



Polymeric Scaffolding based on polyisocyanopeptide based multi-chromophoric arrays: Unraveling the relationship between nanoscale architecture and function in materials for organic electronics

Paolo Samori,^{(1,2)*} Vincenzo Palermo,⁽²⁾ Erik Schwartz,⁽³⁾ Chris E. Finlayson,⁽⁴⁾ Matthijs B.J. Otten,⁽³⁾ Andrea Liscio,⁽²⁾ Sara Trapani,⁽⁵⁾ David Beljonne,⁽⁵⁾ Klaus Müllen,⁽⁶⁾ Richard H. Friend,⁽⁴⁾ Roeland J. M. Nolte,⁽³⁾ Alan E. Rowan⁽³⁾

- (1) ISIS-UdS, 8 allée Gaspard Monge, 67000 Strasbourg, France. Email: samori@isis-ulp.org
 - (2) ISOF-CNR, via Gobetti 101, 40129 Bologna, Italy
 - (3) Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands
 - (4) Cavendish Laboratory, J.J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom.
 - (5) Université de Mons-Hainaut, Place du Parc 20, 7000 Mons (Belgium)
 - (6) Max-Planck Institute for Polymer Research, Ackermannweg 10, 55124 Mainz, Germany.
- * Corresponding author.

The physico-chemical properties of organic (multi)component films for opto-electronics depend on both the mesoscopic and nanoscale architecture within the semiconducting material. Two main classes of semiconducting materials are commonly used: polymers and (liquid)-crystals of small aromatic molecules. While polymers are easily solution-processable in thin uniform layers, small molecules can form highly defined (liquid)-crystals featuring high charge mobilities. Herein, we combine the two material types by employing structurally well-defined polyisocyanopeptide polymers as scaffolds to precisely arrange thousands of electron accepting molecules, i.e. perylene-bis(dicarboximides) (PDIs), in hundreds of nanometer long defined chromophoric wires. The polymer backbone enforces high control over the spatial location of PDI dyes favouring both enhanced exciton and charge transfer.^[1]

Spectroscopic analyses and extensive molecular dynamics studies revealed a well defined 4₁ helix in which the PDIs form four 'helter skelter-like' overlapping pathways along which excitons and electrons can rapidly migrate. The electronic transport properties of thin films based on such a polymeric architecture (P-PDI) forming fibers have been explored by fabricating prototypes of field-effect transistors (FETs) which revealed carrier mobilities of order 10⁻³ cm²/Vs, which are limited by inter-chain transport processes.^[2]

On the other hand, in FETs based on crystalline organic materials the edges of crystals are known to represent bottleneck for charge transport. To tackle this issue, we have co-deposited on insulating surfaces the monomeric PDI derivative (M-PDI) with the polymeric P-PDI. We found conditions for producing crystals of M-PDI which are bridged by fibers of P-PDI, the latter architectures behaving as percolation pathways for charge transport. Compared to pure M-PDI, the bicomponent films (P-PDI + M-PDI) that feature polymer interconnections between crystallites of the monomer display a significant improvement in electrical connectivity and a 2 orders of magnitude increase in charge carrier mobility within the film, as measured in FETs device prototypes.^[3]

When blended with an electron donor system as regioregular poly(3-hexylthiophene) (P3HT), this polymeric P-PDI shows an improved charge generation and diffusion with respect to monomeric/aggregated PDI. Atomic Force Microscopy studies revealed that the two polymers form interpenetrated bundles, having a nanophase segregated character, which feature a high density of contact points between the two different phases. In order to visualize the relationship between the architecture and the photovoltaic efficiency, Kelvin Probe Force Microscopy measurements were carried out on sub-monolayer thick films. This technique allowed for the first time the direct visualization of the photovoltaic activity occurring in such a nanoscale phase segregated ultrathin film with a true nanoscale spatial resolution.^[4]

The use of rigid polymer backbone as a scaffold to achieve a full control over the position and orientation of functional groups is of universal applicability and great interest in the design of building blocks for numerous technologically important functional materials.

References

- [1] *Chem. Eur. J.* **2009**, *15*, 2536-2547.
- [2] *Adv. Funct. Mater.* **2008**, *18*, 3947-3955.
- [3] *J. Am. Chem. Soc.* **2009**, *131*, 7055-7063.
- [4] *J. Am. Chem. Soc.* **2008**, *130*, 14605-14614.