

## Preface

Functional organic materials constitute a combination of diverse fields that range from carbon nanotubes to self-assembled polymers but encompass also nonlinear optical effects, the organic solid state and the construction of chiral materials. We, as the two Editors, have tried to put together an overview over the development of modern functional organic materials in this book. The content is divided into four different sections, which deal with 3-D carbon-rich systems (I), strategic advances in synthesis (II), molecular muscles, switches and electronics (III) and the interplay of electronic interaction and structure (IV). Renowned experts in each field give an introduction to/overview of each of their selected thematic fields, making an easy entry for readers into the respective field. The book is intended both for active scientists working in the field of organic materials, in academe and in industry, and also for graduate students who are interested in this area. Owing to the daunting scope of the topic, the book is not intended to be comprehensive, but rather presents selected highlights that are deemed of particular importance.

In the first part, 3-D carbon-rich systems, *Hirsch and Vostrovski (Chapter 1)* describe the strategies for attaching chemical functionalities to CNTs to make these fascinating materials processable. Solubilization allows tailoring of the interactions of nanotubes with semiconductors and (bio)polymer matrices. The authors describe the chemical and physical functionalization of single-walled and multiple-walled carbon nanotubes, of individual tubes and of bundles. Covalent functionalization of the nanotubes' carbon scaffold can be performed at the tubes' termini, at the sidewalls and at defect sites of enhanced reactivity. Physical functionalization is a noncovalent attachment of functions, based on complexation and adsorption forces, van der Waals and  $\pi$ -stacking effects. The authors discuss the functionalization of nanotubes comprehensively and show how functionalized nanotubes connect to biologically active environs and advanced devices.

In *Chapter 2, Matsuo and Nakamura* describe the synthetic developments of a subgroup of bowl-shaped  $\pi$ -conjugated corannulenes and expand the topic to the discussion of the synthesis of a novel class of organic fluorophores derived from  $C_{60}$ , hoop-shaped condensed aromatic compounds. They are made by selective removal of ten  $sp^2$  carbon centers out of conjugation from the north and south pole regions of  $C_{60}$ . The resulting 40- $\pi$ -electron [10]cyclophenacenes excised

from the equatorial region of the fullerene molecule are chemically stable, yellow-luminescent, non-conventional  $\pi$ -systems.

The second part of the book deals with strategic advances in the synthesis of organic materials. This part is ushered in by the contribution of *Scherf* and colleagues, who describe in *Chapter 3* the synthesis and characterization of cruciform,  $\pi$ -conjugated oligomers. The so-called cruciform approach leads to compounds with increased solubility and allows solution processing of such materials to produce homogeneous thin films and layers. Cruciform oligothiophene dimers have been used as active, semiconducting layer in solution-processed OFETs with a high hole mobility. Other examples of such cruciforms involve oligophenylenevinylene-type, oligophenyleneethynylene-type and oligophenylene-type cruciforms. The approach allows the introduction of donor or acceptor substituents leading to spatially addressable electronic properties in small molecule materials.

The introduction of the heavier main group elements, particularly phosphorus, is reviewed in *Chapter 4* by *Dyer* and *Réau*. The authors describe the use of P-containing building blocks (phospholes, phosphino groups or trivalent phospho- and diphospho-alkenes) for the design of conjugated systems. They illustrate the specific advantages offered by organophosphorus synthons compared with their widely used sulfur or nitrogen analogues. The possibility of chemically modifying P-centers provides a unique way to create structural diversity and to tailor conjugated systems for optoelectronic applications. The coordination ability of P-centers towards transition metals offers additional opportunities to build supramolecular architectures in which the  $\pi$ -systems can be organized in a defined manner and with significant changes to its electronic properties.

In *Chapter 5*, *Müller* provides an overview over multi-component processes, domino reactions and sequential transformations in diversity-oriented syntheses. The author demonstrates that multi-component reactions (MCRs), having found broad application in pharmaceutical high-throughput screening and lead finding, can also be used in the design and construction of functional  $\pi$ -electron systems (chromophores, fluorophores, electrophores). The author shows the developments of the last decade that led to adaptations of diversity-oriented approaches. New strategies, developments and perspectives of diversity oriented syntheses of functional  $\pi$ -electron systems are summarized and highlighted.

Most of the systems described in Chapter 5 contain small- or medium-sized or multinuclear benzenoid and non-benzenoid arenes. In *Chapter 6*, *Höger* gives an overview over the mastery of the synthesis of macro- and megacycles. He shows different approaches towards shape-persistent macrocycles and carefully examines and discusses selected examples that display the advantages and disadvantages of macrocycle synthesis under kinetic and thermodynamic control. The template approach (both supramolecular and covalent) towards functionalized rings is also discussed and introduces a strong motif of supramolecular chemistry, which is much further developed but in a more polymer-oriented topic, in the next chapter.

In *Chapter 7* *Carlise* and *Weck* discuss the design and synthesis of multifunctionalized, architecturally controlled polymers as a prerequisite for a variety of future

applications of polymeric materials. They review recent progress in polymer science that is based on Nature's use of self-assembly in the creation of biomaterials and that utilizes noncovalent interactions such as hydrogen bonding, ionic interactions, electrostatic interactions and metal coordination. These concepts have been employed to synthesize both main-chain and functionalized side-chain polymeric materials. The examples outlined in this chapter demonstrate the great potential of noncovalently functionalized polymers. Weck's group has laid the groundwork for future endeavors in this area.

Although supramolecular assembly is a necessary prerequisite for the construction of molecular machines, it is not sufficient. In Part III, concepts of molecular muscles, switches and molecular electronics are illuminated. In *Chapter 8*, on molecular motors and muscles, *Saha* and *Stoddart* survey bistable rotaxane-based molecular switches and motors, and also muscles that display piston-like linear translational motions, when triggered by chemical, electrical or photochemical inputs. The problematic issues that arise by miniaturization of semiconductor devices by a "top-down" approach can often be circumvented by noncovalent syntheses leading to a "bottom-up" approach, based on molecular recognition and self-assembly. Bistable catenanes and rotaxanes are capable of nanoscale mechanical movements of one component with respect to another in response to external stimuli – a property which makes them one of the best molecular systems that can be made to function like a switch or a machine. These relative movements within interlocked molecules, arising from changes in the noncovalent bonding interactions, can be initiated and controlled by three types of stimuli – chemical, electrical and light.

While the transformation of chemical, electrical and radiation energy into mechanical movement is important, the control of intramolecular magnetic interactions using light is yet another facet of the fascinating world of organic materials. In *Chapter 9*, *Matsuda* and *Irie* discuss and outline attempts to control intramolecular magnetic interactions by photoswitchable materials. The most convenient way to introduce a photoswitching function to molecular systems is to use photochromic units as spin couplers. A particularly interesting group of these couplers are diarylethenes, which reversibly change the  $\pi$ -conjugation and structure upon irradiation. These materials are successfully used to control the intramolecular magnetic interaction and can change these by a factor of >150-fold.

*Matsuda* and *Irie's* chapter on photonic switching gives an excellent transition to the final fourth part of the book, where electronic interaction and structure are discussed. In *Chapter 10*, *Nørgaard*, *Brøndsted Nielsen* and *Bjørnholm* review the current status of conductivity measurements through single molecules with particular emphasis on thiol end-capped  $\pi$ -conjugated oligomers. This field of research has been progressing rapidly over the last few years and aims at developing the methodology and fundamental understanding of sending current through individual molecules – towards the ultimate goal of constructing "single molecule" electronics. The first part of the chapter describes different synthetic approaches towards the fabrication of candidate molecules for these aims, followed by a survey of current experimental methods for measuring the electronic transmission

properties of organic molecules in various two- and three-terminal device configurations.

Going from molecular electronics to molecular photonics, in the elegant *Chapter 11*, Barlow and Marder introduce the general reader to the origin of nonlinear optical effects in conjugated organic systems and to structure–property relationships for  $\pi$ -chromophores. The chapter focuses on two exciting areas of current interest. In the case of second-order nonlinear optics, recent developments in overcoming various challenges in the commercial application of organic chromophores in electrooptic switching devices are described. In the case of third-order nonlinear optics, the chapter summarizes recent breakthroughs in understanding the design of molecules with a high two-photon cross-section and surveys some of the applications that may be facilitated by the availability of these chromophores.

Whereas in all of the preceding chapters non-biological building blocks were used to construct organic materials, Wagenknecht demonstrates in *Chapter 12* that DNA is a viable bioorganic material for molecular electronics, since the unique self-assembling and predictable structure make DNA a superb architectural scaffold. For the investigation of photoinduced electron transfer processes through DNA, it is necessary to modify oligonucleotides with suitable chromophores: The different methods to introduce these into the building-block strategy via phosphoramidite chemistry and also protocols for post-synthetic oligonucleotide modifications are discussed in terms of their ability to prepare structurally and electronically well-defined DNA systems. The author discusses issues of electron transport through DNA on different length scales and concludes that efficient electron transport over longer distances using DNA (>20 nm) requires the development of DNA-based materials which contain the DNA-typical structural features but exhibit improved electron transport capabilities by engineering electronic interactions between – now artificial – bases in single- and double-stranded DNA molecules.

The concept of electron transfer in non-biological systems is deepened in *Chapter 13* by Fukuzumi, who reviews recent developments of electron-transfer systems of functional  $\pi$ -compounds focusing on the specific aspect of their supramolecular organization to construct efficient photovoltaic devices. Specifically, porphyrins and fullerenes exhibit excellent electron-transfer properties. Their small reorganization energies of electron transfer facilitate the design of artificial photosynthetic systems composed of functional  $\pi$ -compounds with fast charge separation but very slow charge recombination. The author discusses the two factors for efficient photocurrent generation. One is charge separation and the other one is charge carrier transport in thin films. Three-dimensional control of  $\pi$ -complexes between porphyrins and fullerenes contributes to both the efficient charge separation and excellent charge carrier transport. Efficient self-exchange electron transfer between porphyrin/porphyrin<sup>+</sup> and between fullerene/fullerene<sup>-</sup> is well established and leads in supramolecular clusters with interpenetrating networks to efficient hopping of holes and electrons in each network.

Charge transfer and charge migration in organic solids are also a critically important issue for the successful fabrication of organic competitive solid-state de-

vices. In *Chapter 14*, Anthony unfurls the relationship between molecular packing and its consequences for linear acenes. Although many high aspect ratio aromatic systems adopt an edge-to-face arrangement referred to as “herringbone” packing, the arrangement predicted to yield the best electronic properties involves the face-to-face interaction of aromatic species, direct  $\pi$ -stacking. The separation between the  $\pi$ -faces of the molecules and even the degree of lateral or longitudinal offset between adjacent aromatic units can lead to dramatic changes in electronic communication between molecules. This chapter discusses modes for enhancing or enforcing  $\pi$ -stacking arrangements in linearly fused aromatic systems and discusses the effect of  $\pi$ -stacking on the properties of devices fabricated from these materials.

From electronic back to optical properties, in the final *Chapter 15*, Rajca and Miyasaka provide an overview of the synthesis of molecules with highly annelated, chiral,  $\pi$ -conjugated systems, primarily of the helicene-type. Tremendous progress has been made in the synthesis of helicenes; however, the corresponding helical, ladder-type polymers remain a significant and attractive challenge. In addition to the synthesis, the configurational stability (barriers for racemization) and chiroptical properties are described and discussed in depth in this chapter. In this context, perspectives for isotropic materials with molecule-based chiroptical properties are outlined.

We hope that this book, *Functional Organic Materials*, gives an effective overview of novel and important aspects in the field. We have not included the area of semiconducting polymers as there is a very recent book [Georges Hadziioannou and George G. Malliaras (Editors), *Semiconducting Polymers, Chemistry, Physics and Engineering*, 2nd edn., Wiley-VCH, Weinheim, 2006] that treats this topic in depth. Neither has this book covered the area of organic materials for light-emitting diodes, as there is an excellent recent monograph (Klaus Müllen and Ullrich Scherf (Editors), *Organic Light Emitting Devices, Synthesis, Properties and Application*, Wiley-VCH, Weinheim, 2005). We hope that readers will enjoy the herein presented developments in organic materials as much as the Editors did in assembling these chapters.

Atlanta and Düsseldorf, November 2006

Uwe H. F. Bunz  
Thomas J. J. Müller