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2009-03

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Advanced Materials, Weinheim, v. 21, n. 10/11, p. 1037-1040, Mar. 2009

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Taming Complexity: From Supramolecules to Suprafuctions

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It is a great pleasure to present this Special Issue on complex functional architectures for organic electronics and nanotechnology. While supramolecular chemistry is a well-established field of science, the use of its principles to fabricate highly ordered and functional 2D and 3D architectures is an emerging interdisciplinary domain. Progress in the field requires contributions from chemists, physicists, and engineers as well as biologists. This Special Issue aims at summarizing some of the supramolecular approaches to organic electronics and nanotechnology, which recently also have been presented at the symposium “Functional Supramolecular Architectures for

Organic Electronics and Nanotechnology” (Strasbourg, May – 2008) within the European Materials Research Society Spring Meeting. This symposium was organized as a networking activity of the European Science Foundation (ESF) – European Collaborative Research program on Self-Organized Nanostructures (SONS). The key role of ESF and the way it has promoted interdisciplinary research in fields such as materials science in the last decade in Europe is thoroughly discussed in the Essay written by Di Trapani. Although this Special Issue is not aimed at providing an exhaustive overview of the research in the field, we hope that the different papers that follow, including a Review, Progress Reports, Communications, and Research News, will offer a broad overview of the current activity in this area, including design and modeling, synthesis, tailoring of bio-hybrid structures, hierarchical self-assembly and nanopatterning, development of approaches for space confinement, multiscale structural, mechanical, optical and electronic characterization of 2D and 3D supramolecular architectures as well as fabrication of device prototypes.

Controlled processing and in particular the patterning of surfaces and interfaces with functional (supra)molecular systems with a nanoscale precision is a milestone for technological application in various fields. The Review article by Cavallini, Albonetti, and Biscarini provides a state-of-the-art overview of the various techniques for processing molecular materials from solutions through up-scalable micro-/nanopatterning approaches. This includes (i) micromolding in capillaries for deposition of nanoparticles, nano-

clusters, biomolecules, and polymers, (ii) lithographically controlled wetting for nanopatterning by lithographically controlled (de)wetting, deposition of organic semiconductors and fluorescent compounds, and (iii) grid-assisted deposition for deposition of organic semiconductors, and its use in combination with electrified stamps.

A thorough multiscale description of supramolecular architectures with controlled properties is one of the crucial goals towards prediction of self-assembly of functional 2D architectures. In this context, De Vita and co-workers provided an overview of advanced atomistic modeling strategies based on quantum formalism to describe and simulate the formation of complex supramolecular architectures based on tectons with controlled mechanical properties, i.e., flexibility, offering enhanced design capabilities in fabricating 2D nanostructures. Interestingly alongside the precise description of supramolecular motifs based on multiple H-bonding, including those based on interactions between abiotic and biotic systems, molecule featuring both spontaneous conformational switching properties as well as the lock-and-key effect have been highlighted, paving the way towards the description of bi-stable architectures.

Among various building blocks for organic electronics, phenylene-based synthetic (macro)molecules, featuring fused benzene rings, represent the chemical solution to one of the currently most studied systems with potential for

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DOI: 10.1002/adma.200900161

electronics, i.e., the graphenes. Müllen and co-workers report an up-to-date account of organic soluble 1D systems based on phenylenes, 2D macrocycles and graphenes with tunable side chains as well as cores exhibiting a diversity of sizes and symmetries. Also by incorporating heterocycles in the fused planar structure, the electronic and optical properties of the materials have been modulated. Globular shape persistent dendrimers have been also introduced and their light-harvesting characteristics discussed.

In recent years, there have been very significant advances in optical microscopy that have enabled researchers to overcome the limits of spatial resolution and push them beyond the acknowledged limits due to diffraction of optical radiation. Hofkens and co-workers describe in their contribution the potential of single-molecule far-field microscopy, and defocused wide-field imaging in particular, to study a range of properties and dynamics of macromolecular systems. For example, by embedding dye molecules in polymers close to the glass transition temperature, useful information could be obtained regarding the dynamics of the polymers in such a regime. Significantly, by combining defocused wide-field imaging with the stochastic nature of processes such as bleaching, a new type of microscopy was introduced, which should make it possible to deduce the conformation of isolated conjugated polymer chains.

The improvement of the performance of field-effect transistors, in particular of the charge carriers mobility, has experienced notable steps forward in the last few years. The Progress Report by McCulloch and collaborators presents an interesting class of semiconducting materials, i.e., thienothiophene copolymers, which have been demonstrated to achieve the highest charge carrier mobilities in solution-processed transistor devices. This account provides a comprehensive overview of the relevant aspects of the science and technology of these materials. These span from the design and synthesis to the description of fundamental physico-chemical properties, processing from solution (to minimize defects) and opti-

mization of device performance through tailoring of interfaces with electrodes and dielectrics. The paper also includes discussion of environmental exposure and fabrication conditions. With specially designed materials, the authors aimed at tuning the position of the frontier levels via control of the conjugation extent, and enable facile packing and interdigitation of the structures with minimization of impurities. Thanks to such an integrated approach, charge carrier mobilities of as high as $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ were achieved in optimized device architectures.

The tuning of the electronics of interfaces represents a crucial aspect for (opto)electronic applications. In their computational study, Sushko and Shluger chose a most relevant case, namely chemisorbed alkanethiols on Au(111) surfaces. The effect of the head-group in the ω -position, including CH_3 , CF_3 , COOH , was explored. It revealed that the polarizability of the polar groups of organic molecules represents a key factor determining the direction of the SAM-induced change in the metal work function.

Bruno and co-workers experimentally demonstrated in thin films of vinylene-fluorinated MEHPPDFVs that the strength and polarization of absorption spectra depend on the self-organization. They showed that the absorption band at approximately 4eV is probably of excitonic origin and is primarily polarized parallel to the polymer chain. These data provide further evidence that self-assembly of polymer chains in the thin films represents a tool for tuning the electronic and optical properties of π -conjugated system.

The importance of a chemical structure of polymer resin in lithographic performance was explored by Hadziioannou and co-workers. To this end, they have synthesized hyperbranched polymers making use of the self-condensing vinyl polymerization strategy. The lithographed samples displayed a good pattern profiles and line edge roughness values comparable of the reference (commercial) resists.

Scaffolding represents a key strategy to achieve a control over the position of functional groups in 2D and 3D. To this end different non-covalent interactions can be employed. Surin, Schenning, and collaborators, in a joint experimental and computational investigation, employed H-bonding between an ss-DNA template and oligophenylene vinylene conjugated oligomers exposing a diaminotriazine moiety to form ordered conjugated arrangements, which were studied both in solution and on surfaces. In another approach, Hosseini, Samori, and co-workers employed metallo-ligand interactions to locate optically active anthracene units on a solid substrate. Interestingly, they revealed that a nanoscale control over both the geometry and the directionality of supramolecular arrays composed of 1D coordination networks can be achieved on surfaces through the design and combination of organic tectons with metal centers/complexes. STM at the solid-liquid interface made it possible to monitor long and shape persistent arrays with either a linear or a zig-zag geometry.

Achieving spatial control and confinement of certain desirable properties is one of the most important objectives of nanoscience and nanotechnology in general. In this regard, two approaches based on structurally different solutions are reported. The former, by Wang, Wegner, and co-workers relies on the use of nanoparticles consisting in a thermoplastic polymer core and a polyelectrolyte corona shell impregnated with conducting domains of polypyrrole (PPy). The conducting PPy composite film assembled from the core-shell particles features excellent surface smoothness, adequate adhesion to ITO substrates, and high transmittance in the visible region. A prototype of light-emitting device (LED) based on a conducting PPy composite film as hole injection layer revealed performance comparable with that of devices based on PEDOT:PSS, while the leakage current is lowered. The latter by De Cola, Whitesides, and collaborators describes the use of microcontact printing technique (MCP) to obtain well-ordered and uniformly oriented zeolite L monolayers on conductive surfaces without any chemical

modification of the zeolite or the substrate. The appropriate choice of fluorescent dyes trapped in the zeolite channels results in patterns featuring a tunable color of the emission dependent on the polarization of the excitation light. Vohra and co-workers also used zeolite as building block for the preparation of electroluminescent polymeric nanofibers embedding dye loaded zeolite L crystals. By exciting the polymer nanofiber, the energy is transferred to the fluorescent dyes inside the zeolite L channels through a two-step Förster Resonant Energy Transfer (FRET) process from the polymer to the host-guest system. In this way it was possible to obtain a hybrid nanofiber emitting in different regions in the visible. Such different emissions were achieved by excitation of the polymer and through energy transfer from the polymer to the dye-loaded zeolite L crystals. This study opens new perspectives in the field of low-cost fabrication technology of flexible nanoscale OLEDs.

Andraud and collaborators report a study on functionalized azabodipy (nitrogen substituted boron-dipyrromethane) dyes which showed to hold a great potential for two-photon absorption (TPA) related applications in the telecommunication spectral range (1300–1500 nm) and in particular for nonlinear transmission. The versatile nature of this highly stable and soluble class of chromophores paves the way to a fine chemical engineering aimed at optimizing the TPA properties in the NIR by additional functionalization of the β position or by rigidification of the lateral π -skeleton.

Burrows and co-workers report on the self-assembly of the anionic conjugated polyelectrolyte poly{1,4-phenylene-[9,9-bis(4-phenoxybutylsulfonate)] fluorene-2,7-diyl} (PBS-PFP) and the cationic Tris(bipyridyl)ruthenium(II) ($\text{Ru}(\text{bpy})_3^{2+}$) in aqueous solutions in the presence of the nonionic surfactant C_{12}E_5 . Efficient Förster energy transfer occurs from the conjugated polyelectrolyte to the metal complex within 30 ps. Further, the emis-

sion in the ruthenium complex is from the lowest triplet state, which is formed on a sub-ps timescale, such that it is possible to funnel all the excitation energy to the lowest triplet state of the metal complex.

Nanowires are basic, yet crucial elements for organic nanoelectronics. Redmond and collaborators report on polyfluorene nanowire Y-junctions that were synthesized by solution-assisted template wetting, exhibiting strongly polarized light emission from the branches and stems. The Y-junctions can be positioned and branching angles may be adjusted by micro-manipulation. Nanowire junctions of this type could ultimately facilitate the incorporation of conjugated polymer materials into highly integrated electronic and photonic circuits and systems.

Hamilton, Anthopoulos, and co-workers describe a blended formulation of semiconducting small molecules in a polymer matrix that exhibits a high electrical performance within thin-film field-effect transistors (OTFTs). In particular the device prototypes were found to combine charge carrier mobilities greater than $2\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$, a good device uniformity and the potential to fabricate devices from routine printing techniques. The use of an insulating polymer matrix demonstrated the improved film-forming properties of the blend system, while use of the field-effect active polymer matrix maintained this and increased the mobility provided by the functionalized oligoacene components in the blend.

Von Seggern and co-workers studied the effect of injection barriers on the performance of ambipolar light-emitting OFETs based on (poly(9,9-di-*n*-octyl-fluorene-*alt*-benzothiadiazole)) (F8BT) as semiconductor, (poly(methyl methacrylate)) (PMMA) as gate dielectric and identical source and drain metals (Au, Ag) with a work function in the midgap of the organic semiconductor. In addition to an unusual narrow ambipolar regime in V_G the authors were

also able to demonstrate the importance of contact (source, drain) formation in ambipolar FETs, via a careful interpretation of the characteristics for different contact metals (Au, Ag).

Veciana, Ocal, and collaborators made use of 3D conducting atomic force microscopy (AFM) to study the IV characteristics of a metal-molecule-metal junction incorporating two different SAMs based on the closed and open-shell form of a polychlorotriphenylmethyl (PTM) derivative. Albeit the two forms exhibit a rather similar molecular structure, their electronic structure is very different, dramatically influencing the transport properties. These results offer new perspectives in the field of molecular electronics and molecular spintronics.

Dinu and Dordick employed kinesin motor protein and its microtubule track to transport multi-walled carbon nanotubes (MWNTs) on engineered surfaces. Using a flow chamber, surface-adsorbed kinesins are demonstrated to transport red-labeled microtubules loaded with green cargos of MWNTs. These results establish a platform for assembling individually addressable MWNT nanostructures using microtubule templates

Viruses are complex architectures that are currently employed as templates for constructing specific nanocontainers; either by hanging the properties of the viruses itself or by copying their compact, shelled structure into engineered materials, which are able to encapsulate various agents.

As a contribution towards the understanding of the properties of biomaterials, Wuite and Roos used indentation of viral capsids by AFM to unravel their material properties. Parameters such as the particle's Young's modulus and the threshold

force for breaking are obtained from analyzing the force response upon indentation. These major advances in understanding the material properties of viral nanocontainers may be relevant for their use in nanotechnological applications.

Brocogens and co-workers reported on the solid-state supramolecular organization of polythiophene chains containing thienothiophene units. In particular they have used molecular modeling and simulation of X-ray diffraction patterns to determine the molecular packing of a thiophene-based polymer showing exceptionally high field-effect mobilities (up to $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This was done by focusing on the organization of the polymer chains in lamellae and the orientation of these crystalline domains with respect to the

substrate in thin films. The analysis is supported by XRD and NEXAFS experiments and is complemented by calculating intermolecular transfer integrals, which govern the charge mobility.

We hope that through the series of excellent contributions covering various scientific domains, this Special Issue will represent a stimulating playground and offer valuable highlights on the design, fabrication, characterization, and exploitation of supramolecular complex architectures. The contributions may ultimately provide unambiguous evidence of the high potential for breakthroughs and innovation that characterize this R&D area. This Special Issue is a follow-up to the one published in 2006 (Vol. 18, Issue 10), also dedicated to topics of interest to

those working on organic and plastic semiconductors, and on supramolecular materials in general. The comparison between these two issues witnesses the notable steps forward in understanding and controlling the relationship between molecular architecture and function. Significantly, supramolecular materials increasingly exhibit improved properties and performance when incorporated as active layers in device prototypes. The next step ahead, alongside the continuation of the supra-path traced thus far, is the simultaneous control over many functions. The field is still very much in its infancy, thus future developments and discoveries are rather unpredictable but will surely expand the molecular toolbox towards a real technology.

February 23, 2009