



Preface

Supramolecular approaches to nano and molecular electronics

At the interface between inorganic and organic chemistry, coordination chemistry has a tremendous role to play in the development of nanomaterials and nanotechnologies. During the top-down years, these fields were intimately linked to silicon and inorganic semi-conductor chemistry. Although a recent issue of *Coordination Chemistry Reviews* (December 2009) has highlighted the development of pure inorganic or hybrid materials, the emergence of plastic electronics and the use of soft materials in devices over the last two decades have largely stimulated the interest of coordination chemists for bottom-up approaches leading to molecular materials for nanotechnologies and molecular electronics. There is no reason that molecular electronics should be different than classical electronics in the sense that the devices and components made of molecular materials are expected to be active in either the propagation or the treatment of an electronic, photonic or magnetic signal. Thus, the term molecular material implicates important challenges, including the design of function or properties at the molecular level and the transposition and implementation of these functions or properties at the device scale, in an organized collective phase of a material. Supramolecular chemistry has developed the tools for self-organization of molecular materials for nanotechnologies, as well as the general rules for the controlled design of molecular electronic functions such as logic operators or switches. Inspired by the work of pioneers, many new ideas or concepts are emerging.

The purpose of this issue is to cover recent and new developments in various areas of supramolecular coordination chemistry such as strategies towards tailor-made self-assembled nanostructures, electronic molecular functions or surface studies.

Signal processing and treatment have a long history in coordination chemistry because photo-induced energy and electron transfer studies in solution on coordination compounds are the archetypal example of electronic output triggered by a photonic signal. Not only is the nature of the input signal to be processed a determining factor in the design of the molecular devices or materials, but also the nature of the output signal. As a result, metal complexes or large aromatic chromophores are frequently used. Two reviews address these issues very specifically. The contribution on chiroptical switches by Jim Canary essentially focuses on the detection of chiral responses from chromophore-based devices that can be triggered by a variety of stimuli such as electron transfer or solvent changes. The detection of chirality changes in coordination complexes appears to be promising tool to monitor molecular events and the potential application of chiroptical switches in sensors is also discussed.

Another review by Alberto Credi presents molecular logic operations performed at the molecular scale, as well as information storage in molecular memories and signal processing in molecular switches. Because the implementation of molecular materials in devices involves their deposition on surfaces, the connection of photo, and electroactive species with surfaces or the studying of these species in soft condensed phases has emerged as a very active field in coordination chemistry. A few supported systems are also presented and critically discussed for a clear definition of perspectives in the field of molecular logic devices.

As a necessary complement to the use of photo or redox triggers for molecular functions, the field of supramolecular magnetic materials is covered by a separate contribution coordinated by Yves Journaux, with research work illustrating the high level of interest for the recent development of spintronics. Molecular programming of ligands is suited to produce complexes of paramagnetic metals in which the multiple spin interactions through aromatic ligands can be controlled, rationalized and predicted. The oligometallocyclic compounds that can be prepared with a class of polyoxalamide ligands appear ideal for the design of molecular magnetic wires and switches.

Aside from the processing of photo, electro or magnetic signal, molecular electronics is also confronted with the demand to transport these signals. Molecular circuitry provides a fantastic opportunity for supramolecular chemistry to demonstrate the power of self-assembly. Because π -electronic density is keen for delocalization, aromatic building blocks are very common in molecular materials geared towards applications in nanotechnologies. Among the aromatic structures intensively used in nanomaterials are porphyrins, or more generally tetrapyrrolic macrocycles. Inspiration easily comes from the biological electron and energy transfer machinery and photo, redox, magnetic activities can be combined within an aromatic ligand. Three reviews of this issue focus on porphyrin derivatives. One by Mike Drain introduces a necessary background of the individual properties of porphyrins before presenting the potential of porphyrin derivatives in molecular electronics, not only as wires, but also as electronic components of functional devices. In a section dedicated to functional devices, selected examples of devices produced by covalent linking of porphyrin scaffolds to electroactive surfaces are detailed. A second article by Joe Otsuki focuses more specifically on the imaging of porphyrin-based nanostructures and the use of near-field microscopies to study electronic properties of porphyrins on surfaces. Particular attention is given to scanning tunneling microscopy (STM), which probes electronic properties at the single molecule

level. A third contribution by Davide Bonifazi reviews porphyrins as privileged building blocks for the construction of nanostructures. Strategies to attain multiporphyrin assemblies in controlled 1D, 2D and even 3D architectures on surfaces are discussed and illustrated. Coverage of supramolecular recognition on surface deposited 2D architectures for the construction of molecular networks shows the possible applications of porphyrin networks in catalysis and sensing.

Wires containing aromatic moieties are not the only solution for nano-circuitry. The supramolecular coordination chemistry toolbox allows the incorporation of metals in linear species with potential or real conducting properties. A contribution by Mark MacLachlan is dedicated to metal containing linear scaffolds. It covers the general coordination chemistry approach to one-dimensional fibers. It details the use of synthetic ligands associating binding sites with peripheral non-covalent interactions that are typically used in molecular recognition to control the organization and interactions between metallic complexes. Application of metal-based wires and fibers in the fields of catalysis, sensors, gas storage, and the potential development of nanosized devices is also discussed.

In general, programming the association of metallic complexes is an essential issue in the controlled generation of nanostructures as the precise positioning and spacing of metallic complexes may define, for example, the generation of redox cascades for conduction, switches or logic operations. Nature contains many examples of materials organized in one dimension, and for this reason, three contributions provide an exhaustive overview of close but distinct approaches towards the use of biomaterials in nanotechnologies. Particular attention is paid to DNA and nanostructures and nanotechnologies that involve metallic complexes. The structure of DNA is a source of inspiration for many reasons. To enhance the potential conduction of charges from short DNA segments to larger species, the possible replacement of one or several base pairs with metallic complexes has been developed in an approach that resembles to the engineering and programming of the helix core, and is reviewed by Mitsuhiro Shionoya. Another approach highlighted in this issue by Hanadi Sleiman is the design of metallic assem-

blies and architectures with the help of DNA programmed building blocks. The design and programming process can be reversed and metal complexation can in turn control the assembly of DNA segments bearing exo or terminal binding sites. Another inspiration from DNA structures is the use of peptide nucleic acids (PNA) in which peptide residues link bases in the strands and allow similar programming of assemblies of nucleobases as well as of metallobases. This approach is extensively discussed by Mary-Beth Williams. Together, the three contributions addressing the use of biomaterials are very complementary.

A major issue in the bottom-up approaches is the step from molecular behavior to collective behavior. How the organizational constraints, to which molecular spin, photo and electroactive species are subjected, modify, enhance or degrade molecular properties is an essential issue in the development of molecular electronics. These organizational aspects are critically addressed in a review by Dario Bassani and Nathan McClenaghan that covers supramolecular ordering of soft matter into the three big categories of molecular electronic devices, namely organic light emitting diodes, organic field effect transistors and organic photovoltaic devices.

I would like to finish this foreword by thanking those who contributed to this issue that compiles a large variety of literature and research, covering the field of supramolecular coordination chemistry for nanotechnologies from the molecule to the nanomaterials. I hope that the readers will have as much pleasure as I, in reading this issue, which was a long term project that could not have been prepared without the perseverance and patience of Prof. Barry Lever.

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