

Spotlight
POLYMAT

Novel Approaches to 2D and Porous Polymers

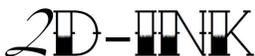
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POLYMAT and the **University of the Basque Country** have initiated a series of workshops, in the framework of the **European Project 2D-INK**, entitled **POLYMAT SPOTLIGHT**.

The objective of this international conference is to increase the visibility of emerging and technologically-relevant macromolecular materials.

This first edition of POLYMAT SPOTLIGHT will be devoted to **Novel Approaches to 2D and Porous Polymers**, including synthesis, properties and applications.

San Sebastian is one of the **most famous tourist destinations in the world**, widely known for its exquisite gastronomy and for hosting the International Film and Jazz Festivals.

The conference will be held in the **Miramar Palace** built in 1893, situated opposite the Bay of La Concha with one of the most spectacular views of the city.

We hope POLYMAT SPOTLIGHT will cultivate **new connections and collaborations**.

Oral Presentations

Porous C₂N and other C_nN_m-species: new 2d-structures by polycondensation accessing special chemical functionalities

Markus Antonietti*

Max Planck Institute of Colloids and Interfaces, Department of Colloid Chemistry, Research Campus Golm, D14424 Potsdam, Germany, e-mail: office.cc@mpikg.mpg.de)

Choosing the right organic starting products, polycondensation and copolycondensation allows to generate a wider range of porous scaffolds, ranging from regular frameworks over disordered systems with however well-defined pores and chemical surface functionality. The electronic properties vary from medium bandgap semiconductors to organic metals within a rather similar family of components. At the same time, following distinct layout rules, such porous materials can be made to be "unexpectedly" stable, i.e. inert against pure oxygen at 500 °C or resistant against boiling sulfuric acid in an oxidative catalytic reaction environment.

I will report on our recent approaches to make such structures, mainly via novel condensation schemes of nitrogen containing monomers, such as nitriles, supramolecularly preorganized complexes, and ionic liquid crystals.

Exemplary applications of such polymer scaffolds as catalysts, catalyst supports, as electrocatalysts, and for energy storage are reported.

Novel Functional Carbon Interfaces

Maurizio Prato

a, Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy

b, CIC BiomaGUNE, Parque Tecnológico de San Sebastián, Paseo Miramón, 182, 20009 San Sebastián (Guipúzcoa), Spain

email address: prato@units.it, mprato@cicbiomaqune.es

Coupling nanomaterials to biological entities is crucial to develop prosthetic applications, where the interfacing surfaces provide minimal undesired perturbation to the target tissue. Ultimately, the (nano)material of choice has to be biocompatible, promoting cellular growth and adhesion with minimal cytotoxicity or dis-regulation of, for example, cellular activity and proliferation.

In this context, carbon nanomaterials, including nanotubes and graphene, are particularly well suited for the design and construction of functional interfaces. This is mainly due to the extraordinary properties of these novel materials, which combine mechanical strength, thermal and electrical conductivity.

Our group has been involved in the organic functionalization of various types of nanocarbons, including carbon nanotubes, fullerenes and, more recently, graphene. The organic functionalization offers the great advantage of producing soluble and easy-to-handle materials. As a consequence, since biocompatibility is expected to improve, many functionalized carbon nanomaterials may be useful in the field of nanomedicine.

We have recently shown that carbon nanotubes and graphene can act as active substrates for neuronal growth, a field that has given so far very exciting results. Nanotubes and graphene are compatible with neurons, but especially they play a very interesting role in interneuronal communication. Improved synaptic communication is just one example.

In addition, in combination with suitable catalysts, carbon nanotubes can serve as versatile interfaces for the splitting of water molecules to give oxygen, but, especially, molecular hydrogen, ideal for clean energy generation. After our initial efforts in the electrochemically catalyzed splitting of water, we move to the more interesting photochemical process.

During this talk, we will show the latest and most exciting results obtained in our laboratory in these fast developing fields.

Two-Dimensional Covalent Polymers and Organic Frameworks: Structural Design and Functional Exploration

Donglin Jiang*

Field of Energy and Environment, School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi 923-1292, Japan

djiang@jaist.ac.jp

Two-Dimensional covalent polymers and organic frameworks are a class of crystalline porous polymers that enable the incorporation of organic building blocks into well-defined primary and high-order structures. In recent years, we have focused on exploring the design principle, synthetic reactions, structural diversity, functional exploration, and potential applications. One significant feature is that the merge of covalent bonds and noncovalent forces enables the precise control over the primary and high-order structures. The geometry-directed covalent bondings direct the growth of two-dimensional atomic layers in which the primary-order structures are precisely controlled, while the noncovalent π - π interactions between two-dimensional layers encode the formation of layered high-order structures, which constitute periodically aligned π -skeletons and nanometer-sized unidirectional open channels. These structural features make them as an attractive platform for designing functional materials and exploring various functions, including CO₂ capture, catalysis, light-emitting, semiconductors, proton conduction, and energy conversion and storage. In this talk, I will discuss our recent work on structural designs and functional explorations.

References

- 1 X. Feng, X. Ding, and D. Jiang, Covalent organic frameworks, *Chem. Soc. Rev.* **2012**, 41, 6010.
- 2 H. Xu, J. Gao, and D. Jiang, Stable crystalline porous covalent organic frameworks as a platform for chiral organocatalysis, *Nat. Chem.* **2015**, 9, 905.
- 3 H. Xu, S. Tao, and D. Jiang, Proton conduction in crystalline and porous covalent organic frameworks, *Nat. Mater.* **2016**, doi: 10.1038/nmat4611.

Ultrathin Films of Electronically active Metal–Organic Frameworks

Victor Rubio-Giménez,^a Sergio Tatay,^a Eugenio Coronado^a and Carlos Martí-Gastaldo^{a*}
a. Instituto de Ciencia Molecular, Universidad de Valencia, Catedrático José Beltrán, 2, 46980, Spain.
 Corresponding author email address: carlos.marti@uv.es

Metal-Organic Frameworks (MOFs) are porous coordination polymers of metal centres connected through organic ligands. MOFs have found interesting applications in gas storage, separations, sensing and catalysis by taking advantage of their intrinsic porosity in the bulk form. Nowadays there is an increasing interest in developing an advanced generation of electronic and optoelectronic devices that make use of electrically active MOFs. However, this type of applications requires the processing of these bulk materials as high-quality nanometric thin films with exquisite control over several parameters that are required for device performance like morphology, density, crystallinity, roughness and orientation.¹ Research involving electrically conductive MOFs is just starting to blossom,² but investigation of the electrical conductivity of MOF thin films at the nanoscale (<100 nm) is still challenging due to the synthetic difficulties in producing smooth films with homogenous coverage and low roughness with nanometric accuracy. The use of advanced thin film preparation techniques by combination of self-assembled monolayer (SAM) functionalization of non-innocent substrates with Langmuir-Blodgett (LB) and Layer-by-Layer (LbL) enables the production of homogeneous MOF ultrathin films with exquisite control over the desired nanometric thickness.³⁻⁵ Electrical properties of these ultrathin films can be analysed in a vertical configuration by using the hanging-mercury-drop electrode technique, a soft contacting method that measures the current (I) flowing between the top electrode (mercury drop) and the bottom electrode (substrate coated with the MOF film) as a function of the applied bias (V).⁵

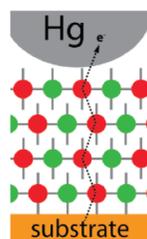


Figure 1. Charge transport operating between electrodes through the MOF film.

References

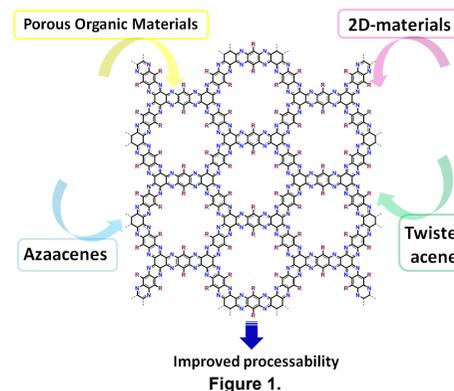
1. M. D. Allendorf, A. Schwartzberg, V. Stavila, A. A. Talin, *Chem-Eur J.* **2011**, *17*, 11372.
2. L. Sun, M. G. Campbell, M. Dincă, *Angew. Chem. Int. Ed.* **2016**, *55*, 3566.
3. R. Makiura, S. Motoyama, Y. Umemura, H. Yamanaka, O. Sakata, H. Kitagawa, *Nature Mater.* **2010**, *9*, 565.
4. S. Sakaida, K. Otsubo, O. Sakata, C. Song, A. Fujiwara, M. Takata, H. Kitagawa, *Nature Chem.* **2016**, *8*, 373.
5. V. Rubio-Giménez, S. Tatay, F. Volatron, F. J. Martínez-Casado, C. Martí-Gastaldo, E. Coronado, *J. Am. Chem. Soc.* **2016**, *138*, 2576.

Twisted Organic Frameworks

A. Belén Marco,^a Diego Cortizo-Lacalle,^a Jan Plas,^b Steven De Feyter,^b Andrei Khlovyostov,^c Manuel Melle-Franco,^d Íñigo Pérez-Miqueo,^e Mario Montes,^e Alessandro Boni,^f Giovanni Valenti,^f Francesco Paolucci^g and Aurelio Mateo-Alonso^{a*}
a. POLYMAT, University of the Basque Country UPV/EHU. Avenida de Tolosa 72, E-20018 Donostia-San Sebastián, Spain.
b. KU Leuven. Department of Chemistry, Celestijnenland 200F, B-3001 Leuven, Belgium.
c. School of Chemistry, University of Nottingham. University Park, Nottingham, UK
d. Centro de Ciências e Tecnologias de Computação, CCTC. Universidade do Minho, 4710-057 Braga, Portugal
e. Dpto. de Química Aplicada. Fac. de C. Químicas, UPV/EHU E-20080 San Sebastián, Spain
f. Università di Bologna. Department of Chemistry "G. Ciamician", Via Selmi 2, 40126 Bologna, Italy.
 Presenting author email address: belen.marco@polymat.eu
 Corresponding author email address: amateo@polymat.eu

The rise of graphene as a novel material with extraordinary perspectives in several fields among materials science, has opened the door to the investigation of a wide variety of related nanomaterials.¹ Some of these emerging structures are designed to make up the lack of electronic gap displayed by graphene, which prevents its use as semiconductor in spite of its high charge mobility. Among them, All conjugated Porous Organic Materials, such as Covalent Organic Frameworks² (COFs) or Conjugated Microporous Polymers³ (CMPs) are soft materials composed of layers which can be exfoliated into 2D-materials. However, their poor processability is still one of their main drawbacks.

In this work we report an unconventional approach to improve the processability of organic frameworks based on the introduction of twists (Figure 1). This has been achieved by overcrowding the nodes with bulky and rigid substituents that are forced above and below the plane using the strategies successfully developed by our group for small azaacene fragments.⁴ The presence of the of nanopores combined with the highly distorted conjugated framework and with an alternating out-of-plane substituents results in twisted aromatic frameworks with an intrinsic band gap that can be handled by liquid-deposition techniques.



References

1. a) G.R. Bhimanapati, Z. Lin, V. Meunier, Y. Jung, J. Cha, S. Das, D. Xiao, Y. Son, M. S. Strano, V. R. Cooper, L. Liang, S. G. Louie, E. Ringe, W. Zhou, S. S. Kim, R. R. Naik, B. G. Sumpter, H. Terrones, F. Xia, Y. Wang, J. Zhu, D. Akinwande, N. Alem, J. A. Schuller, R. E. Schaak, M. Terrones and J. A. Robinson, *ACS Nano*, **2015**, *12*, 11509; b) X. Zhuang, Y. Mai, D. Wu, F. Zhang and X. Feng, *Adv. Mater.*, **2015**, *27*, 403.
2. X. Feng, X. Ding and D. Jiang, *Chem. Soc. Rev.*, **2012**, *41*, 6010.
3. a) Y. Xu, S. Jin, H. Xu, A. Nagai and D. Jiang, *Chem. Soc. Rev.* **2013**, *42*, 8012; b) A. Cooper, *Adv. Mater.*, **2009**, *21*, 1291.
4. a) R. A. Pascal Jr., *Chem. Rev.*, **2006**, *106*, 4809; b) A. Mateo-Alonso, *Chem. Soc. Rev.*, **2014**, *43*, 6311.

Two-Dimensional Networks with Uniformly Decorated Heteroatoms

^a Javeed Mahmood and Jong-Beom Baek*

^a, School of Energy and Chemical Engineering, UNIST, 50 UNIST, 44919, South Korea.

Corresponding author email address: jbbaek@unist.ac.kr

Two-dimensional (2D) networks with uniformly decorated heteroatoms attract immense interest beyond graphene due to their multifunctionality such as exceptional electronic, optoelectronic, magnetic and electrocatalytic properties. Despite recent explorations in 2D networks science and engineering, easy and scalable methods to produce 2D networks with uniformly decorated heteroatoms are limited. To overcome these problems, a new layered 2D network structures with uniformly distributed holes and/or nitrogen atoms were synthesized and their stoichiometry of basal plane is C_2N and/or C_3N .^{1,2} Their structures were confirmed by scanning tunneling microscopy (STM) (Figure 1). Their electronic properties were studied by density-functional theory (DFT) calculations and electrooptical measurements.

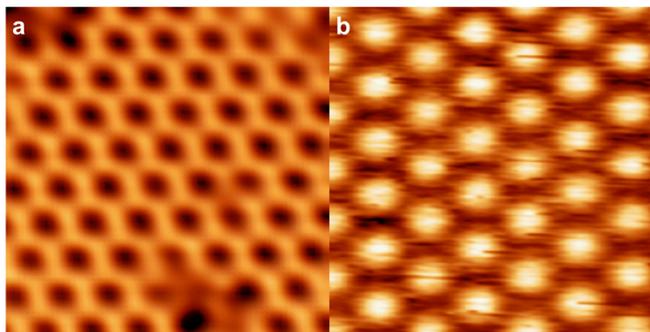


Figure 1. Scanning tunneling microscopy (STM) images of 2D networks: a, C_2N ; b, C_3N .

References

1. J. Mahmood, et al., *Nature Communications*, **2015**, 6, 6486.
1. J. Mahmood, et al., *Proceedings of National Academy of Sciences, USA*, **2016**, online.

Towards the Formation 2D Polymers and Oligomers on Graphitic Substrates

Steven De Feyter

Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium.

Presenting author email address: steven.defeyter@kuleuven.be

In recent years, the synthesis of 2D COFs has gained a lot of interest and has been successfully performed both in ultra-high vacuum and ambient conditions. Linking the building blocks together by covalent bonds creates strong sheets of material with well-defined composition and porosity. Polycondensation reactions involving Schiff bases, or boronic acid derivatives are the most studied so far and under optimal conditions can yield extended porous networks that compete with supramolecular systems, both in terms of domain size and structural quality. We show that some ultrathin COF films might be of interest as insulating coatings for directed layered growth of fullerene and its derivatives. We demonstrate that these host-guest monolayers can be easily patterned with STM lithography under very mild conditions [1].

Self-assembly under nanoconfinement opens up the possibility to synthesise polymers with well-defined dimensions. Using a recently established process, i.e. high density grafting followed by nanoshaving using a STM or AFM probe, it is possible to nanostructure graphitic substrates with an unprecedented precision [2]. The localized nature of the probe allows for the creation of nanoconfined spaces (so-called corrals) where both shape, size and orientation with respect to the substrate lattice symmetry can be tailored. The ability to capture organic reagents within the corrals opens the door for exploring chemical reactions under nanoconfinement conditions, including the synthesis of polymers.

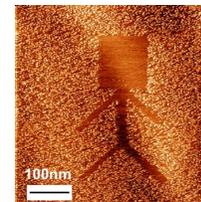


Figure 1. STM image of the result of nanoshaving or degrafting

References

1. J. Plas, O. Ivasenko, N. Martsinovich, M. Lackinger and S. De Feyter, *Chemical Communications*, **2016**, 52, 68.
2. J. Greenwood, T. H. Phan, Y. Fujita, Z. Li, O. Ivasenko, W. Vanderlinden, H. Van Gorp, W. Frederickx, G. Lu, K. Tahara, Y. Tobe, H. Uji-i, S. F. L. Mertens, and S. De Feyter, *ACS Nano*, **2015**, 9, 5520.

Porous 2D Nanostructured Networks via Nucleobase Self-Assembly

Nerea Bilbao,^a Miguel Martín-Arroyo,^a Iris Destoop,^b Steven De Feyter,^b and David González-Rodríguez^{a,*}

^a, Nanostructured Molecular Systems and Materials group, Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain

^b, Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven—University of Leuven, Celestijnenlaan 200 F, B-3001, Leuven, Belgium.

Presenting author email address: david.gonzalez.rodriguez@uam.es

Corresponding author email address: david.gonzalez.rodriguez@uam.es

Our project aims at establishing an unconventional and versatile strategy to prepare cyclic systems¹ whose size, shape, composition and function can be rationally pre-designed and controlled at the nanoscale using concepts and tools of supramolecular chemistry. Cyclic tetramers are formed from 4 monomeric π -conjugated subunits by hydrogen-bonding interactions between nucleobase directors. A proper monomer preorganization affords high chelate cooperativities and thus high cyclization yields in solution²⁻⁴ and onto surfaces.⁵ In the last case, nanostructured porous 2D networks are assembled that can selectively host molecular guests as a function of their size and shape.

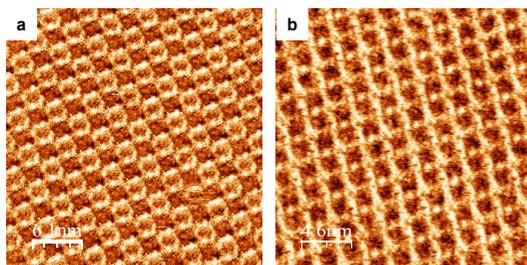


Figure 1. STM images of (a) GC and (b) AU monomers on HOPG.

References

1. M. J. Mayoral, N. Bilbao, D. González-Rodríguez, *ChemistryOpen* **2016**, 5, 10.
2. C. Montoro-García, J. Camacho-García, A. M. López-Pérez, N., Bilbao, S. Romero-Pérez, M. J. Mayoral, D. González-Rodríguez, *Angew. Chem. Int. Ed.* **2015**, 54, 6780. (VIP Paper)
3. S. Romero-Pérez, J. Camacho-García, C. Montoro-García, A. M. López-Pérez, A. Sanz, M. J. Mayoral, D. González-Rodríguez, *Org. Lett.* **2015**, 17, 2664.
4. C. Montoro-García, J. Camacho-García, A. M. López-Pérez, M. J. Mayoral, N., Bilbao, D. González-Rodríguez, *Angew. Chem. Int. Ed.* **2016**, 55, 223.
5. N. Bilbao, I. Destoop, S. De Feyter, D. González-Rodríguez, *Angew. Chem. Int. Ed.* **2016**, 55, 659. (Hot Paper)

Modification of the partially confined electronic states using Xe adsorption in a porous network

Jorge Lobo-Checa^a, Sylwia Nowakowska^b, Aneliia Wäckerlin^b, Ignacio Piquero-Zulaica^c, Meike Stöhr^d, J. Enrique Ortega^e, Lutz H. Gade^f, Thomas A. Jung^g

^a, Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Univ. de Zaragoza, E-50009 Zaragoza, Spain

^b, Department of Physics, University of Basel, Klingelbergstrasse 82, 4056 Basel, Switzerland.

^c, Centro de Física de Materiales (CSIC/UPV-EHU), Manuel Lardizabal 5, 20018 San Sebastián, Spain.

^d, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

^e, Departamento Física Aplicada I, Universidad del País Vasco, 20018 San Sebastián, Spain.

^f, Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.

^g, Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland.

Presenting and corresponding author email address: jorge.lobo@csic.es

Self-assembly at surfaces e.g. by formation of a porous metal-organic network provides an ideal way to manufacture arrays of identical nanoscale units capable of confining the surface electronic states inside the structural pores¹⁻³.

By adding Xe atoms into the pores we demonstrate that we can modify the energetic position and dispersion of these states. Each quantum box exhibits 12 filling levels, which incrementally perturb the quantum box state(s) via Pauli repulsion⁴.

The inter-box coupling can be sustained or significantly weakened by an appropriate arrangement of empty and filled pores. Owing to complementary scanning tunneling microscopy/spectroscopy and angle-resolved photoemission spectroscopy studies we can gain insight into the physics of interacting quantum states on the local level as well as in their cooperative interaction. Such self-assembled two-dimensional quantum box architectures may serve as nanoscale analog of breadboards commonly employed in electronic circuitry.

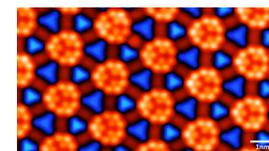


Figure 1. Condensation of Xe on a 2D porous network. STM image of Cu-coordinated 3deh-DPDI network grown on Cu(111) with each pore filled with 12 xenon atoms.

References

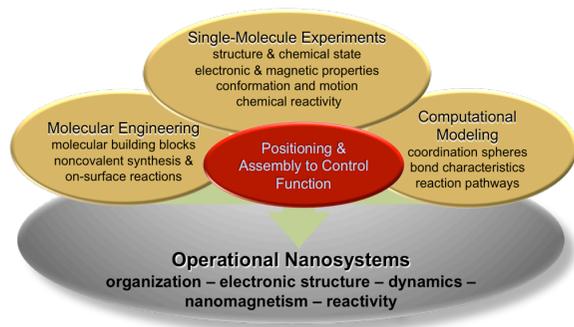
1. Lobo-Checa, J. et al. Band Formation from Coupled Quantum Dots Formed by a Nanoporous Network on a Copper Surface. *Science* 325, 300–303 (2009).
2. Klappenberger, F. et al. Dichotomous Array of Chiral Quantum Corrals by a Self-Assembled Nanoporous Kagomé Network. *Nano Lett.* 9, 3509–3514 (2009).
3. Klappenberger, F. et al. Tunable Quantum Dot Arrays Formed from Self-Assembled Metal-Organic Networks. *Phys. Rev. Lett.* 106, 026802 (2011).
4. Nowakowska, S. et al. Interplay of weak interactions in the atom-by-atom condensation of xenon within quantum boxes. *Nat. Commun.* 6, 6071 (2015).

Design and manipulation of molecular nanosystems at interfaces

JV Barth*

Physik-Department E20, TUM, Garching, Bavaria, Germany
Presenting author email address: jvb@tum.de

The control and organization of molecular species at interfaces is key to advance molecular science, nanochemistry and the development of novel materials. We explore the pertaining bonding, assembly and dynamic behaviour at well-defined homogenous surfaces, textured templates and sp²-sheet layers. The developed bottom-up fabrication protocols employ biological and de novo synthesized building blocks, exploiting error-corrective supramolecular bonding schemes as well as covalent chemistry. Our approach provides a rationale for the interfacial control of single molecular units and the design of nanoarchitectures with remarkable structural features, intricate dynamics and tailored properties.



Towards rational catalyst design? 2D frameworks as platforms for light-driven hydrogen evolution

Bettina V. Lotsch^{a,b,*}

a, Max Planck Institute for Solid State Research, Heisenbergstraße 1, 70569 Stuttgart

b, Department of Chemistry, University of Munich (LMU), Butenandtstraße 5-13, 81377 München, Germany
b.lotsch@fkf.mpg.de

The conversion of sunlight into storable chemical fuels through photocatalysis has been identified as a viable strategy to alleviate future energy shortage. Although a number of potent semiconductors for solar water splitting are at hand, key features such as earth-abundance, stability and low toxicity still need to be addressed, thus calling for new material solutions for sustainable photocatalysis. While heterogeneous systems excel through their stability, homogeneous catalysts offer the potential to tune every step in the photocatalytic mechanism through molecular engineering. Combining the best of both worlds opens up new possibilities for the design of tailor-made photocatalysts.

We have recently developed “soft” photocatalysts based on 1D and 2D molecular frameworks, including covalent organic frameworks (COFs),¹ which are abundant and molecularly tunable organic semiconductors. Our recent progress in the rational design of triazine- and heptazine-based systems for hydrogen evolution will be discussed and possible catalyst optimization strategies will be highlighted – through doping,² exfoliation,³ functionalization,⁴ and active site engineering,⁵ as well as hybridization with bio-inspired co-catalysts.⁶

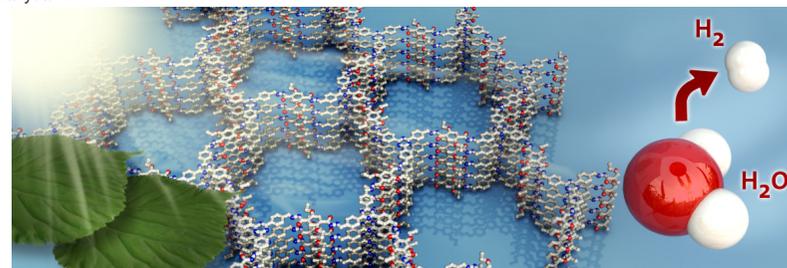


Figure 1. Sketch of a hydrazone-based covalent organic framework for hydrogen evolution.

References

1. L. Stegbauer, K. Schwinghammer and B. V. Lotsch, *Chem. Sci.* **2014**, 5, 2789.
2. K. Schwinghammer, B. Tuffy, M. B. Mesch, E. Wirnhier, C. Martineau, F. Taulelle, W. Schnick, J. Senker and B. V. Lotsch, *Angew. Chem. Int. Ed.* **2013**, 52, 2435.
3. K. Schwinghammer, M. B. Mesch, V. Duppel, C. Ziegler, J. Senker and B. V. Lotsch, *J. Am. Chem. Soc.* **2014**, 136, 1730.
4. V. S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld and B. V. Lotsch, *Nat. Commun.* **2015**, 6, 8508, DOI: 10.1038/ncomms9508.
5. V. W.-h. Lau, M. B. Mesch, V. Duppel, V. Blum, J. Senker and B. V. Lotsch, *J. Am. Chem. Soc.* **2015**, 137, 1064.
6. C. A. Caputo, M. A. Gross, V. W. Lau, B. V. Lotsch and E. Reisner, *Angew. Chem. Int. Ed.* **2014**, 53, 11538.

Iron(II)-Porous Polyiminopyridines (Fe-PIPyS) as heterogeneous catalysts in the synthesis of diesel additives.

Marta Iglesias,^a José G. de la Campa,^b Eva M. Maya^{a*}

^a, New Architectures in Chemistry of Materials, Institute of Material Science of Madrid, CSIC, c/ Sor Juana Ines de la Cruz 3, Cantoblanco, Madrid 28049, Spain.

^b, Applied Molecular Chemistry, Institute of Polymer Science and Technology, CSIC, C/ Juan de la Cierva 3, Madrid 28006, Spain.

Presenting author email address: evamaya@ictp.csic.es

Corresponding author email address: evamaya@ictp.csic.es

Three polyiminopyridines (PIPyS) were synthesized using 2,6-pyridine carboxyaldehyde and three different amines, with functionality two, three and four respectively. Iron (II) heterogeneous catalysts (Fe-PIPyS 2-4, Figure 1) were prepared by direct treatment of the PIPyS with $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$. Iron was selected because can offer significant advantages over precious metals: it is the second most abundant metal in earth's shell, it is much less expensive than other metals and it is a non-toxic metal [1].

The iron contents, determined by ICP, were 3.66, 2.36 and 2.88 w% respectively. **Fe-PIPy2** has a contorted conformation together with a great rigidity that difficult the packing. Thus **Fe-PIPy2** exhibits porosity as it happens to polymers of intrinsic microporosity, PIMs [2]. **Fe-PIPy3** and **Fe-PIPy4** exhibited mesoporous properties with moderate specific surface areas and pores size centered at 16 and 13 nm respectively. All catalysts showed good thermal stability with decomposition temperatures higher than 300 °C.

The three **Fe-PIPyS** catalysts were tested in the acetalization of furfural (F) and hydroxymethylfurfural (HMF) using n-butanol, which increases the number of carbons of F and HMF making them potential additives for diesel fuel [3]. The activity and selectivity of the three catalysts were very high because all of them transformed F and HMF completely (100% conversion) into the corresponding acetal derivatives with 100% yield. Moreover the reactions take place in 30-120 min, depending on the catalysts used, employing very small amounts of catalysts, 0.1 w%. The **Fe-PIPyS** catalysts were reused in at least seven cycles and were faster and more selective than the corresponding soluble catalyst synthesized for comparative purposes.

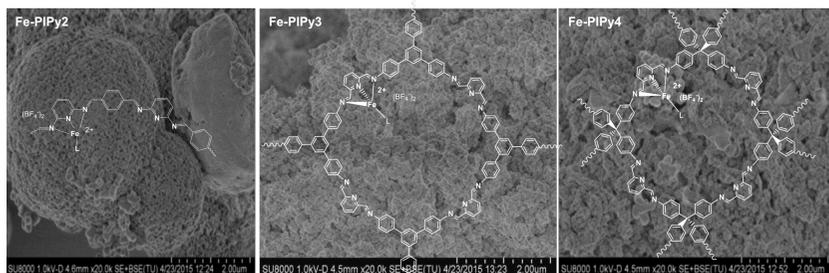


Figure 1. SEM images and structures of Fe-PIPyS catalysts (L = THF)

References

1. S. Enthaler, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2008**, *47*, 3317.
2. N.B. Mckeown, P.M. Budd, K.J. Msayib, B.S. Ghanem, H.J. Kingston, C.E. Tateershall, S. Makhseed, K.J. Reynolds, D. Fritsch, *Chem. Eur. J.*, **2005**, *11*(9), 2610.
3. W. Yu, Y. Tang, L. Mo, P. Chen, H. Lou, X. Zheng, *Bioresour. Technol.*, **2011**, 8241.

New Synthetic Approaches to Planar and Nonplanar Aromatics

Michael Mastalerz*

Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg, Germany
email address: michael.mastalerz@oci.uni-heidelberg.de

Fused aromatic π -systems are attractive compounds for sensing or organic electronics applications, such as organic solar cells, organic light emitting devices or thin-film transistors. In the talk, new synthetic approaches will be presented to construct porous molecular π -systems, new soluble acene derivatives and contorted aromatics. Furthermore, possible applications for sensing and organic electronics will be discussed.

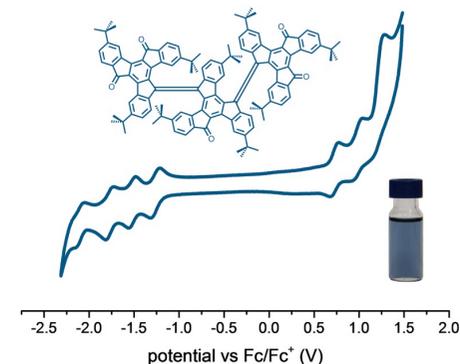


Figure 1. electron accepting truxene trimer

References

1. B. Kohl, F. Rominger, M. Mastalerz, *Org. Lett.* **2014**, *16*, 704-707.
2. B. Kohl, F. Rominger, M. Mastalerz, *Angew. Chem. Int. Ed.* **2015**, *54*, 6051-6056.
3. E. H. Menke, V. Lami, Y. Vaynzof, M. Mastalerz, *Chem. Commun.* **2016**, *52*, 1048-1051
4. G. Zhang, F. Rominger, M. Mastalerz, *Chem. Eur. J.* **2016**, *22*, 3084-3093.
5. G. Zhang, V. Lami, F. Rominger, Y. Vaynzof, M. Mastalerz, *Angew. Chem. Int. Ed.* **2016**, *55*, 3977-3981

Glycofullerenes as active materials for the Ébola virus infection

Nazario Martín*

Department of Organic Chemistry, Faculty of Chemistry, University Complutense, Avenida Complutense s/n, E-28040 Madrid, Spain.

IMDEA-Nanociencia, C/ Faraday 9, Campus de Cantoblanco, E-28049 Madrid, Spain.

nazmar@ucm.es

At the molecular level, there are a wide variety of examples where multivalency drastically enhances the interactions between biomolecules in comparison with the monovalent binding. In particular, multivalency plays a key role in the protein-glycan recognition events which usually take place in the initial steps of pathogenic infection and also at some stages of the immune response. Recently, we have shown that fullerene sugar balls, namely hexakis-adducts of [60]fullerene appended with 12, 24 or 36 mannose moieties, act as strong inhibitors for DC-SIGN in an Ebola infection assay model.¹ Furthermore, a drastic increase in the inhibition process to the subnanomolar scale has been observed when the size and mannoses' number are increased in the recently reported tridecafullerenes endowed with 120 mannose units decorating the periphery of the molecule.²

In this presentation, the aforementioned tridecafullerenes as well as other nanocarbons platforms for the multivalent presentation of carbohydrates in an artificial Ebola virus infection model are presented. Their efficiency to block DC-SIGN mediated viral infection by an artificial Ebola virus has been tested in a cellular experimental assay and the experimental results are discussed.

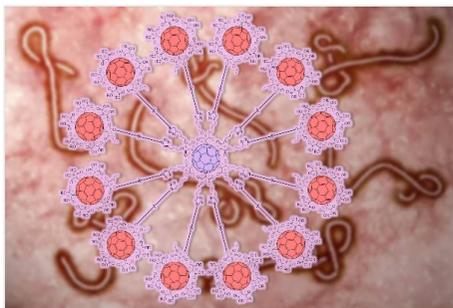


Figure 1. Tridecaglycofullerene molecule on the Ebola virus

References

1. a) J. Luczkowiak, A. Muñoz, M. Sánchez-Navarro, R. Ribeiro-Viana, A. Ginieis, B. M. Illescas, N. Martín, R. Delgado, J. Rojo, *Biomacromolecules* **2013**, *14*, 431; b) J.-F. Nierengarten, J. Iehl, V. Oerthel, M. Holler, B. M. Illescas, A. Muñoz, N. Martín, J. Rojo, M. Sánchez-Navarro, S. Cecioni, S. Vidal, K. Buffet, M. Durka, S. P. Vincent, *Chem. Commun.* **2010**, *46*, 3860; c) M. Sánchez-Navarro, A. Muñoz, B. M. Illescas, J. Rojo, N. Martín, *Chem. Eur. J.* **2011**, *17*, 766.
2. A. Muñoz, D. Sigwalt, B. M. Illescas, J. Luczkowiak, L. Rodríguez, I. Nierengarten, M. Holler, J.-S. Remy, K. Buffet, S. P. Vincent, J. Rojo, R. Delgado, J.-F. Nierengarten, N. Martín, *Nat. Chem.*, **2016**, *8*, 50.

Graphene pillaring: Towards functional nanoporous materials

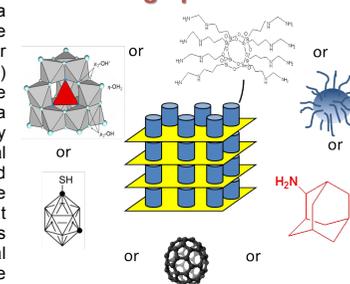
D. Gournis

Department of Materials Science and Engineering, University of Ioannina, 45110 Ioannina, Greece.

dgourni@cc.uoi.gr

Much of the research effort on graphene focuses on its use as building block for the development of novel hybrid structures with well-defined dimensions and behavior suitable for applications among else in gas storage, heterogeneous catalysis, gas/liquid separations, nanosensing and biology. Towards this aim, novel nanostructured pillared materials based on graphene with high surface area, tunable pore size and aromatic functionalities have been synthesized and studied by taking advantage of the concept of intercalation chemistry and the so-called pillaring method. Various cage-shaped and robust species (see Scheme) such as cubic silsesquioxanes, fullerenes (C₆₀), adamantane derivatives, carbon nanodots and nanotubes, nanoparticles and alumina (Keggin ion), as well as, organic precursors (amine derivatives) were successfully intercalated into the interlayer space of chemically oxidized graphene (graphene oxide) and graphite nitrate leading to new pillared graphene structures[1-8]. Pillared graphenes were characterized by a combination of powder X-ray diffraction, X-ray photoemission, Raman and FTIR spectroscopies, thermal analysis (DTA/TGA), surface area measurements and microscopy techniques (TEM, SEM, AFM). Representative case studies addressing cutting edge processes of great importance such as the use of these hybrid nanostructures as cytotoxic agents, effective adsorbents for environmental remediation and hydrogen storage materials will be discussed.

Nano-pillared graphenes



References

1. K. Spyrou, L. Kang, E.K. Diamanti, R.Y. Gengler, D. Gournis, M. Prato, P. Rudolf, *Carbon*, **2013**, *61* 313.
2. T. Tsoufis, G. Tuci, S. Caporali, D. Gournis, G. Giambastiani, *Carbon*, **2013**, *59*, 100.
3. K. Spyrou, G. Potsi, E.K. Diamanti, X. Ke, E. Serestatidou, I.I. Verginadis, A.P. Velapoulou, A.M. Evangelou, Y. Deligiannakis, G. Van Tendeloo, D. Gournis, P. Rudolf, *Adv. Funct. Mater.*, **2014**, *24*, 5841.
4. K. Spyrou, M. Calvaresi, E.A.K. Diamanti, T. Tsoufis, D. Gournis, P. Rudolf, F. Zerbetto, *Adv. Funct. Mater.*, **2015**, *25*, 263.
5. T. Tsoufis, Z. Syrgiannis, N. Akhtar, M. Prato, F. Katsaros, Z. Sideratou, A. Kouloumpis, D. Gournis, P. Rudolf, *Nanoscale*, **2015**, *7*, 8995.
6. V. Georgakilas, A. Demeslis, E. Ntararas, A. Kouloumpis, K. Dimos, D. Gournis, M. Kocman, M. Otyepka, R. Zboril, *Adv. Funct. Mater.*, **2015**, *25*, 1481.
7. A. Kouloumpis, K. Spyrou, K. Dimos, V. Georgakilas, R. P., G. D., *Frontiers in Materials*, **2015**, *2*, Article 10 (11-18).
8. P. Stathi, D. Gournis, Y. Deligiannakis, P. Rudolf, *Langmuir*, **2015**, *31*, 10508.

Subnanometer 2D-confinement of poly(ethylene oxide) in graphene-based materials

Fabienne Barroso-Bujans*

Donostia International Physics Center (DIPC), 20018 San Sebastian, Spain

Materials Physics Center (MPC), 20018 San Sebastian, Spain

IKERBASQUE-Basque Foundation for Science, María Díaz de Haro 3, Bilbao 48013, Spain

fbarroso@ehu.es

The ability to alter and ultimately control the physicochemical properties of a material using the spatial dimension lies at the heart of the nanotechnology revolution. In the case of soft matter, the confinement of both molecular and macromolecular systems at nanometre length scales can lead to significant changes in observables such as glass transition temperature and melting point. In spite of a plethora of experimental and theoretical work, a solid understanding of the underlying factors responsible for changes in macroscopic behaviour remains both elusive and controversial. Graphene-based materials are exceptional hosts to study confined polymers at the subnanometric scale due to the ability to control and tune their degree of oxidation and exfoliation and, therefore, to control the strength of the interaction between host and macromolecules. In this study, we report on the extreme two-dimensional (2D) confinement of poly(ethylene oxide) (PEO) in the interlayer space of graphite oxide (GO) and in the surface of thermally-reduced graphene sheets by using a combination of diffraction, calorimetric, and spectroscopic methods, including high-resolution inelastic neutron scattering (INS).¹⁻³

Careful control over the degree of graphite oxide oxidation and exfoliation reveals three distinct cases of spatial confinement: (i) subnanometer 2D-confinement; (ii) frustrated absorption; and (iii) surface immobilization. Case (i) results in drastic changes to PEO conformational and collective vibrational modes as a consequence of a preferentially planar zigzag (*trans-trans-trans*) chain conformation in the confined polymer phase, which is accommodated in a layer of thickness ~ 3.4 Å within the GO substrate. In case (ii), GO is thermally reduced resulting in a disordered pseudo-graphitic structure. As a result, we observe minimal PEO absorption owing to a dramatic reduction in the abundance of hydrophilic groups inside the distorted graphitic galleries. In case (iii), the INS data unequivocally show that PEO chains adsorb firmly onto graphene sheets, with a substantial increase in the population of gauche conformers. Well-defined glass and melting transitions associated with the confined polymer phase are recovered in case (iii), albeit at significantly lower temperatures than those of the bulk. These results will be compared with those of PEO intercalated in the pores of carbon and organic-resin nanoparticles.⁴

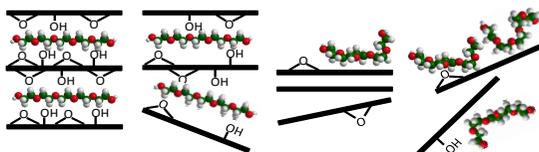


Figure 1. Cartoon illustrating PEO confinement in graphene-based materials.

References

1. F. Barroso-Bujans, F. Fernandez-Alonso, S. Cerveny, S.F. Parker, A. Alegría, and J. Colmenero, *Soft Matter*, **2011**, 7, 7173.
2. F. Barroso-Bujans, F. Fernandez-Alonso, J.A. Pomposo, S. Cerveny, A. Alegría, and J. Colmenero, *ACS Macro Lett.*, **2012**, 1, 550.
3. F. Barroso-Bujans, S. Cerveny, Á. Alegría, and J. Colmenero, *Macromolecules*, **2013**, 46, 7932.
4. F. Barroso-Bujans, P. Palomino, F. Fernandez-Alonso, S. Rudić, A. Alegría, J. Colmenero, and E. Enciso, *Macromolecules*, **2014**, 47, 8729.

Two-Dimensional Conducting Polymers and Supramolecular Polymers

Xinliang Feng*

Center for Advancing Electronics Dresden & Department of Chemistry and Food Chemistry, Technische Universität Dresden, Germany.

xinliang.feng@tu-dresden.de

In the past decade, two-dimensional (2D) materials have emerged as the new paradigm of materials with enormous potentials, ranging from electronics and optoelectronics to energy technology, membrane, sensing and biomedical applications. In contrast to the tremendous exploration of graphene and 2D inorganic materials such as metal dichalcogenides, metal oxides and nitrides, the study on 2D soft materials including the bottom-up organic synthesis of graphene and 2D polymers as well as supramolecular approach to 2D organic nanostructures remains very limited.

In this lecture, we will present our recent efforts toward the chemical synthesis of novel 2D conducting polymers and supramolecular polymers with structural control at the atomic/molecular-level or meso-scale. First, we will briefly report the latest efforts towards the bottom-up synthesis of graphene nanostructures (nanoribbons) with atomically precise structures. This is based on the strategy of designing and synthesis of well-defined dendritic polyphenylenes with different topologies and architectures which can lead to planar graphene nanoribbons upon intramolecular cyclodehydrogenation, when utilizing both solution and on surface approaches. Second, we will discuss the synthetic 2D conjugated polymers including 2D Schiff-base type polymers and 2D metal-dithienene/diamine coordination supramolecular polymers at air-water and liquid-liquid interfaces. The resulting 2D conjugated polymers exhibit single-layer feature, good local structural ordering and with a size of cm^2 . The functional exploration of such 2D single-layer conjugated polymers for the electrical and mechanical properties, as well as serving as efficient electrocatalytic water splitting catalysts will be demonstrated. Third, we will introduce the self-assembly of a host-guest enhanced donor-acceptor interaction, consisting of a tris(methoxynaphthyl)-substituted truxene spacer, and a naphthalene diimide substituted with N-methyl viologenyl moieties as donor and acceptor monomers, respectively, in combination with cucurbit[8]uril as host monomer toward monolayers of an unprecedented 2D supramolecular polymers at liquid-liquid interface. Finally, we will present the supramolecular approaches to 2D conducting polymers, such as polypyrrole and polyaniline nanosheets featuring 2D structures and with adjustable mesopores with/without on various functional free-standing surfaces. The unique structure with adjustable pore sizes (5–20 nm) and thickness (35–45 nm), enlarged specific surface area as well as high electrical conductivity make 2D conducting polymers promising for a number of applications..

References

- Nature*. **2016**, 531, 489-492; *Adv. Mater.* **2016**, in press; *J. Am. Chem. Soc.* **2015**, 137, 14525-14532 ; *Nature Comm.* **2015**, 6, 8817 ; *Angew. Chem. Int. Ed.* **2015**, 54, 12058-12063; *Chem. Soc. Rev.* **2015**, 2015, 44, 6616-6643 ; *Adv. Mater.* **2015**, 27, 403-427.

Superconductivity and ferromagnetism in 2D Materials

S. Mañas-Valero, E. Navarro-Moratalla, Miguel Clemente-León and Eugenio Coronado*
Instituto Ciencia Molecular (ICMol), University Valencia, c/ Catedrático José Beltrán 2, 46100 Paterna, Spain.
Presenting/corresponding author email address: eugenio.coronado@uv.es

Superconductivity and ferromagnetism are two cooperative properties difficult to reach in the 2D limit. The discovery of graphene and other 2D materials has opened the possibility to check these phenomena in this limit. Here we show that, contrarily to the expectation, superconductivity of TaS₂ can be enhanced in the 2D limit¹. On the other hand, we show that coordination chemistry can provide examples of layered coordination polymers exhibiting ferro or ferrimagnetism. These magnetic materials are constructed from a 2D porous anionic network formed by Mn(II) and Cr(III) ions linked through anilate ligands, and by molecular spin-crossover complexes of the type [Fe^{III}(acac₂-trien)]¹ acting as counter-ions, which are placed inside the pores. The result is a layered material formed by neutral layers that can be exfoliated in atomically-thin layers with heights down to 2 nm, using a micromechanical method².

References

1. E. Navarro-Moratalla et al, *Nature Comm.*, **2016**, 7, Article number: 11043.
2. A. Abherve et al, *Chem. Sci.*, **2015**, 6, 4665.

Conjugated Polymers As Molecular Gates for Light-Controlled Release of Gold Nanoparticles

Maria Sanroman-Iglesias,^{a,b} Kai A. I. Zhang,^c Hiromitsu Urakami,^d Felipe Villela,^e Andrey Chuvilin,^{f,g} Charles H. Lawrie,^{b,g} Marek Grzelczak^{a,g,*} and Luis M. Liz-Marzán^{a,g}
^a, CIC biomaGUNE, Paseo de Miramón 182, 20009 Donostia-San Sebastián, Spain
^b, Oncology Area, Biodonostia Research Institute, Donostia-San Sebastián, Spain
^c, Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
^d, Max-Planck Institute of Colloids and Interfaces, Research Campus Golm, 14476 Potsdam, Germany
^e, School of Engineering & Physical Sciences; Heriot-Watt University, Edinburgh, UK
^f, CIC nanoGUNE Consolider, Avenida de Tolosa 76, 20018 Donostia-San Sebastián, Spain
^g, Ikerbasque, Basque Foundation for Science, 48013 Bilbao, Spain
Presenting and Corresponding author email address: mgrzelczak@cicbiomagune.es

The remote release of nano-objects from a container is a promising approach to transduce chemical events into an optical signal.¹ The major challenge in the development of such a system involves the use of a suitable molecular gate that retains aggregated particles and releases them upon applying an external stimulus. We show proof-of-concept experiments for the release of gold nanoparticles into an aqueous solution upon photodegradation of conjugated polymer thin films.² We concluded that the release of nanoparticles was faster when using a polymer that absorbs a wider spectral range matching the features of the incident light. Gold nanoparticles thus transduce light-induced chemical events into an amplified optical signal with a release rate of 2.5 nM per hour, which can be readily detected by the naked eye.

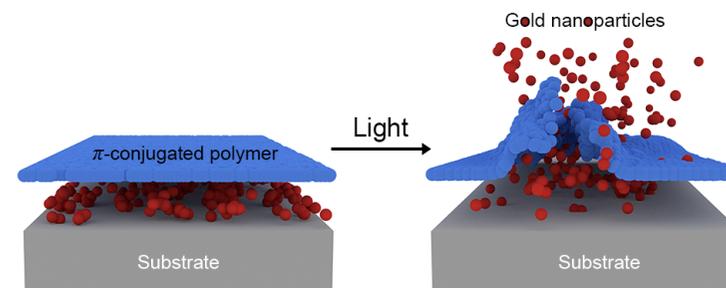


Figure 1. A conjugated polymer thin film covers gold nanoparticle aggregates, preventing their dispersion in water. Under light irradiation, the thin film degrades, allowing nanoparticle release that is detectable by the naked eye. The nanoparticles act as a signal transducer via amplification of structural and chemical changes in the polymer film.

References

1. Kowalczyk, B.; et al.; *Angew. Chem. Int. Ed.* **2010**, 49, 5737
2. Sanroman-Iglesias, M.; et al.; *ACS Appl. Mater. Interfaces* **2015**, 7, 15692

Selectivity in surface-assisted intramolecular cyclodehydrogenations

Alissa Wiengarten,^a Julian A. Lloyd,^a Knud Seufert,^a Joachim Reichert,^{a,*} Willi Auwärter,^a Runyuan Han,^a David A. Duncan,^a Francesco Allegretti,^a Sybille Fischer,^a Seung Cheol Oh,^a Özge Sağlam,^a Li Jiang,^a Saranyan Vijayaraghavan,^a David Eciija,^a Manuela Garnica,^a Anthoula C. Papageorgiou,^{a,*} and Johannes V. Barth,^a

^a, Physik-Department E20, Technische Universität München, James-Frank-Str. 1, D-85748 Garching, Germany

Presenting and corresponding author email address: a.c.papageorgiou@tum.de

Thermally induced cyclodehydrogenation reactions are currently employed in the on-surface syntheses of fullerenes [1], graphene nanoribbons [2], tailored nanographenes [3] as well as carbon nanotubes [4]. Tetraphenyl porphyrins (2H-TPP) on a Ag(111) surface undergo surface intramolecular cyclodehydrogenations (or ring-closing reactions) with a selective outcome [5] (Figure 1, left panel). We propose that the two-fold symmetry of the 2H-TPP's core, which is defined by the position of the H atoms, determines the reaction outcome. This interpretation is substantiated by looking at a corresponding metalated porphyrin, which possesses a higher (four-fold) symmetry: a significant decrease in the selectivity of the ring-closing reactions is observed (Figure 1 right panel). With submolecular resolution of scanning probe microscopes, we identify reaction products and intermediates and compare our findings with density functional theory calculations of the ground state energies of the related species. Based on this model case, we expect *ab initio* calculations of the energetically favoured products to have predictive power for the outcome of surface assisted cyclodehydrogenation reactions and thus contribute towards the targeted design of molecular precursors for conjugated and advanced porphyrin-based architectures at interfaces.

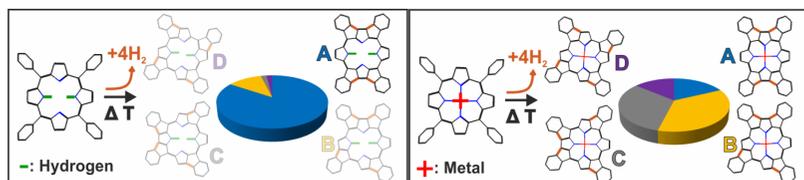


Figure 1. Selectivities of intramolecular cyclodehydrogenation products for a free base (left panel) and a metal (right panel) tetraphenyl porphyrin on the Ag(111) surface.

References

1. G. Otero, G. Biddau, C. Sánchez-Sánchez, R. Caillard, M. F. López, C. Rogero, F. J. Palomares, N. Cabello, M. A. Basanta, J. Ortega, J. Méndez, A. M. Echavarren, R. Pérez, B. Gómez-Lor, and J. A. Martín-Gago, *Nature* **2008**, 454, 865.
2. J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen, and R. Fasel, *Nature* **2010**, 466, 470.
3. M. Treier, C. A. Pignedoli, T. Laino, R. Rieger, K. Müllen, D. Passerone, and R. Fasel, *Nat. Chem.* **2011**, 3, 61.
4. J. R. Sanchez-Valencia, T. Dienel, O. Gröning, I. Shorubalko, A. Mueller, M. Jansen, K. Amsharov, P. Ruffieux, and R. Fasel, *Nature* **2014**, 512, 61.
5. A. C. Papageorgiou, S. Fischer, S. C. Oh, Ö. Sağlam, J. Reichert, A. Wiengarten, K. Seufert, S. Vijayaraghavan, D. Eciija, W. Auwärter, F. Allegretti, R. G. Acres, K. C. Prince, K. Diller, F. Klappenberger, and J. V. Barth, *ACS Nano* **2013**, 7, 4520.

A two-dimensional field-effect spin transistor

Wenjing Yan^a, Oihana Txoperena^a, Felix Casanova^{a,b} and Luis E. Hueso^{a,b,*}

^a, CIC nanoGUNE, San Sebastian, Spain.

^b, IKERBASQUE, Basque Foundation for Science, Bilbao, Spain.

Corresponding author email address: l.hueso@nanogune.eu

The integration of the spin degree of freedom in charge-based electronic devices has revolutionised both sensing and memory capability in microelectronics¹. However, any further development in spintronic devices requires electrical manipulation of spin current for logic operations. The approach followed so far, inspired by the seminal proposal of the Datta and Das spin modulator², has relied on the spin-orbit field as a medium for electrical control of the spin state³. However, the still standing challenge is to find a material whose spin-orbit-coupling (SOC) is weak enough to transport spins over long distances, while also being strong enough to allow their electrical manipulation.

In this talk I will show a radically different approach in the form of an atomically thin van der Waals heterostructure⁴, which combines the superior spin transport properties of graphene⁵ with the strong SOC of the semiconducting MoS₂⁶.

Our results show how the spin transport in the graphene channel is modulated between ON and OFF states by tuning the spin absorption into the MoS₂ layer with a gate electrode. Our demonstration of a spin field-effect transistor using two-dimensional materials identifies a new route towards spin logic operations for beyond CMOS technology.

References

1. A. Fert, *Review Modern Physics*, **2008**, 80, 1517.
2. S. Datta and B. Das, *Applied Physics Letters*, **1990**, 56, 665.
3. H.C. Koo et al., *Science*, **2009**, 325, 1515.
4. A.K. Geim and I.V. Grigorieva, *Nature*, **2013**, 449, 419.
5. W. Han et al., *Nature Nanotechnology*, **2014**, 9, 794.
6. X. Xu et al., *Nature Physics*, **2014**, 10, 343.

Challenges in Graphene Synthesis and Applications

A. Zurutuza

Graphenea S.A., Tolosa Hiribidea 76, 20018 Donostia-San Sebastian, Spain.

Email address: a.zurutuza@graphenea.com

Graphene has emerged as an extremely promising material due to its extraordinary properties. These properties are responsible for the broad range of potential applications that this material could have in the future. Since it first emerged in 2004, the methods to synthesise graphene have advanced considerably however many open issues still remain. During this talk I will cover some challenges related to the synthesis and transfer of graphene as well as challenges that need to be overcome in order to progress towards finding the most promising applications.¹⁻³ As potential application examples I will mention organic light emitting diodes (OLEDs), biosensors and batteries.

As graphene is all surface, the surrounding environment such as the substrate, the atmosphere⁴ as well as the further processing of the material (device fabrication)^{5,6} can really affect its electronic and optical properties, therefore, it is important to protect it from environmental effects.⁵

Finally, I would like to mention that the development of large scale and non destructive characterisation/quality control methods⁷ for graphene is crucial in order to advance towards industrial applications.

References

1. J. Meyer, P.R. Kidambi, B.C. Bayer, C. Weijtens, A. Kuhn, A. Centeno, A. Pesquera, A. Zurutuza, J. Robertson, and S. Hofmann, *Sci. Rep.*, **2014**, 4, 5380.
2. O. Zagorodko, J. Spadavecchia, A. Yanguas Serrano, I. Larroulet, A. Pesquera, A. Zurutuza, R. Boukherroub, and S. Szunerits, *Anal. Chem.*, **2014**, 86, 11211.
3. D. Wei, S. Haque, A. Piers, J. Kivioja, T. Ryhänen, A. Pesquera, A. Centeno, B. Alonso, A. Chuvilin, and A. Zurutuza, *J. Mat. Chem. A*, **2013**, 1, 3177.
4. C. Melios, A. Centeno, A. Zurutuza, V. Panchal, C.E. Giusca, S. Spencer, S.R.P. Silva, and O. Kazakova, *Carbon*, **2016**, 103, 273.
5. A.A. Sagade, D. Neumaier, D. Schall, M. Otto, A. Pesquera, A. Centeno, A. Zurutuza Elorza, and H. Kurz, *Nanoscale*, **2015**, 7, 3558.
6. D.M.A. Mackenzie, J.D. Buron, P.R. Whelan, B.S. Jessen, A. Silajdzic, A. Pesquera, A. Centeno, A. Zurutuza, P. Bøggild, and D.H. Petersen, *2D Mater.*, **2015**, 2, 045003.
7. J.D. Buron, D.M.A. Mackenzie, D.H. Petersen, A. Pesquera, A. Centeno, P. Bøggild, A. Zurutuza, and P.U. Jepsen, *Opt. Express*, **2015**, 23, 30721.

Liposomes as effective exfoliating agents for graphite

Romina Zappacosta,^a Valeria Ettore,^a Mara Di Giulio,^a Caroline Hadad,^b Domenico Bosco,^a Luigina Cellini^a and Antonella Fontana*^a

a, Department of Pharmacy, University "G. d'Annunzio", Via dei Vestini, I-66100 Chieti, Italy.

b, Department of Chemical and Pharmaceutical Sciences, University of Trieste, Via L. Giorgieri 1, I-34027 Trieste, Italy.

c, Molecular Genetics Institute, CNR Unit of Chieti, 66100, Italy

Presenting and Corresponding author email address: antonella.fontana@unich.it

In the last years, graphene and its derivatives, have aroused interest¹⁻³ in many research fields due to their unique physicochemical properties.

For applications in biomedicine, one of the most important and fundamental goal to be achieved is to make graphene soluble in water. Up to now, most of the research on graphene in the biomedical field has been focused on the production and characterization of hydrophilic graphene oxide.⁴

Here we present the preparation of double and few-layer graphene aqueous dispersions by exploiting liposomes as effective exfoliating agents for graphite. Raman measurements evidenced the presence of non-oxidized double layer graphene and ordered phospholipid bilayers. TEM analyses confirmed the embedding of graphene nanosheets in the liposomal bilayer. The as-prepared graphene aqueous dispersions demonstrated to be stable for days highlighting significant antibacterial activity against both Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) strains.

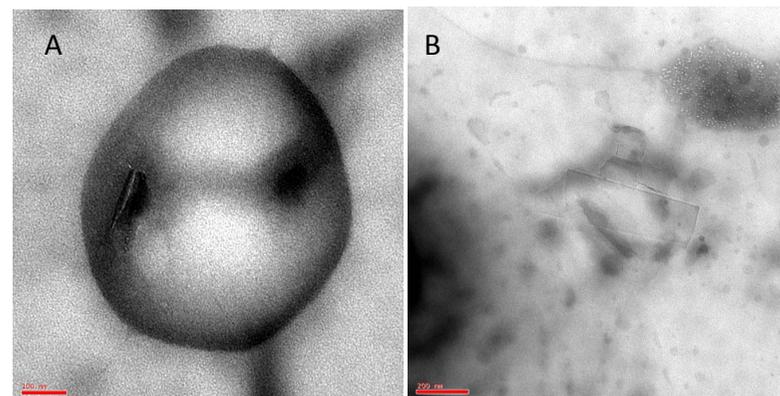


Figure 1. A) Liposome containing graphene flakes. Scale bars: 100 nm; B) Graphene flakes in a liposomal solution. Scale bars: 200 nm

References

1. M. J. Allen, V. C. Tung and R. B. Kaner, *Chem. Rev.*, **2010**, 110, 132.
2. A. K. Geim, *Science*, **2009**, 324, 1530.
3. A. C. Ferrari, F. Bonaccorso, V. Fal'ko, K. S. Novoselov, S. Roche, P. Bøggild, S. Borini, F. H. L. Koppens, V. Palermo, N. Pugno, J. A. Garrido, R. Sordan, A. Bianco, L. Ballerini, M. Prato, E. Lidorikis, J. Kivioja, C. Marinelli, T. Ryhänen, A. Morpurgo, J. N. Coleman, V. Nicolosi, L. Colombo et al. *Nanoscale*, **2015**, 7, 4598.
4. V. Ettore, P. De Marco, S. Zara, V. Perrotti, A. Scarano, A. Di Crescenzo, M. Petri, C. Hadad, D. Bosco, B. Zavan, L. Valbonetti, G. Spoto, G. Iezzi, A. Piattelli, A. Cataldi, A. Fontana, *Carbon*, **2016**, 103 291.

Bio-Based Polymeric Nanocomposites From Acrylated Rapeseed Oil and Hexagonal Boron Nitride Nanosheets

Fatma Selen^a and Gülay Bayramoğlu^{a*}

^a, Polymer Engineering, Yalova University, Yalova, 77100, Turkey.

Presenting author email address: gulayb@yalova.edu.tr

Boron nitride nanosheets (h-BNNSs), so-called “white graphene”, are two-dimensional (2D) layered materials nanomaterials which consist of a regular network of BN hexagons. H-BNNSs exhibit high thermal stability, deep ultraviolet photon emission, good mechanical strength, superb oxidation resistance, electrical-insulating property, and high thermal conductivity¹⁻³. They are promising nanofillers for nanocomposites.

In this study polymeric nanocomposites were synthesized from acrylated rapeseed oil and hexagonal boron nitride nanosheets (h-BNNS) using an *in situ* free radical polymerization reaction. Styrene was also used as a reactive solvent. Acrylated rapeseed oil was synthesized from epoxidized rapeseed oil in our previous studies. H-BNNSs were produced by using molten hydroxides to chemically exfoliate hexagonal boron nitride in a nanoscroll form. The resultant nanocomposites were characterized using X-ray diffraction and atomic force microscopy. The effect of increased H-BNN content on the thermal and mechanical properties of the nanocomposites was investigated using thermogravimetric analysis and dynamic mechanical analysis.

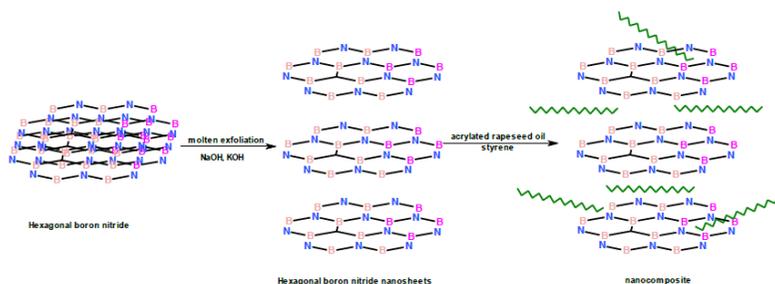


Figure 1: Production of exfoliated h-BNNSs and nanocomposites

Acknowledgment

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References

1. Zeng, X.;Ye, L.; Yu, S.; Sun, R.; Xu, J.; Wong.C.P.; “Facile Preparation of Superelastic and Ultralow Dielectric Boron Nitride Nanosheet Aerogels via Freeze-Casting Process”. *Chem. Mater.*, **2015**, 27 (17), pp 5849–5855
2. Golberg, D.; Bando, Y.; Huang, Y.; Terao, T.; Mitome, M.; Tang, C.; Zhi, C. “Boron Nitride Nanotubes and Nanosheets” *ACS Nano* **2010**, 4, 2979–2993.
3. Meng, W.; Huang, Y.; Fu, Y.; Wang, Z.; Zhi, C. “Polymer composites of boron nitride nanotubes and nanosheets” *J. Mater. Chem. C*. **2014**, 2, 10049–10061.

DNA-Gating in Membranes and Particles

Thomas Schäfer^{a,b}

^a, Polymat, University of the Basque Country, Av. Tolosa 72, Donostia-San Sebastián, 20018, Spain.

^b, Ikerbasque, Basque Foundation for Science, Bilbao, 48013, Spain.

Presenting author email address: thomas.schafer@polymat.eu

Aptamers are oligonucleic acids that can be selected to specifically interact with in principle any kind of target molecule. An important asset of aptamer conjugates is the fact that upon specific binding, their spatial conformation may change drastically, depending on a fine equilibrium between mainly electrostatic and hydrophobic interactions. Recently, it has been shown that this specific conformational change can be exploited for controlled release applications in particles and membranes, where aptamers serve as a “nanovalve” which selectively triggers the opening or closing of a nanopore depending on the presence of a target molecule. Such systems add an important degree of freedom in the design of stimuli-responsive systems which conventionally respond to bulk stimuli such as pH, temperature, light or electrical and magnetic fields. Figure 1 schematically shows as an example the conformational which an AMP-aptamer undergoes upon target binding.

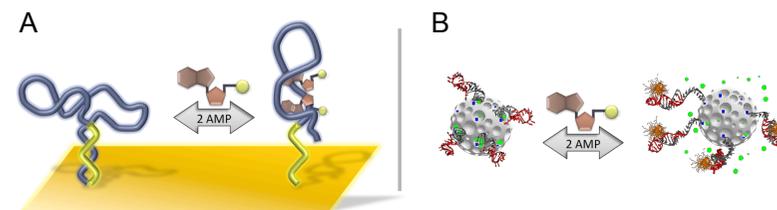


Figure 1. (A) Conformational changes of an AMP-binding aptamer upon exposure to its target; (B) Concept of the gating function of DNA-aptamers immobilized in mesoporous substrates

In this presentation an overview will be given of how DNA can be used as a gating element in nanodevices and membranes [1]. Particular attention will be given to the potential of using DNA-aptamers as nanovalves that selectively interact with small molecules, such as adenosine-triphosphate (ATP), which has hardly been explored until today for nanodevices. For elucidating interactions and conformational changes that lead to the function of aptamer-based nanovalves, some analytical techniques will be critically discussed, namely surface plasmon resonance (SPR), dual polarization interferometry (DPI) and the quartz crystal microbalance with dissipation monitoring (QCM-D). It will be shown how these techniques can help us to verify the function of aptamer films, but also how much one needs to be aware of underlying measurement principles in order to avoid possible pitfalls. The presentation will on one hand demonstrate how far modular concepts such as the one presented here will have a tremendous potential in controlled release and drug delivery applications, but on the other also critically evaluate current bottlenecks and possible limitations.

Reference

1. T.Schäfer and V.C. Özalp. *Chem Commun*, **2015**, 51, 5471.

Pyrene as the Cornerstone in the Synthesis of Designed Pi Systems with Unusual and Interesting Properties

Kiran Sagar Unikela,^a Joshua C. Walsh,^a Kerry-Lynn M. Williams,^a David T. Hogan, and Graham J. Bodwell^{a*}

^a Department of Chemistry, Memorial University of Newfoundland, St. John's, NL, Canada, A1B 3X7.

Presenting author email address: gbdowell@mun.ca

Corresponding author email address: gbdowell@mun.ca

Pyrene is a tremendously popular system and has been used extensively for decades as a fluorescent probe for microenvironments. More recently, it is becoming increasingly important as a building block (instead of a decoration) for the construction of a variety of designed pi systems.¹ Impediments to progress in this area are problems with selectivity in the synthesis of functionalized pyrenes and low solubility. We have recently developed methods to address both of these issues and parlayed them into the synthesis of pyrene-based oligomers,² planar PAHs,³ cyclophanes with bent PAHs,^{4,5} polymers⁶ and macrocycles.^{7,8} A number of unusual and interesting properties have been observed in these compounds.

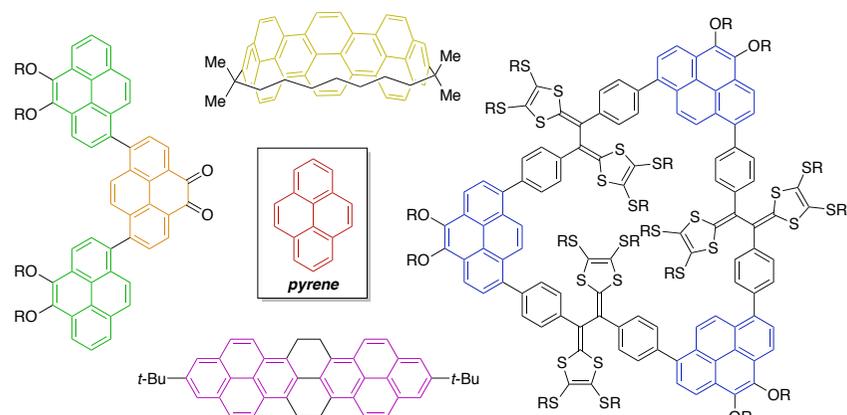


Figure 1. Pyrene and some interesting systems it can be converted into.

References

1. T. M. Figueira-Duarte, and K. Müllen, *Chem. Rev.*, **2011**, 111, 7260.
2. J. C. Walsh, D. T. Hogan, and G. J. Bodwell, *unpublished results*.
3. K. S. Unikela, and G. J. Bodwell, *unpublished results*.
4. B. L. Merner, L. N. Dawe, and G. J. Bodwell, *Angew. Chem. Int. Ed.* **2009**, 48, 5487.
5. E. A. Younes, K.-L. M. Williams, J. C. Walsh, C. M. Schneider, G. J. Bodwell, and Y. Zhao, *RSC Adv.* **2015**, 5, 23952.
6. B. L. Merner, K. S. Unikela, L. N. Dawe, D. W. Thompson, and G. J. Bodwell, *Chem. Commun.* **2013**, 49, 5930.
7. G. Venkataramana, P. Dongare, L. N. Dawe, D. W. Thompson, Y. Zhao, and G. J. Bodwell, *Org. Lett.* **2011**, 13, 2240.
8. M. Khadem, J. C. Walsh, G. J. Bodwell, and Y. Zhao, *Org. Lett.* **2016**, 18, 2403.

Supramolecular Polymerization of Electroactive Systems: A Theoretical Insight

Enrique Orti[†] and Joaquín Calbo

Instituto de Ciencia Molecular, Universidad de Valencia, Catedrático José Beltrán 2, 46100 Paterna (Valencia), Spain.

enrique.orti@uv.es

Supramolecular 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 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 types of monomeric units: a bisurea macrocycle bearing electron-donor di(methylthio)tetrathiafulvalene (DMTTF) groups (**1**) and N-centered and CO-centered oligo(phenylene ethynylene)s (OPEs) trisamides endowed with paraffinic side chains bearing chirally active groups (**2**). Calculations show that **1** polymerize into supramolecular nanotubes through a combination of urea-urea hydrogen bonds and π - π stacking (Figure 1a). The aggregation process in solution can be controlled in a reversible way electrochemically.¹ Trisamides **2** polymerize into helical columnar stacks due to the π -stacking aromatic interactions between the OPE cores and the threefold H-bonding arrays formed by the amide groups (Figure 1b).^{2,3} The connectivity of the amide functional groups attached to the OPE core in **2** has no influence on the handedness of the helical aggregates that only depends on the absolute configuration (S or R) of the stereogenic centers located on the peripheral alkyl chains. Calculations help to assign the helical sense of the aggregate and to energetically discriminate between right-handed P-helices and left-handed M-helices. Both **1** and **2** follow a cooperative mechanism in which an initial nucleation process, where the stability of the aggregate rapidly increases with the number of monomeric units, is followed by an elongation process, where the incorporation of new units has no additional effect.

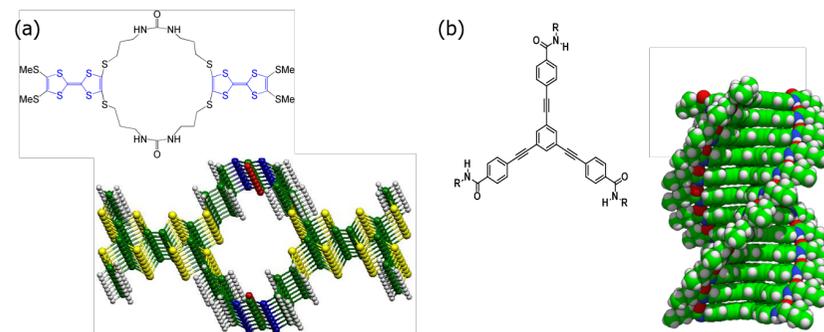


Figure 1. a) Chemical structure and supramolecular nanotubes of **1**. b) Chemical structure and supramolecular helical aggregates of **2**.

References

1. J. L. López, E. M. Pérez, P. M. Viruela, R. Viruela, E. Orti, and N. Martín, *Org. Lett.* **2009**, 11, 4524.
2. F. García, P. M. Viruela, E. Matesanz, E. Orti, and L. Sánchez, *Chem. Eur. J.* **2011**, 17, 7755.
3. B. Nieto-Ortega, F. García, G. Longhi, E. Castiglioni, J. Calbo, S. Abbate, J. T. López Navarrete, F. J. Ramírez, E. Orti, L. Sánchez, and J. Casado, *Chem. Commun.* **2015**, 51, 9781.

Centrohexaindane Functionalization

Jens Linke, Dietmar Kuck*

Department of Chemistry, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld, Germany.
dietmar.kuck@uni-bielefeld.de

Centrohexaindane (**1**, Figure 1, X = H), a rigid, T_d -symmetrical, truly three-dimensional hydrocarbon bears twelve equivalent peripheral positions at its six electronically independent benzene rings.¹ We have studied single, six-fold and twelve-fold functionalization of **1**, each of which represents a challenging task for different reasons. Examples of each type will be given. Most exciting, however, and probably also most promising in terms of molecular and supramolecular architecture, is the exhaustive functionalization of the outer periphery of **1**, which leads to likewise T_d -symmetrical derivatives, such as the dodecabromo (**3**, X = Br) and dodecaiodo (**4**, X = I) derivatives. In contrast to the previously known dodecamethoxy congener (**4**, X = OMe),² the dodecahalo derivatives **2** and **3** are accessible in good yields and, in spite of their extremely poor solubility, both represent highly valuable substrates for the construction of large hydrocarbon cores that bear twelve identical branches stretching into the 3-space. Remarkably efficient model extension reactions of the centrohexaindane core by twelve-fold Pd-catalyzed C-C cross coupling of **3** and **4**, leading to hydrocarbons **5** (X = phenylethynyl) and **6** (X = phenyl), respectively, have been performed successfully.

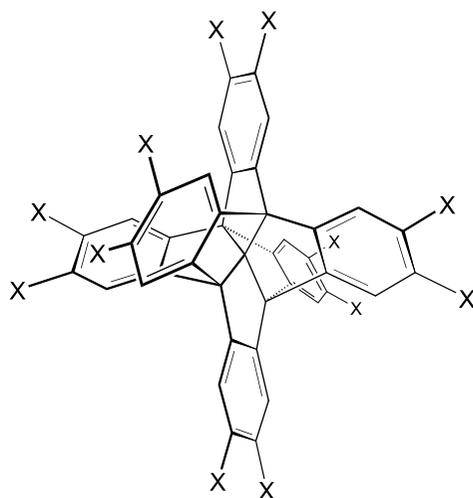


Figure 1. Centrohexaindane **1** (X = H) and some derivatives **2–6** (X = OMe, Br, I, CPh and Ph) with twelve-fold peripheral functionalization or skeletal extension

References

1. D. Kuck, *Chem. Rev.* **2006**, *106*, 4885.
2. M. Harig, D. Kuck, *Eur. J. Org. Chem.* **2006**, 1647.

Realistic Models for Carbon Nanotechnology

Manuel Melle-Franco

CIGECO, Department of Chemistry, Universidade de Aveiro, Aveiro, 3810-193, PORTUGAL.
manuelmelle.research@gmail.com

Computer modelling has played a determinant role in the development of nanotechnology by predicting and confirming electronic novel properties of carbon nanomaterials. Through the years (and in a more modest scale) we have used and developed different computer models to explain complex experimental results in carbon systems. We will illustrate, with a **special emphasis in experiment and in a fully non-technically manner**, how computer modelling has been a helpful tool to understand the physics and chemistry of different carbon nanostructures, like fullerenes¹, carbon nanotubes², graphite³, graphene⁴ and polyaromatic hydrocarbons⁵.

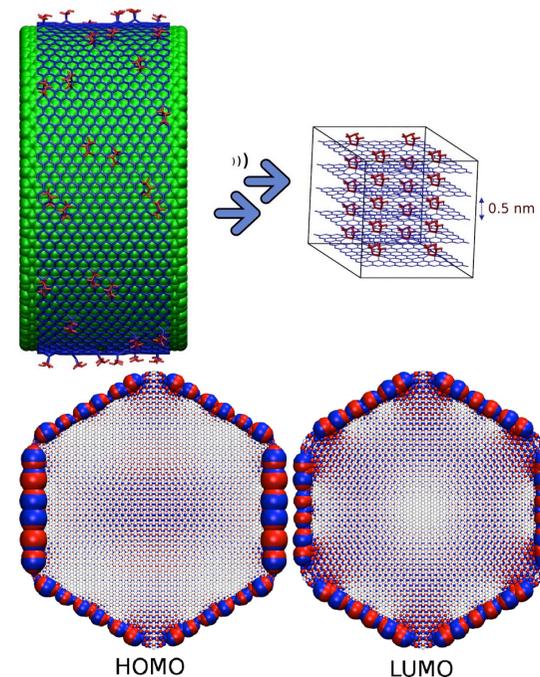


Figure 1. Nanoribbons from unzipping of carbon nanotubes (top) and reactive frontier electrons in graphene islands (bottom)

References

1. Melle-Franco, M.; Brinkmann, G.; Zerbetto, F. Modeling Nanotube Caps: The Relationship Between Fullerenes and Caps. *J Phys Chem A* **2015**, *119* (51), 12839.
2. Paolucci, D.; Franco, M. M.; Iurlo, M.; Marcaccio, M.; Prato, M.; Zerbetto, F.; Pénicaud, A.; Paolucci, F. Singling out the Electrochemistry of Individual Single-Walled Carbon Nanotubes in Solution. *J. Am. Chem. Soc.* **2008**, *130* (23), 7393.
3. Strutyński, K.; Gomes, J. A. N. F.; Melle-Franco, M. Accuracy of Dispersion Interactions in Semiempirical and Molecular Mechanics Models: The Benzene Dimer Case. *J. Phys. Chem. A* **2014**, *118* (40), 9561–9567.
4. Dallavalle, M.; Calvaresi, M.; Bottoni, A.; Melle-Franco, M.; Zerbetto, F. Graphene Can Wreak Havoc with Cell Membranes. *ACS Appl. Mater. Interfaces* **2015**, *7* (7), 4406.
5. Melle-Franco, M. Uthrene, a radically new molecule? *Chem. Commun.* **2015**, *51* (25), 5387.

Transmission Electron Microscopy of Molecular Materials: Challenges and Opportunities

Andrei N. Khlobystov^{a,b,*}

a. School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

b. Nanoscale & Microscale Research Centre (nmRC), University of Nottingham, University Park, Nottingham, NG7 2RD, U.K.

Presenting author email address: andrei.khlobystov@nottingham.ac.uk

Transmission electron microscopy (TEM) is one of the most direct methods for imaging individual molecules with atomic resolution, in direct space and real time. The latest achievements in high-resolution TEM not only provide exquisite structural information, but also help to answer some of the most fundamental and challenging questions of chemical science.

Atomically thin materials, such as graphene, 2D covalent organic frameworks (COFs) or carbon nanotubes, are ultimate nanoscale materials that are ideally suited for TEM imaging. The electron beam of TEM penetrates these structures and has a potential to enable structural characterisation with sub-Angstrom resolution, as well as time-resolved imaging of the reactions taking place in these materials. The level of structural information is usually limited by the stability of the material under the e-beam, with COFs and other organic materials representing the most significant challenge. Highly energetic electrons employed for TEM imaging (20 – 200 keV) transfer some of their kinetic energy to the atoms of the material with the maximum of transferrable energy (T) described by the formula:

$$T = \frac{2 \cdot M \cdot E (E + 2m_e \cdot c^2)}{(M + m_e)^2 \cdot c^2 + 2M \cdot E}$$

where E – energy of incident electrons, m_e – mass of electron, c – speed of light and M – atomic weight of the element. T is strongly dependent and inversely proportional to the atomic weight of the element (M), so that under TEM imaging conditions lighter elements receive significantly more energy from the e-beam. For example, from the 80 keV e-beam, often utilised for imaging molecular materials, a transition metal would receive 1.0 – 3.5 eV depending on its atomic weight. For carbon and the neighbouring elements (e.g. O and N) the transferable energy is about 15-16 eV, which is high enough to knock-out relatively weakly bound atoms from the molecular material (e.g. carbon atoms of alkyl chains), but strongly bound atoms such as sp^2 -C in graphene or in a polyaromatic molecule, can withstand the impact of the 80 keV e-beam. Hydrogen, however, being the lightest atom, receives a vastly higher amount of energy from the e-beam under same conditions (~185 eV from the 80 keV e-beam) which means that hydrogen atoms are removed from the material almost instantaneously under standard TEM conditions.¹ Therefore, structural characterisation of hydrogen-containing molecular materials, including the COFs, is challenging and requires development of new innovative TEM methodologies specifically for this class of materials which then can be applied to a broad range of other organic materials, including molecular 3D porous structures, liquid crystals and polymers.

Beyond the simple structural characterisation, TEM may present a new exciting opportunity, if atomistic mechanisms of interactions between fast electrons and molecules are understood. Indeed, we can embrace the changes in materials triggered by the act of observation to reveal valuable chemical information. Activated by the electron beam, the energy and dose rate of which can be set precisely, molecules undergo different chemical transformations determined by the imaging conditions. Some types of the reactions revealed under the e-beam are familiar to chemists (i.e. polymerisation) and their mechanisms can be studied and interpreted with the atomic precision, while others are newly discovered by TEM.² The concept of the electron beam simultaneously acting as an imaging probe and a source of energy to drive chemical transformations offers an entirely new tool for studying chemical reactions of individual molecules with atomic resolution.

References

1. T.W. Chamberlain et al., *Small*, **2015**, 11, 622.
2. T. Zoberbier et al., *Small*, **2016**, 12, 1649

Nanochemistry inside carbon nanotubes as toolbox to novel hybrid materials

Thomas Pichler

Faculty of Physics, University of Vienna, Boltzmanngasse 5 1090 Vienna

Presenting author email address: thomas.pichler@univie.ac.at

In this contribution I will present recent progress in the synthesis of novel materials based on filled carbon nanotubes followed by nanochemical reactions. This covers the bulk growth of metallobenzenes inside single walled carbon nanotubes and the bulk growth of metal chains [1] and of carbyne inside double walled carbon nanotubes [2]. I will show recent progress on unraveling the influence of charge transfer, local strain and hybridization on their electronic transport properties. As selective examples I will present a gas sensing model based on external functionalization and shows how the interaction with reactive gases like nitric oxides can be tailored by advanced filling reactions with metallocenes and metalacetylacetonates towards room temperature selectivity and sensitivity. As a last example I will review how stabilized carbyne chains with more than 6000 carbon atoms length exhibit novel electronic and optical properties such as a huge resonance Raman signal and act as functional elements enhancing the photoluminescence of inner tubes [3].

Work supported by FWF and the EU.

[1] Hidetsugu Shiozawa et al. *Scientific Reports* 5:15033 (2015); DOI: 10.1038/srep15033

[2] Lei Shi et al. *Nature Materials* (2016); DOI: 10.1038/NMAT4617

[3] Philip Rohringer, Paola Ayala, Thomas Pichler, *Advanced Functional Materials* (2016); DOI: 10.1002/adfm.201505502

From Molecules to Materials

Prof. Colin Nuckolls^a

a, Department Name, University Name, Address, Zip/Postcode, Country.

Presenting author email address: cn37@columbia.edu

This presentation will describe our research in designing molecules for solar energy conversion. In one series we create nanobowls that self-assemble to create molecularly defined pn-junctions. The well-defined nature of this interface has important consequences on the properties in solar cells. In a second series, we create nanowires that form a new class of chromophores for singlet fission. The design and characterization will be discussed along with plans to implement them into solar cells. In the third series, we create nanoribbons of graphene that are atomically defined. The nanoribbons are robust electron acceptors that have high conversion efficiency in solar cells.

References

1. Y. Zhong, B. Kumar, S. Oh, M. Trinh, Y. Wu, K. Elbert, P. Li, X. Zhu, S. Xiao, F. Ng, M. L. Steigerwald, and C. Nuckolls, *J. Am. Chem. Soc.* **2014**, *136* (22), 8122.
2. Y. Zhong, M. Trinh, R. Chen, W. Wang, P. P. Khlyabich, B. Kumar, Q. Zhu, C.-Y. Nam, M. Sfeir, C. Black, M. Steigerwald, S. Xiao, F. Ng, X.-Y. Zhu, and C. Nuckolls, *J. Am. Chem. Soc.* **2014**, *136* (43), 15215-15221.
3. Y. Zhong, M. Trinh, R. Chen, G. E. Purdum, P. P. Khlyabich, M. Sezen, S. Oh, H. Zhu, B. Fowler, B. Zhang, W. Wang, C.-Y. Nam, M. Sfeir, C. Black, M. L. Steigerwald, Y.-L. Loo, F. Ng, X.-Y. Zhu, and C. Nuckolls, *Nat. Comms.* **2015**, *6*, doi: 10.1038/ncomms9242.

Flash/Poster Presentations

P1 Molecular Self-assembly of Hydrogen-bonded Macrocycles Built from DNA Bases

Nerea Bilbao,^a Iris Destoop,^b Steven De Feyter,^b and David González-Rodríguez^{a*}

^a, Nanostructured Molecular Systems and Materials' group, Organic Chemistry Department, Universidad Autónoma de Madrid, c/ Francisco Tomás y Valiente 7, 28049, Spain.

^b, Division of Molecular Imaging and Photonics, Department of Chemistry, KU Leuven–University of Leuven, Celestijnenlaan 200 F, 3001 Leuven, Belgium.

Presenting author email address: nerea.bilbao@uam.es

Corresponding author email address: david.gonzalez.rodriguez@uam.es

This project aims at the development of an innovative methodology,¹⁻⁴ based on molecular self-assembly for the nanostructuring of surfaces which are able to selectively recognize functional guest molecules. The main objectives are: i) the synthesis of the molecular components; ii) the study of the self-assembly process; iii) the formation of nanostructured monolayers; iv) the study of the molecular recognition on surfaces.

The preparation of the different nucleobase derivatives and molecular building-blocks, connected via Sonogashira coupling reactions will be explained.⁵ The mentioned building-blocks will allow us to obtain supramolecular functional nanostructures such as rectangular tetrameric macrocycles via selective hydrogen-bonding between complementary nucleobases. The ability of these molecular building-blocks to self-assemble, as well as its hosting capacity, will be studied by Scanning Tunneling Microscopy (STM) in ultra-high vacuum⁶ and at the solid-liquid interface⁷ (Figure 1).

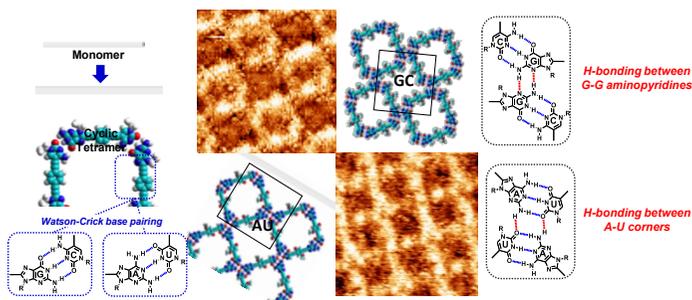


Figure 1. Hierarchical hydrogen-bonding leading to 2D porous networks able to host size-complementary guests.

References

- 1 J. Camacho-García, C. Montoro-García, A.M. López-Pérez, N. Bilbao, S. Romero-Pérez, D. González-Rodríguez, *Org. Biomol. Chem.* **2015**, *13*, 4506.
- 2 C. Montoro-García, J. Camacho-García, A.M. López-Pérez, N. Bilbao, S. Romero-Pérez, M.J. Mayoral, D. González-Rodríguez, *Angew. Chem. Int. Ed.* **2015**, *54*, 6780. (VIP article).
- 3 S. Romero-Pérez, J. Camacho-García, C. Montoro-García, A. M. López-Pérez, A. Sanz, M. J. Mayoral, D. González-Rodríguez, *Org. Lett.* **2015**, *17*, 2664.
- 4 C. Montoro-García, J. Camacho-García, A.M. López-Pérez, M.J. Mayoral, N. Bilbao, D. González-Rodríguez, *Angew. Chem. Int. Ed.* **2015**, DOI: 10.1002/anie.201508854.
- 5 N. Bilbao, V. Vázquez-González, M. Aranda, D. González-Rodríguez, *Eur. J. Org. Chem.* **2015**, *32*, 7160.
- 6 R. Otero, W. Xu, M. Lukas, R. E. A. Kelly, E. Loegsgaard, I. Stensgaard, J. Kjems, L. N. Kantorovich, F. Besenbacher, *Angew. Chem. Int. Ed.* **2008**, *47*, 9673.
- 7 N. Bilbao, S. Destoop, S. De Feyter, D. González-Rodríguez, *Angew. Chem. Int. Ed.* **2015**, DOI: 10.1002/anie.201509233 (Hot Paper).

P2 NEW POROUS GRAPHENE OXIDE BIOMATERIALS WITH POTENTIAL APPLICATION IN BONE REPAIR

Andreea Madalina Pandele^{a,b}, Sorina Alexandra^a, Garea, Horia Iovu^{a*}

^a, Advanced Polymer Materials Group, Department of Bioresources and Polymer Science, University Politehnica of Bucharest, 132 Calea Grivitei, Bucharest 010072, Romania

^b, Department of Analytical Chemistry and Environmental Engineering, Faculty of Applied Chemistry and Material Science

Presenting author email address: pandele.m.a@gmail.com

Corresponding author email address: iovu@tsocm.pub.ro

The idea of developing a biomaterial, appropriate for bone repair applications, with both osteoconductive and osteoinductive features is still a question of basic research.

Chitosan (CHT) is a promising material that encounters all the requirements for these applications, but as other polysaccharide shows low mechanical properties and poor procesability¹. To mitigate these drawbacks, graphene can be used as reinforcing agent. Assimilation of graphene into CHT matrix in order to expand the properties of the final material is a major challenge due to difficulty to achieve a good dispersion of the nanofiller within the biopolymer. In order to overcome this disadvantage the use of graphene oxide (GO), a graphene derivative, was proposed. The functional groups present on GO surface, epoxy(bridging oxygen atoms), carbonyl (C=O), hydroxyl (-OH) groups, bring an increase of the hydrophilic character to GO and favored interactions between the GO and polymer³.

The aim of this study is synthesis of composites scaffold based on CHT and different GO concentrations using freeze-drying method (see figure 1). Studies such as morphology, swelling, enzymatic biodegradation, biological tests and mineralization assays were performed.

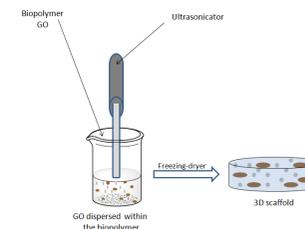


Figure 1. Experimental protocol used for the obtention of CHT/GO composites with different composition

References

1. P. A. L. Lima, C. X. Resende, G. Dulce de Almeida Soares, K. Anselme and L. Eduardo Almeida, *Mat. Sci. Eng. C-BIOMIM*, **2013**, *33*, 3389
2. M. Fang, J. Long, W. Zhao, L. Wang and G. Chen, *Langmuir*, **2010**, *26*, 16771
3. W. Zhang, C. Zhou, W. Zhou, A. Lei, Q. Zhang, Q. Wan, B. Zou, *Bulletion of Environmental Contamination and Toxicology*, **2011**, *87*, 86.

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P3 Self-Assembled Mixed-Stacks of Acene Derivatives: From Supramolecular Intercalation to 1D Solids

Cristian Gozálviz,^a Jose L. Zafra,^b Juan Casado,^b Akinori Saeki,^c Aurelio Mateo-Alonso^{a,d,*}

^a, POLYMAT, University of the Basque Country UPV/EHU, Avenida de Tolosa 72, E-20018 Donostia-San Sebastian, Spain.

^b, Department of Physical Chemistry, University of Málaga, Campus de Teatinos s/n, 229071 Málaga, Spain.

^c, Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan.

^d, Ikerbasque, Basque Foundation for Science, Bilbao, Spain

Presenting author email address: cristian.gozalvez@polymat.eu

Corresponding author email address: amateo@polymat.eu

Organic semiconductors have awakened considerable research interest in the development electronic devices on account of their great potential. They offer the advantage to be processed by solution methods lowering the production costs, plus the fabrication of light weight, flexible and large area devices in contrast with the actual inorganic counterparts, although their intrinsically lower mobility. Organic materials are based on π -conjugated molecules where the π delocalized electrons are the responsible of the conduction and even if the exact relationship between structure and efficiency it is not completely understood, it is known that well-ordered structures and face to face packing of the aromatic moieties with significant intermolecular π -orbital overlap allows for enhance charge transport properties.

Research in our group focuses on the design of new polycyclic aromatic hydrocarbons and on controlling their supramolecular organization for organic electronic applications [1-4]. We have designed a new method to obtain polymolecular organized assemblies of organic semiconductors based on polycyclic aromatic hydrocarbons like acenes and azaacenes able to recognize each other by supramolecular interactions with an optimal distance, between 3.5 Å and 4 Å, for the electrical conduction. The characterization of these systems was carried out in solution by NMR, UV-Vis and in solid state using X-ray diffraction that confirmed the desired packing of the supramolecular assemblies. Finally, these systems were characterized by time-resolved microwave conductivity (TRMC) in order to study their photoconducting properties.

References

1. A. Mateo-Alonso, *Chem.Soc.Rev.*, **2014**, *43*, 6311.
2. S. Choudhary, **C. Gozálviz**, A. Higelin, I. Krossing, M. Melle-Franco, A. Mateo-Alonso, *Chem. Eur. J.*, **2014**, *20*, 1525.
3. G. Tregnago, C. Fléchon, S. Choudhary, **C. Gozálviz**, A. Mateo-Alonso, F. Cacialli, *App. Phys. Lett.*, **2014**, *105*, 143304.
4. A. B. Marco, D. Cortizo-Lacalle, **C. Gozálviz**, M. Olano, A. Atxabal, X. Sun, M. Melle-Franco, L. E. Hueso, A. Mateo-Alonso, *Chem. Commun*, **2015**, *51*, 10754.

P4 Halogen Bonding in Polymer Self-Assembly: A New Route Towards Functional Materials.

Valentina Dichiarante,^a Nikolay Houbenov,^b Olli Ikkala,^b Roberto Milani,^c Pierangelo Metrangolo,^{a,c} Arri Priimagi,^{b,d} Giuseppe Resnati,^a and Gabriella Cavallo^{a,*}

^a, Dept. Chemistry, Materials, and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via Mancinelli 7, 20131 Milan, Italy

^b, Dept. Applied Physics, Aalto University School of Science, Aalto, Finland

^c, VTT Technical Research Centre of Finland, Espoo, Finland

^d, Dept. Chemistry and Bioengineering, Tampere University of Technology, Tampere, Finland

Presenting author email address: gabriella.cavallo@polimi.it

Corresponding author email address: gabriella.cavallo@polimi.it

Polymer self-assembly is gaining significant interest in several fields, including organic electronics, nanotechnology, biomedicine and material science, since it allows for manipulation and production of nanostructured materials characterized by a high degree of internal order. The choice of strong and directional interactions can lead to shape-persistent nanostructures and new functionalities respect to similar covalent polymers may arise. Recently halogen bonding (XB), the non-covalent interaction involving halogen atoms as electrophilic species,¹ has proven to be one of the most effective way to assemble halogenated organic compounds and polymers with suitable electron-donor groups into stable macromolecular structures.² It has also been established that fluorination of molecular backbone around certain halogenated building blocks enhances their ability to work as halogen bonding donors, giving rise to particularly strong interactions.

Herein, we show that the XB strength and directionality, coupled with the segregation tendency of perfluoroalkyl and alkyl chains, might open the way to several new possibilities for structure control and molecular imprinting of polymeric materials, as well as for the tuning of their functional properties.^{2,3} Moreover, photoresponsive XB-donors can be highly effective also for light-induced surface patterning applications, showing interesting possibility in photonics and nanotechnology.⁴

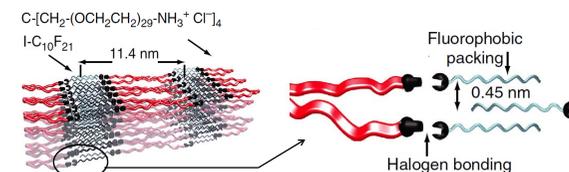


Figure 1. Fluorophobic packing and halogen bonding in polymer self-assembly (adapted from ref. 3).

References

1. G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* **2016**, DOI: 10.1021/acs.chemrev.5b00484
2. A. Priimagi, G. Cavallo, A. Forni, M. Gorynsztejn-Leben, M. Kaivola, P. Metrangolo, R. Milani, A. Shishido, T. Pilati, G. Resnati, G. Terraneo, *Adv. Funct. Mater.* **2012**, *22*, 2572
3. N. Houbenov, R. Milani, M. Poutanen, J. Haataja, V. Dichiarante, J. Sainio, J. Ruokolainen, G. Resnati, P. Metrangolo, O. Ikkala, *Nature Commun.* **2014**, *5*:4043, 1.
4. A. Priimagi, G. Cavallo, P. Metrangolo, G. Resnati, *Acc. Chem. Res.* **2013**, *46*, 2686.

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P5 Thermal and dynamical properties of filled and unfilled cross-linked rubber blends

Lucía Ortega,^{a,*} Mathias Meyer,^b Nihat Isitman,^b Stephan Westermann,^b Silvína Cerveny^c and Gustavo A. Schwartz^c

^a, Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain

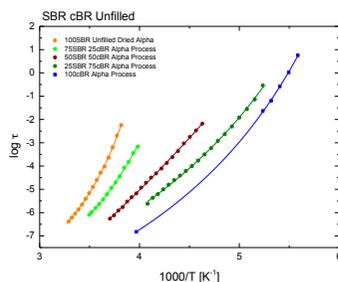
^b, Global Materials Science, Goodyear Innovation Center Luxembourg, Avenue Gordon Smith, L-7750 Colmar-Berg, Luxembourg

^c, Centro de Física de Materiales (CFM, CSIC/UPV) – Materials Physics Center (MPC), Paseo Manuel de Lardizabal 5, 20018 San Sebastián, Spain

Presenting author email address: lortega022@ikasle.ehu.es

Corresponding author email address: lortega022@ikasle.ehu.es

Rubber compounds are often composed of filled and cross-linked polymer blends. Some advantages in the use of blended materials include the possibility of tuning the properties of the compounds, obtaining in general materials with superior properties than the neat components and avoiding the synthesis of new materials, which is expensive and lengthy. In this work different compounds based on standard styrene-butadiene rubber (SBR) and its functionalized counterpart (fSBR), high cis polybutadiene rubber (cBR) and blends of these polymers have been studied. Unfilled and precipitated silica filled compounds were prepared using an internal mixer and then vulcanized under pressure. The samples so obtained have been measured by means of differential scanning calorimetry (DSC) and broadband dielectric spectroscopy (BDS) in a broad frequency (10^{-2} - 10^7 Hz) and temperature (100 - 350K) range. From the calorimetric measurements, the temperature (T_g) and broadness of the glass transition as well as the heat capacity increment (ΔC_p) were obtained and its dependence with the blend concentration and the polymer microstructure has been analyzed. From the dielectric measurements, the dynamics of the neat compounds and the blends has also been analyzed. In particular, the fragility has been correlated with the polymer microstructure.



Temperature dependence of the relaxation time for the α -process for unfilled SBR/cBR blends.

P6 Design and applications of a chemical hydrogel network of chitosan synthesized via Diels–Alder reaction

O. Guaresti, C. García–Astrain, A. Eceiza and N. Gabilondo *

^{*}Materials + Technologies' Group, Dept. of Chemical and Environmental Engineering, Engineering College of Gipuzkoa, University of the Basque Country, Pza. Europa 1, 20018 Donostia–San Sebastián, Spain.

Presenting author email address: olatx.guaresti@ehu.es

Corresponding author email address: nagore.gabilondo@ehu.es

Chemically cross-linked chitosan-based hydrogel was synthesized through Diels–Alder reaction. Chitosan, a natural cationic polysaccharide¹, has great economic impact because of its multiple possibilities to be structurally modified for numerous applications². Besides, 'click' type reactions have lately been used in polymer science to design polymer-based hydrogels for drug delivery systems or as scaffolds for tissue engineering, among others applications³. Thereby, the importance of this research work lies in the fact that two complementary chitosan units were functionalized and then cross-linked to synthesize a novel biomaterial via click chemistry. Namely, the ϵ -amino groups present in the principal chain of chitosan were modified with furfuraldehyde (Cs-Fu) and maleimide-functionalized amino acid (Cs-AMI) separately, so as to obtain the two complementary diene and dienophile polymeric precursors, respectively. For the cross-linked hydrogel formation the Diels–Alder reaction was conducted between both derivatives (HGEL Cs–Fu/Cs–AMI). The as-designed hydrogel was analysed in terms of microstructure, rheological and thermal behaviour or swelling capacity and pH sensitivity in different media. Finally, specific properties of the hydrogel were evaluated facing the possible use in various applications. Thus, controlled-drug delivery studies in a simulated intestinal fluid, dehydration kinetics or antibacterial activity analysis were carried out.

In conclusion, a new material was successfully synthesized by a complementary functionalized strategy, were chitosan derivatives reacted via Diels–Alder chemistry. This hydrogel showed to be highly pH-sensitive, an especially suitable property for targeted-drug delivery, which was reflected on the swelling rate. Furthermore, it can be concluded that this material showed promising properties for its application in the biomedical field as wound protector or drug delivery system.

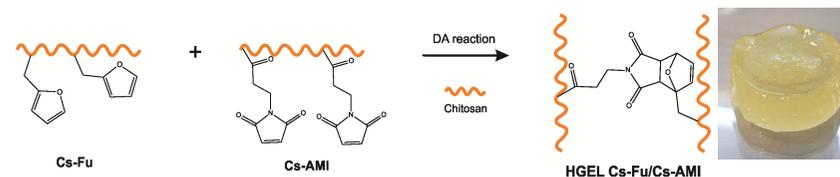


Figure 1. Hydrogel network formation through DA reaction between Cs-Fu and Cs-AMI and a picture of the final hydrogel.

References

1. T.K. Giri, A. Thakur, A. Alexander, Ajazuddin, H. Badwaik and D.K. Tripathi, *Acta Pharmaceutica Sinica B*, **2012**, 2 (5), 439.
2. C.K.S. Pillai, W. Paul and C.P. Sharma, *Progress in Polymer Science*, **2009**, 34 (7), 641.
3. C. García–Astrain, I. Ahmed, D. Kendziora, O. Guaresti, A. Eceiza, L. Fruk, M.A. Corcuera and N. Gabilondo, *RSC Advances*, **2015**, 5, 50268.

P7 Nanoporous Amide Networks Based on Tetraphenyladamantane for Selective CO₂ Capture¹

Sonia Zulfiqar,^{a,b} Daniele Mantione,^a Omar El Tall,^a Muhammad Ilyas Sarwar,^{b,c} Fernando Ruipérez,^a Alexander Rothenberger^d and David Mecerreyes^{a,f}

a, Department of Chemistry, School of Natural Sciences (SNS), National University of Sciences and Technology (NUST), Islamabad 44000, Pakistan

b, POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018 Donostia-San Sebastián, Spain

c, Analytical Core Laboratories, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

d, Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan

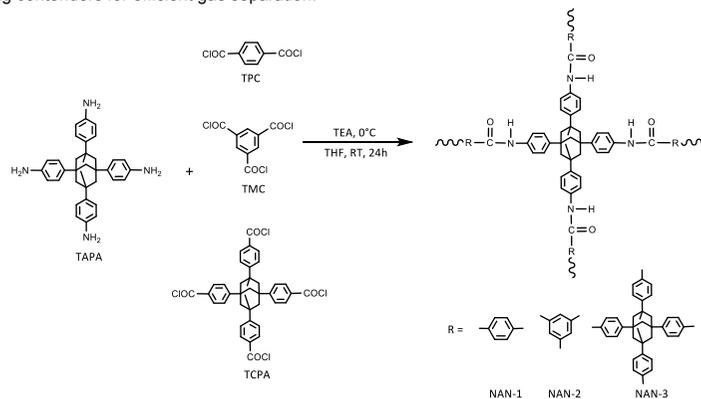
e, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Kingdom of Saudi Arabia

f, Ikerbasque, Basque Foundation for Science, E-48011, Bilbao, Spain

Presenting author email address: daniele.mantione@ehu.es

Corresponding author email address: soniazulfiqar@sns.nust.edu.pk, soniazulfiqar@yahoo.com.

Diminution of anthropogenic CO₂ emissions and CO₂ separation from post-combustion flue gases are among the imperative issues in spotlight at present. Hence, it is highly desired to develop efficient adsorbents for mitigating climate change with possible energy savings. Here, we report the design and facile one pot catalyst free synthetic protocol for the generation of three different nitrogen rich nanoporous amide networks (NANs) based on tetraphenyladamantane. Besides the porous architecture, CO₂ capturing potential, up to 65 mg/g, and high thermal stability, these NANs possess notable CO₂/N₂ selectivity with reasonable retention while increase in temperature from 273K to 298K; passing from 74 to 66. The quantum chemical calculations also suggest that CO₂ interact mainly in the region of the polar amide groups (-CONH-) present in NANs and this interaction is much stronger than with N₂ thus leading to better selectivity and affirming them as promising contenders for efficient gas separation.



Scheme 1. Synthetic route to NANs

References

1. S. Zulfiqar, D. Mantione, O. Tall, M. I. Sarwar, F. Ruipérez, A. Rothenberger and D. Mecerreyes, *J. Mater. Chem. A.*, **2016**, submitted.

P8 New A-D-A Small Molecules based on Rhodanine-fluorene acceptor.

Rafael Sandoval,^a Alexey Gavrik,^b Jose Santos,^a Vladimir Dyakonov^b and Nazario Martin^{a,*}

a, Imdea-Nanoscience, C/ Faraday, 9. Campus Cantoblanco, E-28049, Madrid, Spain.

b, Experimental Physics VI, Julius-Maximilians Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Presenting author email address: rafael.sandoval@imdea.org

Corresponding author email address: nazmar@quim.ucm.es

In recent years, organic photovoltaics has experienced a meaningful progress. With polymer-based bulk heterojunction cells having reached PCE values of 10-11%, it seems that there is little room for improvement. Therefore, much attention has been re-directed to small molecules in order to try to overcome the morphological issues (cross-linking, reproducibility...) dragging their polymeric counterparts. Nevertheless, cross-linking defects derived from their polymeric nature seem to drag further improvement. Being well-defined molecular structures, small molecules have the potential of providing highly ordered phases, along with the ability of easy fine-tuning their electronic energy levels.¹

Many examples have arisen in the literature about the use of rhodanine (Rh) as an electron accepting moiety in high efficiency devices.² All these systems incorporate Rh subunit after condensing it with an aldehyde, herein we present the first example of a Rh unit directly linked to rigid fluorene frame. Incorporation of arylamine groups as donor moieties gave rise to D-A-D-SMs (donor-acceptor-donor small molecules) systems.

Different substitution patterning over the arylamine groups allows modulating and enhancing their light absorption properties. Resulting molecules show intense broad absorption in the visible range (as observed in Figure 1), along with calculated HOMO/LUMO levels fitting the electronic requirements to fabricate blends with PCBM derivatives. Currently, BHJ cells are currently under fabrication and characterization.

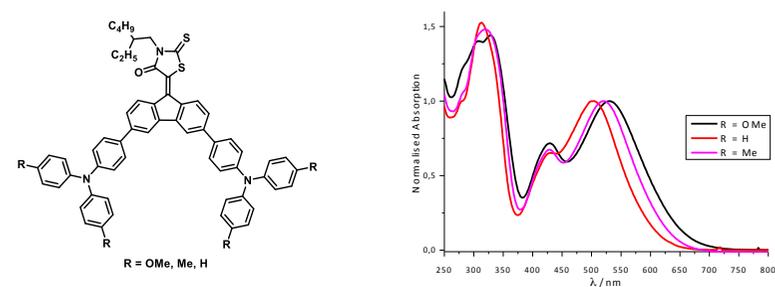


Figure 1. UV-Visible spectra of D-A-D-SMs systems in DCM (right). Structure of D-A-D-SMs (left)

References

1. Y. Cao *et al.*, *Nat. Photonics*, **2015**, *9*, 174.
2. P. Bäuerle *et al.*, *Angew. Chem., Int. Ed.*, **2012**, *51*, 2020.
3. W. Ni. *et al.*, *Chem. Mater.*, **2015**, *27*, 6077.

P9 Synthesis of a novel photocurable urethane spiroorthocarbonate acrylate monomer (SOCUDMA) and their study of antishrinking properties in dental composite resins

Luis Alberto Reyna Medina^{a*}, María Lydia Berlanga Duarte^a.

^aCentro de Investigación en Química Aplicada CIQA, Blvd. Enrique Reyna 140, C.P.25294. Saltillo, Coahuila, México

E-mail: luis_albertorm@live.com.mx

*Correspondence to: Luis Alberto Reyna Medina. ^aCentro de Investigación en Química Aplicada CIQA, Blvd. Enrique Reyna 140, Saltillo, Coahuila, México. C.P.25294. Phone No. + 52 (844) 438 98 30 Ext. 1339.

One of the main drawbacks that presents a dental resin nowadays is the shrinkage that occurs in the photopolymerization, this leads to gaps formation between the interface of the tooth and resin, promoting recurrent caries¹; and low conversion of acrylic double bonds.²

This research contemplates the use of spiro orthocarbonates in dental resin³. Consist in the preparation of a novel acrylate monomer SOCUDMA which has the ability of a double ring open polymerization, producing a volumetric expansion which may counteract the shrinkage that occurs during the polymerization. The SOCUDMA monomer, was synthesized using the spiro orthocarbonates (DIOL SOC_s)⁴ and 2 isocyanato ethyl methacrylate in a single step reaction. The SOCUDMA dimethacrylate monomer was confirmed by ¹HNMR and FT-IR spectroscopy techniques.

The SOCUDMA was evaluated in dental formulations by real time infrared spectroscopy (RT-FTIR) using this technique to determine the reactivity by conversion kinetics, obtaining higher conversions than the Bis-GMA used as reference. The shrinkage and stress that accompanies curing of dental composites was measured with a Polymerization Stress Tester device, where SOCUDMA was effective in reducing the shrinkage compared with Bis-GMA reference in the dental composite, moreover the life time of these materials also increases. The SOCUDMA can be considered as a possible replacement of BIS-GMA,

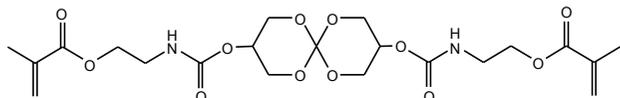


Figure 1. SOCUDMA Acrylate monomer

References

1. Chung, C.M., Kim and M.S., Kim, J.G. *J Biomed Mater Res.* **2002**, 62,622.
2. Moore, J.E. *Coat. Plast. Prep.* **1976**, 36, 747
3. Ricardo Acosta Ortiz and Luis Alberto Reyna Medina, *J Mater Sci* **2013** 24:2077
4. Acosta. O. R and Berlanga D. M.L., *Polymer International.* **2010**, 59; 680.

P10 New Hole-Transporting Materials for Perovskite Solar Cells

Inés García-Benito^a, Agustín Molina-Ontoria^a and Nazario Martín^{b*}

^a, IMDEA-Nanoscience, C/ Faraday, 9. Campus Cantoblanco, 28049, Madrid, Spain.

^b, Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, 28040, Madrid, Spain.

ines.garcia@imdea.org

agustin.molina@imdea.org; nazmar@ucm.es

Recently, the organometal halide perovskites (CH₃NH₃PbX₃, X = Cl, Br, I)⁵ have experienced a scientific research blast for photovoltaic applications due to their appropriate direct band gap, large optical absorption and excellent carrier mobility among others great characteristics.

An impressive photovoltaic performance has been achieved using 2,2',7,7'-tetrakis-N,N-di (4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) as hole transporting material (HTM). Actually, power conversion efficiency (PCE) of 21.1 % has recently been achieved.¹ However, Spiro-OMeTAD is a relatively expensive material because a rather complicated synthetic protocol is required. Besides, a sublimation-grade of this compound is an essential requirement in order to achieve high PCEs devices.² Therefore, the development of cost-effective HTMs with high efficiency along with a better stability is an important task to address.

We report herein on three new star-shaped benzotrithiophene (BTT) based HTM: *BTT-1*, *BTT-2* and *BTT-3* (figure 1) which have been obtained through a straightforward synthetic route by crosslinking triarylamine-based donor moieties with a BTT core. Power conversion efficiencies in the range of 16.0 % to 18.2 % have been achieved under AM 1.5 sun with the three derivatives tested on solution processed lead trihalide perovskite based solar cells.³

These values are comparable to those obtained with today's most commonly used HTM Spiro-OMeTAD, which point them out as promising candidates to be used as readily available and cost-effective alternatives in perovskite solar cells.

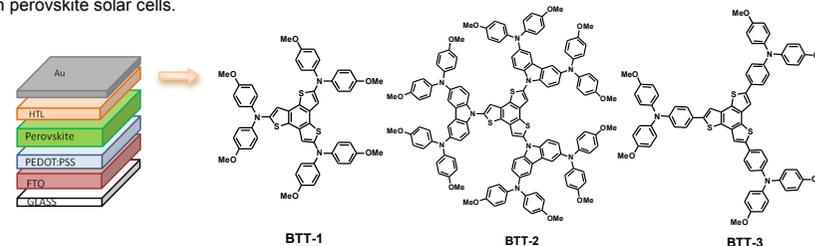


Figure 1. Schematic perovskite solar cells and new star-shaped hole-transporting materials.

References

1. M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M.K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate, A. Hagfeldt and M. Grätzel, *Energy Environ. Sci.*, **2016**, DOI: 10.1039/c5ee03874j.
2. P. Gratia, A. Magomedov, T. Malinauskas, M. Daskeviciene, A. Abate, S. Ahmad, M. Graetzel, V. Getautis, M. K. Nazeeruddin, *Angew. Chem. Int. Ed.*, **2015**, 54, 11409.
3. A. Molina-Ontoria, I. Zimmermann, I. Garcia-Benito, P. Gratia, C. Roldán-Carmona, S. Aghazada, M. Graetzel, M. K. Nazeeruddin, N. Martín, *Angew. Chem. Int. Ed.*, **2016** (accepted).

P11 Magnetic composite scaffolds of Polycaprolactone/nFeHA, for bone-tissue engineering

M.B. Valle,^a E. Díaz^{b*} and J. M. Barandiarán^c

^a, Department Applied Chemistry, Facultad de Químicas UPV/EHU, Pº Manuel Lardizabal 3, 20018 Donostia - San Sebastián, Spain.

^b, Department of Mining Metallurgy Engineering & Materials Science, Escuela de Ingeniería de Bilbao UPV/EHU, María Díaz de Haro 68, 48920 Portugalete, Spain.

^c, BCMaterials, Parque Tecnológico de Bizkaia, Derio, 48160, Spain.

Presenting author email address: mariablanca.valle@ehu.es

Corresponding author email address: esperanza.diaz@ehu.es

Magnetic composite scaffolds of Polycaprolactone/ Fe doped nanohydroxyapatite (PCL/nFeHA) with different composition ratios have been fabricated by thermally induced phase separation (lyophilization) for the purpose of bone-tissue engineering. Magnetic measurements reveal some interaction between the Fe particles that decreases steadily as the nFeHA is diluted in the polymer. All the scaffolds were characterized before and after in-vitro degradation for over 28 weeks. The SEM results showed that the amount of nFeHA strongly affected the pore morphology of the scaffolds. The introduction of Fe anions in nHA increased the scaffold water absorption rates, a complex system consisted of hydrophilic nFeHA and hydrophobic polymeric matrix has a more probable tendency to absorb aqueous medium than pure polymer. The nFeHA nanoparticles decreased the initiation rate of hydrolytic degradation. After 16 weeks degradation, thermograms of the first heating revealed two melting peaks, which could be attributed to the presence of crystals of two different sizes. GPC results indicated that Mw and Mn and the polydispersity index were unaffected by the weeks of degradation with no cleavage of the macromolecular chains.

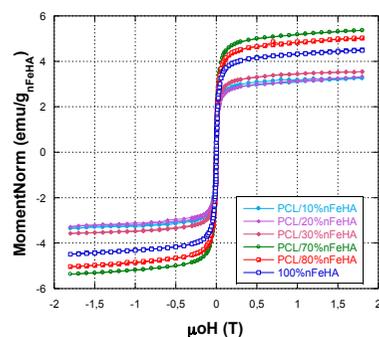


Figure 1. Magnetization curves for different contents of nFeHA in PCL at T=300 K (human body temperature)

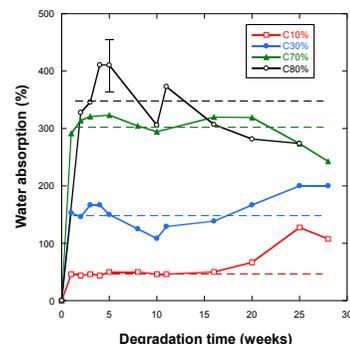


Figure 2. Water absorption, for PCL/nFeHA composite scaffolds, as a function of degradation time

P12 Organogelators with Nonlinear Optical activity

B. Marco,^a F. Aparicio,^b L. Faour,^b K. Iliopoulos,^b B. Sahraoui,^b D. Gindre,^b S. Franco,^a R. Andreu,^a D. Canevet,^{b*} M. Sallé.^{b*}

^a, Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, Pedro Cerbuna 12, 50009 Zaragoza, Spain

^b, Laboratoire MOLTECH-Anjou, Université d'Angers 2, Bd Lavoisier, 49045 Angers Cedex 01, France

Presenting author email address: fatima.aparicioherandez@univ-angers.fr

Corresponding author email address: marc.salle@univ-angers.fr

Organic nonlinear optically (NLO)-active compounds are continuously investigated as precursors for Second Harmonic Generation (SHG) active materials given their potential in a variety of applications including photonics, optoelectronics or anti-counterfeiting.^{1,2}

Our strategy³ lies on the supramolecular gelation of (NLO)-active substances. The corresponding materials display a SHG response without any need for pre-processing and this activity proves to be stable over several months (Figure 1). These findings, based on an intrinsic structural approach, are supported by favorable supramolecular interactions, which locally promote a non-centrosymmetric NLO-active organization. By this method, SHG active materials are generated avoiding the use of expensive or heavy-to-handle external techniques usually utilized to promote dipoles alignment.

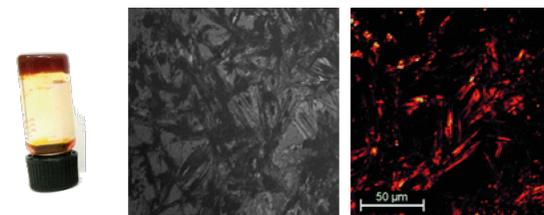


Figure 1. An organogel (left) and its corresponding optical micrograph (center) and SHG image (right) after evaporation of the solvent (xerogel state).

References

1. G. Zerbi, *Organic Materials for Photonics: Science and Technology*, Elsevier, 1993.
2. K. Iliopoulos, O. Krupka, D. Gindre and M. Sallé, *J. Am. Chem. Soc.* **2010**, 132, 14343.
3. B. Marco, F. Aparicio, L. Faour, K. Iliopoulos, B. Sahraoui, D. Gindre, S. Franco, R. Andreu, D. Canevet and M. Sallé, *Submitted*.

P13 Low Temperature Synthesis and Characterization of CMK-3 Ordered Mesoporous Carbons with High Surface Areas

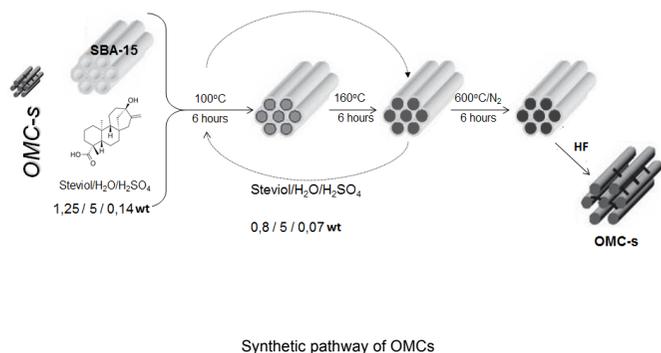
M. A. Karakassides^a, V. Kostas^a, K. Dimos^a, A. Bourlinos^b, M. Baikousi^a, A. Avgeropoulos^a

^aDepartment of Materials Science and Engineering, University of Ioannina, 45110, Ioannina, Greece.

^bPhysics Department, University of Ioannina, 45110, Ioannina, Greece

mkarakas@cc.uoi.gr

So far, sugar is the most common carbon source that has been used for synthesis of this kind of ordered mesoporous carbon materials. Although many other chemical compounds have been used for this purpose such as furfuryl alcohol, acrylonitrile, acetylenedicarboxylic acid, etc..[1-4] In this study, ordered mesoporous carbons, OMCs, with high surface areas have been synthesized via a nanocasting process using SBA-15 as a template and steviol as a carbon source instead of sugar at various temperatures between 300 °C and 900 °C. The as derived mesoporous carbon materials were characterized by means of X-ray diffraction (XRD), Fourier-transform infrared (FT-IR), Raman, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), thermal (DTA/TGA) and surface analysis (BET) methods. The experimental results showed that mesoporous carbons which were synthesized at high temperatures, exhibit similar basic structural and morphological features with common CMK-3 carbons [5,6]. However, carbon samples which have been synthesized at lower temperatures (i.e. 500 °C, 600 °C) showed higher specific surface areas (up to 1900m²/g), better thermal stability (>100 °C), different pore size distribution (PSD) and tuneable surface chemistry.



References

- Lu, A. H.; Schmidt, W.; Spliethoff, B.; Schüth, F. Synthesis of Ordered Mesoporous Carbon with Bimodal Pore System and High Pore Volume. *Advanced Materials* **2003**, *15*, 1602-1606.
- Fuertes, A. B.; Nevskaja, D. M. Template Synthesis of Mesoporous Carbons from Mesostructured Silica by Vapor Deposition Polymerisation. *J. Mater. Chem.* **2003**, *13*, 1843-1846.
- Lu, A.; Kiefer, A.; Schmidt, W.; Schüth, F. Synthesis of Polyacrylonitrile-Based Ordered Mesoporous Carbon with Tunable Pore Structures. *Chem. Mater.* **2004**, *16*, 100-103.
- M. Baikousi, C. Daikopoulos, Y. Georgiou, A. Bourlinos, R. Zbořil, Y. Deligiannakis, and M. A. Karakassides. Novel Ordered Mesoporous Carbon with Innate Functionalities and Superior Heavy Metal Uptake. *J. Phys. Chem. C*, **2013**, *117*, 16961-16971
- Shin, H. J.; Ryoo, R.; Kruk, M.; Jaroniec, M. Modification of Sba-15 Pore Connectivity by High-Temperature Calcination Investigated by Carbon Inverse Replication. *Chemical Communications* **2001**, 349-350.
- Kruk, M.; Jaroniec, M.; Ryoo, R.; Joo, S. H. Characterization of Ordered Mesoporous Carbons Synthesized Using Mcm-48 Silicas as Templates. *J. Phys. Chem. B* **2000**, *104*, 7960-7968.
- Ryoo, R.; Joo, S. H.; Kruk, M.; Jaroniec, M. Ordered Mesoporous Carbons. *Advanced Materials* **2001**, *13*, 677-681.

P14 Raman Spectroscopy and DFT calculations for the Electronic Structure Characterization of Conjugated Polymers

Rafael C. González-Cano^a, Juan T. López Navarrete^a and M. Carmen Ruiz Delgado^{a*}

^a Department of Physical Chemistry, University of Málaga, Campus de Teatinos s/n, Málaga, 29071, Spain.

Presenting author email address: rafacano@uma.es

Corresponding author email address: carmenrd@uma.es

In the last three decades, there has been a broad academic and industrial interest in conjugated polymers as semiconducting materials for organic electronics. Their applications in polymer light-emitting diodes (PLEDs), polymer solar cells (PSCs), and organic field-effect transistors (OFETs) offer opportunities for the resolution of energy issues as well as the development of display and information technologies¹. Conjugated polymers provide several advantages including low cost, light weight, good flexibility, as well as solubility which make them readily processed and easily printed, removing the conventional photolithography for patterning². A large library of polymer semiconductors have been synthesized and investigated with different building blocks, such as acenes or thiophene and derivatives, which have been employed to design new materials according to individual demands for specific applications. To design ideal conjugated polymers for specific applications, some general principles should be taken into account, including (i) side chains (ii) molecular weights, (iii) band gap and HOMO and LUMO energy levels, and (iv) suited morphology.³⁻⁶

The aim of this study is to elucidate the impact that substitution exerts on the molecular and electronic structure of π -conjugated polymers with outstanding performances in organic electronic devices. Different configurations of the π -conjugated backbones are analyzed: (i) donor-acceptor configuration, (ii) 1D linear or 2D branched conjugated backbones, and (iii) encapsulated polymers (see Figure 1). Our combined vibrational spectroscopy and DFT study shows that small changes in the substitution pattern and in the molecular configuration have a strong impact on the electronic characteristics of these polymers. We hope this study can advance useful structure-property relationships of conjugated polymers and guide the design of new materials for organic electronic applications.

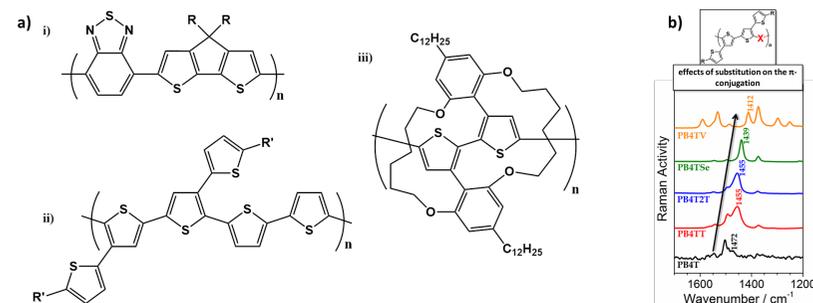


Figure 1. a) Chemical structures of different types of π -conjugated polymers under study and b) Raman analysis of the effect of chain elongation on the π -conjugational properties of branched polythiophenes.

References

- L. Y. Bian, E. W. Zhu, J. Tang, W. H. Tang, F. J. Zhang. *Prog. Polym. Sci.* **2012**, *37*, 1292.
- S. Kola, J. Sinha, H. E. Katz. *J. Polym. Sci. Part B: Polym. Phys.* **2012**, *50*, 1090.
- X. Guo, M. Baumgarten, K. Müllen. *Progress in Polymer Science*, **2013**, *38*, 1832.
- M. Goll, A. Ruff, E. Muks, F. Goerigk, B. Omiecienski, I. Ruff, R. C. González-Cano, J. T. López Navarrete, M. C. Ruiz Delgado, S. Ludwigs. *Beilstein J. Org. Chem.*, **2015**, *11*, 335.
- D. Herrero-Carvajal, A. de la Peña, R. C. González-Cano, C. Seoane, J. T. López Navarrete, J. L. Segura, J. Casado, M. C. Ruiz Delgado, *J. Phys. Chem. C*, **2014**, *118*, 9899.
- M. Scheuble, Y. M. Gross, D. Trefz, M. Brinkmann, J. T. López Navarrete, M. C. Ruiz Delgado, and S. Ludwigs, *Macromolecules*, **2015**, *48*, 7049.

P15 Gate-controlled energy barrier at a graphene/molecular semiconductor junction

S. PARUI^{1,*}, L. PIETROBON¹, D. CIUDAD¹, S. VÉLEZ¹, X. SUN¹, F. CASANOVA^{1,2}, P. STOLIAR¹, L. E. HUESO^{1,2}

¹CIC nanoGUNE, 20018 Donostia-San Sebastian, Basque Country, Spain

²IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Basque Country, Spain

Presenting author email address: s.parui@nanogune.eu

Corresponding author email address: s.parui@nanogune.eu

The formation of an energy barrier at a metal/molecular semiconductor junction is both a ubiquitous phenomenon as well as the subject of intense research in order to improve the performance of molecular semiconductor-based electronic and optoelectronic devices [1-3]. For these devices, a junction with a large energy barrier provides rectification, leading to a diode behavior, whereas a relatively small energy barrier provides nearly-ohmic behavior, resulting in efficient carrier injection into (or extraction from) the molecular semiconductor [2]. Typically, a specific metal/molecular semiconductor combination leads to a fixed energy barrier [3], which crucially determines the device performance and efficiency; therefore, the possibility of a gate-controlled energy barrier is very appealing from the point of view of possible advanced applications.

In this work [4] we present a graphene/C₆₀ vertical field-effect transistor in which we demonstrate control of the interfacial energy-barrier such that the junction switches from a highly rectifying diode at negative gate voltages to a nearly-ohmic behavior at positive gate voltages and at room temperature. From the experimental data, we extract an energy-barrier modulation of up to 660 meV, a transconductance of up to five orders of magnitude and a gate-modulated photocurrent. The ability to tune the graphene/molecular semiconductor energy-barrier provides a promising route towards novel, more performing molecular devices.

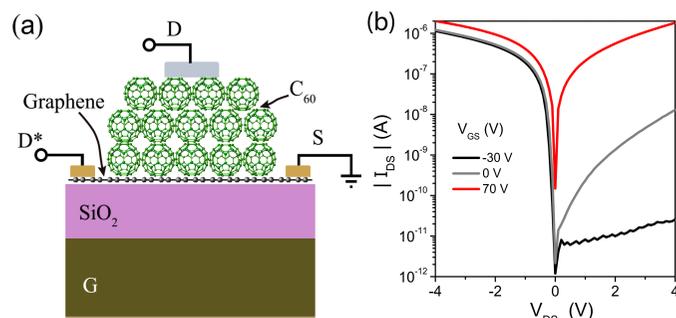


Figure 1: (a) Cross-sectional schematic diagram of our device, which acts as a lateral graphene field effect transistor as well as a graphene/C₆₀-based vertical field effect transistor. (b) A controllable switch of the energy-barrier of a graphene/C₆₀ junction from a highly rectifying diode to a nearly-ohmic junction at room temperature.

References

- [1] S. Braun, W. R. Salaneck, and M. Fahlman, *Adv. Mater.* **2009**, 21, 1450.
- [2] Y. Shen, A. R. Hosseini, M. H. Wong, and G. G. Malliaras, *ChemPhysChem* **2004**, 5, 16.
- [3] M. Gobbi, L. Pietrobon, A. Atxabal, A. Bedoya-Pinto, X. Sun, F. Golmar, R. Llopis, F. Casanova, and L. E. Hueso, *Nat. Commun.* **2014**, 5, 4161.
- [4] S. Parui, L. Pietrobon, D. Ciudad, S. Vélez, X. Sun, F. Casanova, P. Stoliar, and L. E. Hueso, *Adv. Fun. Mat.* **2015**, 25, 2972.

P16 Azaacene-based Surfactants for Carbon Nanotubes

Valentina Montagna,^a Philip Rohringer, Thomas Pichler^b and Aurelio Mateo Alonso^{a,c*}

^a Polymat, University of the Basque Country, Avenida de Tolosa 72, 20018, San Sebastian, Spain.

^b Faculty of Physics, University of Vienna, Strudlhofgasse 4, A-1090, Wien, Austria.

^c Ikerbasque, Basque Foundation for Science, Bilbao, Spain.

Presenting author email address: montagna89v@gmail.com

Corresponding author email address: amateo@polymat.eu

Carbon nanotubes (CNT) constitute promising materials for use in the aerospace, textile, and electronics industries, since they possess high chemical and thermal stability, mechanical strength, flexibility, electrical and thermal conductivity, as well as low weight. CNTs do not exist individually, but form bundles, which are difficult to characterize and process due to their low solubility in organic or aqueous solvents. Exfoliated CNT dispersions can be prepared in certain solvents or mixtures of solvents and surfactants¹. Although this approach is very convenient for optical characterisation, traditional surfactants (e.g. sodium dodecyl sulphate) are insulators and difficult to remove. To develop electronic applications, it will be desirable to disperse and manipulate SWCNTs with surfactants based on molecules more suitable for this purpose that can complement or enhance the inherent properties of CNT and also that do not disturb their inherent properties. In this regard, acene derivatives have demonstrated a great potential as organic semiconductors². In this communication, we will describe a series of novel pyrene-fused azaacene based surfactants. We will show that the combination of large π electron deficient surfaces with optimal solubilising groups provide stable dispersions of doped CNTs.

References

- (1) Connell, M. J. O. Band Gap Fluorescence from Individual Single-Walled Carbon Nanotubes. **2010**, 593, 593–597.
- (2) Anthony, J. E. Functionalized Acenes and Heteroacenes for Organic Electronics. *Chem. Rev.* **2006**, 106, 5028–5048.

P17 Toward on-surface synthesis of low dimensional conjugated nanomaterials

Li Jiang,^a Anthoula C. Papageorgiou,^{a,*} Seung Cheol Oh,^a Özge Sağlam,^a Joachim Reichert,^{a,*} David A. Duncan,^a Yi-Qi Zhang,^a Florian Klappenberger,^a Yuanyuan Guo,^a Francesco Allegretti,^a Sandeep More,^{b,c,d} Rajesh Bhosale,^{c,d} Aurelio Mateo-Alonso,^{d,e,*} and Johannes V. Barth^a

^a, Physik Department E20, Technische Universität München, James-Frank-Str. 1, D-85748 Garching, Germany.

^b, POLYMAT, University of the Basque Country UPV/EHU, E-20018 Donostia-San Sebastian, Spain

^c, Freiburg Institute for Advanced Studies (FRIAS), School of Soft Matter Research, Albert-Ludwigs-Universität Freiburg, Albertstraße 19, 79104 Freiburg, Germany

^d, Institut für Organische Chemie und Biochemie, Albertstraße 21, 79104 Freiburg, Germany

^e, Ikerbasque, Basque Foundation for Science E-48011 Bilbao, Spain

Presenting author email address: li.jiang@tum.de

Corresponding author email address: a.c.papageorgiou@tum.de, joachim.reichert@tum.de, amateo@polymat.eu

Recently, graphene nanoribbons, especially doped with heteroatoms have spurred extensive attention and exploration¹ and covalent organic frameworks (COF) have been successfully synthesized based on Schiff base formation.² Inspired by these findings, we systematically investigated the coupling reaction of a tetraamine molecule with a tetraketone molecule on the three coinage close packed metal surfaces Au, Ag and Cu under ultrahigh vacuum conditions by scanning tunneling microscopy. On all three substrates the reactants readily intermix at room temperature forming two-dimensional bi-component networks (eg. Figure 1a). We demonstrated the feasibility to form Schiff base conjugated oligomers (Figure 1b) on the Ag(111) surface by thermal treatment. Statistical analysis of the reaction products as a function of reactant stoichiometry and further investigations with the X-ray photoelectron spectroscopy provide mechanistic insight in the on-surface polymerization process. In contrast to the behavior on Ag(111), the monomers desorb from the Au(111) surface before they react, whereas on the Cu(111) surface undesired thermal decomposition is observed after annealing at lower temperatures than that of imine formation.

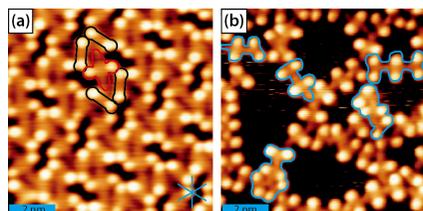


Figure 1. Scanning tunnelling microscopy images of (a) 2-D nanostructures of tetraketone molecules (examples outlined in black) intermixed with tetraamine molecules (example outlined in red) on Ag(111) and (b) the corresponding reaction products (examples outlined) after annealing to 510 K.

References

1. L. Zhao, R. He, K. T. Rim, T. Schiros, K. S. Kim, H. Zhou, C. Gutierrez, S. P. Chockalingam, C. J. Arguello, L. Palova, D. Nordlund, M. S. Hybertsen, D. R. Reichman, T. F. Heinz, P. Kim, A. Pinczuk, G. W. Flynn, and A. N. Pasupathy, *Science* **2011**, 333, 999.
2. L. Stegbauer, K. Schwinghammer, and B. V. Lotsch, *Chem. Sci.* **2014**, 5, 2789.

P18 Effect of graphene oxide on the properties of water-borne pressure sensitive adhesives

Victoria Padilla¹, Raquel Ledezma¹, Beatriz Reyes and Esther Trevino^{1,*}

¹ Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna 140, Saltillo, Coah., 25294, México
Presenting and corresponding author email address: esther.trevino@ciqa.edu.mx

Pressure-sensitive adhesives (PSAs) undergo adhesion to a specific surface upon application of light pressure and also can be easily removed through a light pulling force without leaving any residues on the surface.¹ Water-borne PSAs, with 30 wt % of solids, are prepared by dropping a mixture of butyl acrylate/methyl methacrylate (95/5; wt/wt) onto an aqueous solution of graphene oxide (GO) and sodium dodecyl benzene sulfonate (SDBS). Polymerizations are carried out at 70°C using potassium persulfate as initiator. Films without GO as well as films with 0.08 wt % of GO are used to evaluate their: tack (ability to adhere quickly), peel strength (ability to resist removal through peeling), and shear strength (ability to hold in position when shear forces are applied). The effect of nano-fillers on the performance of the adhesives has been scarcely studied. For solvent-borne acrylic PSAs, Park *et al.*² observed a reduction of peel strength with the addition of graphene, while Czech *et al.*^{3,4} reported a reduction of tack and peel adhesion, but an increase of shear strength, with the addition of carbon black and carbon nanotubes. The results presented in Figure 1 are opposed to the expected since, as a result of the incorporation of GO, tack is improved but peel strength and shear strength are negatively affected. This behaviour could be explained by differences in the film formation mechanisms between solvent- and water-based products. Apparently, once the water has been evaporated, the GO platelets interfere with the appropriate diffusion of polymer chains between particles to the subsequent development of entanglements. If so, the lack of continuity of the polymeric film could lead to failures in the cohesive forces.

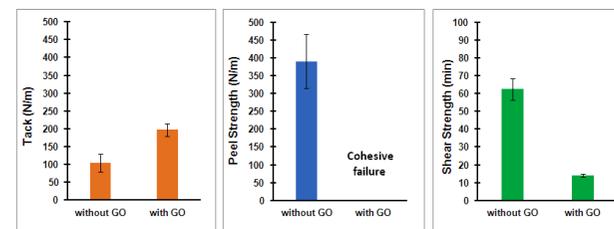


Figure 1. Effect of GO on the adhesive properties.

References

1. I. Benedek, "Pressure-Sensitive Adhesives and Applications", 2nd edition Marcel Dekker, Inc., New York **2004**, Chap. 1.
2. G. H. Park, K. T. Kim, Y. T. Ahn, H. Lee, and H. M. Jeong, *J. Ind. Eng. Chem.*, **2014**, 20 (6), 4108.
3. Z. Czech, R. Pelech, A. Kowalczyk, A. Kowalski, and R. J. Wróbel, *Polish J. Chem. Tech.*, **2011**, 13 (4), 77.
4. Z. Czech, A. Kowalczyk, R. Pelech, R. J. Wróbel, L. Shao, Y. Bai, and J. Swiderska, *Int. J. Adhes. Adhes.*, **2012**, 36, 20.

P20 Toward Hydrogen-bonded Porous Organic Frameworks from a DNA-base Toolkit

Miguel Martín-Arroyo^a, Nerea Bilbao^a and David González-Rodríguez^{a*}
^a, Nanostructured Molecular Systems and Materials group, Departamento de Química Orgánica, Universidad Autónoma de Madrid, C/ Francisco Tomás y Valiente 7, Madrid, 28049, Spain.
 Presenting author email address: miguel.martina@uam.es
 Corresponding author email address: david.gonzalez.rodriguez@uam.es

Supramolecular Organic Frameworks (SOFs) present advantages over other types of materials as COF's or MOF's because of their lower molecular weight and better processability. Recent studies have achieved great 2D SOF's strength that significantly improve previous results¹ and ensures a new generation of materials with enhanced characteristics to use in different fields like gas storage or catalysis.

Our aim is to take advantage of the knowledge acquired in our group regarding the use of ditopic nucleobase monomers to form supramolecular structures² and use them to obtain 2D networks (Figure 1a). Previously, we have obtained STM images in the solid-liquid interface that prove the formation of 2D networks³ of cyclic tetramers formed by Watson-Crick interactions between complementary bases. The network is stabilized by other interactions as H-Bonding or Van der Waals.

In this work, we intend to join two of these monomers using different "fusing-motifs" so that network formation depends essentially on the Watson-Crick interactions between the nucleobases. Here we present the first steps in the design and synthesis of these "fused monomers", as well as some preliminary characterization of the self-assembled systems formed.

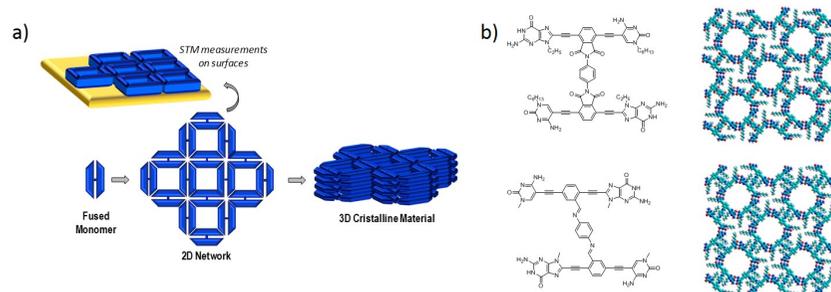


Figure 1. a) Scheme showing the formation of H-bonded networks and multilayered frameworks, b) Two monomer designs and the corresponding network models.

References

1. M. Pfefferman, R. Dong, R. Graf, W. Zajaczkowski, T. Gorelik, W. Pisula, A. Narita, K. Müllen, X. Feng, *J. Am. Chem. Soc.*, **2015**, 137, 14525.
2. a) C. Montoro-García, J. Camacho-García, A. M. López-Pérez, N. Bilbao, S. Romero-Pérez, M. J. Mayoral, David González-Rodríguez, *Angew. Chem. Int. Ed.*, **2015**, 54, 6780. (VIP) b) C. Montoro-García, J. Camacho-García, A. M. López-Pérez, M. J. Mayoral, N. Bilbao, D. González-Rodríguez, *Angew. Chem. Int. Ed.*, **2016**, 55, 223.
3. N. Bilbao, I. Destoop, S. De Feyter, David González-Rodríguez, *Angew. Chem. Int. Ed.*, **2016**, 55, 659. (HOT)

P21 Polycyclotrimers of 1,4-diethynylarenes and 1,3,5-triethynylbenzene: Preparation and Properties

Hynek Balcar^{a,*}, Martin Kubů^a, Arnošt Zukal^a, Eva Slováková^b, Jan Sedláček^b
^a, Department Synthesis and Catalysis, J. Heyrovský Institute of Physical Chemistry of the ASCR, v. v. i., Dolejškova 3, 182 23 Prague, Czech Republic.
^b, Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University in Prague, Hlavova 2030, CZ-128 40 Prague 2, Czech Republic.
 Presenting author email address: hynek.balcar@jh-inst.cas.cz
 Corresponding author email address: hynek.balcar@jh-inst.cas.cz

Microporous organic polymers (MOPs) have attracted much attention because of their potential use for gas separation and reversible storage, heterogeneous catalysis, optoactive materials and sensors¹. The aim of this contribution is to report the synthesis and properties of microporous polycyclotrimers,^{2,3} prepared with catalytic system TaCl₅ + Ph₃Sn: (i) polycyclotrimers of several 1,4-diethynylarenes, and (ii) polycyclotrimers of 1,3,5-triethynylbenzene (Fig.1). Application of Ta catalyst system allows to use milder reaction conditions and lower amount of catalyst in comparison with earlier reported polycyclotrimerizations catalyzed with Co₂(CO)₈ (ref.²). All polycyclotrimers were yellow-orange solids, insoluble (and non-swellable) in common organic solvents. Their structure was confirmed by ¹³C CP/MAS NMR and FTIR. N₂ adsorption/desorption isotherms (77 K) showed the BET surface area and sorption capacity depended strongly on arene linker, the highest S_{BET} values were found for polycyclotrimers of 1,4-diethynylbenzene (polyDEB) and of 1,3,5-triethynylbenzene (polyTEB) (1300 and 1270 m²/g, respectively). The sorption capacity (in mmol/g) for hydrogen (100 kPa, 77 K) and for CO₂ (100 kPa, 273 K) were 6.3 and 2.45 (polyDEB) and 7.1 and 2.7 (polyTEB). The kinetic effects in the adsorption of CO₂ were observed.

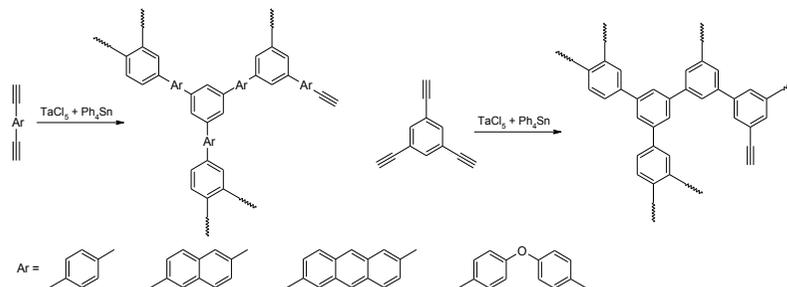


Figure 1. Polycyclotrimerization of 1,2-diethynylarenes and 1,3,5-triethynylbenzene

Acknowledgement

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References

1. J.X. Jiang, and A.I. Cooper in Functional Metal-Organic Frameworks: Gas Storage, Separation and Catalysis (M.Schröder, Ed.), *Top. Curr. Chem.* **2010**, 293, 1.
2. S. Yuan, B. Dorney, D. White, S. Kirklín, P. Zapol, L. Yu, and D.-J. Liu, *Chem. Commun.* **2010**, 46, 4547.
3. A. Zukal, E. Slováková, H. Balcar, and J. Sedláček, *Macromol. Chem. Phys.*, **2013**, 214, 2016.

P22 Acrylate based core – shell microspheres

Andreas M. Kreuzer^a and Christian Paulik^{a*}

a, Institute for Chemical Technology of Organic Materials, Johannes Kepler University, Altenbergerstrasse 69, 4040 Linz, Austria.

Presenting author email address: Andreas.Kreuzer@jku.at

Corresponding author email address: Christian.Paulik@jku.at

Polymeric microspheres with a core – shell structure, in contrast to microcapsules, are by definition small spheres which have no distinct outer layer or membrane and are therefore susceptible for diffusion phenomena¹. This leads to a wide variety of fields of application, such as in the food industry or in the medical field as drug delivery system²⁻⁴. When the core of such a sphere is comprised of a volatile substance, the sphere becomes expandable upon reaching the shells glass transition temperature and the core substances boiling point. This has been used in industry since the 1970s for different purposes such as coating agents, in adhesive applications or thermal insulation enhancement⁵.

This work is focused on the synthesis of microspheres with a core-shell structure, whereas the core is an inert carbohydrate and the shell is acrylate based. The reactions are carried out as oil in water (OIW) suspensions and as free radical polymerisations. Several different monomers (acrylonitrile, methyl methacrylate, acrylic acid, dipropylene glycol diacrylate and vinyl acetate) and initiators (AIBN and DLPO) are used. Through the variation of the monomer ratios, initiator variation and the OIW ratio, different shell composition can be observed. The characterization conducted with differential scanning calorimeter reveals as expected different glass transition temperatures and melting points for the shell. Scanning electron microscopy is used to characterize the shape and size of the microspheres.

References

1. Vert M., Doi Y., Hellwich K.-H., Hess M., Hodge P., Kubisa P., Rinaudo M., Schué F., *Pure and Applied Chemistry*, **2012**, 2, 84
2. Diarrassouba F., Garrait G., Remondetto G., Alvarez P., Beyssac E., Subirade M., *Food Chemistry*, **2015**, 173, 1066
3. Sagis L. M., *Microencapsulation and microspheres for food applications*, **2015**, Academic Press, London
4. Ferrari M., *BioMEMS and biomedical nanotechnology*, **2006**, Springer, New York
5. Morehouse D. S., Tetreault R. J., US Patent 3.615.972, **1971**

P23 Polymer hybrid composite thin-films with tailored hydrophobic properties

Gianina Dodi*, Doina Hritcu, Dan Draganescu, Marcel Ionel Popa

Faculty of Chemical Engineering and Environmental Protection, Technical University of Iasi, D.Mangeron Rd, 700050, Romania.

Presenting author email address: gianina.dodi@yahoo.co.uk

Corresponding author email address: gianina.dodi@yahoo.co.uk

This paper presents a simple and novel strategy to prepare hydrophobic composite coatings with unique micro/nano hierarchical surface roughness. The coatings were applied in a layer-by-layer configuration, with the hybrid polymeric matrix first, followed by iron oxide nanoparticle dispersion. Chitosan bearing surface vinyl groups, subsequently cross-linked with ethylene glycol dimethacrylate using thermal initiation was tested as a polymeric matrix. The magnetite nanoparticles, capable of self-assembling during the curing stage were prepared by mild oxidation of ferrous ions in alkaline solution, followed by amination with (3-aminopropyl) triethoxysilane. The third film component, pre-hydrolyzed/precondensed sol-gel solution of hexadecyltrimethoxy silane, was incorporated both into the matrix and the nanoparticle suspension, in order to promote the interfacial adhesion and to decrease the surface tension of the coatings. Hybrid nanoparticle-polymer films prepared by spraying were deposited on glass slides and cured by heating. The effects of the matrix composition, the nanoparticles concentration and the polymerization regime of the base layer were studied in order to yield coatings with high wetting angle and good adherence to the substrate in a reproducible manner (Figure 1). The morphologies, surface microstructure, wettability performance and adhesion to substrate of the hybrid coatings were systematically investigated by scanning electron microscopy (SEM), water contact angle (WCA) measurements and scratch tests. The resulting coatings exhibited excellent hydrophobicity and wetting stability driven by the formation of hierarchical roughness. The fabricated environmental friendly hydrophobic surfaces with excellent water-repellant properties will be promising for practical applications.

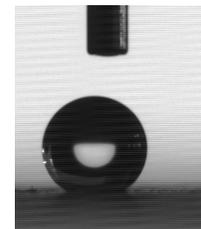


Figure 1. Water drop sitting on hybrid composite coating deposited by the optimum procedure (drop volume: 20 μ l, average wetting angle: 148 $^{\circ}$)

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P24 Polythiophene Thin Films by Surface-Confined Polymerization

Sang Gil Youm, Fatemeh Khamespanah, and Evgueni E. Nesterov*

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States.

Department Presenting author email address: fkhame1@lsu.edu

Corresponding author email address: een@lsu.edu

An ability to control nanoscale morphology and molecular organization in organic semiconducting polymer thin films is an important prerequisite for enhancing efficiency of organic thin-film devices including organic light-emitting and photovoltaic devices. Current "top-down" paradigm to such devices is based on utilizing solution-based processing (e.g. spin-casting) of soluble semiconducting polymers. This approach typically provides only modest control over nanoscale molecular organization and phase separations. A promising alternative to using solutions of pre-synthesized semiconducting polymers would be a "bottom-up" approach to prepare surface-grafted semiconducting polymer thin films by surface-confined polymerization of small-molecule monomers. In this presentation, we describe development of an efficient method to prepare polythiophene thin films utilizing surface-confined Kumada catalyst transfer polymerization. In this study, we provide evidence that this surface-confined polymerization happens by the controlled (pseudo-"living") chain-growth mechanism. Further optimization of this method enabled reliable preparation of polythiophene thin films with thicknesses up to 100 nm. Extensive structural studies of the resulting thin films using X-ray and neutron scattering methods as well as ultraviolet photoemission spectroscopy revealed detailed information on molecular organization and bulk morphology of the films, and enabled further optimization of the polymerization protocol. One of the most remarkable findings from the structural studies was that surface-confined polymerization delivers polymer thin films with uniform alignment of the polymer molecules in the direction normal to the film surface. In addition to improved bulk morphology and molecular alignment, a unique feature of the surface-confined polymerization is that it can be used for the preparation of large-area uniformly nanopatterned polymer thin films. This was demonstrated using combination of particle lithography and surface-confined polymerization.

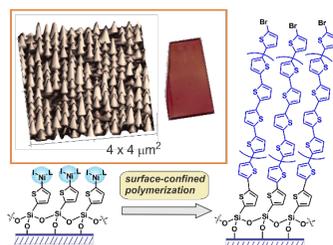


Figure 1. General scheme of surface-confined polymerization, and an AFM image of the nanostructured polythiophene thin film prepared by this approach.

P25 A novel bio-based photocurable acrylate monomer (ISDHUDMA) for application in restorative dental resins

María Lydia Berlanga Duarte^{a*}, Luis Alberto Reyna Medina^a, Cesar Eduardo Fuentes Camacho^b.

^aCentro de Investigación en Química Aplicada CIQA, Blvd. Enrique Reyna 140, C.P.25294.Salttillo, Coahuila, México

^bFacultad de Odontología de la Universidad Autónoma de Coahuila, Unidad Saltillo. Ave. Dra. Cuquita Cepeda S.N. Col. Adolfo López Mateos, C.P. 25125.Salttillo, Coahuila, México.

E-mail: lydia.berlanga@ciqa.edu.mx

*Correspondence to: María Lydia Berlanga Duarte ^aCentro de Investigación en Química Aplicada CIQA, Blvd. Enrique Reyna 140, Saltillo, Coahuila, México. C.P.25294. Phone No. + 52 (844) 438 98 30 Ext. 1339.

This work considers the preparation of a novel bio-based acrylate monomer called ISDHUDMA which is derived of a raw material of natural origin, such as the isosorbide (IS) [1] and the 4,4-methylenebis(cyclohexil isocyanate) [4,4-HMDI]. Once that HMDI reacts with IS turns to a polyurethane that is chemically inert[2]. Isosorbide is considered non-toxic, derived from glucose approved by the FDA[3]. In this study a new bio-based monomer was obtained and used as organic matrix of dental resin composite. The ISDHUDMA can be considered as a possible replacement of BIS-GMA, which was synthesized via two steps route. The ISDHUDMA dimethacrylate monomer (Figure 1) was confirmed by ¹HNMR and FT-IR spectroscopy techniques. The ISDHUDMA was evaluated in dental formulations by real time infrared spectroscopy (RT-FTIR) to determine the reactivity by conversion kinetics, obtaining higher conversions than BIS-GMA. Also were evaluated flexural strength, sorption and solubility water according to the international standard ISO 4049 [4], which sets the allowed values for these evaluated properties. All the results obtained show concordance with the International standard 4049, being this new bio-based monomer highly potential for application in dental resins.

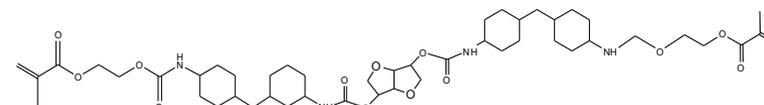


Figure 1. Bio-based ISDHUDMA monomer

References

1. Lukaszczyk, Jan., Janicki, Bartosz. *J Mater Sci: Mater Med.* **2012**, 23, 1149.
2. Demehl CU Journal Of Occupational and Environmental Medicine. **1966**.
3. Malhorta, S.V., Kumar V., East, A., Jaffe, M. *The bridge.* **2007**, 37, 17-24.
4. International Organization for Standardization. Dentistry- Polymer-Based Restorative Materials ISO 4049-**2009**.

P26 Green nanocomposites based on nanofibrillated cellulose and natural based epoxy oligomers

Aysun Ekinci^a and Gülay Bayramoğlu^{a*}

^a, Polymer Engineering, Yalova University, Yalova, 77100, Turkey.

Presenting author email address: ekinci_aysun@hotmail.com

Corresponding author email address: gulayb@yalova.edu.tr

In recent years, researches are focused on renewable biobased materials due to the increasing concern about environmental issues and limiting supply of petroleum and fossil fuel. The demand for vegetable oils which are considered to be among the most promising renewable raw materials for polymers and alternatives to petroleum, is growing because of their ready availability, inherent biodegradability, and their many versatile applications¹. Among the vegetable oils, especially epoxidized vegetable oils have unlimited and bright future prospects. Epoxidized vegetable oil possesses epoxy ring in their backbone chain and produces flexibility and elasticity when it is treated with thermoplastic or thermosetting polymer along with suitable curing agent².

For the purpose of replacing the materials coming from fossil resources, cellulose nano-fibres and nanocrystals have nowadays drawn a considerable attention in the production of functional biomaterials³. As a matter of fact, they may provide many potential applications namely as nano-reinforcement to produce bionanocomposites with high mechanical performance. To achieve this objective, the knowledge and control of the physico-chemical properties at the nanoscale, are of key rule to build-up bionanocomposites.

In this study rapeseed, corn and sesame oils were epoxidized using glacial acetic acid and hydrogen peroxide. The epoxidation was confirmed by iodine value, FTIR analysis and NMR analysis. Also epoxidized gallic acid was synthesized as a crosslinking agent. Nanofibrillated cellulose from agricultural crops residues was synthesized and used as a reinforcing nanofiller to elaborate nanocomposite films with improved mechanical properties. The effect of increased nanofiller loading in thermal and mechanical properties of the nanocomposites was investigated by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA).

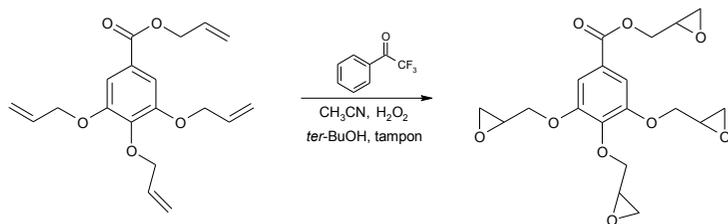


Figure 1. Synthesis of gallic acid based crosslinking agent.

References

1. Industrial Uses of Vegetable Oils (Ed.: S. Z. Erhan), AOCS Press, Champaign, IL, **2005**
2. Y.X. Xu, M. A. Hanna, S.J. Josiah. Industrial Crops and Products, 26 (1), **2007**, 69–76
3. C. J. Chirayil, L. Mathew, S. Thomas,. "Review of recent research in nano cellulose preparation from different lignocellulosic fibers" Rev.Adv. Mater. Sci. 37, **2014**, 20-28

P27 Determination of energy level alignment at metal/molecule and polymer/metal interfaces by in-device electrical spectroscopy

A. Atxabal^a, X. Sun^a, M. Gobbi^{a,b}, S. Parui^a, L. Pietrobon^a, A. Bedoya-Pinto^a, R. Llopis^a, F. Casanova^{a,c} & L.E. Hueso^{a,c}

^a, CIC nanoGUNE, Tolosa Hiribidea 76, 20018 Donostia-San Sebastian, Spain.

^b, Institut de Science et d'ingénierie Supramoléculaires (I.S.I.S.), Université de Strasbourg 8, allée Gaspard Monge, F-67083 Strasbourg, France.

^c, IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain.

Presenting author email address: aatxabal@nanogune.eu

Corresponding author email address: lhueso@nanogune.eu

Flexibility, processability and low cost are some of the advantages that polymers offer to devices¹ such as Organic Light Emitting Diodes (OLED), Organic Field Effect Transistors (OFET) and Organic Photovoltaic cells (OPV). However, the performance of all those devices is directly related with the energy barriers built up between the metal Fermi energy and the molecular levels devoted to charge transport^{2, 3, 4}, which limits the charge injection from metals to polymeric semiconductors. So far, even if information about energetics of metal/molecule and metal/polymer interfaces has been most commonly gained by photoemission spectroscopy techniques⁵ and Kelvin Probe measurements⁶, which require experimental conditions far from the real device operation, our group have already reported a three-terminal vertical device based on ballistic injection of hot electrons (Figure 1) that allows the acquisition of spectroscopic information about the metal/molecule energy alignment in real operative conditions⁷ into molecular level devoted to charge transport. But, now we go a step further and we show that this three-terminal vertical device allows us to gain spectroscopic information about the metal/polymer energy alignment in real operative conditions with interesting implications for organic electronics. As a proof of principle, we have measured the energy barrier height between Au and spin coated N2200 polymer.

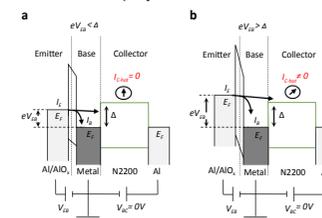


Figure 1: (a, b) Scheme of the energetics of the device. The tunnelling current I_E flows when a bias V_{EB} is applied at the emitter/base terminals. When the bias V_{EB} is lower than the energy barrier Δ at the metal/N2200 interface, I_E flows into the base where it is measured as base current I_B . In this case, no current is measured into the N2200 (a). When the bias V_{EB} is higher than Δ , part of the tunnelling current I_E flows into the N2200 and is measured as collector current I_{C-hot} even in the absence of an external voltage directly applied across N2200 ($V_{BC}=0$) (b).

References

- 1 Gustafsson, G. *et al. Nature*. **1992**, 357,477,
- 2 Friend, R. H. *et al. Nature* **1999**, 397, 131
- 3 Sirringhaus, H. *Adv. Mater.* **2005**, 17, 2411
- 4 Tada, A. *et al. Nature Mater.* **2011**, 10, 450
- 5 Hwang, J., Wan, A. & Kahn, A. *Mater. Sci. Eng. R Rep.* **2009**, 64, 1
- 6 Pfeiffer, M., Leo, K. & Karl, N. *J. Appl. Phys.* **1996**, 80, 6880
- 7 Gobbi, M. *et al. Nat. Commun.* **2014**, 5, 4161

P28 Materials design for ambipolar devices: Tuning orbital energetics in oligothiophene-naphthalimide semiconductors.

Iratxe Arrechea Marcos,^a A. de la Peña,^b M.J. Mancheño,^b J.L. Segura^{a,b}, J.T. López Navarrete,^{a*} R. Ponce Ortiz,^{a*}

^a, Department of Physical Chemistry, University of Málaga, Málaga, 29071, Spain.

^b, Department of Organic Chemistry, Complutense University of Madrid, Faculty of Chemistry, Madrid 28040, Spain.

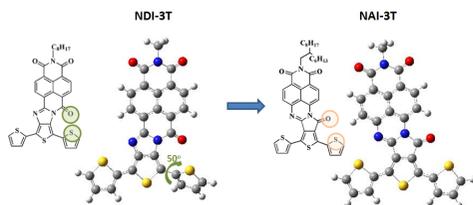
Presenting author email address: larrechea@uma.es

Corresponding author email address: rocioponce@uma.es

Ambipolar organic field-effect transistors (OFETs), which can efficiently transport both holes and electrons,^[1] using a single type of electrode, are currently of great interest due to their possible applications in complementary metal oxide semiconductor (CMOS)-like circuits, sensors, and in light-emitting transistors.^[2]

One factor that can compromise ambipolar transport in organic semiconductors is poor solid state overlap between the HOMO (p-type) or LUMO (n-type) orbitals of neighboring molecules in the semiconductor thin film. In the search of low-bandgap ambipolar materials, where the absence of skeletal distortions allows closer intermolecular π - π stacking and enhanced intramolecular π -conjugation, a new family of oligothiophene-naphthalimide assemblies have been synthesized and characterized, in which both donor and acceptor moieties are directly conjugated through rigid linkers.

In previous works^[3] we found that oligothiophene-naphthalimide assemblies connected through amidine linkers (NDI derivatives) exhibit skeletal distortions (50-60°) arising from steric hindrance between the carbonyl group of the arylene core and the sulphur atom of the neighbored thiophene ring. In the present work we report novel oligo- and polythiophene-naphthalimide analogues NAI-3T, NAI-5T and poly-NAI-8C-3T, in which the connections of the amidine linkage have been inverted in order to prevent steric interactions (see Figure).



The FET performance for vapor-deposited films of NAI-3T show remarkably balance mobilities for electrons and holes of around $10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. Finally, these planar semiconductors are compared with their NDI derivatives analogues, which exhibit only n-type mobility, in order to understand the origin of the ambipolarity in this new series of molecular semiconductors.

References

1. H. Jiang, *Macromolecular Rapid Communications* **2010**, *31*, 2007.
2. F. Dinelli, R. Capelli, M. A. Loi, M. Murgia, M. Muccini, A. Facchetti, T. J. Marks, *Advanced Materials* **2006**, *18*, 1416
3. a) R. P. Ortiz, et al., *Journal of the American Chemical Society* **2010**, *132*, 8440; b) R. P. Ortiz, et al. *Chemistry – A European Journal* **2012**, *18*, 532.

P29 Multifaceted Regioregular Oligo-Thieno[3,4-b]Thiophenes: an Experimental and Theoretical Study of their Oxidized and Reduced Species

Guzmán L. Espejo,^a Feng Liu,^b Shuhai Qiu,^b María Moreno Oliva^{a,c}, João Pina,^c J. Sérgio Seixas de Melo,^c Xiaozhang Zhu,^b Rocío Ponce Ortiz,^{a,*} and Juan Casado^{a,*}

^a, Dpt. of Physical Chemistry, University of Málaga, 29071 Málaga, Spain.

^b, Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China.

^c, Coimbra Chemistry Centre, Department of Chemistry, University of Coimbra, Rua Larga Coimbra, 3004-535, Portugal.

Presenting author email address: guzman@uma.es

Corresponding author email address: rocioponce@uma.es; casado@uma.es

The family of the thieno[3,4-b] oligothiophenes (Figure 1) have been studied, both theoretically and experimentally.¹ The band wavelengths of the low-energy lying electronic absorptions show a continuous red-shift from the monomer to the hexamer. This shift and consequent band gap contraction is ascribed to a progressive quinoidization.

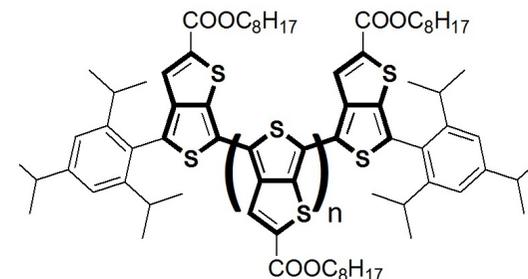


Figure 1. Chemical structure of the family of oligothiophenes under study.

In this presentation, a competition between the constant aromaticity of the outer [3,4-b]thiophene regarding the variable aromaticity of the linearly conjugating thiophenes is proposed. In addition, a characterization of the redox properties is fully provided by using a variety of spectroscopies. Characterization of the oxidized species brings us another unprecedented result: an inversion of the position and trend of the optical band wavelengths and optical gaps of radical cations versus dications. All experiments have been supported with a complete and exhaustive array of different DFT and time-dependent DFT calculations. These molecules represent a new family of organic π -conjugated systems with promising application in organic electronics.²

References

1. F. Liu, G.L. Espejo, S. Qiu, M. Moreno Oliva, J. Pina, J.S. Seixas de Melo, J. Casado, X. Zhu, *J. Am. Chem. Soc.*, **2015**, *137*, 10357.
2. C. Zhang, Y. Zang, E. Gann, C.R. McNeill, X. Zhu, C. Di, D. Zhu, *J. Am. Chem. Soc.*, **2014**, *136*, 16176.

P30 Star-shaped POSS-poly lactide-graft-doxorubicin

Rozga-Wijas Krystyna*, Kurjata Jan, Stanczyk Włodzimierz Andrzej
 Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences,
 Sienkiewicza 112, 90-363 Lodz, Poland.
 Presenting author email address: krysia@cbmm.lodz.pl
 Corresponding author email address: krysia@cbmm.lodz.pl

In this presentation we report on the conjugation of doxorubicin (DOX) with terminal reactive groups of functional star-shaped POSS-poly lactide copolymers. Polyoctahedral oligomeric silsesquioxanes (POSS) of the formula $(RSiO_{1.5})_8$ belongs to the silica nanoparticles group. It is a hybrid particle with cubic symmetry and of high thermal resistance and biocompatibility. POSS bearing hydroxyl terminal groups [1] was used as initiator for ring opening polymerization of L,L-dilactide catalyzed with tin(II) octoate to produce hybrid materials (POSS-PLA-OH) with octasilsesquioxane cage in the middle and poly lactides arms. The (Bu-PLA-OH) and star-shaped (POSS-PLA-OH) polymers were transformed through highly efficient esterification into a novel aldehyde modified hybrid (POSS-PLA-CHO) and linear (Bu-PLA-CHO) as model. The POSS-poly lactide-doxorubicin (POSS-PLA-DOX), was synthesized by the reaction of aldehyde group of (POSS-PLA-CHO) with the primary amine group of (DOX) to form acid-sensitive Schiff base linkage between polymer and drug. Chemical structure of the resulting (POSS-PLA-DOX) was verified by 1H NMR spectroscopy and MALDI TOF analysis.

This work was realized in a frame of the project—LACMAN” (PBS2/A1/12/2013; ID: 210366) and financed by NCBiR.

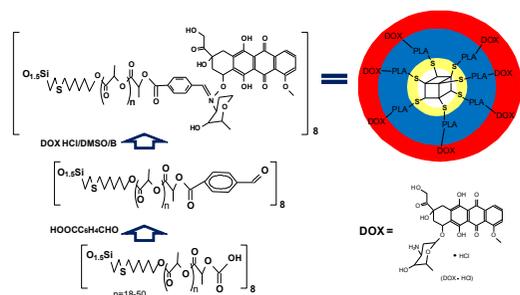


Figure 1. Synthesis of POSS-PLA-DOX.

References

1. Rozga-Wijas K., Stanczyk W.A., Kurjata J., Kazmierski S., *Materials* **2015**, *8*, 4400-4420.

P31 K-Conjugated Pyrene-fused Azahexacenes

Gabriella Antonicelli^a and Aurelio Mateo-Alonso^{a,b}
 a, POLYMAT, University of the Basque Country UPV/EHU. Avenida de Tolosa 72, E-20018 Donostia-San Sebastián, Spain
 b, Ikerbasque, Basque Foundation for Science, 48011 Bilbao, Spain
 Presenting author email address: gabriella.antoniceili@polymat.eu
 Corresponding author email address: amateo@polymat.eu

Pyrene-fused azaacenes are receiving a lot of interest as precursors of narrow nanoribbon-like structures for organic electronic applications because of their enhanced length/stability relationship.¹ Most of the recent studies have focused on obtaining elongated pyrene-fused azaacenes by different means. However, an important factor that has received little attention and that can play an important role in the properties is the conjugation along the K-region. Decades ago Clar already noted spectral differences in the β band absorption along the pyrene/benzo[e]pyrene/dibenzo[e,*l*]pyrene series² and more recently some our research group has shown that the conjugation along the K-region can dramatically affect the absorption and emission properties of short pyrene-fused azaacenes.³

In this communication, we report the synthesis and properties of two asymmetric K-conjugated pyrene-fused hexacenes. Our results show that these K-conjugated pyrene-fused systems constituted of six members rings show similar energy gaps than pyrene-fused azaacenes with ten linearly-fused rings⁴ in which the K-conjugation is diluted in an aromatic sextet. In addition their longest-wavelength absorption falls between that of TIPS-pentacene ($\lambda_{max} = 635$ nm) and TIPS-hexacene ($\lambda_{max} = 733$ nm), indicating that K-conjugated pyrene-fused hexacenes with an acene character between that of pentacene and hexacene.

References

1. A. Mateo-Alonso, *Chem. Soc. Rev.*, **2014**, *43*, 6311.
2. E. Clar, J.F. Guye-Vuillème, S. McCallum, I.A. Macpherson, *Tetrahedron*, **1963**, *19*, 2185.
3. R. García, M. Melle-Franco, A. Mateo-Alonso, *Chem. Commun.*, **2015**, 51,8037.
4. Z. Wang, J. Miao, G Long, P.Gu, J. Li, N. Aratani, H.Yamada, B. Liu, Q. Zhang, *Chem. Asian J.* **2016**, *11*, 482.

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