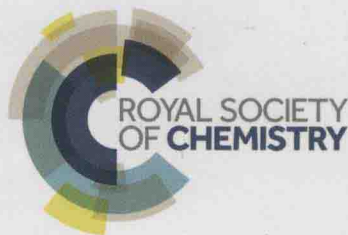




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Supramolecular Materials for Opto-Electronics

Edited by Norbert Koch



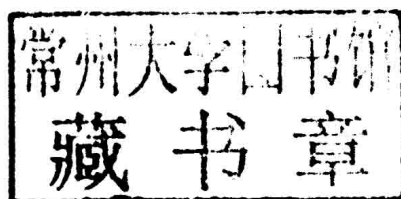
Supramolecular Materials for Opto-Electronics

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RSC Smart Materials

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Preface

The power of supramolecular assembly strategies, where mostly non-covalent interactions between individual building blocks are exploited, to form well-defined two- and three-dimensional architectures is impressive. Careful design of molecules to facilitate directed hydrogen-bonding, π - π , and electrostatic interactions can lead to hierarchically ordered structures spanning the nano- to the macroscale. In addition, covalent bonds between molecules are used to form supramolecular assemblies, and the properties of the subunits can be largely retained by keeping their direct electronic coupling strength low. In an overarching scheme, complex multi-component structures are assembled first and subsequently locked into position by initiating covalent bonds. Achieving an appropriate balance of all intermolecular forces to reach the desired bulk structures is challenging.

When aiming to use supramolecular systems in electronic and optoelectronic devices, such as transistors, light emitting diodes, photovoltaic cells, and memory elements, the challenges increase rapidly. Key for device functionality is the proper combination of conducting, semiconducting, and insulating materials, some or even all of which may be provided for by supramolecular assemblies and on various length scales. Furthermore, typical device structures are composed of numerous layers of materials and it has transpired that the interfaces between layers are of paramount importance for device performance.

Consequently, the interaction between a substrate – often an electrode – and the assembly building blocks introduces another degree of freedom for steering structure formation, which thus differs from the bulk. The same holds when considering the formation of heterojunctions of different supramolecular materials, where adverse side effects such as intermixing and induced orientations may occur. In addition, since optoelectronic components are two- or multi-terminal devices, the question of how

electronic equilibrium across the entire layer stack is established must be addressed. We can think of the stack as a sequence of materials with varying energy gaps (*i.e.*, semiconductors), where the alignment of energy levels to a common Fermi-level may introduce space charges, mostly close to the interfaces. This induced charge density represents yet another source of interaction that influences the supramolecular structure formation.

For opto-electronic functionality, the requirements regarding structural perfection are tremendous. Every defect will widen the energy spread of the density of states where charge carrier transport takes place, thus reducing carrier mobility. Furthermore, radiative exciton recombination, *e.g.*, in a light emitting diode, can be tremendously reduced by defects, particularly trapped charges. Therefore, the envisioned devices require either extreme structure control or, at least, fault-tolerant architectures must be implemented.

To comprehensively understand supramolecular materials for opto-electronic applications and to derive reliable material design guidelines, experiment and theory must go hand in hand. True multiscale modeling must be applied, starting from an *ab initio* approach for the building blocks or moderately large assemblies to unravel fundamental electronic and optical properties, and continuing to larger length- and time-scales through parameterization of electrons and eventually atoms to predict structure formation up to device-relevant scales.

All these topics and challenges are discussed in the chapters of this book. Experts, who define the frontiers of the respective fields, present state-of-the-art understanding of supramolecular assemblies consisting of conjugated molecular moieties to achieve opto-electronic functionality, and show how these formidable challenges are presently tackled. Research towards supramolecular systems for opto-electronics remains vivid and will benefit from increasingly tight interactions of chemistry, physics, material science, and electrical engineering.

Norbert Koch
Berlin

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CHAPTER 1

Self-assembled Supramolecular Materials in Organic Electronics

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1.1 Introduction

Organic electronics¹ is of great fundamental interest in materials science and is also recognized as one of the most promising and competitive markets for industry. In particular, its expansion will be supported by the development of active components being easily processable, flexible, energy friendly, cheap, and compatible with their downscaling towards nano-devices. In this research field, high-molecular-weight conjugated polymers in the form of thin plastic films are easy to synthesize and to process for incorporation in devices.² However, these materials show limitations in the precise ordering of their crystalline layers in the bulk, thus impacting the mobilities of charge-carriers required for enhanced performances. Conversely, recrystallization or vapor-phase deposition of low-molecular-weight π -conjugated organic molecules leads to 100% crystalline orientation, but single crystals are impractical to process.³ At the smallest scales, the very intriguing electronic properties of single molecules have also been

demonstrated, but problems arise from contacts with the electrodes and from thermal noise producing undesired orientation and conformational motions.⁴

Quite recently, so-called supramolecular electronics⁵ has been proposed as a promising intermediary-scale approach that rests on the design of electronic components at a length of 5–100 nm, that is, between plastic electronics (μm) and molecular electronics (\AA). Supramolecular engineering, which programs self-assembly processes under thermodynamic control,^{6,7} represents a key bottom-up strategy to build and process relatively soft functional objects while introducing “pseudo-crystalline” electroactive domains corresponding to this typical intermediate length scale. In the past ten years, since the seminal works of several groups who demonstrated the potential of this approach with supramolecular assemblies such as gels and liquid crystals, several soft nanoribbons, nanotubes, nanorods, and nanowires of low dimensionality have been designed and incorporated into organic electronic devices.^{8,9} In the following sections, we discuss some recent examples of supramolecular electroactive nanostructures displaying various electronic properties such as conducting materials, field-effect transistors, light-emitting diodes, and photovoltaic devices. Within each of these sections, electroactive self-assemblies are classified along with the molecular structure of their components.

1.2 Conducting Supramolecular Materials

This section specifically focuses on soft self-assemblies made of small organic molecules, or of short monodisperse oligomers, and yielding to π -stacked one-dimensional (1D) conducting nano-objects with high aspect ratio, a geometry attracting much attention for its crucial impact on advanced nanosciences.¹⁰ These supramolecular structures are classified according to their chemical composition, such as for instance: (i) thiol-based heterocycles such as thiophenes and tetrathiafulvalenes (TTFs); (ii) nitrogen-containing heterocyclic molecules; (iii) aromatic molecules including perylene-tetracarboxylic diimides (PTCDIs), fluorenes, anthracenes, and hexabenzocoronenes (HBCs); derivatives; and (iv) triarylamine. For each category, we shall emphasize the most remarkable advances achieved in the recent literature regarding three interlinked aspects of crucial importance for further developments in organic electronics: structure, conductivity properties, and processability.

1.2.1 Thiophene Derivatives

Conjugated polymers of thiophenes are among the best candidates for thin film (opto)electronic devices because of their small band gap, their relatively high charge carrier mobility, and their high quantum yield for fluorescence. Feringa and van Esch first described an alternative supramolecular approach in which bis-urea derivatives incorporating mono- or bis-thiophene spacers

can self-assemble by hydrogen bonds into ribbons that enforce the π -stacking of the central heterocycles.¹¹ Lamellar fibers with lengths of 20–100 μm and breadths of 2–10 μm were imaged by electronic microscopy and molecular modeling studies of the closely packed layers were also found to be coherent with X-ray powder diffraction analyses. The charge mobility properties of these materials were determined by a pulse radiolysis time-resolved microwave conductivity technique (PR-TRMC) technique, which minimizes effects of domain boundaries and impurities. The authors measured values up to $5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, thus showing that supramolecular cofacial ordering provided by the bis-urea interactions can improve the through-space mobility of charge carriers close to that measured in covalent conjugated polythiophenes ($7 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). Along the same lines, other groups developed symmetric oligothiophene¹² and oligo(thienylene-vinylene)¹³ derivatives with lateral hydrogen bond forming segments, yielding conducting gels with values reaching $4 \times 8 \cdot 10^2 \text{ S m}^{-1}$ upon I_2 doping and by solvent evaporation casting in a four-probe configuration. In these cases, non-linear I/V curves indicate contact resistance due to a charge injection barrier. All the aforementioned examples highlight the role of the self-assembly and of the gelation process to achieve electronic properties that can rival covalent conducting molecules.

Recently, the group of Barbarella described the synthesis of octa- and tetrathioether-substituted octathiophenes and studied the morphology and conductivity of the corresponding self-assemblies.¹⁴ Scanning electron microscopy (SEM) and atomic force microscopy (AFM) imaging revealed that the sulfur-overrich molecule formed superhelices and even double helices of superhelices with lengths ranging from 100 nm up to 5 μm whereas the core tetra-substituted molecule formed tape-like fibrils of similar lengths. Both types of fibers grown on ITO (indium tin oxide) were then analyzed by tunneling atomic force microscopy in torsion mode (Tr-TUNA), which allows simultaneous surface topography and nanoscale conductivity measurement. Finally, charge carrier mobilities of both octathiophenes were determined using conductive-AFM (C-AFM) ($9.8 \times 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the octa-substituted system *versus* $5 \cdot 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the tetra-substituted one) and could be rationalized based on X-ray diffraction of the fibers films, which shows that the presence of substituents on the outermost rings induces disorder and therefore influences the distance between parallel octathiophene rows.

In another approach, Stupp and co-workers¹⁵ achieved the self-assembly of short oligothiophene rod-coils by conjugation to a dendron capable of self-associating by hydrogen bonding. These molecules can be dissolved at high temperature in toluene/THF mixtures and form birefringent gels (1 wt%) after cooling at room temperature. These gels present blue-shifted absorbance and red-shifted fluorescence compared to solutions, in agreement with the formation of H-aggregates. A TEM (transmission electron microscopy) micrograph illustrates the formation of ribbons with a width of a single dendron dimer ($9.7 \pm 0.3 \text{ nm}$), while AFM revealed a thickness of

