Functional Supramolecular Architectures

Over twenty years have passed since the Nobel Prize in Chemistry was awarded to Donald Cram, Jean-Marie Lehn, and Charles J. Pedersen "for their development and use of molecules with structure-specific interactions of high selectivity". The area of study developed to become its own research field, known as "supramolecular chemistry". The supramolecular approach, based on the design and synthesis of molecules with the capacity to undergo self-recognition events and form multicomponent structures, has been applied to the development of complex systems. Over the course of the last decade, researchers have started to lay the foundations for a change in the focus of research, from structure to function. This is because the supramolecular approach is, above all, a very powerful strategy for investigating, with a high degree of precision, the relationship between architecture and function in both macroscopic and nanoscopic systems when it is applied to functional materials and devices. It is also a versatile approach to the development of complex materials with tunable properties, which can ultimately be employed for the fabrication of devices with improved performance and innovative functionalities.

In the year 2000, the Nobel Prize in Chemistry was awarded to Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa "for the discovery and development of conductive polymers". That achievement paved the way towards the use of polymers for the fabrication of electronic and optoelectronic devices by solution-processing of film-forming polymers.

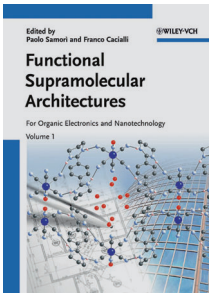
The publication of these two volumes, edited by Professors Paolo Samorì and Franco Cacialli, is particularly important and timely. It successfully bridges between the supramolecular and the conjugated-polymers worlds, by providing the most valuable examples of supramolecular engineering of materials and devices. To this end, over 30 chapters gather together the collective knowledge of the experts currently exploring this field, providing a complete picture of the blossoming realm.

The book is structured in eight main parts: "Modeling and Theory" (3 chapters), "Supramolecular Synthetic Chemistry" (5 chapters), "Nanopatterning and Processing" (4 chapters), "Scanning Probe Microscopies" (4 chapters), "Electronic and Optical Properties" (4 chapters), "Field-Effect Transistors" (4 chapters), "Solar Cells" (4 chapters), and "LEDs/LECs" (2 chapters).

Various theoretical and computational methods can be employed to apply supramolecular concepts to the field of organic electronics. Chapter 1 (J. L. Brédas, D. Beljonne, J. Cornil, R. Lazzaroni, C. Zannoni, and co-workers) is focused on the multiscale modeling of charge transport in organic semiconductors, including single crystals based on acenes, as well as architectures of the tetrathiafulvalene, polythiophene, or phthalocyanine types; the role played by polymeric dielectrics is also explored. Chapter 2 (M. A. Ratner and co-authors) describes the Monte Carlo approach to unraveling the phase transition and cooperative motion in Langmuir monolayers containing internal dipoles. Chapter 3 (N. Sändig, F. Zerbetto) deals with molecules adsorbed on gold surfaces, both by chemisorption and by physisorption, including adsorption in the presence of an electric field.

The synthesis of complex molecules pre-programmed to undergo self-assembly, thus forming materials that incorporate sophisticated functions, is a challenging goal that offers a wealth of potential directions of development. Chapter 4 (M. Levine, T. W. Swager) deals with the design, synthesis, and use of water-soluble conjugated polymers for sensing and detection, especially for proteins, DNA, and bacteria. Here changes in aggregation, or a response to a temperature change, serve as signals. In Chapter 5, A. E. Rowan and R. J. M. Nolte discuss the use of multi-chromophoric arrays based on poly(isocyanides) as macromolecular scaffolds to control the position of functional groups in space, as well as related applications in organic electronics. Electro- and opto-active polyphenylene-based motifs, including 1D, 2D, and 3D structures, are described in Chapter 6 (M. Baumgarten, K. Müllen). Thanks to its extended conjugation, this class of systems exhibits an exceptional capacity to undergo self-assembly by π–π stacking, to form both n- and p-type architectures. Ordered networks and crystals can be developed by applying principles of molecular tectonics. One solution relies on the use of charge-assisted hydrogen bonding (S. Ferlay, M. W. Hosseini, Chapter 7). In fact, the opto-electronic properties of π-conjugated materials can also be modulated by doping a carbon-based module with heteroatoms (D. Bonifazi and co-workers, Chapter 8). The introduction of electron-rich elements such as sulfur, selenium, or tellurium, or of electron-deficient elements such as boron, offers access to unique self-assembly properties, and also to unconventional photophysical and electrical characteristics for technological applications.

Techniques for self-assembly and nanopatterning at surfaces and interfaces with nanoscale precision are essential to any technological applications based on molecules. In this regard, spatial confinement is a hallmark of nanoscience. Inor-



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ganic nanocontainers based on zeolites have been shown to be versatile building-blocks for hosting functional units and controlling their physical properties such as stability and luminescence. These multi-component systems, unique in their design, have been employed successfully for electronic, opto-electronic, and biomedical applications (L. De Cola and co-workers, Chapter 9). In nanopatterning, it is not generally possible to control key parameters such as long-range order, precision, accuracy, and registration by using conventional bottom-up procedures. On the other hand, soft lithography approaches (J. Huskens and co-workers, Chapter 10) are highly versatile methods to form ordered arrays of molecules, biomolecules, or nanoparticles for electronics as well as for cell and tissue engineering, sensing, or bioanalysis. Semiconducting polymer nanospheres can be formed from almost all types of conjugated polymers, and can be employed in the fabrication of electronic and opto-electronic devices (E. Fisslthaler, E. J. W. List, Chapter 11). Regardless of the sizes of the nanospheres, they can be processed using soft methods such as ink-jet printing, paving the way towards their use for large-scale patterning. Chapter 12 (C. Ober, G. Malliaras, and co-workers) is devoted to the use of photolithography approaches to pattern surfaces and interfaces with organic electronic materials.

Scanning probe microscopy methods (SPMs) are very powerful tools to investigate structures and physicochemical properties of supramolecular architectures, with nanoscale spatial resolution. In particular, scanning tunneling microscopy (STM) at the solid–liquid interface provides a direct view of intermolecular interactions in multi-component structures, geared towards 2D crystal engineering of functional systems (P. Samorì and co-workers, Chapter 13). As well as imaging, STM is also a crucial method to gain direct insight into supramolecular materials for applications in electronics and nanotechnology. It can be used to nanopattern surfaces by initiating and controlling chemical reactions, as well as to study local-scale properties of adsorbates at surfaces, such as spin–electron interactions (F. Rosei and co-workers, Chapter 14). Ordered assemblies of conjugated molecules, as visualized by the use of atomic force microscopy (AFM) and other SPM techniques, can be obtained by π–π stacking or by using either a macromolecular or a supramolecular scaffold. The scale is in the order of 1 nm to 100 nm, which makes it possible to control properties of the materials for applications in electronics and opto-electronics (M. Surin, R. Lazzaroni, P. Leclère, and co-workers, Chapter 15). The electrical characteristics of single molecules or biomolecules in a metal–molecule–metal junction can be explored by STM-based approaches (S. J. Higgins, R. J. Nichols, Chapter 16).

The optimization of the electronic and optical properties of conjugated materials can be accomplished through a number of careful studies addressed to well-defined photophysical and electronic properties. The role of charge-transfer excitons in supramolecular semiconducting nanostructures is discussed in Chapter 17 (C. Silva, D. Beljonne, and co-workers), where it is demonstrated that in organic semiconductors the supramolecular coupling energy dominates the nature of the primary photoexcitations. Chapter 18 (D. Comoretto and co-workers) is focused on the optical properties and electronic states in anisotropic conjugated polymers. The roles played by inter- and intra-chain effects are explored by making use of different spectroscopic techniques, including polarized photoluminescence, as well as Raman scattering. Spectroscopic characterization can be carried out on very small objects within the realm of single-molecule spectroscopies (E. Da Como, J. M. Lupton, Chapter 19). In particular, polarization anisotropy provides insight into the shape of the conjugated chain, and more generally demonstrates a correlation between architecture and spectroscopic characteristics of single polymers. The electronic structure of a material can be engineered by incorporating intermolecular polar bonds (G. Heimel, N. Koch, Chapter 20). Ultraviolet photoelectron spectroscopy is a powerful tool to investigate the energetics of interfaces, properties that depend on the orientation of the molecules at the surface and are crucially important for optimal charge injection and extraction in electronic devices.

Organic field-effect transistors (OFETs) are not only basic tools for studying the electrical characteristics of molecules and arrays thereof, but are also of importance for technological applications including computing and sensing. The relationship between structure and field-effect transistor performance in devices based on single crystals (including pentacene, TTF, and oligothiophenes) as the electro-active component is discussed in Chapter 21 (M. Mas-Torrent, C. Rovira). Recognition is a hallmark of supramolecular chemistry. Organic field-effect transistors can also be employed for sensing analytes in vapors or to recognize the presence of biomolecules in complex liquid media (L. Torsi and co-workers, Chapter 22). This can be accomplished by immobilizing recognition elements on sensor surfaces. Ambipolar OFETs could form the basis of organic complementary metal oxide semiconductor (CMOS) logic circuits, by enabling the development of robust, low-noise, low-power organic electronics. Ambipolar properties in OFETs can be obtained by using multicomponent structures with tailored interactions between the components in the bulk heterojunction (A. Bonfiglio, P. Cosseddu, Chapter 23).

Processing is a key issue in materials science and in particular in organic electronics. Alongside the possibility of using non-toxic, cheap, and upscalable approaches, the reproducibility of the self-assembly depends very much on the methodology used. Both the processing and post-processing of molecules on surfaces are crucial to obtaining full control over the interplay of kinetics and thermodynamics of the process. Chapter 24 (N. Stingelin) shows that many of the approaches common to polymer processing and technology can be applied to blends of conjugated macromolecules as a way of combining multiple functions in a single material.

In a time in which science is called upon to exert an impact on society at large by addressing its most pressing issues, the search for alternative energy sources is becoming an ever more important activity. Supramolecular architectures have a significant role to play in this, both for the insight that they can provide as model systems, and for direct application in functional devices. Although primary excitations in organic semiconductors and dyes are generally bound to hole–electron pairs or excitons, it is possible to separate them by adopting a "type II heterojunction" approach, so as to improve efficiency to levels that become interesting for commercial exploitation. Among solar cells, hybrid organic–inorganic photovoltaic diodes represent a particularly interesting solution, taking advantage of the heterojunction approach and also delivering efficiencies of 10% or more in the most favorable cases. Chapter 25 (H. J. Snaith) describes hybrid organic–inorganic solar cells, with a particular focus on the photochemical action at the heterojunction and charge collection through mesostructured composites. Chapter 26 (L. Schmidt-Mende) is concerned with the use of various metal-oxide-based inorganic blends with controlled morphologies. On the other hand, for organic bulk heterojunctions the current challenge is to achieve nanoscale and microscale control over the structure within the blend, based either on polymers (D. Neher, Chapter 28) or on a mixture of small molecules and polymers, through a tuning of the chemical structure of the components and processing techniques, to improve charge and exciton dynamics. Interestingly, modeling now makes it possible to predict the molecular packing (C. J. Brabec, I. McCulloch, J. Nelson, Chapter 27).

The optimization of light-emitting devices also requires self-assembly with nanoscale precision. This is the case for light-emitting electrochemical cells that depend on ionic self-assembly (L. Edman, Chapter 29), and also in more conventional light-emitting diodes, in which a modulation of intermolecular interactions obtained by rotaxination makes it possible to improve some of the photophysical properties of the device, such as its lifetime and blue light emission (S. Brovelli, F. Cacialli, Chapter 30).

Overall, these two books excel in achieving their goal of presenting chemical solutions to problems of organic electronics and nanotechnology, by highlighting a number of complementary methodologies to best exploit the supramolecular approach in molecular materials. This book will be a most valuable tool for graduate students, but also for more experienced scientists working in interdisciplinary fields at the crossroads of chemistry, physics, biology, and engineering in the burgeoning fields of materials, nanoscience, and nanotechnology. I am proud to have it in my collection.

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