABLE GLASSES FOR OLEDs FROM COARSE-GRAINED SIMULATIONS

Christoph Scherer,<sup>\*1</sup> Anirban Mondal,<sup>1,2</sup> Sebastian Reineke,<sup>3</sup> and Denis Andrienko<sup>1</sup> <sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany <sup>2</sup>current address: Chemical and Biological Engineering, Princeton University, Princeton, USA

<sup>3</sup>Technische Universität Dresden, Dresden, Germany

*scherer@mpip-mainz.mpg.de, denis.andrienko@mpip-mainz.mpg.de, anirbanm@princeton.edu*

TPBi (2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)) is a host material for organic light-emitting diodes (OLEDs). It has been shown that the external quantum efficiency and lifetimes of OLEDs can be improved by depositing the host material at about 80% - 85% of its bulk glass transition temperature  $T_g$  [1]. To understand morphological differences between "cold" and "hot" depositions, we develop a coarse-grained model of TPBi based on a bottom-up structure based scheme [2] with a bulk glass transition temperature close to the experimental one of  $T_g=400$  K (127 °C) [3]. We then carry out coarse-grained molecular dynamics simulations, depositing one molecule at a time and letting enough time for it to diffuse on a substrate. Finally, we examine the temperature dependence of the density and the molecular ordering of deposited layers and their impact on the density of states and charge carrier mobility.



**Figure 1.** Left: Snapshot of coarse-grained TPBi deposition simulations. Right: Volume-Temperature curve of bulk coarse-grained TPBi indicating the glass transition temperature  $T_g$ .

**Acknowledgments:** We thank Anton Melnyk for providing the scripting framework. DFG is acknowledged for financial support through the collaborative research center TRR 146.

## REFERENCES

- [1] J. Ràfols-Ribé et. al., Science Advances, 2018; 4:eaar8332, 2018
- [2] V. Rühle, C. Junghans, A. Lukyanov, K. Kremer and D. Andrienko, JCTC, 2009; 5, 3211
- [3] Z. Wang et. al., J. Mater. Chem., 2011; 21, 5451-5456



## FUNCTIONAL ALL-CARBON SUPRA-STRUCTURES COMPRISING CARBON NANOTUBES SCAFFOLDS AND FULLERENE NANO-CRYSTALS

Rachel Yerushalmi – Rozen <sup>\*1,2</sup>, Evgenee Yekimov<sup>1</sup> and Eugene A. Katz<sup>2,3</sup>

<sup>1</sup> Chemical Engineering, Ben-Gurion University of the Negev Beer-Sheva 84105, Israel

<sup>2</sup> The Ilse Katz Institute for nanoscience and Technology, Ben-Gurion University of the Negev, Beer-Sheva 84105 Israel  
*rachely@bgu.ac.il aaaa.bbb*

<sup>3</sup> Department of Solar Energy and Environmental Physics, Swiss Institute for Dryland Environmental and Energy Research, Jacob Blaustein Institute of Desert Research, Ben-Gurion University of the Negev, Sde-Boker Campus, Midreshet Ben-Gurion 8499000, Israel

Random 3D- networks of carbon nanotubes (CNT) decorated by fullerene crystallites are an example of carbon-based electronic materials that may combine the geometrical, electrical and mechanical properties of the two carbonaceous nano-structures. Unlike covalent exohedral CNT- fullerene hybrids *non-covalent*, Van-der-Waals (vdW)-type hybrids are preserve the intrinsic properties of the components while enabling control over the nano-morphology of the fullerenes phase. It is well known that the size of the fullerene domains plays an important role in the kinetics of exciton splitting in bulk-heterojunction polymer-fullerenes solar cells, where the fullerene phase morphology is crucial for high efficiency. Yet, solution-processing of polymer-fullerene mixtures into quenched thin solid films does not provide reliable pathways for controlling the domain-size. Here we report the preparation and characterization of hybrids comprising 3D (random) networks of CNT and fullerene crystallites of controlled size and density. Electron imaging followed by electron diffraction suggests that the assemblies are C<sub>60</sub> nano-crystals with *fcc* structure, Raman scattering indicates non-covalent vdW-type interactions among the components. The structures are metastable and surface migration of the fullerenes on the MWNTs surface leads to coarsening of the nanocrystals. We find that controlled induction of SP<sup>3</sup> point defects on the CNTs surface (via UV/O<sub>3</sub> treatment) traps the initial nano-morphology and preserves the nano-dimensions and structure of the fullerene crystals. The nano-morphology of the treated nanotubes is preserved also when the hybrid is coated by a polymer layer (Poly(3-hexylthiophene-2,5-diyl), P3HT), and the polymer-hybrid films show significant quenching of the photoluminescence, indicating that these hybrids could be useful in photovoltaic applications where the typical size of the nano-domains and the degree of crystallinity of the fullerenes play an important role in light-matter interactions.

**ON THE NATURE OF THE SINGLET AND TRIPLET EXCITATIONS MEDIATING THERMALLY  
ACTIVATED DELAYED FLUORESCENCE**

**Y. Olivier<sup>1</sup>, L. Muccioli<sup>2</sup>, J.-C. Sancho-Garcia<sup>3</sup>, B. Yurash<sup>4</sup>, D. Hall<sup>5</sup>, A. Pershin<sup>6</sup>, V. Lemaury<sup>7</sup>, C. Adachi<sup>8</sup>, T.-Q. Nguyen<sup>9</sup>, E. Zysman-Colman<sup>10</sup>, D. Beljonne<sup>11</sup>**

<sup>1, 5, 6, 7, 11</sup> Laboratory for Chemistry of Novel Materials, University of Mons, Mons, BELGIUM *yoann.olivier@umons.ac.be, dh82@st-andrews.ac.uk, Anton.PERSHIN@umons.ac.be, Vincent.LEMAUR@umons.ac.be, David.BELJONNE@umons.ac.be*

<sup>2</sup> Department of Industrial Chemistry "Toso Montanari", University of Bologna, Bologna, ITALY  
*luca.muccioli@unibo.it*

<sup>3</sup> Departamento de Química Física, University of Alicante, Alicante (Spain)  
*jc.sancho@ua.es*

<sup>4, 9</sup> Department of Chemistry and Biochemistry, Center for Polymers and Organic Solids, University of California, Santa Barbara, Santa Barbara, (United States of America) *byurash@ucsb.edu, quyen@chem.ucsb.edu*

<sup>5, 10</sup> University of St Andrews, St Andrews (United Kingdom)

*dh82@st-andrews.ac.uk, eli.zysman-colman@st-andrews.ac.uk*

<sup>8</sup> Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, Fukuoka (Japan)  
*adachi@cstf.kyushu-u.ac.jp*

Thermally Activated Delayed Fluorescence (TADF) process is the new paradigm for Organic Light-Emitting Diodes (OLEDs). Despite all the efforts, a complete mechanistic understanding of TADF materials has not been fully uncovered yet. Part of the complexity arises from the apparent dichotomy between the need for small energy difference between the lowest singlet and triplet excited states ( $\Delta E_{ST}$ ) which has to carry a significant charge transfer (CT) character; and for a significant spin-orbit coupling which according to El-Sayed rules requires the involved singlet and triplet excited states to have very different natures [1]. In this contribution, we will show:

(i) How this dichotomy can be resolved once accounting in a fully atomistic model of reference carbazole derivatives for thermal fluctuations of the molecular conformations and discrete electronic polarization effects in amorphous films [2]. Using both computational and experimental techniques [3], we demonstrate that, electronic excitations involved in the TADF process have a mixed CT-locally excited character being dynamically tuned by torsional vibrational modes. Hence, we will demonstrate that the conversion of triplet-to-singlet and light emission in TADF materials are both electronic processes that are vibrationally-assisted.

(ii) Unlike conventional TADF chromophores, how color purity is achieved together with small  $\Delta E_{ST}$  and high photoluminescence quantum yield in boron-centered azatriangulene-like molecules [4]. Here, using highly correlated quantum-chemical calculations, we report this is driven by short-range reorganization of the electron density taking place upon electronic excitation of these multi-resonant structures. Based on this finding, we design a series of  $\pi$ -extended boron- and nitrogen-doped nanographenes as promising candidates for efficient TADF emitters with concomitantly decreased  $\Delta E_{ST}$ , improved oscillator strength and core rigidity compared to previously reported structures, permitting both emission color purity and tunability across the visible spectrum.

## REFERENCES

- [1] Olivier, Y.; Sancho Garcia, J.C.; Muccioli, L.; D'Avino, G.; Beljonne, D. *J. Phys. Chem. Lett.* 2018, 9, 6149.
- [2] Olivier, Y.; Yurash, B.; Muccioli, L.; D'Avino, G.; Mikhnenko, O.; Sancho-Garcia, J.C.; Adachi, C.; Nguyen, T.Q.; Beljonne, D. *Phys. Rev. Mater.* 2017, 1, 075602.
- [3] Evans, E.W.; Olivier, Y.; Puttisong, Y.; Myers, W.K.; Hele, T.J.H.; Menke, S.M.; Thomas, T.H.; Credgington, D.; Beljonne, D.; Friend, R.H.; Greenham, N.C. *J. Phys. Chem. Lett.* 2018, 9, 4053.
- [4] Pershin, A.; Hall, D.; Lemaury, V.; Sancho-Garcia, J.C.; Muccioli, L.; Zysman-Colman, E.; Beljonne, D.; Olivier, Y. *Nat. Commun.* 2019, 10, 597.

## BENZOTHIENOBENZOTHIOPHENE BASED HIGH-PERFORMANCE HUMIDITY SENSOR

Marc-Antoine Stoeckel<sup>\*1</sup>, Félix Devaux<sup>2</sup>, Camila Cendra<sup>3</sup>, Matilde Eredia<sup>1</sup>, Basab Chattopadhyay<sup>2</sup>, A. Salleo<sup>3</sup>,  
Y. H. Geerts<sup>2</sup> and P. Samorì<sup>1</sup>

<sup>1</sup> Institut de Science et d'Ingénierie Supramoléculaires (I.S.I.S.), 8 allée Gaspard Monge, 67083, Strasbourg, France.  
*marc-antoine.stoeckel@etu.unistra.fr eredia@unistra.fr samori@unistra.fr*

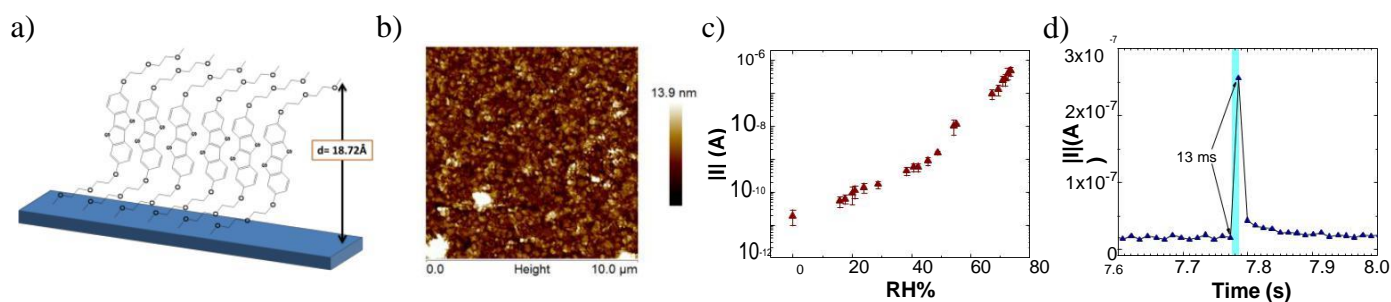
<sup>2</sup> Laboratoire de Chimie des Polymères, Faculté des Sciences, Université Libre de Bruxelles (ULB), Boulevard du  
Triomphe CP206/O1, 1050 Brussels, Belgium  
*felix.devaux@ulb.ac.be bchattop@ulb.ac.be ygeerts@ulb.ac.be*

<sup>3</sup> Department of Materials Science and Engineering, Stanford University, Stanford, USA  
*ccendra@stanford.edu asalleo@stanford.edu*

Achieving a control over the environmental humidity is central in many aspects of everyday life. While the relative humidity for the human's comfort should be around 50%, more dry environments are required in clean rooms and a greater humidity is needed in hospital's operating rooms.<sup>[1]</sup> Consequently, the development of hygrometers (or humidity sensors) based on different detection strategies to attain high sensitivity, selectivity and response speed combined with full reversibility, is a technologically relevant task.

Low-dimensional nanostructures featuring a highest surface-to-volume ratio and physical properties strongly susceptible to environmental changes are ideal candidates as active components for chemical sensing. Suitably designed organic molecules can be self-assembled into highly organized low-dimensional and electroactive nanostructures.<sup>[2,3]</sup> Among semiconducting molecules, alkyl substituted BTBTs displayed high-charge carrier mobilities when integrated in OFETs.<sup>[4]</sup>

In this work we have functionalized BTBT with ethylene glycol side-chains, as active building block for humidity sensing. The ethylene glycol chains can be expected to interact via dipole-dipole interactions with water molecules. Upon absorption of water molecules present in the atmosphere, doping is expected to take place thereby enhancing the charge transport through a molecular film integrated in 2-terminal electrical devices. This leads to devices possessing a fast response speed below 13 ms with a 4-orders-of-magnitude increase of the current when the relative humidity is ranging from 0 to 75%. This compound exhibits a high selectivity for water molecules adsorption, in a fully reversible manner.



**Figure 1.** Cartoon of the BTBT molecules oriented on the surface, b) topographic AFM image of such BTBT film, c) calibration curve between 0 and 75% RH and d) response time under a pulse of humid air of BTBT device measured

### REFERENCES

- [1] H. Farahani, R. Wagiran, M. N. Hamidon, *Sensors* **2014**, *14*, 7881.
- [2] M. A. Squillaci, L. Ferlauto, Y. Zagranyarski, S. Milita, K. Müllen, P. Samorì, *Adv. Mater.* **2015**, *27*, 3170.
- [3] M. A. Squillaci, A. Cipriani, M. Melucci, M. Zambianchi, G. Caminati, P. Samorì, *Adv. Electron. Mater.* **2017**, 1700382.
- [4] Y. Yuan, G. Giri, A. L. Ayzner, A. P. Zoombelt, S. C. B. Mannsfeld, J. Chen, D. Nordlund, M. F. Toney, J. Huang, Z. Bao, *Nature Communications* **2014**, *5*, DOI 10.1038/ncomms4005.

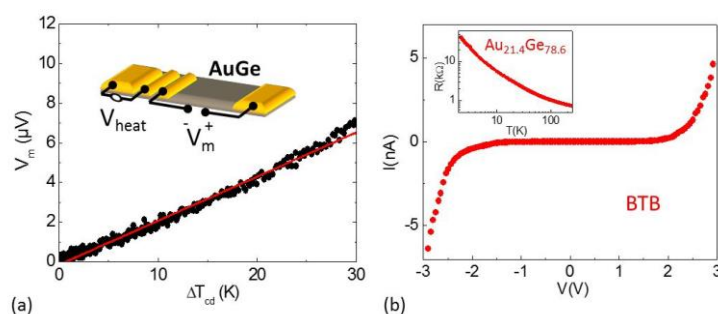
## SEEBECK COEFFICIENT OF $Au_xGe_{1-x}$ THIN FILMS CLOSE TO THE METAL-INSULATOR TRANSITION FOR MOLECULAR JUNCTIONS

C. Salhani, J. Rastikian, C. Barraud, P. Lafarge, and M. L. Della Rocca

Laboratoire MPQ, Université Paris Diderot, Sorbonne Paris Cité, UMR 7162, CNRS, 10 rue Alice Domon et Léonie Duquet, 75205 Paris Cedex 13, France  
 maria-luisa.della-rocca@univ-paris-diderot.fr

Thermal transport at the nanoscale has recently been the subject of renewed interest both theoretically and experimentally, due to the ability to tailor the electronic properties of materials by quantum design. In particular, exciting results have been achieved in the field of molecular thermoelectricity [1-4]. Most results in this field have been obtained on systems consisting of single or few molecules, whereas the thermoelectric properties of large-area molecular junctions remain unexplored. Probing the thermopower of large-area molecular junctions requires the current through the junctions to be measured while simultaneously heating only one of the contacts and measuring the temperature difference across the junction *in situ*. Another general issue is to reduce as much as possible any spurious thermoelectric signal, such as that related to the junction electrodes. As a consequence, the device design and the choice of materials for exploring the thermoelectricity of molecular films are crucial aspects that need to be investigated in detail.

Here, we report on the growth and thermoelectric characterization of  $Au_xGe_{1-x}$  thin-film alloys ( $x = 19.5\%$ ) and on the fabrication of large-area molecular junctions with a  $Au_xGe_{1-x}$  top contact. We discover that for this particular composition, where the alloy is close to its metal-insulator transition (MIT) [5], the Seebeck coefficient is very close to that of pure Au films up to 200 K (fig. 1a), while the alloy preserves good thermosensor properties. This aspect is particularly appealing for thermoelectric applications. We demonstrate the possibility of directly depositing the alloy on a nanometric-thick molecular layer covalently bonded onto a gold electrode, in order to achieve a large-area molecular junction in a cross-bar configuration (fig. 1b) [6]. A  $Au_xGe_{1-x}$ -based junction electrode with such a low Seebeck coefficient can fulfill the double requirement of being resistive enough to generate Joule heating and having a resistance that is sensitive enough to temperature to be used as a local thermometer, opening up new perspectives for molecular thermoelectricity.



**Figure 1.** (a) Thermoelectric voltage measured on the of the  $Au_{19.5}Ge_{80.5}$  thin-film alloy heated following the nonlocal scheme represented in the inset at a temperature of the environment of  $T_{env} = 200$  K. (b) Current-voltage ( $I$ - $V$ ) characteristics at  $T = 2$  K of a junction including a molecular layer BTB and having an  $Au_xGe_{1-x}$  electrode. Inset: temperature dependence of the  $Au_xGe_{1-x}$  top electrodes resistance.

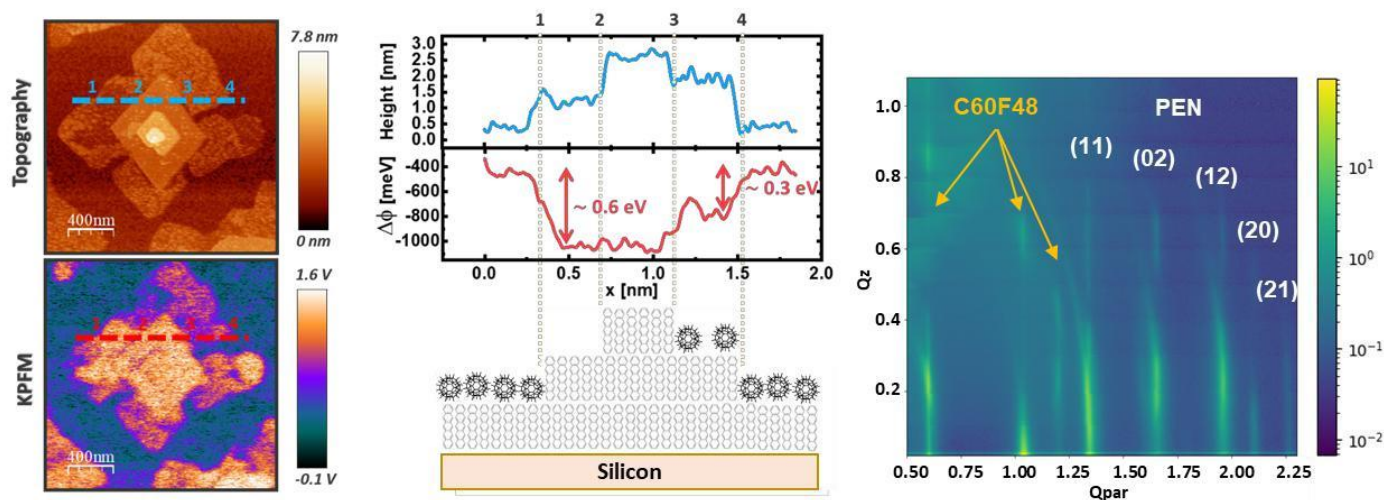
### REFERENCES

- [1] P. Reddy, S.-Y. Jang, R. A. Segalman, and A. Majumdar, Thermoelectricity in molecular junctions, *Science* 2007, *315*, 1568.
- [2] J. R. Widawsky, P. Darancet, J. B. Neaton, and L. Venkataraman, Simultaneous determination of conductance and thermopower of single molecule junctions, *Nano Lett.* 2012, *12*, 354.
- [3] Y. Kim, W. Jeong, K. Kim, W. Lee, and P. Reddy, Electrostatic control of thermoelectricity in molecular junctions, *Nat. Nanotech.* 2014, *9*, 881.
- [4] J. P. Bergfield, M. A. Solis, and C. A. Stafford, Giant thermoelectric effect from transmission supernodes, *ACS Nano* 2010, *4*, 5314.
- [5] B. W. Dodson, W. I. McMillan, J. M. Mochel, and R. C. Dynes, Metal-Insulator Transition in Disordered Germanium-Gold Alloys, *Phys. Rev. Lett.* 1981, *46*, 46.
- [6] C. Salhani, J. Rastikian, C. Barraud and P. Lafarge, M.L. Della Rocca, Seebeck Coefficient of  $Au_xGe_{1-x}$  Thin Films Close to the Metal-Insulator Transition for Molecular Junctions, *Phys. Rev. Appl.* 2019, *11*, 014050.

## DOPANT INDUCED STRUCTURAL AND ELECTRICAL CHANGES AT THE C60F48/PENTACENE INTERFACE

F. Silvestri<sup>1</sup>, A. Babuji<sup>1</sup>, N. Tessler<sup>2</sup>, O. Solomeshch<sup>2</sup>, C. Ocal<sup>1</sup>, E. Barrena<sup>1</sup> <sup>1</sup>Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), 08193 Bellaterra, Barcelona, Spain <sup>2</sup>Electrical Engineering Department, Nanoelectronic Center, Technion, Haifa 32000, Israel  
*fsilvestri@icmab.es*

Doping organic semiconductors (OSCs) with organic molecules to adequately modify their electrical properties is key for device functionality and still poorly understood [1,2]. Recent results have shown that the doping mechanism strongly depends on the electronic coupling between the OSC and the dopant molecule, and consequently, on the structure of the OSC/dopant system [3]. Doping of OSCs is usually achieved by incorporating the molecular dopant into the OSC film. Here we focus on surface doping, where a new p-type dopant from the family of fluorinated fullerenes, namely C<sub>60</sub>F<sub>48</sub>, is deposited on the surface of the OSC. The C<sub>60</sub>F<sub>48</sub> molecule has the advantage of low volatility, bulkier shape (to prevent diffusion within the  $\pi$ -stacking of the OSC) and higher thermal stability than other used dopants [4]. Pentacene (C<sub>22</sub>H<sub>14</sub>) has been chosen as benchmark organic semiconductor. The combination of grazing incidence x-rays diffraction (GIXD) and atomic force microscopy (AFM) with photo-electron spectroscopy (UPS/XPS) and Kelvin probe force microscopy (KPFM) allows to correlate the structural properties of the donor/acceptor system with the surface transfer doping mechanisms at nanoscale level. The crystalline quality of pentacene has strong impact on the adsorption and crystalline growth of C<sub>60</sub>F<sub>48</sub> on top. The change in the local surface potential (of up to 0.8 eV) indicates charge transfer and interface dipole formation. The structural properties and thermal stability of the organic-organic interface have been determined by GIXD.



**Figure 1.** Topography and surface potential images (left) with relative line profiles and sketch (middle) and reciprocal space map (right) of a pentacene sample covered with C<sub>60</sub>F<sub>48</sub>.

## REFERENCES

- [1] Jacobs I. E. and Moule A. J., Controlling Molecular Doping in Organic Semiconductors, *Adv. Mater.*, 29, 1703063 (2017)
- [2] Mendez H., Heimel G., Winkler S., Frisch J., Opitz A., Sauer K., Wegner B., Oehzelt M., Rothel C., Duhm S., Tobbens S., Koch N., Salzmann I., Charge-transfer crystallites as molecular electrical dopants, *Nat. Commun.*, 6, 8560 (2015)
- [3] Duva G., Pithan L., Zeiser C., Reisz, B., Dieterle J., Hofferberth B., Beyer P., Bogula L., Opitz A., Kowarik S., Hinderhofer A., Gerlach A., Schreiber F., Thin-Film Texture and Optical Properties of Donor/Acceptor Complexes. Diindenoperylene/F6TCNNQ vs Alpha-Sexithiophene/F6TCNNQ, *J. Phys. Chem. C*, 122, 18705 (2018)
- [4] Li J., Rochester C. W., Jacobs I. E., Friedrich S., Stroeve P., Riede M., Moule A. J., Measurement of Small Molecular Dopant F4TCNQ and C60F36 Diffusion in Organic Bilayer Architectures, *ACS Appl. Mater. Interfaces*, 7, 28420 (2015)

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**EFFICIENT NON-DOPED NEAR-INFRARED CHROMOPHORES FOR SOLUTION-PROCESSED ORGANIC LIGHT-EMITTING DIODES**

**Patteera Funchien\***, Taweesak Sudyoasuk and Vinich Promarak Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Wang Chan, Rayong 21210, THAILAND. *patteera.f\_s16@vistec.ac.th*

Nowadays, near-infrared (NIR) fluorescent materials have received much attention, because of a lot of their practical uses such as fluorescent tag for bioimaging, OLEDs for optical communication applications including a night-vision displays. To achieve the NIR colour, it is necessary to modify low bandgap of the organic compounds. Donor-acceptor-donor structure is the simplest way to design for NIR molecules. In term of application in OLEDs, there is a few researches which can achieve a high performance of OLEDs devices in NIR colour, so this is more challenging for studying about the NIR materials for OLEDs. Nevertheless, the most of NIR materials are fabricated by vapor evaporation which is not effective cost for the mass production. So, in this work, the development of efficient NIR molecules for non-doped devices was studied and importantly, fabrication by solution process such as spin coating are needed. Derivatives of naphthobenzothiadiazole (**3Hex-NBTz** and **4Hex-NBTz**) were synthesized with D-A-D structure. They exhibited emission above 690 nm and high photoluminescence quantum yields. They were fabricated as emissive layer of OLEDs devices with structure of ITO/PEDOT:PSS/**3Hex-NBTz** and **4Hex-NBTz**/TPBi/LiF/Al. The non-doped OLEDs of **4Hex-NBTz** demonstrated long EL emission at 763 nm and high radiance of 10,608 mW Sr<sup>-1</sup> m<sup>-2</sup>. These results confirm that **4Hex-NBTz** are suitable for efficient solution-processed non-doped OLEDs.

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## SYNTHESIS AND CHARACTERIZATIONS OF CONJUGATED CO-POLYMERS WITH THERMALLY ACTIVATED DELAYED FLUORESCENCE FOR ORGANIC LIGHT-EMITTING DIODES

Praetip Khammultri<sup>\*1</sup>, Taweesak Sudyoadsuk<sup>1</sup>, Supawadee Namuangruk<sup>2</sup> and Vinich Promarak<sup>1</sup>

<sup>1</sup> Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand.

<sup>2</sup> National Nanotechnology Center (NANOTEC), Thailand Science Park, Patumthani 12120, Thailand. s15\_namthip.k@vistec.ac.th, vinich.p@vistec.ac.th

In the last decade, organic light-emitting diodes (OLEDs) have become popular technology due to their potential application in solid-state lighting, low-cost and flexible display. In general, organic molecules were used as emitting materials in OLEDs and shown the maximum internal quantum efficiency only in 25%. The new generation of emitting materials namely thermally activated delayed fluorescence (TADF) recently has been developed, owing to outstanding of internal quantum efficiency up to 100% theoretically. This property effect to enhance external quantum efficiency of OLEDs devices. TADF polymers have become attractive because of they can be solution process fabrication, which can be reducing cost in up-scale processing. In this work, new TADF polymers were designed using 2-(4-(diphenylamino)phenyl)-9H-thioxanthen-9-one 10,10-dioxide (**TXO-TPA**) as TADF core monomer copolymerized with carbazole and fluorene monomers by Suzuki-Miyaura coupling polymerization. The fluorene monomer unit was modified with *tert*-butyl carbazole to ensure hole-transport property. The new polymers, **PCZTXO-FG** containing fluorene monomer and **PCZTXO** having no fluorene monomer, were obtained in molecular weights ( $M_n$ ) of the ranging from 9,000-22,000 Dalton. They were studied the photophysical and the TADF properties by UV-VIS spectrophotometer, steady state, fluorescence lifetime and phosphorescence lifetime spectrometer (FLS). **PCZTXO** displayed emission wavelength in 668 nm while adding fluorene spacing units in **PCZTXO-FG** leading to blue-shifted emission to 620 nm. However, **PCZTXO-FG** showed lifetime in neat film of 29 ns which was longer than that of **PCZTXO** (9 ns). **PCZTXO** and **PCZTXO-FG** showed photoluminescence quantum yields in solution 80% and 62%, respectively. All polymers demonstrated outstanding TADF properties that result from larger integrating area of photoluminescence and longer lifetime compare between air-saturated and degassed solution. The OLED devices with structure of ITO/PEDOT:PSS/TADF polymers/TmPyPb/LiF/Al, were fabricated and evaluated.

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## DIRECT POLYMERIZATION OF COBALT CHALCOGENIDE CLUSTERS FOR HYBRID PHOTVOLTAIC MATERIALS

Brycelyn M. Boardman\*<sup>1</sup>, Daniel A. Corbin<sup>1</sup>, Devon M. Shircliff<sup>1</sup> and Brian J. Reeves<sup>1</sup><sup>1</sup>Department of Chemistry and Biochemistry, James Madison University, Harrisonburg, VA, USA.

boardmbm@jmu.edu, Daniel.Corbin@colostate.edu, devon.shircliff@gmail.com, reevesbj@rams.colostate.edu

The bulk hetero-junction (BHJ) photovoltaic architecture is applicable to a wide variety of materials and recently conjugated polymers and inorganic semiconductor nanoparticle systems have been investigated.<sup>1-3</sup> These materials are advantageous for organic photovoltaic (OPV) applications because they combine the strong light harvesting capabilities of the inorganic component with the ability to solution process well-ordered structures for efficient charge separation and migration of the organic component. Colloidal semi-conducting nanocrystals or nanoparticles are often used as the inorganic component in these types of devices, but are often plagued by aggregation of the inorganic particles rather than the preferred dispersion throughout the polymer matrix.<sup>4,5</sup> Therefore a distinctly different approach has been taken to alleviate these issues associated with hybrid systems by the copolymerization of a functionalized cobalt chalcogenide cluster ( $\text{Co}_6\text{Se}_8((\text{Ph})_2(\text{C}_4\text{H}_2\text{SBr}))_6$ ) (**1**) with 2,5-bistrimethylstannylthiophene and 2,5-dibromo-3-hexylthiophene to yield a type III metallopolymer.<sup>6</sup> This

approach differs from simple mixing of the organic and inorganic blocks because of the covalent attachment of the two materials. This covalent attachment is between the ligands of the cluster and the  $\pi$ -conjugated blocks, not the metal-ligand dative bonds. The ratio of cluster to the other comonomers are varied to yield three new copolymers, poly-cluster-co-thiophene-co-3-hexylthiophene, **PCLHTa-c**. **PCLHTa** has the shortest polymer chains between the cluster co-monomers (largest cluster loading), **PCLHTb** has intermediate lengths, and **PCLHTc** has the longest polymer chains between the clusters (smallest

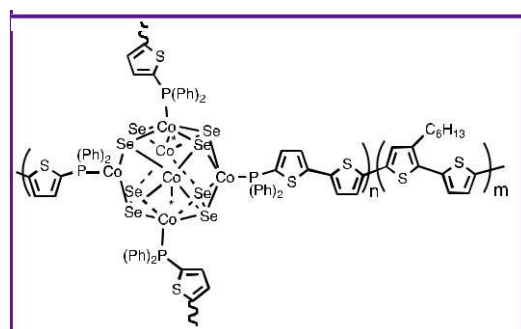
loading) (Figure 1). Structural characterization was performed with NMR, GPC and UV-visible spectroscopy. DFT calculations and experimental results were used to determine the impact of attachment on the polymer chain conjugation. Charge transfer from the polymer to the cluster moieties is observed in all of the cluster-thiophene copolymers. Increased charge transfer is observed with increased cluster incorporation. Fluorescence quenching experiments

comparing simple cluster-polymer mixtures to the polymerized clusters indicate that covalent attachment of the cluster into the polymer chain can result in improved charge transfer. Optical and electronic characterization of thin films of **PCLHTa-c** supports formation of uniform films and suggests that increasing polymer chain lengths lead to increased order in the solid-state.

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## REFERENCES

- [1] Beek, W.J.E., Wienk, M.M. & Janssen, R.A.J., Hybrid polymer solar cells based on zinc oxide, *Journal of Materials Chemistry*, **2005**, 15, 2985-2988.
- [2] Seo, J., Cho, M.J., Lee, D., Cartwright, A.N. & Prasad, P.N., Efficient heterojunction photovoltaic cell utilizing nanocomposites of lead sulfide nanocrystals and a low-bandgap polymer, *Advanced Materials*, **2011**, 23, 3984-3988.
- [3] Yen, W.C., Lee, Y.H., Lin, J.F., Dai, C.A., Jeng, U.S. & Su, W.F., Effect of TiO<sub>2</sub> nanoparticles on self-assembly behaviors and optical and photovoltaic properties of the P3HT- b -P2VP block copolymer, *Langmuir*, **2011**, 27, 109-115.
- [4] Dayal, S., Reese, M.O., Ferguson, A.J., Ginley, D.S., Rumbles, C. & Kopidakis, N., The effect of nanoparticle shape on the photocarrier dynamics and photovoltaic device performance of poly(3-hexylthiophene):CdSe nanoparticle bulk heterojunction solar cells, *Advanced Functional Materials*, **2010**, 20, 2629-2635.
- [5] Huynh, W.U., Dittmer, J.J. & Alivisatos, A.P., Hybrid nanorod-polymer solar cells, *Science*, **2002**, 295, 2425-2427.
- [6] Corbin, D. A., Shircliff, D. M., Reeves, B.J., & Boardman, B. M., Metallopolymers from direct polymerization of functionalized cobalt chalcogenide clusters and thiophene comonomers., *Polymer Chemistry*, **2017**, 8, 3801-3809



**Figure 1.** Illustration of polymeric structures **PCLHTa-c**. The value of  $n$  increases from **PCLHTa** to **PCLHTc** effectively decreasing the cluster loading in the copolymers.



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## ELECTRONIC STRUCTURE, ELECTRON-PHONON COUPLING AND CHARGE TRANSPORT IN CRYSTALLINE RUBRENE UNDER MECHANICAL STRAIN

Michael T. Ruggiero<sup>1</sup>, Sergio Ciuchi<sup>2</sup>, Simone Fratini<sup>3</sup> and Gabriele D'Avino\*<sup>3</sup>

<sup>1</sup> Department of Chemistry, University of Vermont, 82 University Place, Burlington (USA)

<sup>2</sup> Department of Physical and Chemical Sciences, University of L'Aquila, Via Vetoio, L'Aquila (Italy)

<sup>3</sup> Institut Néel, CNRS and Grenoble Alpes University, Grenoble, (France)  
gabriele.davino@neel.cnrs.fr

Motivated by the potential for application of organic semiconductors in flexible electronics, we present a theoretical study aiming at elucidating the interplay between mechanical strain and electronic, vibrational and charge transport properties of the prototypical high-mobility molecular semiconductor rubrene.[1]

Our study considers several factors that can play a role in the electro-mechanical response of a soft, van-der-Waals bonded, molecular crystal, such as intermolecular charge transfer integrals, lattice dynamics and electron phonon coupling. We find that compressive strain leads to an increase in magnitude of charge transfer integrals but also of the energetic disorder hampering the mobility. Charge transport simulations, based on the transient localization framework [2] and fed with first-principles inputs, reveal a remarkably different response to strain applied along different crystal axes, in line with most recent experiments. The critical interplay between energetic disorder of intrinsic and extrinsic nature on the mobility-strain relationship is also discussed.

The theoretical approach proposed in this work paves the way for the systematic study of the electro-mechanical response of different classes of high-mobility molecular semiconductors.

### REFERENCES

[1] M. T. Ruggiero, S. Ciuchi, S. Fratini, G. D'Avino, submitted (2019)

[2] S. Fratini, S. Ciuchi, D. Mayou, G.T. de Laissardiere, A. Troisi, Nature Materials **16**, 998 (2017)

## LIST OF PARTICIPANTS

Name	First name	E-Mail	Institute	Status	Country
Ahlang	Christian	cahlang@abo.fi	Physics Abo Akademi University	PhD student	Finland
Ajdari	Mohsen	Mohsen.Ajdari@stud.uni-heidelberg.de	University of Heidelberg	PhD student	Germany
Alfonsi	S�everine	Severine.Alfonsi@u-cergy.fr	LPPI - Cergy-Pontoise University	Academic	France
Andrienko	Denis	denis.andrienko@mpip-mainz.mpg.de	Max Planck Institute for Polymer Research	Academic	Germany
Babuji	Adara	ababuji@icmab.es	ICMAB – Barcelone	PhD student	Spain
Baessler	Heinz	heinz.baessler@uni-bayreuth.de	University of Bayreuth	Academic	Germany
Bao	Zhenan	zbao@stanford.edu	Stanford University	Academic	USA
Barrena	Esther	ebarrena@icmab.es	Instituto de Ciencia de Materiales de Barcelona	Academic	Spain
Bedolla-Valdz	Zaira Itzel	zbedolla@ucdavis.edu	Renewable Energy Electronics Lab	Academic	USA
Beljonne	David	David.Beljonne@umons.ac.be	LCNM, University of Mons	Academic	Belgium
Boardman	Brycelyn	boardmbm@jmu.edu	James Madison University	Academic	USA
Bonard	Nelly	nelly.bonard@u-cergy.fr	LPPI - Cergy-Pontoise University	Academic	France
Boudrioua	Azzedine	boudrioua@univ-paris13.fr	LPL - Paris 13 University	Academic	France
Br�edas	Jean-Luc	jean-luc.bredas@chemistry.gatech.edu	Georgia Institute of Technology	Academic	USA
Brunel	Damien	damien.brunel@univ-amu.fr	Institut de Chimie Radicalaire Aix-Marseille University	PhD student	France
Bui	Thanh-Tu�n	tbui@u-cergy.fr	LPPI - Cergy-Pontoise University	Academic	France
Carbonera	Chiara	chiara.carbonera@eni.com	Solar Energy Department - Eni SpA	Non Academic	Italy
Cerda Calatayud	Jesus	jesus.cerda@uv.es	Universitat de Valencia	PhD student	Spain
Chaihan	Komsun	komsun.nchai@gmail.com	LPPI - Cergy-Pontoise University	PhD student	France
Chakaroun	Mahmoud	chakaroun@univ-paris13.fr	LPL - Paris 13 University	Academic	France
Charrier	Anne	charrier@cinam.univ-mrs.fr	CINaM - Aix-Marseille University	Academic	France
Chawanpunyawat	Thanyarat	1530315@vistec.ac.th	Vidyasirimedhi institute of science and technology	PhD student	Thailand
Chepelianskii	Alexei	alexei.chepelianskii@u-psud.fr	Laboratoire de Physique des Solides - Paris-Sud University	Academic	France
Chikh	Linda	linda.chikh@u-cergy.fr	LPPI - Cergy-Pontoise University	Academic	France
Comin	Massimiliano	massimiliano.comin@neel.cnrs.fr	Institut N�eel CNRS - Grenoble University	PhD student	France
Cornil	J�r�me	Jerome.Cornil@umons.ac.be	LCNM, University of Mons	Academic	Belgium
Coropceanu	Veaceslav	coropceanu@gatech.edu	Georgia Institute of Technology	Academic	USA
Daiber	Benjamin	b.daiber@amolf.nl	Center for Nanophotonics	PhD student	Netherlands
Dautel	Olivier	olivier.dautel@enscm.fr	Institut Charles Gerhardt of Montpellier	Academic	France
D'Avino	Gabriele	gabriele.davino@neel.cnrs.fr	Institut Neel CNRS	Academic	France
De Monfreid	Thybault	thybault.de-monfreid@u-cergy.fr	LPPI- Cergy-Pontoise University	PhD student	France
De Silva	Piotr	pdes@dtu.dk	DTU Energy	Academic	Denmark
Dehbi	Lynda	dehbi.lynda@yahoo.fr	LPL - Paris 13 Universit�	PhD student	France
Della Rocca	Maria Luisa	mldellaro@gmail.com	Laboratoire Mat�riaux et Ph�nom�ne Quantiques - Paris Diderot University	Academic	France
Delmas	Vincent	vincent.delmas@univ-rennes1.fr	ISCR – Rennes 1 University	PhD student	France
Diez Cabanes	Valentin	valentin.diezcabanes@umons.ac.be	Laboratory for Chemistry of Novel Materials - Mons University	Academic	Belgium
Dreessen	Chris	chris.dreessen@uv.es	University of Valencia	PhD student	Spain
Dreiser	Jan	jan.dreiser@psi.ch	Paul Scherrer Institut - Swiss Light Source	Academic	Swiss
Duhm	Steffen	duhm@suda.edu.cn	Soochow University	Academic	China
Dumur	Frederic	frederic.dumur@univ-amu.fr	Institut de Chimie Radicalaire - Aix-Marseille University	Academic	France
Dzhagan	Volodymyr	volodymyrdzhagan@gmail.com	V Lashkaryov Institute of Semiconductors Physics	Academic	Ukraine
Ebeling	Ren�	r.ebeling@fz-juelich.de	PGI-7 - Forschungszentrum Juelich GmbH	PhD student	Germany
Engels	Bernd	bernd.engels@uni-wuerzburg.de	Institut for Theoretical Chemistry	Academic	Germany
Fichet	Odile	Odile.Fichet@u-cergy.fr	LPPI - Cergy-Pontoise University	Academic	France
Filho	Demetrio	dasf@fis.unb.br	University of Brasilia	Academic	Brazil

Fornari Rocco	Peter	rocfor@dtu.dk	ASM DTU Energy	Academic	Netherlands
Fratini	Simone	simone.fratini@neel.cnrs.fr	Institut Néel – CNRS	Academic	France
Friend	Richard	rhf10@cam.ac.uk	Cambridge University	Academic	UK
Frisbie	Dan	frisbie@umn.edu	Minnesota University	Academic	USA
Funchien	Patteera	patteera.f_s16@vistec.ac.th	Vidyasirimedhi Institute of Science and Technology	PhD student	Thailand
Geesi	Mohammed	m.geesi@psau.edu.sa	Prince Sattam Bin Abdulaziz University	Academic	Saudi Arabia
Gomez-Lor	Berta	bgl@icmm.csic.es	CSIC	Academic	Spain
Gorenflot	Julien	julien.gorenflot@kaust.edu.sa	King Abdullah University of Science and Technology	Academic	Saudi Arabia
Goubard	Fabrice	fabrice.goubard@u-cergy.fr	LPPI - Cergy-Pontoise University	Academic	France
Hamdad	Sarah	sarah.hamdad@univ-paris13.fr	LPL - Paris 13 University	PhD student	France
Hantush	Martin	m.hantusch@ifw-dresden.de	IFW Dresden	Academic	Germany
Harbuzaru	Alexandra	harbuzaru@uma.es	Physical Chemistry - Malaga University	PhD student	Spain
Hirsch	Lionel	lionel.hirsch@ims-bordeaux.fr	University Of Bordeaux	Academic	France
Hnid	Imen	im.hnid@gmail.com	ITODYS - Paris-Diderot University	PhD student	France
Kahn	Antoine	kahn@princeton.edu	Princeton University	Academic	USA
Karthaeuser	Silvia	s.karthaeuser@fz-juelich.de	Forschungszentrum Juelich GmbH, PGI-7	Academic	Germany
Kassal	Ivan	ivan.kassal@sydney.edu.au	School of Chemistry University of Sydney	Academic	Australia
Katan	Claudine	claudine.katan@univ-rennes1.fr	University of Rennes 1	Academic	France
Khammultri	Praetip	s15_namthip.k@vistec.ac.th	Vidyasirimedhi Institute of Science and Technology	Academic	Thailand
Koch	Norbert	norbert.koch@physik.hu-berlin.de	Hu Berlin, Institut Für Physik, Germany	Academic	Germany
Kouki	Mohamed Hedi	koukimedhed02@gmail.com	ITODYS - Paris-Diderot University	Academic	France
Krinichnyi	Victor	kivirus@gmail.com	Institute of Problems of Chemical Physics of RAS	PhD student	Russia
Kungwan	Nawee	naweekung@gmail.com	Department of Chemistry	PhD student	Thailand
Lacroix	Jean-christophe	lacroix@univ-paris-diderot.fr	ITODYS - Paris-Diderot University	Academic	France
Lartigau-Dagron	Christine	christine.lartigau-dagron@univ-pau.fr	IPREM - University of Pau	Academic	France
Lee	Hyunbok	hyunbok@kangwon.ac.kr	Kangwon National University	Academic	South Korea
Lemaur	Vincent	vincent.lemaur@umons.ac.be	Laboratory for Chemistry of Novel Materials – Mons University	Academic	Belgium
Lim	Kyung-Geun	kglim@kriss.re.kr	Korea Research Institute of Standards and Science	Academic	South Korea
Liu	Wenlan	liuwenlan@mpip-mainz.mpg.de	Max Planck Institute for Polymer Research	Academic	Germany
Londi	Giacomo	Giacomo.LONDI@umons.ac.be	Chemistry of Novel Materials - Mons University	Academic	Belgium
MacQueen	Rowan	rowan.macqueen@helmholtz-berlin.de	Helmholtz-Zentrum Berlin	Academic	Germany
Marcus	Rudolph A.	ram@caltech.edu	California Institute of Technology	Academic	USA
Marder	Seth	seth.marder@chemistry.gatech.edu	Georgia Institute of Technology	Academic	USA
Markina	Anastasia	markina@mpip-mainz.mpg.de	Max Planck Institute for Polymer Research	PhD student	Germany
Martin	Pascal	pascal.martin@univ-paris-diderot.fr	ITODYS - Paris-Diderot University	Academic	France
Martinez José	Ignacio	joseignacio.martinez@icmm.csic.es	ICMM-CSIC	Academic	Spain
Martins	Gabriel	gabriel_ma21@hotmail.com	BioISI Faculdade de Ciencias de Lisboa	Academic	Portugal
Masoomi	Saghar	smasoomigoda@student.unimelb.edu.au	Functional Organic Materials - Melbourne University	Academic	Australia
Mayou	Didier	didier.mayou@neel.cnrs.fr	Institut Néel CNRS	Academic	France
McGovern	Luci	L.McGovern@amolf.nl	AMOLF - Hybrid Solar Cells group	PhD student	Netherlands
Michaud	Alexandre	alexandre.michaud@u-cergy.fr	LPPI - Cergy-Pontoise University	Academic	France
Mishra	Arpit	arpit.mishra@edf.fr	EDF Lab Paris-Saclay	Academic	France
Momeni	Anouchah	anouchah.momeni@u-psud.fr	ISMO- Paris-Sud University	PhD student	France
Mrkyvkova	Nada	nada.mrkyvkova@savba.sk	Institute of Physics - Slovak Academy of Sciences	PhD student	Slovakia
Neher	Dieter	neher@uni-potsdam.de	Postdam University	Academic	Germany
Niederhausen	Jens	jens.niederhausen@helmholtz-berlin.de	Helmholtz-Zentrum Berlin	Academic	Germany
Ocal	Carmen	cocal@icmab.es	Institut de Ciencia de Materials de Barcelona	Academic	Spain

Ojeim	Charles	charles.ojeimi@elementar.fr	Elementar	Industrial Sponsor	
Olivier	Yoann	yoann.olivier@umons.ac.be	Laboratory for Chemistry of Novel Materials – Mons University	Academic	Belgium
Ortmann	Frank	frank.ortmann@tu-dresden.de	Center for Advancing Electronics Dresden	Academic	Germany
Ounnunkad	Kontad	suriyacmu@yahoo.com	Department of Chemistry	Academic	Thailand
Peralta	Sébastien	sebastien.peralta@u-cergy.fr	LPPI - Cergy-Pontoise University	Academic	France
Pigot	Corentin	pigotcorentin2@gmail.com	ICR CROPS - Aix-Marseille University	PhD student	France
Ponce Ortiz	Rocio	rocioponce@uma.es	University of Malaga	PhD student	Spain
Ponyaev	Alexander	ponyaev2002@mail.ru	Research Department - St Petersburg University	Academic	Russia
Poriel	Cyril	cyril.poriel@univ-rennes1.fr	ISCR - Rennes 1 University	Academic	France
Promarak	Vinich	vinich.p@vistec.ac.th	Vidyasirimedhi Institute of Science and Technology	Academic	Thailand
Puigdollers	Joaquim	joaquim.puigdollers@upc.edu	Universitat politècnica Catalunya	Academic	Spain
Remidi	Kamel	remidikam@gmail.com	Isic ENS Kouba Alger	Academic	Algeria
Richler	Kevin-Davis	kevin.richler@googlemail.com	institut Néel université de Grenoble	PhD student	France
Riera-Galindo	Sergi	sergi.riera-galindo@liu.se	Linköping University	Academic	Sweden
Ros Costals	Eloi	eloi.ros@upc.edu	Electronic Engineering - Polytechnical Catalonia University	PhD student	Spain
Rovira	Concepcio	cun@icmab.es	National Res. Council	Academic	Spain
Ruiz Delgado	MariCarmen	carmenrd@uma.es	University of Malaga	Academic	Spain
Sallenave	Xavier	xavier.sallenave@u-cergy.fr	LPPI - Cergy-Pontoise University	Academic	France
Salman	Seyhan	salmansay@yahoo.com	Gwinnett Coll., Atlanta, USA	Academic	USA
Salzillo	Tommaso	tsalzilla@icmab.es	Institut de Ciència de Materials de Barcelona	Academic	Spain
Sassella	Adele	adele.sassella@unimib.it	University of Milano - Bicocca	Academic	Italy
Scherer	Christoph	scherer@mpip-mainz.mpg.de	Max Planck Institute for Polymer Research - Mainz	Academic	Germany
Sebastia Luna	Paz	paz.sebastia@uv.es	ICMM-CSIC	PhD student	Spain
Silvestri	Francesco	fsilvestri@icmab.es	ICMAB – Barcelone	PhD student	Spain
Sini	Gjergji	gjergji.sini@u-cergy.fr	LPPI - Cergy-Pontoise University	Academic	France
Small	Cephas	Cephas.Small@nature.com	Nature Communications	Associate Editor	
Smith	Hannah	hannahsmith@princeton.edu	Princeton University	PhD student	USA
Stinguelin	Natalie	natalie.stingelin@mse.gatech.edu	Georgia Institute of Technology	Academic	USA
Stoeckel	Marc-Antoine	marc-antoine.stoeckel@etu.unistra.fr	ISIS - Strasbourg University	Academic	France
Susic	Isadora	susic@uv.es	ICMOL - Valencia University	PhD student	Spain
Taffet	Elliot	etaffet@princeton.edu	David Beljonne - Mons University	PhD student	Belgium
Torkhani	Asma	torkhaniasma92@gmail.com	ITODYS - Paris-Diderot University	PhD student	France
Torsi	Luisa	luisa.torsi@uniba.it	Bari University	Academic	Italy
Ulanski	Jacek	jacek.ulanski@p.lodz.pl	Lodz University of Technology K-32	Academic	Poland
Van Dyck	Colin	cvandyck@gmx.com	Nanotechnology Research Centre - University of Alberta	Academic	Canada
Vercouter	Alexandre	Alexandre.VERCOUTER@umons.ac.be	Laboratory of Chemistry of Novel Materials - Mons University	Academic	Belgium
Voisin	Pierre-Julien	pierre-julien.voisin@htds.fr	HTDS	Industrial Sponsor	
Wiscons	Ren	renwis@umich.edu	Matzger Group - University of Michigan	PhD student	USA
Witte	Gregor	gregor.witte@physik.uni-marburg.de	Laboratoire Herr - University of Marburg	Academic	Germany
Xu	Zijun	zijun.xu@outlook.com	ITODYS - Paris-Diderot University	PhD student	France
Yao	En-Ping	EnP.Yao@physik.uni-muenchen.de	Chair for Photonics and Optoelectronics LMU Munich	Academic	Germany
Yao	Xinlei	yxlei676@gmail.com	ITODYS - Paris-Diderot University	PhD student	France
Yerushalmi-Rozen	Rachel	rachely@bgu.ac.il	Ben-Gurion University of the Negev	Academic	Israel
Yoneya	Makoto	makoto-yoneya@aist.go.jp	AIST	Academic	Japan
Yunusova	Kamila	kam.chaos@gmail.com	Laboratoire de Physique des Solides - Paris-Sud university	PhD student	France
Zappia	Stefania	s.zappia@ismac.cnr.it	ISMAL-CNR	Academic	Italy
Zojer	Egbert	egbert.zojer@tugraz.at	Graz University of Technology, Austria	Academic	Austria