Introduction to papers dedicated to the 3rd International Symposium on Molecular Materials (MOLMAT)

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These papers are dedicated to the 3rd International Symposium on Molecular Materials (MOLMAT) held in Toulouse, France in July 2008. This symposium aimed to gather different research topics from chemical synthesis to solid-state physics, nanotechnology and the theory of molecular materials based on inorganic and organometallic chemistry.

The interdisciplinary goals set forth at the outset of this symposium series remain the key aspect of MOLMAT meetings, with the aim of encouraging interactions among molecular scientists working in the fields of chemistry, solid-state physics, theory and nanotechnology. The symposium program was thus structured around twelve invited speakers of high international recognition, among whom we had the honour of receiving Albert Fert, the winner of the 2007 Nobel Prize in Physics.

Several research fields making use of molecular materials are growing strongly, such as nanoelectronics, optoelectronics, molecular and nanomagnetism, photomagnetism (Mathonière *et al.*, DOI: 10.1039/b902833a), switchable molecular materials, nanopatterned molecular thin films, conducting molecular materials, non-linear optics (Barille *et al.*, DOI: 10.1039/b823216d) and dielectric properties, coordination nanoparticles (Larionova *et al.*, DOI: 10.1039/b900918c) and dendrimers (Astruc, DOI: 10.1039/b903188j), liquid crystals, luminescence (Gerbier *et al.*, DOI: 10.1039/b900780f) and electroluminescence, accompanied by quantum and statistical theories, not only because of the fundamental interests they represent, but also because of their use in novel applications and as alternatives to conventional materials. Indeed, the molecular scale is increasingly being considered as a possible solution for the miniaturization of components used in the construction of devices, for instance in the fields of data storage and processing, sensing, and solar energy conversion. The current top-down approach, based on silicon technology, forces solid-state chemists, physicists and electronic engineers to machine progressively smaller and smaller quantities of matter. In contrast, the bottom-up approach of molecule-based devices offers prospects of sensitivity and selectivity levels that cannot be reached with conventional solid-state materials. As a prerequisite, it is however necessary to reproduce traditional physical (electronic/optical/magnetic) functions at the molecular scale. This objective must be the first of successive steps towards achieving the supreme goal of bringing transition metal complexes or organic materials towards new frontiers in materials science.

Gaining knowledge of the physical processes that take place at the molecular scale, which ultimately govern the macroscopic properties of the material, requires the use of dedicated experimental tools and theoretical approaches. The complexity of the architecture, the intrinsically multi-configurational character of the states involved, the role of relativistic effects (through spin–orbit interactions), the necessity to go from accurate first principle calculations to model Hamiltonians in order to match the experimental data and the consideration of time evolution constitute a real challenge for theoreticians.

Switching through external stimuli, such as a variation in temperature and pressure, or by irradiation with light, is one of the key functions necessary for constructing any type of device. Several systems are promising in this respect. In so-called spin-crossover compounds, which are the subject of several contributions of the current issue, namely by Chernyshov *et al.* (DOI: 10.1039/b823514g), Real *et al.* (DOI: 10.1039/b905674b), Salmon *et al.* (DOI: 10.1039/b902811k) and Faulmann *et al.* (DOI: 10.1039/b901779h), all three stimuli can be employed to control the spin state of the transition metal centers. Of particular interest in this respect are their photophysical properties, which confer on these compounds the properties necessary for all-optical read, write and erase memory devices. Similarly, redox-active ligands allow for intramolecular control of the valence state of the central metal ion, as for instance in the well-known catecholate complexes. Along the same line, heteronuclear mixed valent systems, such as the polynuclear cyanide complexes discussed by Marvaud *et al.* (DOI: 10.1039/b902889g) or Prussian Blue analogs, exhibit intramolecular charge transfer phenomena that can be induced by temperature and light. This may be combined with magnetic order, which adds a second functionality to the material. Single molecule magnets, that is polynuclear complexes with strongly coupled spins and a large spin anisotropy, show magnetic order at the molecular level, resulting in interesting quantum phenomena, as shown in the contributions by Wernsdofer *et al.* (DOI: 10.1039/b822305j) and Clérac *et al.* (DOI: 10.1039/b903399h).

Regarding the computational tools for the study of magnetism, two families of approaches are used. The easiest one makes use of density functional theory (DFT) in its single-determinantal Kohn–Sham version, with one of the most efficient exchange-correlation potentials; geometry optimizations are feasible and reliable at this level. For the study of magnetic properties, due to the intrinsic multi-determinantal character of most states, symmetry-broken solutions are used to determine the energies of an Ising-like Hamiltonian. This DFT procedure may also be employed for periodic systems, and it has received applications that to go

beyond standard bicentric spin coupling determinations, for instance four-body effects in plaquettes, biquadratic and three-body operators in $S = 1$ systems, provided that the Fock exchange potential is revised with respect to its standard value. Spin–orbit effects may be incorporated along the same line, and Neese has recently presented an exhaustive review concerning this strategy (*Coord. Chem. Rev.*, 2009, **253**, 526). The more rigorous wave function-based methods, which explicitly treat the dynamic correlation effects either perturbatively or variationally, are computationally much more demanding, and their domain of application is still limited, though they make possible a more detailed analysis of the physical phenomena and a grounded foundation of model Hamiltonians. Methodologists have worked intensively to improve the efficiency of these strict *ab initio* methods in the challenging domain of magnetic materials (Chibotaru *et al.*, DOI: 10.1039/b903126j). Bencini has recently presented an interesting comparative discussion of the two approaches (*Inorg. Chim. Acta*, 2008, **361**, 3820).

These molecular materials represent an extremely stimulating field for the creative imaginations of chemists, physicists who have sophisticated their modes of interpellation and theoreticians who have been summoned to make progress with their tools.

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