

Supramolecular Magnetic Materials

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The incorporation of localized unpaired electrons into molecules and molecular materials provides the basis for a wealth of fascinating and rapidly developing science. Beyond an interest in the intrinsic properties of systems with localized spins (i.e. relating to attributes such as colour, magnetic moment, and chemical reactivity) comes a diverse range of magnetic and electronic phenomena in which transitions can be induced between different spin and spin-ordered states, with dramatic resulting changes in properties observed. Such phenomena perhaps most notably span the field of molecular magnets, in which the unpaired spins align with respect to each other through exchange-coupled pathways to give a rich array of spin-ordered ground states, and the field of spin-crossover, in which transition metal centres may be switched between alternate spin states in response to stimuli such as temperature, pressure, and light irradiation. Of further interest under this broad umbrella are properties such as valence tautomerism, in which spin-switching is achieved through metal-ligand intervalence charge transfer, and mixed-valency, in which differing oxidation states (commonly involving unpaired spins) may exist within the one system, including with varying degrees of delocalization.

A unifying feature of all of these phenomena, other than that they involve unpaired electrons, is that they depend intimately on various types of communication between the electronic spins, each of which are subject to considerable variation through molecular, supramolecular, and materials design. Accordingly, a particularly intriguing aspect of this science – one that is in abundant display in the contributions that make up this Research Front – is the highly complex nature of the links between structure and resulting function for these systems. This complexity makes advances in this area dependent on a multidisciplinary approach in which new molecules and materials are synthesized, their structures and properties determined, relationships between these gleaned, and, subsequently, new systems are designed and synthesized, subject to the considerable whims of molecular self-assembly. Driving these efforts are a fascination with the endless complexity of this chemistry and, increasingly, the desire to

achieve useful electronic and magnetic function at the nanoscale through a ‘bottom-up’ (i.e. chemical) rather than ‘top-down’ (i.e. engineering) approach to miniaturization; among a range of device-oriented goals here include data storage, molecular electronics, quantum computing, magnetic refrigeration, visual displays, and molecular sensing.

Leading off this Research Front is a comprehensive review by Keith Murray^[1] that lays an over-arching foundation for the fields of molecular magnetism and spin-crossover, and in doing so sets the scene for the eight subsequent research contributions. Through description of these phenomena with reference to several examples, this review addresses the chemical features that impart both spin-ordering and spin-crossover to polynuclear clusters and materials. Among several areas covered are the novel chemistry and physics of single molecule magnets, structure–property correlations in molecule-based magnets such as supramolecular grids and coordination polymers, the nature of communication between spin-crossover centres within dinuclear complexes, and the extrapolation of these considerations to spin-crossover framework materials. Further, the incorporation of other functions into these systems, such as reversible guest-exchange in porous phases, leading to interesting new synergies and novel materials properties, is described.

Several interesting research contributions that broadly span magnetic clusters and spin-crossover systems follow. In a communication from Annie Powell and coworkers,^[2] the synthesis and characterization of a novel hydrogen-bonded network based on the spin-frustrated, trinuclear basic iron(III) carboxylate unit and a dinuclear lanthanoid carboxylate are described. Such work is of considerable interest both in the design of targeted magnetic architectures, and in delineating the influence of supramolecular interactions and crystal packing on intra- and intermolecular magnetic exchange coupling. Also exploring the influence of intermolecular interactions, but this time on single-molecule magnetism, is a full article by Euan Brechin and coworkers,^[3] which reports the structure and properties of a family of ferromagnetically coupled trinuclear Mn^{III} complexes, each of which



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exhibits the $S = 6$ ground state at low temperature. An examination of the quantum tunnelling properties reveals large energy barriers to magnetization reversal, with the very interesting observation that this can be modulated through variation of the supramolecular exchange interactions within this family of hydrogen-bonded materials.

Four articles follow that collectively report the magnetic properties of a diverse range of discrete polynuclear complexes. Each of these contributions combines ligand design and synthesis, complexation to form clusters, and characterization of the structure and magnetic properties of the new systems. In the first of these, Sally Brooker and coworkers^[4] report a novel tetranuclear mixed-valent Mn^{II}/Mn^{III} complex with near planar geometry in which weak antiferromagnetic coupling dominates the magnetic properties. This is complemented by the report by Colette Boskovic and coworkers^[5] of a new tetranuclear mixed-valent $Co^{II}Co^{III}$ cluster in which there is weak antiferromagnetic coupling between trigonal bipyramidal Co^{II} centres; the synthesis and structure of a novel pentanuclear $Co^{II}Co^{III}_4$ cluster are also presented. Further variation in ligand design sees the generation by Guillem Aromi and coworkers^[6] of a chain configuration of four Co^{II} ions within an antiferromagnetically coupled tetranuclear cluster – a system that may potentially be systematically modified through the exchange of labile methanol molecules. Rounding off the contributions on magnetic clusters, and targeting increased polynuclearity – an important goal for the achievement of high net spin states should ferro- or ferromagnetic coupling be achieved – comes a contribution from Stuart Batten and coworkers^[7] on the synthesis and characterization of a novel octanuclear cluster that incorporates a disk-shaped $Fe^{III}_8O_3$ core. Magnetic characterization of this system shows that the Fe^{III} spins couple antiferromagnetically at low temperature.

Following these contributions on magnetic exchange coupling are two articles that target, among other things, the achievement (and fickle nature) of spin-crossover in dinuclear complexes and coordination polymers. At the forefront of ligand design comes an article from Christopher Sumby and coworkers^[8] that explores the complexation chemistry of three

new bridging bis-tridentate ligands. This paper reports a range of interesting dinuclear clusters and assemblies of paramagnetic and diamagnetic transition metal ions, highlighting the colourful spectrum of complexes that is achievable through the molecular self-assembly process. This is followed by an article from Anna Gaspar and coworkers^[9] that reports four new two-dimensional grid phases in which Fe^{II} nodes are bridged by dicyanoargentate(1)/aurate(1) ions. In this very interesting series, the serendipity of the spin-crossover phenomenon is evident through an acute dependency of the switching behaviour on crystal packing and intra- and intermolecular effects.

To conclude, these papers provide a glimpse of current developments in the very broad field encompassed by the banner ‘Supramolecular Magnetic Materials’. Armed with increasingly sophisticated synthetic strategies and understandings of structure–property relationships within this area, as derived from this and other work, we can anticipate ever more impressive systems to emerge in future years.

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