

Conference on

Progress in Organic Optoelectronics

18.-19.12.2017

Valencia

SPAIN

organized by

Begoña Milián Medina ^{1,2}

Larry Lürer ²

Johannes Gierschner ²

¹ University of Valencia, ² IMDEA Nanoscience Madrid

**Conference on
Progress in Organic Optoelectronics**

BOOK OF ABSTRACTS

18.-19.12.2017

Valencia, SPAIN

<https://www.uv.es/milian/ConferenceValencia2017.html>

SCIENTIFIC COMMITTEE

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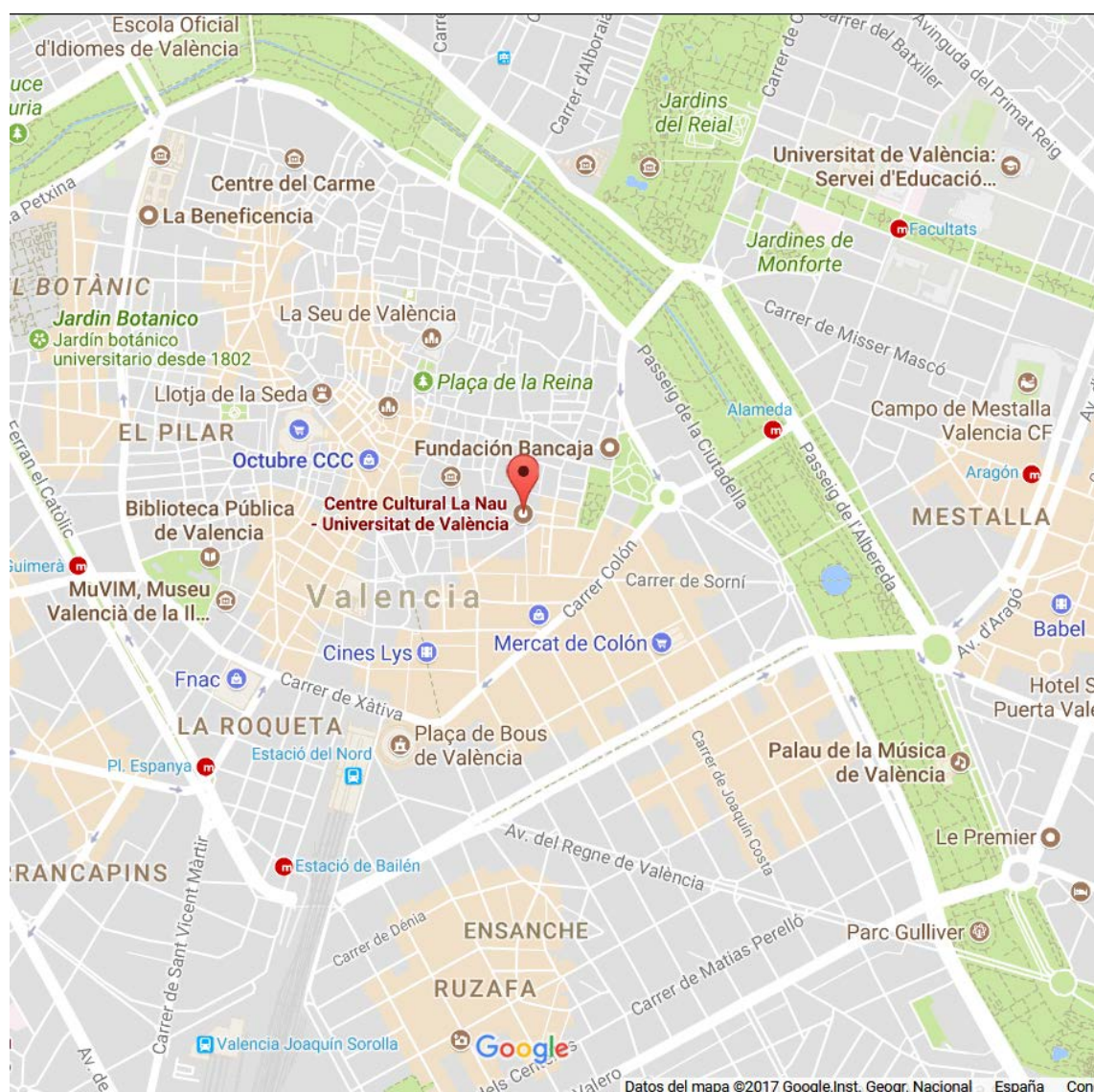
CONTENTS

Venue	p. 1
Program at a glance	p. 3
Program	p. 4
Keynote presentations	p. 8
Invited presentations	p. 12
Oral communications	p. 28
Poster contributions	p. 42

VENUE

La Nau (old University), Calle de la Universitat 2, Valencia (Aula Seminario)

coordinates: 39.471944°, -0.372778°.



Lunch will be served in the Cloister of *La Nau*.



Coffee Breaks will be held in front of the Seminar Room

Poster Sessions will be held during all coffee breaks in the Seminar Room.

Reception will be held at Restaurante *Orio* (Calle San Vicente 23, Valencia),
Sun, 17.12. 20:00h

Conference Dinner will be held at Restaurante *Los Sabores* (Carrer de Landerer, 1, 46003 Valencia)

PROGRAM AT A GLANCE

Progress in Organic Optoelectronics Valencia, 17.-19.12.2017				
time \ day	Su 17.12.	Mo 18.12.	Tu 19.12.	
8:30	 Arrival Valencia 	Registration		
9:00		Welcome & Intro	Key note lecture	
9:30		Key note lecture	Oral contributions	
10:00		Oral contribution		
10:30		Coffee & Poster	Coffee & Poster	
11:00				
11:30		Oral contributions	Oral contributions	
12:00				
12:30				
13:00				
13:30		Lunch	Lunch	
14:00				
14:30		Oral contributions	Oral contributions	
15:00				
15:30				
16:00		Coffee & Poster	Coffee & Poster	
16:30		Oral contributions	Oral contributions	
17:00		City Walk		Closing remarks
17:30				
18:00				
18:30		Social activity		
19:00				
19:30				
20:00	Dinner			
20:30				
21:00		Conference Dinner		
21:30				

PROGRAM

Sun, 17.12.2017

17:00-19:00 **Valencia walk**

20:00 **Reception** (Restaurante Orió, Calle San Vicente 23)

Mon, 18.12.2017

08:30 Registration

09:00 **Welcome:** B. Milián Medina, L. Lüer, J. Gierschner

09:10-09:30 **Introduction:** *MultiCrom an (Inter)National Project* (J. Gierschner)

Session 1 Novel Materials I [Chair: Johannes Gierschner]

09:30-10:15 Soo Young Park (Seoul Nat. Univ.), **keynote:** *De Novo Strategies for Color-Specific Photoswitching*

10:15-10:30 Junqing Shi (IMDEA Nanoscience, Madrid): *Solid State Luminescence Enhancement in π -Conjugated Materials: Unraveling the Mechanism beyond the Framework of AIE/AIEE*

10:30-11:00 Coffee Break & Poster Session (Seminar Room, 2nd Floor, La Nau)

Session 2 Novel Materials II [Chair: M^a Carmen Ruiz Delgado]

11:00-11:30 Blanca Ros (Univ. Zaragoza), **invited:** *Stimuli-Responsive Materials with Bent-Core Liquid Crystals*

11:30-12:00 Rosario Nuñez (ICMAB, Barcelona), **invited:** *Photoluminescence in Boron Clusters-Containing Molecular Materials*

12:00-12:30 Gianluca Farinola (Univ. Bari), **invited:** *Materials for Optoelectronics from Photosynthetic Microorganisms*

12:00-12:30 Dong Ryeol Whang (Univ. Linz), **invited:** *Artificial Photosynthesis: Learning from Nature*

13:00-14:40 Lunch (Cloister, La Nau)

Session 3 Next Generation Solar Cells [Chair: Larry Lüer]

14:40-15:10 Henk Bolink (ICMol, Valencia), **invited:** *Vapor Phase Deposited Perovskite Solar Cells*

15:10-15:30 Markus Scharber (Univ. Linz): *Progress in Organic Solar Cells*

15:30-16:00 Andreas Distler (ZAE Bayern), **invited:** *Towards the Commercialization of Organic Photovoltaics*

16:00-16:30 Coffee Break & Poster Session (Seminar Room, 2nd Floor, La Nau)

Session 4 Modeling of Processes [Chair: Juan Carlos Sancho García]

16:30-17:00 David Beljonne (Univ. Mons), **invited:** *Probing Local Intermolecular Interactions with Light: Modeling Insights*

17:00-17:30 Daniel Roca (ICMol, Valencia), **invited:** *Non-Adiabatic Chemical Mechanisms of Interest in Organic Optoelectronics*

17:30 Social Activity: Old University visit 17:30-18:30, Library visit 18:30-19:30 (Christmas Concert Chapel 19:30-20:30)

21:00 Conference Dinner (Restaurante Los Sabores, Carrer de Landerer 1)

Tue, 19.12.2017

Session 5 Excited State Design [Chair: Enrique Ortí]

09:00-09:45 Jinsang Kim (Univ. Michigan, Ann Arbor), **keynote:** *Metal-Free Purely Organic Phosphors: Molecular Design and Applications*

09:45-10:15 Juan Carlos Sancho García (Univ. Alicante), **invited:** *Thermally Activated Delayed Fluorescence: Insights from Theory and Simulations at the Nanoscale*

10:15-10:30 Juan Aragón (ICMol, Valencia): *Theoretical Insights into the Charge-Separation and -Recombination Rate Constants in Donor-Acceptor Buckybowl-Based Supramolecular Complexes*

10:30-11:00 Coffee Break & Poster Session (Seminar Room, 2nd Floor, La Nau)

Session 6 Supramolecular Systems [Chair: Daniel Roca]

11:00-11:30 Roland Resel (Univ. Graz), **invited:** *Crystal Structure Solution of Substrate Induced Phases: the Example of a Dicyano-Distyrylbenzene Derivative*

11:30-12:00 Emilio Perez (IMDEA Nanoscience, Madrid), **invited:** *Noncovalent Chemistry of SWNTs Inside Out*

12:00-12:30 Enrique Ortí (ICMol, Valencia), **invited:** *Self-Assembly of Electroactive Systems: From Dimers to Supramolecular Polymers*

12:30-12:45 Nandajan, P. C. (IMDEA Nanoscience, Madrid): *Water-Soluble Highly Fluorescent Low-Dimensional Host-Guest Supramolecular Polymers: Structure and Energy Transfer Dynamics Revealed by Polarized Fluorescence Spectroscopy*

12:45-13:00 Javier Segarra (Univ. Lyon): *Two-Dimensional Electronic Spectroscopy as a Tool to Separate Conformations in Molecular Aggregates*

13:00-14:50 Lunch (Cloister, La Nau)

Session 7 Photoinduced Processes I [Chair: Juan Aragón]

14:50-15:10 Juan Cabanillas (IMDEA Nanoscience, Madrid): *Chemical Sensing Schemes Combining Fluorescence, Colorimetry and Amplified Spontaneous Emission of Conjugated Systems*

15:10-15:25 Vladimir Chirvony (ICMol, Valencia): *Why Organic-Inorganic Metal Halide Perovskites are so Efficient Photovoltaic Materials? The Mechanism Responsible for Extended Lifetime of Photogenerated Charge Carriers*

15:25-15:40 Pedro Braña (Univ. Erlangen): *Dynamical Simulation of Singlet Fission in Covalent Bonded Pentacene Dimers*

15:40-16:00 Reinhold Wannemacher (IMDEA Nanoscience, Madrid): *Photophysics of Carbon Dots: Spectroscopy and Applications*

16:00-16:30 Coffee Break & Poster Session (Seminar Room, 2nd Floor, La Nau)

Session 8 Photoinduced Processes II [Chair: Begoña Milián Medina]

16:30-16:50 M^a Carmen Ruiz Delgado (Univ. Malaga): *Impact of the Intermolecular Interactions on the Electronic and Charge-Transport Properties of Organic Materials: A Joint Experimental and Theoretical Approach*

16:50-17:05 Chen Sun (IMDEA Nanoscience, Madrid): *Amplified Spontaneous Emission in Supramolecular Controlled Self-Encapsulated Polythiophenes*

17:05-17:35 Shinto Varghese (IACS, Kolkata), **invited:** *Exciton Diffusion Studies in Small Molecular Donors for Solar Cells*

17:35 Conclusion: B. Milián Medina, L. Lüer, J. Gierschner

Poster Contributions

- P01 Ana Claudia Santos Camilo (Univ. Malaga): *Modelling Charge Transport of Discotic Liquid-Crystalline Triindoles: the Role of Peripheral Substitution*
- P02 Andres Perez Guardiola (Univ. Alicante): *Why are some Organic Nanorings Synthesized and not Others? Insights from the Fractional Occupation Density Method*
- P03 Begoña Milián Medina (Univ. Valencia): *Exciton and MO Localization in Donor-Acceptor Copolymers*
- P04 Benedikt Schrode (Univ. Graz): *The Substrate-Induced Phase of C8O-BTBT-OC8 Detected by Mid-Infrared and Lattice Phonon Raman Spectroscopy*
- P05 Changhoon Yu, Youngmoo Kim (UNIST Korea): *A molecular design for efficient photoredox catalysis and their application for light-driven atom transfer radical polymerization (ATRP)*
- P06 Jesus Cerda Calatayud (ICMol Valencia): *Theoretical Estimates of the Charge-Separation and -Recombination Rates in Donor-Acceptor Buckybowl-Based Supramolecular Complexes in Solution*
- P07 Joaquín Calbo (Univ. Valencia): *A Dispersion-Corrected Density Functional Theory Investigation on Pyreneimidazole-Based Supramolecular Polymers*
- P08 Johannes Gierschner (IMDEA Nanoscience, Madrid): *Mixed- & Separated Stack Charge-Transfer Co-Crystals: Tunable Bright Emitters with Ambipolar Charge Transport Characteristics*
- P09 Junqing Shi & Larry Lüer (IMDEA Nanoscience, Madrid): *Designing High Performance All Small Molecule Solar Cell with Nonfullerene Acceptor: Comprehensive Studies on Photoexcitation Dynamics and Charge Separation Kinetics*
- P10 Larry Lüer (IMDEA Nanoscience, Madrid): *Lévy Defects in Matrix-Immobilized J Aggregates: Tracing Intra- and Inter-Segmental Exciton Relaxation*
- P11 Maria Izquierdo (ICMol, Valencia): *Charge Transfer States in Bulk Heterojunction Organic Photovoltaics*
- P12 Martín Castillo (Univ. Zaragoza): *Study on the Morphology and Optical Properties of Organic Nanoaggregates*
- P13 Ricardo Ortiz Cano (Univ. Alicante): *Electrical Spin Manipulation in Graphene Nanostructures*
- P14 Sergio Gámez Valenzuela (Univ. Malaga): *Using Novel Push-Pull Chromophores to Prepare Single Waveguide Silicon-Organic Hybrid Modulators*

KEYNOTE PRESENTATIONS

De Novo Strategies for Color-Specific Photoswitching

Soo Young Park, Dojin Kim, Ji Eon Kwon

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Fluorescence photoswitching system, which can turn on/off fluorescence by light irradiation, is attracting much attention because of its potential in various optoelectronic applications including optical memory, bioimaging, and super-resolution microscopy. Particularly, a dual-color fluorescent photoswitching system remains an important subject due to its capability of ratiometric imaging, which can reduce background cell autofluorescence in bioimaging field, and of multistate switching, which means displaying multi-distinguishable emission signals upon a single wavelength excitation. [1-5] However, it is still challenging because it demands elaborate manipulation of intermolecular energy transfers (ET) between fluorophores and photoswitchable chromophores.

In this presentation, we report simple and innovative strategies to achieve dual-color photoswitchable systems. The first is the rationally designed color-specific photoswitching system composed of two excited-state intramolecular proton transfer (ESIPT) fluorophores and a color-specific photoswitchable diarylethene.[6] Based on their unique photophysical properties, this system demonstrates an entirely new principle of color-specific photoswitching, which includes the frustration of ET between two fluorophores and the selective ET from only one specific fluorophore to the photochromic switch. The second is the two component system comprising the turn-on type fluorescent diarylethene and one ESIPT dye. This system is far excellent compared to the first system in terms of the fluorescence on/off ratio and non-destructive read-out capability. We synthesized water-soluble and biocompatible nanoparticle containing the two components to make fluorescence imaging agent for bio-system.

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- [1] J. Fölling, S. Polyakova, V. Belov, A. Blaaderen, M. L. Bossi, and S. W. Hell, *Small*, 4, 134 (2008).
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Metal-free Purely Organic Phosphors: Molecular Design and Applications

Jinsang Kim

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Phosphorescent materials are enhancing and broadening the usefulness of organic compounds in a wide variety of applications including OLED, photovoltaics, and sensors. OLEDs and solid-state lighting (SSL) research in both academic and commercial settings are driven by the promise of highly efficient devices manufactured via economic and versatile processes. Of the emissive materials employed in OLEDs and SSL, phosphorescent compounds produce much higher efficiency devices than those based on fluorescent emitters by utilizing spin-parallel electrons and emitting photons from the decay of triplets. Organo-metallic compounds are thus often doped into organic hosts to impart a phosphorescent pathway into otherwise triplet-forbidding carbon-based materials. However, phosphorescence from metal free, purely organic, compounds is almost always either strictly forbidden or only extremely weakly allowed, leaving pure organics undesirable for useful applications. Our recent development of highly emissive and metal-free purely organic phosphorescence materials will be presented.^[1-5] Directed intermolecular heavy atom effects are uniquely implemented in aromatic carbonyl molecules to promote spin-orbit coupling and suppress vibrational dissipation. Color tuning by electron density modulation, highly sensitive oxygen sensors, and prototype PhOLED have been demonstrated. Molecular design strategies and applications of purely organic phosphors will be discussed.

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3. Min Sang Kwon⁺, Dongwook Lee⁺, Sungbaek Seo, Jaehun Jung, Jinsang Kim "Engineering Intermolecular Interactions for Efficient Room Temperature Phosphorescence from Purely Organic Materials in Amorphous Polymer Matrices" *Angew. Chem. Int. Ed.* **2014**, 53, 11177.
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6. Youngchang Yu⁺, Min Sang Kwon^{+*}, Jaehun Jung, Yingying Zeng, Mounngon Kim, Kyeongwoon Chung, Johannes Gierschner, Ji Ho Youk^{*}, Sergey Borisov^{*}, Jinsang Kim^{*} "Room Temperature Phosphorescence based Dissolved Oxygen Detection by Core-Shell Polymer Nanoparticles having Metal-free Organic Phosphors" *Angew Chem* **2017** (10.1002/anie.201708606).

INVITED PRESENTATIONS

Stimuli-Responsive Materials with Bent-Core Liquid Crystals

M. Martínez-Abadía,^{1,4} B. Robles-Hernández,² M. R. de la Fuente,² S. Varghese,^{3,5}
J. Gierschner,³ R. Giménez,¹ M. B. Ros¹

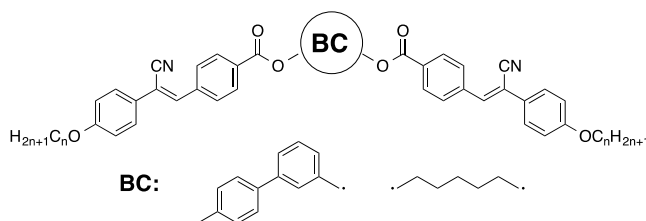
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Novel cyanostilbene¹ compounds characterized by a bent-shaped structure, with photoluminescent properties and photochemical activity in solution, liquid crystal and crystal phases have been obtained. Structural modifications such as the position of the cyano group on the C=C bond (α - or β -isomers), the number of cyanostilbene units in the molecule (one or two), the terminal chain length (-OC₄H₉ or -OC₁₄H₂₉), as well as the presence of a rigid (3,4'-biphenylene) or flexible (-CH₂)₅- structure as the origin of the bent-shape have been considered.² The 2D molecular-shape of these molecules promotes a variety of crystal polymorphs and bent-core mesophases, offering the unique chance to study the stimuli-responsive properties of the cyanostilbene unit in different supramolecular organizations, attaining very attractive functional materials with high light-sensitivity and different photoresponses such as luminescence switching or macroscopic polarization modulations.



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- [2] M. Martínez-Abadía *et al.*, *J. Mater. Chem. C*, **2015**, *3*, 3038, *Phys.Chem.Chem.Phys.*, **2015**, *17*, 11715, *Adv. Mater.* **2016**, *28*, 6586 and *Adv. Optical Mater.*, **2017**, 1600860.

This work was financially supported by MICINN-FEDER and MINECO-FEDER of Spain-UE (Projects MAT2011-27978-C02-02, CTQ2011-27317, MAT2012-38538-C03-01 and -02), the Gobierno de Aragón and FSE (Project E04), the Gobierno Vasco (GI/IT-449-10), the Comunidad de Madrid (Project S2009/MAT-1726, S2009/PPQ-1533) and by the Campus of International Excellence

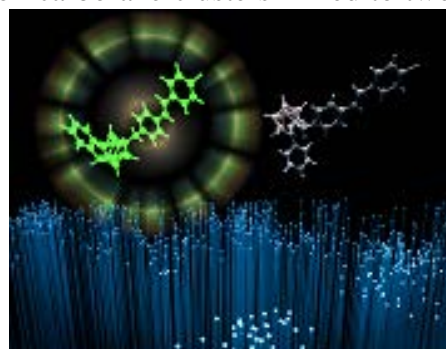
Photoluminescence in boron clusters-containing molecular materials

Rosario Núñez

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Icosahedral carborane clusters are well-known boron-cluster compounds that can be characterized for their unique three-dimensional (3D) structure, their electronic properties as well as their high thermal and chemical stabilities. During the last decade, these boron clusters have been investigated as excellent building blocks for luminescent materials because of their exceptional properties.^[1] The influence of the nature and geometry arrangement of the substituents bonded to the C atoms, the electronic nature of the cage (*closo* or *nido*) and the relative position of the two C atoms within the cluster (*o*-, *m*- and *p*-) have shown a critical effect on the PL behavior. It is noticeable the uniqueness of the *o*-carborane isomer that largely affects the PL of any fluorophore directly attached to the C atom. This is due to the electron-withdrawing ability of the cluster, which leads to a rapid charge transfer (CT) from the fluorophore to the C-C unit producing a quenching of the fluorescence in solution.^[1]

Our group has also contributed to the advancement of luminescent molecular materials based on carborane derivatives linked to different fluorescent π -conjugated systems and their emission properties have been evaluated.^{[1],[2],[3]} Different triads based on carborane clusters linked to two stilbenes through the C atoms, POSS hybrids with extended conjugation containing *o*- and *m*-carborane-substituted vinylstilbenes and tetraphenylene-ethylene-cored stilbene compounds substituted in the terminal carbon for *o*-carboranes are some of the developed systems. Their preparation as well as their photophysical properties in solution and solid state will be exhibited in this presentation.^[3]



References

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Materials for Optoelectronics from Photosynthetic Microorganisms

Gianluca M. Farinola,¹ Roberta Ragni,¹ Marco Lo Presti,¹ Simona la Gatta,¹ Francesco Milano,²
Angela Agostiano,^{1,2} Massimo Trotta²

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The lecture will present our studies on bio-hybrid photoactive materials based on the combination of Photosynthetic Reaction Centers (RCs) from the bacterium *Rhodobacter sphaeroides* and functional organic molecules.

RCs are photoenzymes capable to convert solar energy into charge separated states with almost unitary efficiency. We are investigating the possibility of taking advantage of this unmatched efficiency to create photoactive materials for bioelectronics.¹ We have first demonstrated the functionalization of the bacterial RC in specific sites with tailored fluorophores acting as antennas to enhance its light harvesting capability. The resulting hybrid systems outperform the native protein in the photogeneration of charges and in the photoenzymatic activity.² We have also built-up smart supramolecular architectures combining multiple enzymes assembled with tailored linkers, which are able to perform manifold functions. Finally, we have developed protocols for anchoring the RC on thin films of molecular³ or polymeric semiconductors or on metal electrodes, ultimately building up optoelectronic devices where the RC acts as the photoactive unit.

Our study discloses general concepts for the generation of bio-hybrid supramolecular materials for sunlight photoconversion and for light-triggered bioelectronics, from the combination of highly efficient photo-active natural structures, optimized in billions of years of evolution, with tailored functional molecules.

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Artificial Photosynthesis: Learning from Nature

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Artificial photosynthesis has been devised and investigated in pursuit of solving 21th century's energy problem. Despite such advances in recent decades, applying the technology in real life is still a challenging subject for the scientists. As the term "artificial photosynthesis" stems from mimicking the natural photosynthesis, we can learn from the nature's strategies which have been evolved for 3.4 billion years. This talk highlights our recent progress on developing highly efficient and robust artificial photosynthetic systems by mimicking the important strategies of natural photosynthesis. Starting with a brief description of photosystem II in natural photosynthetic autotrophs, two relevant bioinspired strategies are discussed in this talk: i) accumulative charge transfer and ii) self-healing. Finally, remaining challenges and perspectives for future development of artificial photosynthesis are discussed.

Vapor phase deposited perovskites for photovoltaic applications

Henk Bolink

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Perovskite based solar cells, mostly employ solution processed perovskite layers. Evaporated methylammonium lead iodide perovskite layers have also been reported and been employed in solar cells. Our group has developed several perovskite based solar cells, using vacuum based perovskite preparation methods. These metal oxide free p-i-n type perovskite cells exhibit high power-conversion efficiencies. We have extended this work to fully evaporated perovskite devices reaching power conversion efficiencies as high as 20 % in a planar single junction device and similar performance in tandem devices. Avenues to further increase the device performance by using multiple cation perovskite prepared via sublimation will also be presented.

Towards the Commercialization of Organic Photovoltaics

A. Distler, H.-J. Egelhaaf, E. Tam, Ph. Maisch, P. Schilinsky, Ch. Iftikhar,
M. Winkler, C.J. Brabec

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In terms of efficiency, OPV is certainly still inferior to other technologies, including perovskites, although the performance of commercial OPV modules has continuously increased from 2% in 2007 to about 5 % in 2016, and recent developments on stable and efficient materials suggest that the OPV technology will meet the milestone of 10% module efficiency within the next two or three years.

However, the strength of OPV rather lies in the fact that it offers several unique advantages in terms of high power-to-weight ratio and attractive visual appearance. These advantages include semitransparency, abundant colour choices and freedom of shape and size. Thus, focusing on integrated portable solutions (“wearables”) is certainly today’s strongest marketing concept of the OPV technology. Such a tight integration with products requires a module’s optical appearance to match perfectly with the product of concern, i.e., it should be “invisible” to the user.

Digital printing of organic photovoltaics has been demonstrated by several groups to be a promising approach to address this issue, because its drop-on-demand process allows the arbitrary deposition of materials. The last hurdle on the path to design and process “invisible” OPV modules is a technological solution to mask the cell interconnection regions without compromising performance. Traditional OPV modules typically display cell interconnection gaps of several millimetres in width, which are visually obtrusive.

In order to overcome this final obstacle, we have developed a new strategy to achieve effective, yet visually inconspicuous interconnects by making use of the strengths of ink jet printing. In our approach, all layers except the top and bottom electrodes are printed as continuous homogenous layers. The cell interconnects are produced in a very simple and robust way by ink jet-printing highly conductive silver bridges onto the bottom electrodes to provide conductive paths to the top electrodes. In order to precisely measure the extraordinarily low interconnection resistance provided by this new technology, we have also developed a novel measurement architecture, which is particularly suited for the characterization of printed photovoltaic modules.

Finally, we demonstrate the potential of the bridge interconnection method for creating “shy” photovoltaics by ink jet printing a P3HT:PCBM based “solar module portrait” of Nobel Prize winner Alan Heeger with an active area of 84 cm².

Probing local intermolecular interactions with light: Modeling insights

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The optoelectronic properties of conjugated organic materials are notoriously sensitive to the supramolecular arrangement of their constituent molecules. Because intermolecular interactions in molecular materials are driven by relatively weak van der Waals forces, various supramolecular organizations are possible in the solid state, which translates into multiple polymorphs in crystalline samples. The situation is even more complex in polycrystalline thin films where local microstructure may vary substantially, while impacting significantly fundamental processes such as (photoinduced) charge transfer. Here, we will present some recent modeling studies aiming at deriving structure-property relationships between local packing of electroactive conjugated molecules and function, in the context of molecular doping, charge photogeneration and singlet exciton fission. We will in particular discuss the electronic structure of doped and mixed molecular crystals based on pentacene. Such theoretical studies provide the needed framework for the interpretation of experimental investigations using light, namely ultraviolet photoelectron and (transient) optical spectroscopy, as a probe for local intermolecular interactions.

Non-Adiabatic Chemical Mechanisms of Interest in Organic Optoelectronics

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Non-adiabatic chemistry refers to chemical phenomena taking place via internal conversions (ICs) or intersystem crossings (ISCs). Such processes are important in optoelectronics, for instance in the design of photoinduced switches, solar cells and luminescent materials. Within the framework of the Born-Oppenheimer approximation, non-adiabatic chemistry corresponds to electronic transitions between potential energy surfaces without the absorption or emission of light. Conical intersections (CIs) and singlet-triplet crossings (STC) are key structures in the IC and ISC processes, respectively. In this contribution, we will mainly focus on the findings that we have obtained in the study of the photo-responses of the indoline donor unit used in solar cell dyes;¹ the indan-1-ylidene and fluoren-9-ylidene malononitriles,² which are of interest for the design of photoinduced switches or optical devices based on charge separation processes; cyano-substituted distyrylbenzene,³ with solid-state luminescent enhancement properties; and an inorganic-organic composite based on boron hydride clusters and pyridine ligands,⁴ with potential use as luminescent and solar light concentration materials. These studies shall illustrate some of the roles of CIs/STCs in optoelectronics.

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Thermally Activated Delayed Fluorescence: Insights from Theory and Simulations at the Nanoscale

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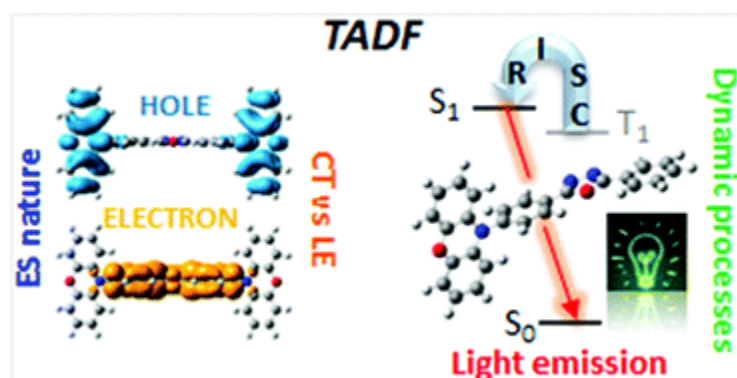
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We present some advances and investigations related with a new mechanism for light-emitting conjugated molecules, dubbed as Thermally Activated Delayed Fluorescence (TADF) and seeking to harvest both the singlet and triplet excitons generated under electrical excitation. The new strategy may disclose the use and manufacturing of 3rd generation OLEDs, although a complete understanding of the mechanism is not fully uncovered yet. Therefore, we will review our recent efforts to address some challenging issues using fully atomistic models [1-3]. Among them, we will remark how the nature of the excited-states involved (charge-transfer or locally-excited) ultimately control the singlet-triplet energy difference, and how this is a dynamic process mediated by conformational fluctuations.



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Crystal Structure Solution of Substrate Induced Phases: The Example of a Dicyano – Distyrylbenzene Derivative

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The presence of unknown polymorphs is frequently observed when a substrate surface is present during the crystallization process [1]. We present a short overview about this class of polymorph phases frequently found in organic electronics and pharmaceuticals. Of special emphasis will be a combined experimental – theoretical approach for solving the crystal structures from thin films. As an example the molecule ((2Z,2'Z)-3,3'-(1,4-phenylene)bis(2-(3,5-bis(trifluoromethyl)phenyl)acrylonitrile), (CN-TFPA) is chosen [2]. Two new crystal structures are observed within thin films, both of them show considerable different molecular packing (see Figure).

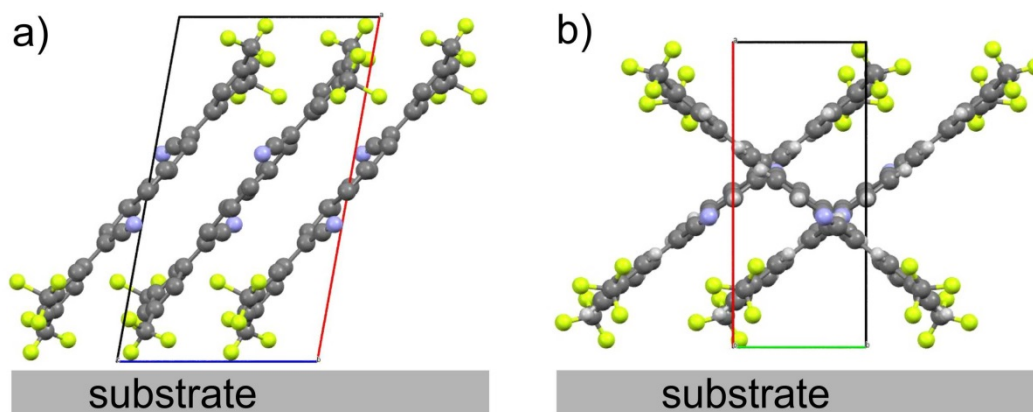


Figure: Molecular packing of the molecule CN-TFPA within two different crystal structures induced by the presence of a substrate during the crystallization process: the “blue film phase (a) and the “green film phase(b).

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Noncovalent Chemistry of SWNTs inside-out

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Here, we present novel strategies to interface molecules and single-walled carbon nanotubes (SWNTs).

In particular, we will present the synthesis of mechanically interlocked derivatives of SWNTs (MINTs), which are rotaxane-type materials, the first example of, a 0D-1D mixed dimensional heterostructure interfaced through the mechanical bond.^[1] We will also show that the effect of the mechanical bond on the properties of SWNTs is unique, and clearly different from the noninterlocked, supramolecular compounds.^[2]

We will also show that the encapsulation of viologen derivatives into metallic single-walled carbon nanotubes (SWNTs) results in the opening of a band gap, making the SWNTs semiconducting. Raman spectroscopy, thermogravimetric analysis, and aberration-corrected high-resolution transmission electron microscopy confirm the encapsulation process. Through the fabrication of field-effect transistor devices, the change of the electronic structure of the tubes from metallic to semiconducting upon the encapsulation is confirmed.

In summary we present two novel noncovalent strategies to functionalize the outside and the inside of SWNTs, with direct consequences to their electronic properties.

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Self-Assembly of Electroactive Systems: From Dimers to Supramolecular Polymers

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Supramolecular aggregates and polymers are macromolecular entities that grow up by the non-covalent interaction of suitable monomeric units. In the search for new materials for optoelectronic applications through self-assembly, the control over the assembly process is one of the most sought-after characteristics. This control is usually achieved by a proper design of the monomeric structure and of the self-assembling motifs (H-bonds, π -stacking, dispersion forces or electrostatic interactions).

In this communication we first present the self-assembly of donor-acceptor supramolecular dimers formed by fullerene fragments (buckybowls) and tetrathiafulvalene (TTF)-based electron donors. In a following step, we discuss the polymerization mechanism and the structural properties of the supramolecular aggregates formed by monomeric units incorporating electroactive fragments. The discussion is mainly based on theoretical density functional theory (DFT) calculations and includes two type of monomeric units: a bisurea macrocycle bearing electron-donor DMTTF moieties (**1**) and CO-centered oligo(phenylene ethynylene)s (OPEs) trisamides endowed with paraffinic side chains bearing chirally active groups (**2**).

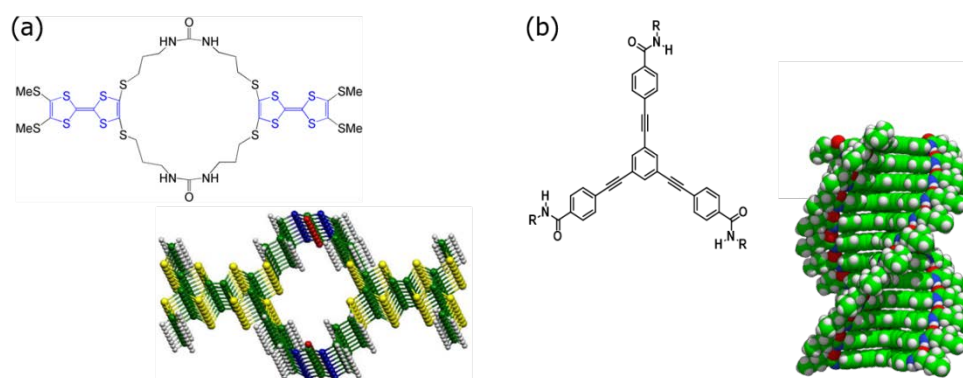


Figure 1. a) Chemical structure and supramolecular nanotubes of **1**. b) Chemical structure and supramolecular helical aggregates of **2**.

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Exciton Diffusion Studies in Small Molecular Donors for Solar Cells

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Exciton generation, migration and dissociation are basic processes in the operation of organic solar cells, which need to be understood and tuned to utilize the full potential of these devices.¹ In a bulk heterojunction solar cell, the exciton formed in one component (donor) of the blend must diffuse to an interface with the acceptor, at which the offset of the energy levels leads to charge separation. Understanding organic solar cells therefore requires the understanding of exciton diffusion.² Materials with high exciton diffusion coefficient are desirable as solar cell materials, as this will ensure the excitons generated in the active layer reach the donor-acceptor interface and generate charges. Conversely in organic light-emitting diodes and lasers, small exciton coefficients are desirable to minimize the exciton-exciton annihilation.

Exciton diffusion in the thin film of DTG-F and F2 derivatives were investigated by time resolved fluorescence quenching at a planer interface. The thin films of varying thickness were spin coated on cross linked PCBM layer and fluorescence quenching was measured using a streak scope and modelled using one dimensional diffusion model to derive the diffusion coefficients. The diffusion coefficient of the DTG-F ($1.4 \times 10^{-3} \text{cm}^2 \text{s}^{-1}$) is found to be three times higher than that of DTG-F2 ($0.47 \times 10^{-3} \text{cm}^2 \text{s}^{-1}$). To further understand the effect of additive and thermal annealing on exciton diffusion coefficients, exciton annihilation studies were carried out. Substantial enhancement in diffusion coefficient was observed with small amount of additive (Diiodooctane) and under thermal annealing. These aspects along with structural and morphological features will be discussed in the talk.

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ORAL COMMUNICATIONS

Solid State Luminescence Enhancement in π -Conjugated Materials: Unraveling the Mechanism beyond the Framework of AIE/AIEE

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Solid state luminescence enhancement (SLE) of conjugated organic materials has found a great impact in materials science,¹ but a deep understanding has been rather limited to date. For this, we investigate a prototype example of SLE materials, cyanosubstituted distyrylbenzene (DCS), by varying systematically and subtly the substitution pattern (inter alia of the position of the cyano-substituent) to give largely different photoresponse in fluid and solid solution as well in the crystalline state.² The combination of quantitative (ultra)fast optical spectroscopic techniques, appropriate quantum-chemical methods, and structural (X-ray) data allows us to elucidate and rationalize all details of the SLE process, including steric versus electronic factors, radiative versus nonradiative decay channels, and *intra*- versus *intermolecular* contributions, providing a first holistic picture of SLE.²



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Progress in Organic Solar Cells

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Organic solar cells (OPVs) offer many advantages and this technology has been explored intensively over last years. OPVs can be printed, can be light weight and flexible, have a very short energy pay-back time and the potential to be manufactured at very low cost. Despite all the advantages, the application of organic solar cells is still limited to small niche markets.

In my presentation, I will summarize the current status of OPV and analyze the discrepancy between the large potential and their moderate market success. As it turns out, achieving higher power conversion efficiencies is the most critical issue for this technology. While state-of-the-art organic solar cells based on conjugated polymer – fullerene blends appear to have reached their efficiency limit (~ 12 %), a recently discovered material class called non-fullerene acceptors (NFAs) has the potential to overcome the current limitations. OPVs with NFAs replacing the fullerene acceptor material show significantly higher open circuit voltages and in some cases also higher radiative recombination quantum yields. In my presentation I will discuss the effect of NFAs and our recent work on the new acceptor material class.

Theoretical insights into the charge-separation and -recombination rate constants in donor-acceptor buckybowl-based supramolecular complexes

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Fullerenes and their derivatives are one of the most important electron-acceptor (A) compounds in organic electronics.¹ In particular, the fullerene fragments such as the C₃₀H₁₂ (Hemifullerene) can effectively interact supramolecularly with, for instance, the electron-donor (D) truxene-tetrathiafulvalene (truxTTF).^{2,3} The resulting D–A supramolecular complexes exhibit an efficient photoinduced electron transfer process (Figure 1) in solution. In this contribution, we present a theoretical protocol to estimate charge-separation and charge-recombination rate constants in D–A buckybowl-based supramolecular complexes in the presence of solvent. The protocol makes use of the Marcus–Levitch–Jortner rate expression^{4,5} where the relevant transfer parameters are carefully evaluated from electronic structure and molecular mechanics calculations. A detailed analysis of how to assess the most important parameters for the electron-transfer processes for these complicated D–A supramolecular associates is provided.

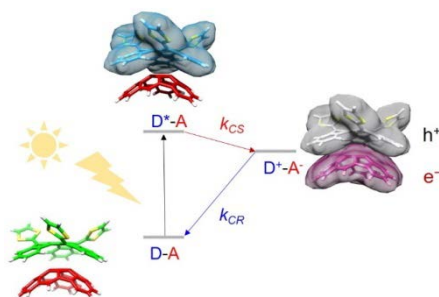


Figure 1. Diagram of the supramolecular organization between truxTTF and C₃₀H₁₂ and the photoinduced electron transfer mechanism.

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Insight into Water-Soluble Highly Fluorescent Low-Dimensional Host-Guest Supramolecular Polymers: Structure and Energy Transfer Dynamics Revealed by Polarized Fluorescence Spectroscopy

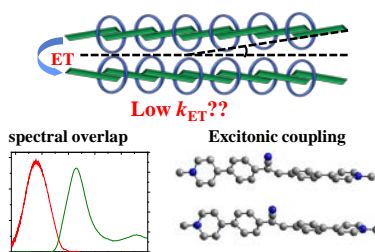
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Host-guest supramolecular assemblies finds extensive applications in biology and materials due to the well-ordered structures and tunable optical properties.¹ But details of the host-guest interactions remains scarcely explored. In this context, we investigate the structural and energy transfer details of quasi-1D supramolecular polymer (SP) based on para-di-pyridyl-cyanostilbene (**G**) enclosed in cucurbituril CB[8] in a 1:1 molar ratio. **G** monomer shows remarkable luminescence changes as non-fluorescent in solution to highly emissive in the SP, due to aggregation induced enhanced emission (AIEE) by synergetic control of the non-/radiative decay channels. The monomer shows weak J-type aggregation in the SP (PM5 calculations^{2a}), while in the solid state it exhibits H-type interactions.^{2c} Steady-state polarized PL measurements reveal the inter-strand arrangement within the SP bundles, being close to the PM5 predictions; single particle investigations allow for insights to the heterogeneity of the system. Dynamic polarized PL reveals slow energy transfer process,^{2c} which can be directly correlated to the small spectral overlap compared to well-studied host-guest assemblies.³ Further to have more insights about the energy transfer process happens in the host-guest assemblies, we compare the SP formed by **G** molecule with SPs of **B** and **R**, which confirms the importance of spectral overlap for the efficient energy transfer processes.^{2b}



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Two-dimensional electronic spectroscopy as a tool to separate conformations in molecular aggregates

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The specific conformation featured by molecular systems in condensed phases is difficult to ascertain due to the vast conformational space accessible to macromolecular species and the molecular systems enclosed. This is endorsed by the extreme difficulties faced in locating and assigning specific spectroscopic fingerprints pertaining to a given unique molecular conformation for its unequivocal characterisation. Intermolecular interactions strongly modulate the photophysical properties of materials, their characterisation being of paramount interest. A computational strategy to simulate two-dimensional electronic spectra (2DES) is here introduced, which allows us to analyse, sample and measure different conformations attained by flexible molecular systems in condensed phases. An explicit mixed quantum mechanics/molecular mechanics (QM/MM) approach is employed for the evaluation of the necessary electronic excited state energies and transition dipole moments. The usefulness of the protocol is exemplified by assessing the ground state dynamics of a water-solvated adenine-adenine monophosphate (ApA),[1] a system featuring two interacting adenine moieties that display various intermolecular arrangements. Molecular dynamics simulations and clustering analyses are used to extract the main molecular conformations, reducing the complexity of the flexible ApA conformational space. By using a Sum-Over-States (SOS) approach [2] to obtain 2DES spectra for each of these selected conformations, we can discern spectral changes and relate them to specific nuclear arrangements (stacked/interacting *vs* unstacked/non-interacting). 2DES maps reveal spectral fingerprints associated with specific molecular conformations, being a promising option to enable their quantitative spectroscopic detection beyond standard 1D pump-probe techniques. This technique enables monitoring photophysical properties, such as energy/charge transfer processes, ascertaining the concrete impact held by their specific molecular conformation.

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Chemical sensing schemes combining fluorescence, colorimetry and amplified spontaneous emission of conjugated systems

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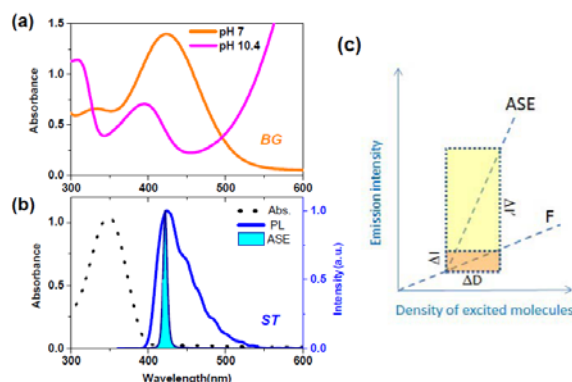
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In this work we present a chemosensing scheme based on a combination of ASE from a laser dye and the colorimetric response of a pH indicator. This principle allows for pH resolution with sensitivity down to 0.05 pH units. The on/off nature of the sensor response is suitable to neatly identify low pH fluctuations. We investigated the response range of our sensor in 10.28–10.93 by ammonia doping of mixtures of a stilbene dye and bromocresol green in order to demonstrate the proof-of-concept. Furthermore, we have taken advantage of the optical gain properties of Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] films to exploit ASE quenching as a sensitive method for acid sensing. When the ASE signal is used, a strong quenching is observed for very low acid concentrations, reaching a limit of detection in the sub-ppm range (40 ppb). This procedure led to the lowest limit of detection for formic acid vapors described in the literature for an optical chemosensing set-up to the best of our knowledge.



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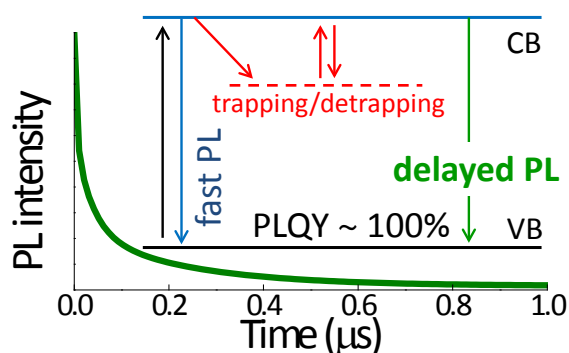
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Why organic-inorganic metal halide perovskites are so efficient photovoltaic materials? The mechanism responsible for extended lifetime of photogenerated charge carriers

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In just four years, hybrid organic-inorganic lead halide perovskites became the most studied semiconductor materials in the field of photovoltaics. The reason for such interest is in low price and simplicity of solution-processed solar cells based on perovskite layers in a combination with their high efficiency (now more than 22%). One of the most salient features of hybrid lead halide perovskites is the extended lifetime of their photogenerated charge carriers, although it is such a long lifetime of charge carriers that is considered to be responsible for the effective separation of charges in perovskite-based solar cells. Here we studied the photophysics of well-passivated methylammonium lead bromide perovskite nanocrystals ($\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs) with a photoluminescence (PL) quantum yield close to unity. We show that, in spite of microsecond-long PL decay time, the lifetime of the spontaneous radiative recombination in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs is as short as 2 ns, which is expected considering the direct bandgap character of perovskites. All longer (up to microseconds) PL decay components result from the rapid reversible processes of multiple trapping and de-trapping of carriers with a slow release of the excitation energy through the spontaneous emission channel. As our modeling shows, the trap (dark) and excitonic states are coupled by the trapping-de-trapping processes so that they follow the same population decay kinetics, while a majority of excited carriers are in the dark state. The lifetime of such “delayed luminescence” (see the Figure below) is found to be determined by the depth of the trap states, lying from a few tens to hundreds meV below the emitting excitonic state [1]. The proposed model changes the paradigm of the description of the PL formation and electron transport in metal halide perovskites.



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Intramolecular Singlet Fission: Insights from Quantum Dynamical Simulations

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Singlet fission (SF) is a spin-allowed process by which two triplet excitons are generated from a singlet exciton.¹ It has received great attention recently as a feasible way to overcome the Shockley-Queisser limit,² which could enable the development of more efficient solar cells. In this contribution, we discuss the dynamics of intramolecular SF (iSF) in a series of modified pentacene dimers covalently bonded to a phenylene spacer in *ortho*-, *meta*-, and *para*-conformations employing multireference perturbation theory and quantum dynamical methods.³⁻⁶ The results provide insight into the different contributions of the direct and mediated mechanisms to the global iSF process, disentangling the key roles that molecular vibrations and the conformation of the chromophores have in the process.

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Photophysics of Carbon Dots: Spectroscopy and Applications

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Carbon dots (CD) currently attract intense interest in the scientific community due to their bright photoluminescence (PL), high quantum yield, high chemical and photo-stability, comparatively easy and low-cost preparation, and excellent biocompatibility, compared, for example, to semiconductor quantum dots. Applications range from bio-imaging, biosensors and drug delivery to photo-catalytic applications like, for example, water splitting and CO₂ conversion. Preparation of CD is typically based either on top-down nano-cutting techniques or bottom-up carbonization. In the case of CD prepared by bottom-up techniques the importance of molecular species for their optical and photo-physical properties has been recently unequivocally demonstrated. Many details, however, are still waiting to be clarified in this context.

In the present study nitrogen-doped CD were prepared from ethylenediamine and citric acid by hydrothermal means, as well as from urea and citric acid by application of microwaves. The samples obtained were characterized by standard UV/VIS, PL, FTIR and Raman spectroscopy, as well as HRTEM, XRD and WAXS. Fluorescence spectra of CD incorporated in polyvinylpyrrolidone (PVP) obtained at 1.5 K with tunable excitation by an optical parametric oscillator exhibit no significant line narrowing compared to room temperature spectra. In addition, CD were mixed with gold nanoparticles (AuNP) and spin-coated on clean silicon substrates. The association with AuNP completely quenches the fluorescence of CD, which allows to obtain SERS spectra with visible light excitation. SERS spectra of both types of CD reveal D and G bands of the graphitic core of the CD, as well as signals from molecular species. CD were also aggregated with anatase TiO₂ nanoparticles and the photo-catalytic activity of these nanocomplexes under visible light excitation was studied. Photo-catalytic action spectra obtained in these experiments will be discussed.

Impact of the Intermolecular Interactions on the Electronic and Charge-Transport Properties of Organic Materials: A Joint Experimental and Theoretical Approach

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The use of organic materials to design electronic devices has actually presented a broad interest because they constitute an ecological and suitable resource for our current "electronic world". These materials provide several advantages (low cost, light weight, good flexibility and solubility to be easily printed) that cannot be afforded with silicon.[1] They can also potentially interact with biological systems, something impossible with inorganic devices. The performance of the organic-based electronic devices critically depends not only to the intrinsic properties of the conjugated cores but also to the supramolecular arrangement.[2] In this contribution, we present some of our more recent investigations on this field dealing with the better understanding of the complex structure-properties relationships of organic nanomaterials.[3] For this purpose, we use a joint experimental and theoretical approach that includes spectroscopic measurements and molecular modeling.

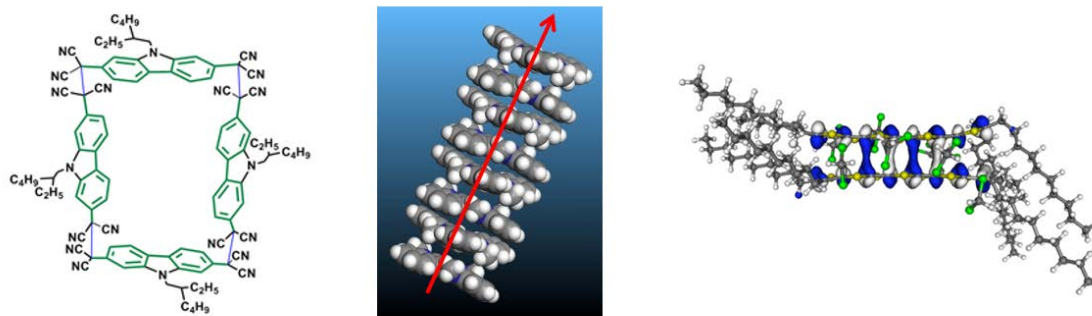


Figure 1. Examples of the supramolecular arrangements recently studied.

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Amplified Spontaneous Emission in Supramolecular Controlled Self-Encapsulated Polythiophenes

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During the past decades, π -conjugated polymers (CP) and oligomers have attracted extensive attentions on account of their peculiar optical properties, high conductivities and low-cost fabrication process.¹ However, in general, π -conjugated polymers still have some drawbacks, especially closed π - π stacking always experiences a tradeoff with the effective fluorescence resulting. Recently, IMWs have attracted considerable attention because of their potential applicability as next-generation monomolecular electronic device to obtain high PLQE. We report on the outstanding optical gain properties of self-encapsulated red-emitting polythiophenes whose conjugated molecular wire is sheathed within its own cyclic side chains: PSTB (bearing one thread every two thiophene rings) and $\frac{1}{2}$ PSTB (one thread every four thiophene rings).² The lowest thresholds for ASE were achieved in PSTB spin-coated films (0.09 mJ/cm²) in contrast with $\frac{1}{2}$ PSTB (1.09 mJ/cm²) and P3HT (ASE action has not been observed).

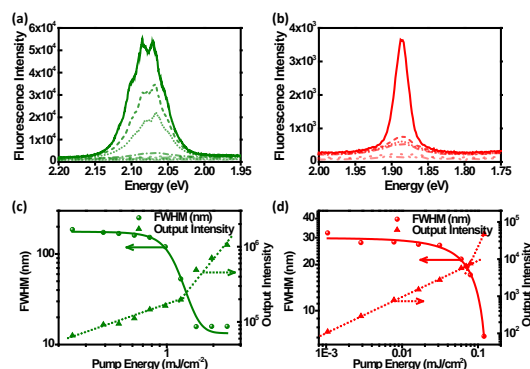


Figure 1. ASE experiments for photoluminescence spectra under different excitation powers of (a) $\frac{1}{2}$ PSTB and (b) PSTB. Input-output characteristics of (c) $\frac{1}{2}$ PSTB and (d) PSTB: FWHM (solid line) and peak intensity (dash line) versus pump power.

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POSTER CONTRIBUTIONS

Modelling charge transport of discotic liquid-crystalline triindoles: the role of peripheral substitution

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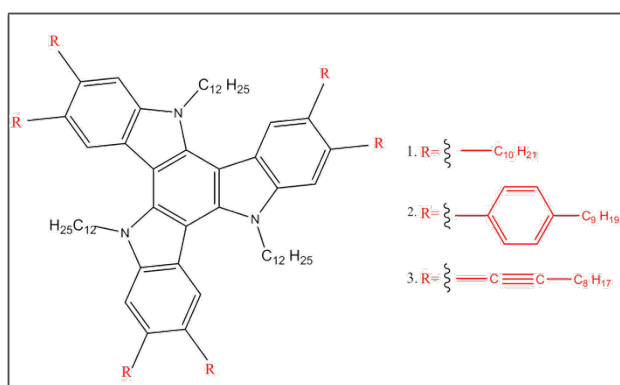
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Charge mobility is one of the key parameter controlling the efficiency of the devices based on organic semiconductors. Recently, a charge mobility as high as $1.4 \text{ cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ was observed for discotic liquid-crystalline Triindole¹. Since then many strategies have been explored to enhance the charge mobility of these systems. One of the approaches investigated is related with the enhancement of the intermolecular order within the stacks by distancing the central aromatic cores and the flexible peripheral chains with linkers such as alkyne or phenyl. Herein, we present a theoretical study about the influence of the peripheral substitution on the charge transport properties of discotic liquid-crystalline triindoles², see Scheme 1. To achieve this goal, we combine Quantum Mechanical (QM) calculations and atomistic Molecular Dynamics (MD) methods. In conclusion, the study reveals that the insertion of alkynyl spacer between the external flexible alkyl chains and triindol cores would be a promising strategy to obtain high mobility in columnar phases.



Scheme 1. Chemical structure of Triindoles 1-3 used in this study.

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Why are synthesized some organic nanorings and not others? Insights from the fractional occupation number weighted density

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Recently developed analysis tools, as fractional occupation number weighted electron density (ρ^{FOD})^[1] have been employed to characterize the nature of electron-correlation effects in carbon nanorings and nanobelts, such as cycloparaphenylene (CPPs) and cyclacene (CCs)^[2] molecules of increasing size. Further comparison with linear oligomers has allowed to establish a relation between these strong-correlation-effects and their bi- or polyradical character. We have also explored how minor structural modifications of cyclacenes can modify the radical character, showing the potential use of these systems as molecular templates for the growth of well-shaped carbon nanotubes as well as the usefulness of the theoretical tools to disclose structure-property relationships.



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P03.- Begoña Milián

Exciton and MO Localization in Donor-Acceptor Copolymers

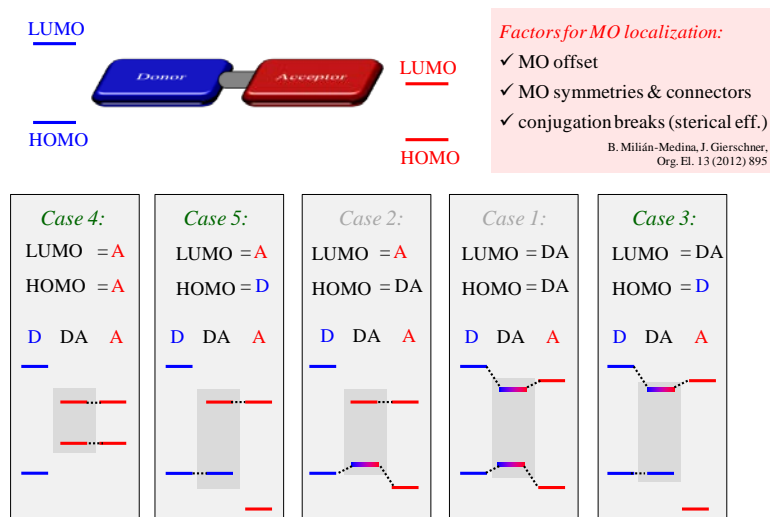
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Molecular orbital (MO) and exciton localization in conjugated homo- and co-polymers originating from electronic, geometrical and symmetry reasons, may have significant impact on the resulting features and fates of excitons and charges, and this on the resulting device performance in organic optoelectronics. We present here a systematic approach towards localization phenomena in (co)polymers, elaborating criteria on how these situations can be realized in practice, giving guidelines on how excited states can be properly calculated, establishing structure-property-relationships, and discussing how these particular properties can be utilized in practical applications.



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The Substrate-Induced Phase of C₈O-BTBT-OC₈ Detected by Mid-Infrared and Lattice Phonon Raman Spectroscopy

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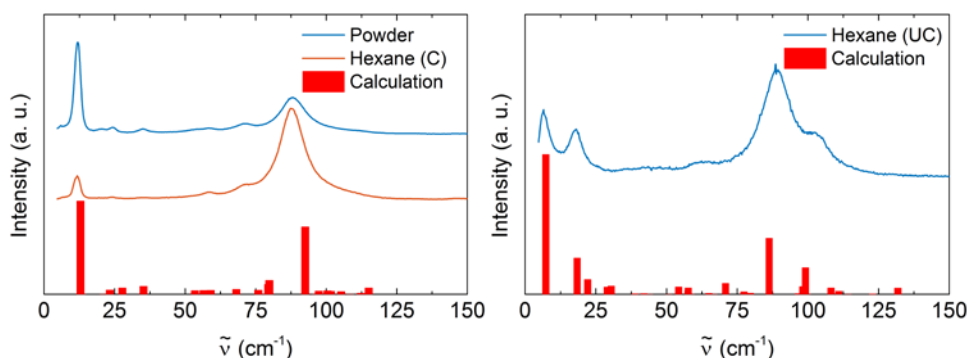
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The presence of a substrate-induced polymorph of the molecule 2,7-dioctyloxy[1]benzothieno[3,2-*b*]benzothiophene is probed on microscopic crystals and within thin films. Two experimental techniques are used: lattice phonon Raman and infrared spectroscopy. Raman spectra of crystals grown from different solvents can be unambiguously assigned to the type of polymorph. Comparison of this experimental data with recently published results from DFT calculations including many-body dispersion van der Waals corrections (Figure) show agreement within 5 cm⁻¹ (0.6 meV) [2]. Drop cast and spin coated films are investigated in the as-prepared state and after solvent-vapor annealing. With decreasing film thickness Raman spectroscopy became less sensitive, so that infrared spectroscopy is a more feasible tool for phase detection. It is found that the surface-induced phase is dominantly present in the as-prepared state of thin films, while the bulk phase is always present after solvent vapor annealing.



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A molecular design for efficient photoredox catalysis and their application for light-driven atom transfer radical polymerization(ATRP)

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Visible light photoredox catalysis, formerly inaccessible redox-neutral reaction scaffolds, has enabled significant development of radical chemistry in organic and polymer synthesis. So far, most progress in this field has been made with transition metal complexes, yet several aspects of current transition-metal photoredox catalysis still remain important challenges. Although organic photoredox catalysis has been recently investigated as an attractive alternative of transition metal catalysis, only limited class of organic dyes has been employed as organic catalysts. In this presentation, we will discuss about a rational molecular design for an efficient visible-light organic photoredox catalysts with the broad diversity in structure and properties. Also, we will talk about their synthetic applications for light-driven atom transfer radical polymerization.

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Theoretical estimates of the charge-separation and -recombination rates in donor-acceptor buckybowl-based supramolecular complexes in solution

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Fullerenes and their derivatives are one of the most important electron-acceptor (A) compounds in organic electronics.¹ In particular, the fullerene fragments such as the C₃₀H₁₂ (Hemifullerene) can be supramolecularly recognized by, for instance, the electron-donor (D) truxene-tetrathiafulvalene (truxTTF).^{2,3} The resulting supramolecular complexes exhibit an efficient photoinduced electron transfer process (Figure 1) in solution. In this contribution, we present a theoretical protocol to estimate charge-separation and charge-recombination rate constants in D-A buckybowl-based supramolecular complexes in the presence of solvent. This protocol makes use of the Marcus-Levitch-Jortner rate expression,^{4,5} obtaining the parameters required from electronic structure and molecular mechanics calculations. A detailed analysis of how the most relevant transfer parameters can be carefully evaluated is provided.

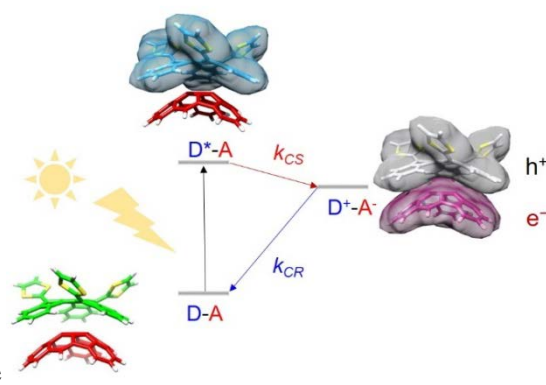


Figure 1. Diagram of the photoinduced electron transfer mechanism.

truxTTF and C₃₀H₁₂ and the photoinduced

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A dispersion-corrected density functional theory investigation on pyreneimidazole-based supramolecular polymers

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Pyrene is one of the most studied polycyclic aromatic compounds due to its attractive electronic and photophysical properties. However, its application as a blue-emitting material is limited by the strong tendency to form excimers that red-shifts the emission of pyrene and reduces its intensity. The optimization of the functional unit of pyrene and the control of its supramolecular organization are therefore essential to design novel derivatives in which supramolecular order and blue-emitting features coexist.

The supramolecular polymerization of a pyreneimidazole derivative endowed with a peripheral amide group substituted with an alkyl chain has been recently described (Figure 1).¹ Theoretical calculations at the DFT level using the latest version of the Grimme's dispersion correction (D3) show that, among the amazing scenario of possibilities to self-assemble, the pyreneimidazole derivative aggregates in a supramolecular polymer that grows up through strong H-bonding interactions and stabilizing C–H \cdots π forces. Interestingly, π - π interactions between vicinal pyrene units in the supramolecular aggregate are hindered by the presence of the aliphatic chains. This prevents the formation of excimers upon aggregation and explains the preservation of the blue-emitting properties in the organogel.

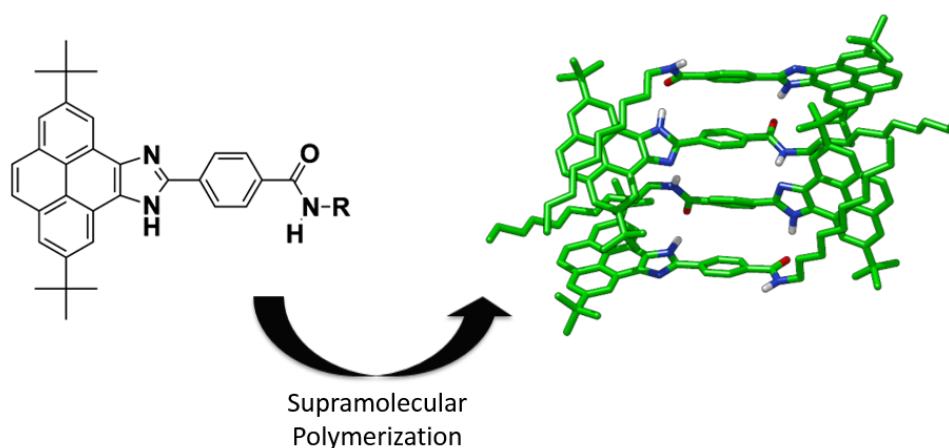


Figure 1. Chemical structure of the pyreneimidazole derivative (left) and side view of the B97D3/6-31G**-optimized geometry calculated for the tetramer (right).

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Mixed-& Separated Stack Charge-Transfer Co-Crystals: Tunable Bright Emitters with Ambipolar Charge Transport Characteristics

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In the last few years co-crystals of conjugated organic compounds have attracted much attention as next-generation composite materials for organic optoelectronics. The vivid interest is driven by targeted materials design concepts *inter alia* via the isometric approach,[1] creating segregated or mixed stacked co-crystal systems. Reversible segregated-mixed stack conversion can be induced by external multi-stimuli, generating large color changes by switching between exciton vs. charge-transfer (CT) emission.[2] Combined pump-probe, low-temperature PL and atomistic quantum-chemical studies reveal spectral signature and kinetics of optical excitation and deactivation.[3] Switching from 1D to 2D mixed-stacking motif gives rise to well-balanced ambipolar charge transport materials.[4] This allowed for the demonstration of the first CT crystal-based light emitting field effect transistor, opening new path towards electrically driven light emitting devices.

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Designing high performance all-small-molecule solar cells with non-fullerene acceptors: comprehensive studies on photoexcitation dynamics and charge separation kinetics

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Solution-processable all-small-molecule organic solar cells (OSC) have shown a dramatic progress in improving stability and photovoltaic efficiency. However, knowledge of photoexcitation dynamics in this novel class of materials is very limited. To fully exploit the design capacities inherent in small molecule chemistry, the elementary processes and branching yields must be known in detail. Here, we present a combined computational-experimental study of photoexcitation dynamics of a prototypical all-small-molecule photovoltaic blend, p-DTS(FBTTh2)2 as donor and NIDCS-MO as acceptor. Femtosecond spectroscopy data show that excitonic coupling is small and that the charge transfer states are localized, at first glance contradicting the high internal quantum efficiency (IQE) and open circuit voltage (VOC) of this material. A target analysis on the femtosecond spectra yields exciton dissociation rates of 1/(25 ps) and 1/(100 ps) for the as-deposited and annealed blend, respectively. These rates are far slower than in typical polymer based organic solar cells. Still, internal quantum yields are high because parasitic quenching processes are found to be even slower. In the framework of semiclassical Marcus theory, we demonstrate that our system shows near-optimum energy conversion and charge separation yields, due to negligible activation energy for charge generation but high activation energy for charge recombination, allowing enough time to separate localized charge transfer states. We thus justify both the high internal quantum yields and the high open circuit voltage found in this system. Finally, we predict that highly efficient and stable low-optical bandgap systems can be realized by reducing the electronic coupling between donor and acceptor.

Lévy defects in matrix-immobilized J aggregates: Tracing Intra-and Inter-Segmental Exciton Relaxation

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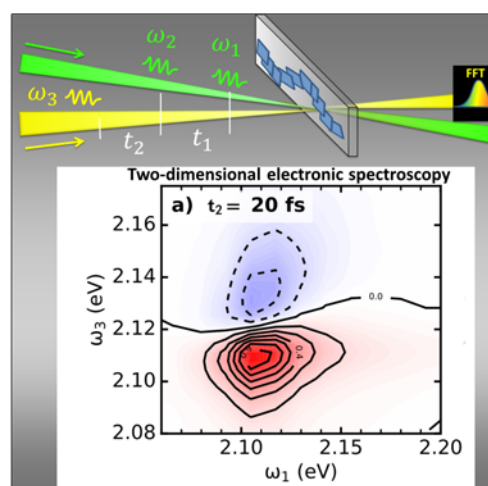
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One-dimensional J aggregates present narrow and intense absorption and emission spectra which are interesting for photonics applications. [1] Matrix immobilization of the aggregates, as required for most device architectures, has recently been shown to induce a non-Gaussian (Lévy type) defect distribution with heavy tails, expected to influence exciton relaxation.[2] Here we perform two-dimensional electronic spectroscopy (2DES)[3] in one-dimensional J aggregates of the cyanine dye TDBC, immobilized in a gel matrix, and we quantitatively model 2DES maps by non-linear optimization coupled to quantum mechanical calculations of the transient excitonic response. We find that immobilization causes strongly non-Gaussian off-diagonal disorder, leading to a segmentation of the chains. Inter-segmental exciton transfer is found to proceed picosecond time scale, causing a long-lasting excitation memory. These findings can be used to inform the design of optoelectronic devices on J aggregates, as they allow for control of exciton properties by disorder management.[4]



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Charge transfer states in bulk heterojunction organic photovoltaics

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Organic photovoltaics (OPVs), unlike inorganic ones, lead to an exciton or bound electron-hole pair after absorption of a photon. The generation of free charges then depends on the exciton binding energy and the absorption properties of the materials used [1]. In the modelling of more efficient OPVs, we have combined a conjugated polymer with a fullerene derivative in bulk heterojunction architectures (see Figure 1). In such architectures, the excitons formed on the absorber polymer are separated through electron transfer process that lead to charge transfer (CT) states at the interface of the polymer and fullerene based molecule. We have computed the energies of the CT and fully charge separated (CS) states in bulk heterojunctions by using Density Functional Theory and its Time Dependent extension, coupled with the Discrete Reaction Field method as implemented in the Amsterdam Density Functional modeling suite [2]. Our preliminary results are in line with experimental ones; especially good agreement in terms of the CT state energies has been found. Our results also indicate that the environment stabilizes the CS states. Further computations of the electron transfer rates and potential energy surfaces are intended [3].

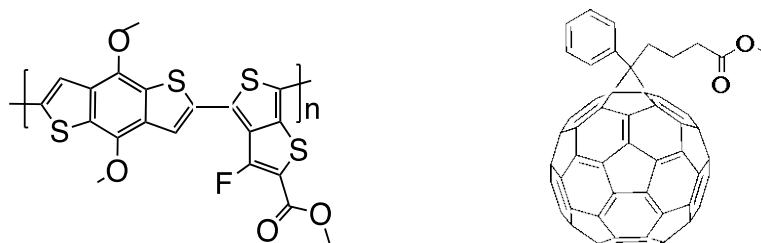


Fig.1 Molecular structure of potential OPV materials used in the modeling of CT and CS states. Left, electron-rich type conjugated polymer (PTB7); Right, acceptor C60 based molecule (PCBM).

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Study on the morphology and optical properties of organic nanoaggregates

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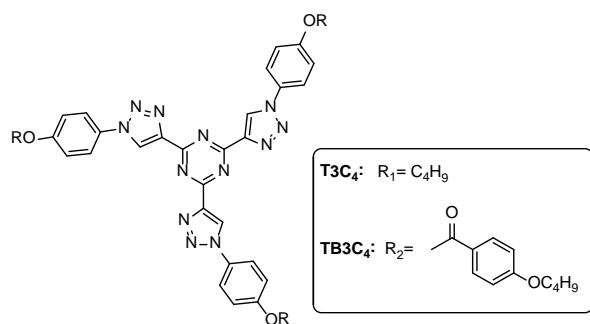
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In recent years, organic nanomaterials have aroused great interest due to their unique properties in comparison with their bulk counterparts.^[1] Since size and shape of the nanomaterials strongly affect their properties, there is a great interest in controlling their morphology. Some organic nanomaterials have shown aggregation-induced emission enhancement (AIEE),^[2] which makes them interesting for optoelectronic applications.

Star-shaped compounds based on 2,4,6-tris(triazolyl)-1,3,5-triazine (TTT) were described by our group and show high tendency to self-assemble in bulk forming liquid crystal phases.^[3] In this work, we show that this kind of π -conjugated molecules can also self-assemble in solvents forming nanostructures. Two different TTT derivatives, T3C₄ and TB3C₄, were synthesized in order to study the formation of the nanoaggregates and their optical properties. A variety of morphologies, such as spherical particles, one-hole hollow spheres, toroids, twisted fibers, screws or corrugated tubes were obtained. The so-obtained aggregates showed emission quenching for T3C₄ and emission enhancement for TB3C₄. Quantum chemical calculations were performed in order to better understand the aggregation processes and the optical properties of the nanostructures of the two star-shaped compounds.



Scheme 1. Chemical structure of the TTT derivatives.

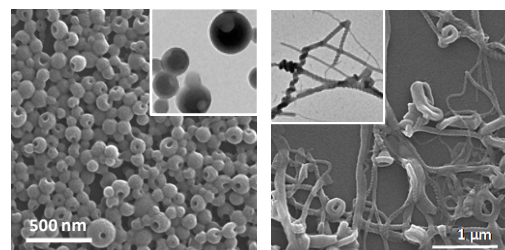


Figure 1. Electron microscopy images of the aggregates.

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Electrical spin manipulation in graphene nanostructures

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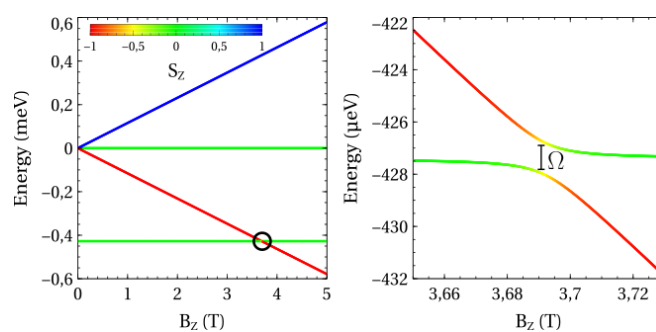
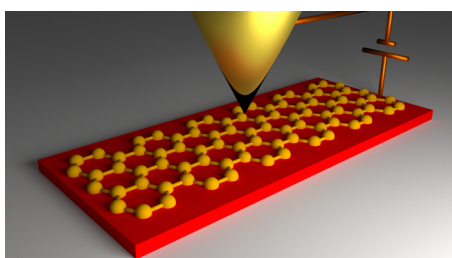
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We propose a mechanism to excite singlet-triplet spin transitions in a wide class of graphene nanostructures that present pairs of in-gap zero modes at half filling, localized at opposite sublattices. Examples are rectangular nanographenes with short zigzag edges [1], armchair ribbon heterojunctions with topological in-gap states [2] and graphene islands with sp^3 functionalization [3]. The interplay between hybridization of zero modes and Coulomb repulsion leads to symmetric exchange interaction that favours a singlet ground state. Application of an off-plane electric field to the graphene nanostructure adds an additional Rashba spin-orbit coupling [4], which results in antisymmetric exchange interaction that mixes $S = 0$ and $S = 1$ manifolds. We show that modulation in time of either the off-plane electric field or the applied magnetic field permits to perform electrically driven spin resonance in a system with very long spin relaxation times [5].



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Novel push-pull chromophores to prepare electro-optic modulators

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In recent years, a large number of push-pull organic molecules have been proposed as promising candidates for electronic and optical applications. Generally, the main effort has been focused on the design of chromophores with large first hyperpolarizability values (β); this would result in a wide variety of nonlinear optical (NLO) applications, such as modulators.^[1,2] In this work, we report an experimental and theoretical investigation of the NLO properties of novel push-pull systems derived from the dicyanomethylene-4*H*-chromene (DCM) group. Particular attention will be paid to better understand the molecular and electronic properties of these systems by using vibrational spectroscopic techniques and electrochemistry. Furthermore, these materials have been tested in a silicon-organic hybrid modulator based on an integrated dual-mode interferometer.^[3]

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