

Molecule-based magnets

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Abstract. The conventional magnetic materials used in current technology, such as, Fe, Fe₂O₃, Cr₂O₃, SmCo₅, Nd₂Fe₁₄B etc are all atom-based, and their preparation/processing require high temperature routes. Employing self-assembly methods, it is possible to engineer a bulk molecular material with long-range magnetic order, mainly because one can play with the weak intermolecular interactions. Since the first successful synthesis of molecular magnets in 1986, a large variety of them have been synthesized, which can be categorized on the basis of the chemical nature of the magnetic units involved: organic-, metal-based systems, hetero-bimetallic assemblies, or mixed organic–inorganic systems. The design of molecule-based magnets has also been extended to the design of poly-functional molecular magnets, such as those exhibiting second-order optical nonlinearity, liquid crystallinity, or chirality simultaneously with long-range magnetic order. Solubility, low density and biocompatibility are attractive features of molecular magnets. Being weakly coloured, unlike their opaque classical magnet ‘cousins’ listed above, possibilities of photomagnetic switching exist. Persistent efforts also continue to design the ever-elusive polymer magnets towards applications in industry. While providing a brief overview of the field of molecular magnetism, this article highlights some recent developments in it, with emphasis on a few studies from the author’s own lab.

Keywords. Molecular lattices; spin–spin interaction; photo-induced magnetism; single molecule magnets.

1. Introduction

Most molecular materials are organic in nature. Molecular crystals are made up of well-defined molecules, which do not change their geometries appreciably upon entering the crystal lattice. This is because intermolecular interactions are non-covalent in nature, viz. hydrogen bonding, Van der Waals interactions, donor–acceptor charge transfer, etc that are much weaker than the energies of typical chemical bonds, ionic or covalent. This provides an interesting possibility to modify the properties of a molecular solid in a predetermined way by attaching a function to the building-block (i.e. the molecule), and thus engineer a bulk molecular material with designer characteristics. Chemical synthesis, at ambient temperature, provides immense flexibility towards the synthesis of new molecular materials designed to perform several functions originally attributed to the metallic lattices, such as, high electric conductivity or photoactivity in polymers, and superconductivity in charge-transfer organic complexes/fullerenes. Quite obviously, there has been a strong urge to develop ferro(ferri)magnetic molecular materials, too, by designing new combinations of interactions between magnetic centres in organic (or polymeric) materials, preferably with *p*-orbital based spins. Theoretical models did predict the possibility of attaining long-range magnetic order in molecular materials. However, organic

compounds are mostly diamagnetic, with closed-shell structures, and even if one (or more) unpaired electron is maintained stably per organic molecule, stabilization of a triplet state (parallel alignment of spins) requires that the orthogonality conditions are satisfied (Hund’s rules), which is difficult, so they prefer to get antiferromagnetically coupled with no spontaneous magnetic moment. No wonder, the conventional magnetic materials used in present-day technology, such as, Fe, Fe₂O₃, Cr₂O₃, SmCo₅, Nd₂Fe₁₄B, etc are all atom-based materials, in which magnetic order arises from co-operative spin–spin interactions between unpaired electrons located in *d*-orbitals or *f*-orbitals. But their synthesis typically depends on solid-state chemistry or high temperature metallurgical routes.

Typical synthetic approach to design molecule-based magnets consists of choosing molecular precursors, each bearing a unpaired spin (the function, as shown in figure 1), and assembling them in such a way that there is no compensation of spins at the scale of the crystal lattice (Kahn 1993; Itoh and Kinoshita 2000; Miller 2000). The design of molecular magnets has also employed the tools of supramolecular chemistry (Kahn 1996). Magnetism being a co-operative effect, the spin–spin interaction must extend to all the three dimensions, either through space or through bond. The interactions between spin carriers may occur through space, in which case we have a genuine molecular lattice, or, through bond when we are faced with a polymeric or extended structure. In the latter case, the interactions are usually much stronger,

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particularly so when the bridging ligands are conjugated. The design of a molecular magnet requires that: (a) all the molecules in the lattice have unpaired electrons; and (b) the unpaired electrons should have their spins aligned parallel along a given direction (Yakhmi 2003).

2. Purely organic magnets

The first two ferro(ferri)magnetic molecular compounds exhibiting a spontaneous magnetization below a certain temperature, T_c , were reported in 1986 (Miller *et al* 1986; Pei *et al* 1986), and subsequently molecular magnets of many different categories have been synthesized and interest in the field of molecule-based magnets has been growing steadily. The discovery of ferromagnetism involving p -electrons in iron-containing organic-based material (Miller *et al* 1986) was an important step forward because magnetism in metal-free compounds must involve electrons from p -orbitals, which was considered impossible not long ago. Despite a significant progress made in the preparation of π -conjugated oligomers and polymers with large values of spin quantum number, S , persistent efforts to design polymer magnets have not borne fruit yet, though success in this endeavour, if and when achieved, would have a huge impact on applications in industry (Ovchinnikov 1978; Itoh and Kinoshita 2000; Rajca *et al* 2001). Multi-orbital ferromagnets such as TDAE- C_{60} (Allemand *et al* 1991) are known, but

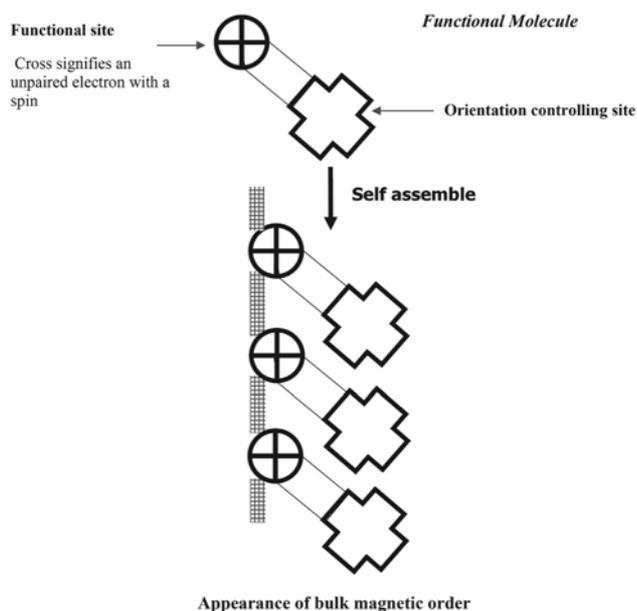


Figure 1. Cartoon depicting the assembly of a molecule-based magnet from functional molecules (precursors), each bearing an unpaired spin (the function), in such a way that there is no compensation of spins at the scale of the crystal lattice, yielding a three-dimensional lattice with a long-range magnetic order.

organics exhibiting (single-)band ferromagnetism have yet to be synthesized. Spin density functional calculations (Arita *et al* 2002) have proposed the possibility of band ferromagnetism in purely organic polymeric structures like PAT [poly(4-amino 1,2,4 triazole)], which are chains of five-membered rings. They predict that when the flat band of such materials is made half-filled, with appropriate dopings using, say, a field-effect transistor structure, the ground state will become ferromagnetic.

Magnetism being a co-operative effect, the spin–spin interaction must extend to all the three dimensions. Specific occurrence of spin delocalization and spin polarization in molecular lattices, unlike in the case of ionic/metallic compounds, is helpful in bringing about ferromagnetic interaction by facilitating necessary intermolecular exchange interactions. The delocalization of spin density in certain molecules makes it possible for magnetic interactions to take place across extended bridges between magnetic centres far apart from each other, propagating through conjugated bond linkages, which act as molecular wires. Spin polarization, i.e. the simultaneous existence of positive and negative spin densities at different locations within a given radical is crucial for intermolecular exchange interactions to bring about ferromagnetic interaction between organic radicals, as per McConnell's (1963) model. Spin density across different regions of the nitronyl nitroxide radical NITR (R = alkyl), a versatile building block with spin $S = 1/2$ ground state (figure 2), for instance, shows positive values, equally delocalized between N and O within each N–O group, and a small negative value on the bridging sp^2 carbon, due to spin polarization. By substituting different alkyl groups (like R = benzyl, isopropyl, methyl, ethyl, phenyl, etc) in NITR, one can tune the single-radical ground state to establish new exchange pathways through varied coordination sites. For instance, ferromagnetism at 0.6 K arises solely from p -orbital spins in the β -phase of R = phenyl compound (4-nitrophenylnitronyl nitroxide) (p -NPNN, with formula $C_{13}H_{16}N_3O_4$, shown in figure 2), a metal-free organic magnet which contains only C, H, N, and O elements (Tamura *et al* 1991).

Ferromagnetism has also been obtained for the purely organic fullerene-based charge-transfer material, [tetrakis

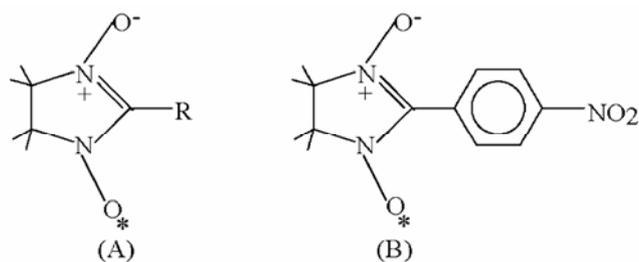


Figure 2. The chemical structure of (A) NITR and (B) p -NPNN (* indicates an unpaired electron).

(dimethylamino)ethylene][C₆₀] with T_c of 16.1 K (Allemand *et al* 1991). Fullerene has no intrinsic magnetic moment. For a magnetic moment to exist, an electron must be transferred to C₆₀ from a donor molecule. Another example of a fullerene-based ferromagnet was the cobaltocene-doped derivative, which has a T_c of 19 K (Mrzel *et al* 1998). The highest ordering temperature reported to date for an organic magnet has been for the β -phase of the 4'-cyanotetrafluorophenyldithiadiazolyl, a sulfur-based free radical, which was found to be a weak ferromagnet below 35.5 K (Banister *et al* 1996; Palacio *et al* 1997). Under a pressure of 16 kilobars, this temperature can be raised to 65 K (Mito *et al* 2001).

3. Ferrimagnetic building-blocks

A powerful strategy, pioneered by O Kahn, to build a molecule-based magnet is based on the use of ferrimagnetic chains containing alternating spins of unequal magnitude, $S_A \neq S_B$, and assembling them in such a way that there is a net spin, leading to a long-range magnetic order in the lattice (Kahn 1993, 1995). Here, S_A stands for the large spin and S_B for the small spin on two different spin carriers, A and B, such as Mn^{II} ions ($S = 5/2$) and Cu^{II} ions ($S = 1/2$), respectively, within the same molecular precursor (figure 3). A large number of molecular (ferro)ferrimagnets have been assembled using this technique, the spin carriers in them being either two different metal ions (Nakatani *et al* 1989; Okawa *et al* 1994) or a metal ion and an organic radical (Caneschi *et al* 1989; Broderick *et al* 1990; Inoue and Iwamura 1994; Inoue *et al* 1996), with intervening ligands which serve as effective exchange pathways.

Heterobimetallic species, in which two different metal ions are bridged by extended bisbidentate ligands such as oxamato (Kahn *et al* 1988; Stumpf *et al* 1993a), oxamido (Nakatani *et al* 1989; Pei *et al* 1991), or oxalato (Okawa *et al* 1994), in particular, allow a variety of spin topologies.

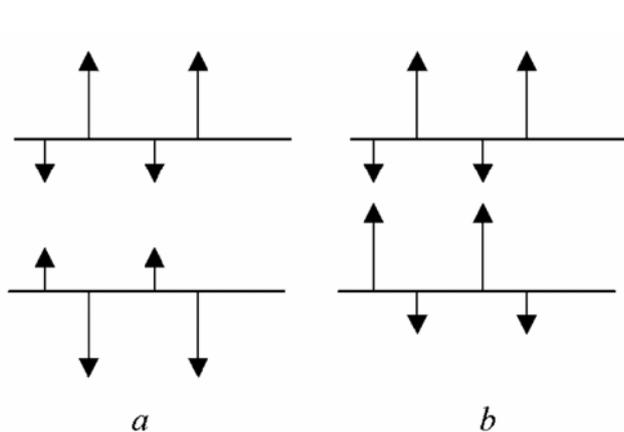


Figure 3. Assembly of ferrimagnetic chains leading to a net a. zero, or b. non-zero magnetic moment in bulk.

Using this principle, Kahn's group synthesized several Mn(II)Cu(II) molecular magnets in which the ferrimagnetic interactions are propagated through bisbidentate ligands, viz. MnCu(*opba*)·0.7DMSO which is synthesized by reacting the Cu(II) precursor $\text{Cu}(\textit{opba})^{2-}$ (figure 4), where *opba* stands for *ortho*-phenylenebis(oxamato), with a divalent ion, Mn(II) in a 1 : 1 stoichiometry. This compound is an amorphous magnet with a spontaneous magnetization below $T_c = 6.5$ K. Aiming at increasing the Curie temperatures of this class of compounds, they synthesized 2 : 3 Mn(II)Cu(II) compounds $\text{A}_2\text{M}_2[\text{Cu}(\textit{opba})]_3 \cdot n$ solv with two-dimensional character, by employing $[\text{Cu}(\textit{opba})]^{2-}$ to cross-link the chains in a two-dimensional network, in the presence of two equivalents of the cation A^+ . Among them is $(\text{NBu}_4)_2\text{Mn}_2[\text{Cu}(\textit{opba})]_3 \cdot 6\text{DMSO} \cdot 1\text{H}_2\text{O}$, exhibiting a transition at $T_c = 15$ K towards a ferromagnetically ordered state (Stumpf *et al* 1993a), the T_c value of which rises to 22.5 K when all the solvent molecules are removed (Stumpf *et al* 1993a; Chavan *et al* 1996). Elucidation of structure of 1 : 2 Mn(II)Cu(II) compound $(\text{NBu}_4)_2\text{Mn}[\text{Cu}(\textit{opba})]_2$ by us revealed a new crystallographic arrangement among the class of '*opba*' molecular magnets (Neels *et al* 2001), which were known till then to exist as one-dimensional chains when the ratio is 1 : 1, or as planar graphite-like sheets for the 2 : 3 ratio.

An effective process for assembling spin-bearing precursors is when polymerization is associated with dehydration. When the precursors are linked to each other after polymerization, the interaction involving a spin carrier A from a given unit and a spin carrier B from the adjacent unit becomes large, and the resulting ground state spin of the polymer $[\text{AB}]_n$, where n is the number of units, becomes $n(S_A - S_B)$. If n is infinite and the system is three-dimensional, a long-range ferrimagnetic ordering should occur, which can also be considered as a ferro-

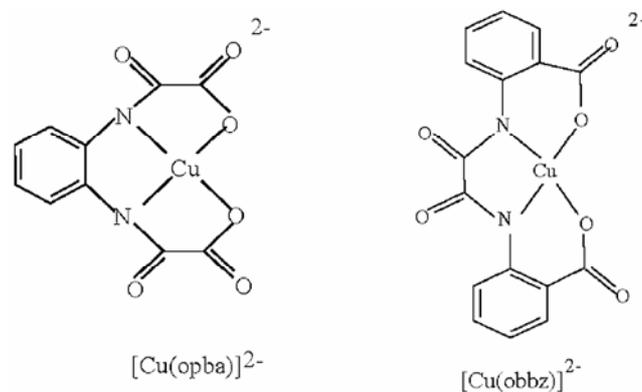


Figure 4. A schematic of the copper dianion precursors $[\text{Cu}(\textit{opba})]^{2-}$ and $[\text{Cu}(\textit{obbz})]^{2-}$, where '*opba*' and '*obbz*' stands for *ortho*-phenylenebis(oxamato) and oxamido bis(benzoato), respectively.

magnetic coupling of the ground state spin $|S_A - S_B|$ of the AB units, which in the case of Mn(II)Cu(II)-based compounds is, $S = 2$. The compound $\text{MnCu}(\text{obbz}) \cdot 5\text{H}_2\text{O}$ (Nakatani *et al* 1989), obtained by the polymerization of ferrimagnetic molecular precursor units prepared by reacting the copper dianion $[\text{Cu}(\text{obbz})]^{2-}$ (figure 4), where *obbz* is the ligand oxamido bis(benzoato), with Mn(II) ions, exhibits a minimum at 44 K in its $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility and T the temperature, a signature of a one-dimensional ferrimagnet, and a sharp maximum at 2.3 K due to a three-dimensional antiferromagnetic ordering. Upon dehydration, it yields the monohydrate, $\text{MnCu}(\text{obbz}) \cdot \text{H}_2\text{O}$, which orders ferromagnetically below the critical temperature (T_c) of 14 K, due to the non-compensation of the magnetic moments on Mn(II) and Cu(II) (Nakatani *et al* 1989; Chavan *et al* 1995). Subsequently, Ni(II)-, Fe(II)- and Co(II)-based bimetallic chain compounds have also been synthesized using the $[\text{Cu}(\text{obbz})]^{2-}$ precursor (Nakatani *et al* 1989; Chavan *et al* 1995; Larionova *et al* 1997; Kahn *et al* 1999; Sra *et al* 2001). Using the mixed metal ion spin-organic radical spin approach, a 46 K magnet was synthesized by the reaction of a trinitroxide radical, with three parallel spins ($S = 3/2$), with bis(hexafluoroacetylacetonato)Mn(II), $[\text{Mn}(\text{II})(\text{hfac})_2]$ (Inoue *et al* 1996).

The Mn(II) ion is not able to prevent the domains from rotating freely under an applied field because it is a magnetically isotropic ion. Most of the Mn(II)Cu(II)-based magnets, though exhibit a high value of T_c (12 to 30 K), are soft ferromagnets, therefore, exhibiting rather narrow magnetic hysteresis loops below T_c with rather weak coercive field values ($H_c < 50$ Oe at 4.2 K) (Stumpf *et al* 1993a, b, 1994a, b). The same is generally true for Fe(II)Cu(II)-based magnets. It is the coercivity of a magnet which confers a memory effect on it. Stronger coercive fields are expected for Co^{2+} -based molecular magnets where Co^{2+} ion in distorted octahedral environment, being magnetically anisotropic, can assume preferred orientations. Replacing Mn(II), with an orbital singlet state (${}^6\text{A}_1$), by Co(II) with an orbital triplet ground state (${}^4\text{T}_1$) in $(\text{cat})_2\text{Mn}_2[\text{Cu}(\text{opba})]_3 \cdot \text{S}$ (Stumpf *et al* 1993a, b, 1994a) resulted in a dramatic rise in coercivity. For instance, $H_c = 3000$ Oe for $(\text{NBu}_4)_2\text{Co}_2[\text{Cu}(\text{opba})]_3 \cdot 3\text{DMSO} \cdot 3\text{H}_2\text{O}$ and 3100 Oe for $(\text{rad})_2\text{Co}_2[\text{Cu}(\text{opba})]_3 \cdot 0.5\text{DMSO} \cdot 3\text{H}_2\text{O}$ (Stumpf *et al* 1994b), where 'rad' stands for the radical cation 2-(4-N-methylpyridinium)-4,4,5,5-tetramethylimidazolin-1-oxyl 3-oxide and 'opba' denotes ortho-phenylene-bis(oxamato).

$[(\text{Etrad})_2\text{Co}_2\{\text{Cu}(\text{opba})\}_3(\text{DMSO})_{1.5}] \cdot 0.25\text{H}_2\text{O}$ exhibits high coercivity, up to 24 kOe at 6 K (Vaz *et al* 1999). These values are much higher than that for the commercial atom-based materials, Fe_2O_3 or CrO_2 . The synthetic procedures employed to obtain molecular materials are different from those employed in solid state chemistry and the molecular crystal lattice is characteristically soft, as compared to the ionic/metallic lattices. We have exploited these attributes

to demonstrate that for certain molecular magnets, assembled from Co(II)Cu(II) based ferrimagnetic chains, it is possible to modify the magnetic properties dramatically and reversibly through a mild dehydration-rehydration process, and have named this class of compounds as molecular magnetic sponges (Turner *et al* 1996; Larionova *et al* 1997; Chavan *et al* 1998; Kahn *et al* 1999). This is because they show 'sponge'-like characteristics, viz. a reversible cross-over under dehydration to a polymerized long range magnetically ordered state with spontaneous magnetization, and transforming back into the isolated units underlying the initial non-magnetic phase by reabsorbing water, i.e. re-hydration of both non-coordinated and coordinated water molecules (figure 5). Coercivity values for these sponges are high and for some of them a colour change, too, occurs reversibly and simultaneously with the change in magnetic properties at the transition temperature corresponding to the dehydration-rehydration process. In the case of $\text{CoCu}(\text{obbz}) \cdot n\text{H}_2\text{O}$, we confirmed that the Co-O bonds could be broken and created without destroying the essence of the molecular architecture. The main features of the four Co(II)Cu(II)-based molecular magnetic sponges synthesized by our group, viz. $\text{CoCu}(\text{pbaOH})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$, $\text{CoCu}(\text{pba})(\text{H}_2\text{O})_3 \cdot 2\text{H}_2\text{O}$, $\text{CoCu}(\text{obbz})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ and $\text{CoCu}(\text{obze})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ are high values of T_c (38, 33, 25 and 25 K, respectively) and H_c (5.66, 3, 1.3 and 1 kOe, respectively).

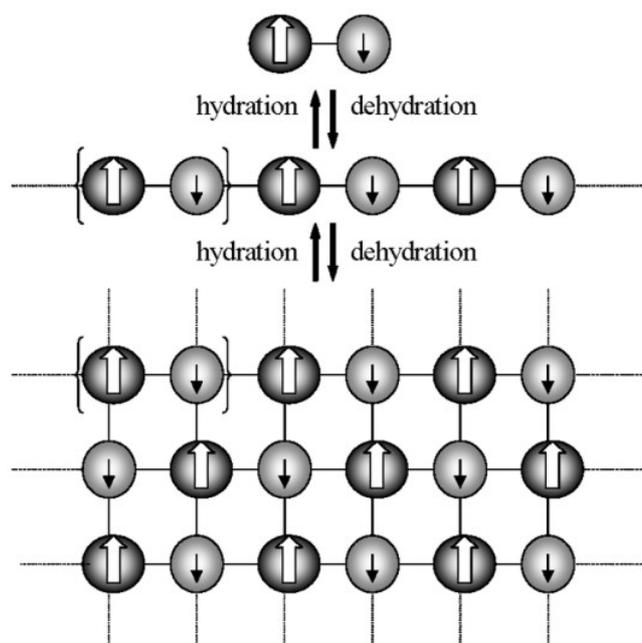


Figure 5. The dehydration-polymerization process, typically applicable to the reversible sponge-like behaviour of the molecular magnet, $\text{CoCu}(\text{obbz}) \cdot n\text{H}_2\text{O}$. Reproduced from Kahn *et al* (1999) with permission from Wiley-VCH Verlag GmbH & Co. KgaA (copyright).

4. Polycyanometallates

A unique feature of the molecular magnets is that they are usually weakly coloured unlike the opaque classical magnets. Design of molecular ferromagnets of low density that are transparent and have a tunable high T_c is a cherished goal and photomagnetic switching has been reported in molecular magnets, especially where hexacyanometallates, $[M(CN)_6]^{n-}$, are used as molecular building blocks. Most metal hexacyanometallates have a cubic (*fcc*) structure and are analogues of the well-known Prussian Blue salt, $Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot 15H_2O$, whose structure was described by Ludi and Gudel (1973) as highly disordered cubic cell consisting of alternating ferrocyanide and ferric ions, with linear $Fe^{III}-N-C-Fe^{II}$ bridges. In the case of Prussian Blue analogues, $A_k[B(CN)_6]_x \cdot zH_2O$, the transition metal ions, A and B, are situated at the corners of the cube (figure 6), and the cyanide groups bridge the metal ions along the cube edges, the metal ions being octahedrally coordinated by the nitrogen or carbon end of the cyanide group. Depending on the charged-state of the N- and C-coordinated metal ions, a certain number of cations can occupy interstitial positions for charge compensation. These interstitial metal ions may be the same as the N- and C-coordinated metal ions, or they may be alkali metal ions.

The cyano bridge is known to mediate strong anti-ferromagnetic or ferromagnetic interactions (Entley and Girolami 1995). T_c values above room temperatures, viz. 376 K (Holmes and Girolami 1999), have been reported for hexacyanometallates but their high *fcc* symmetry is often accompanied by inherent disorder among different

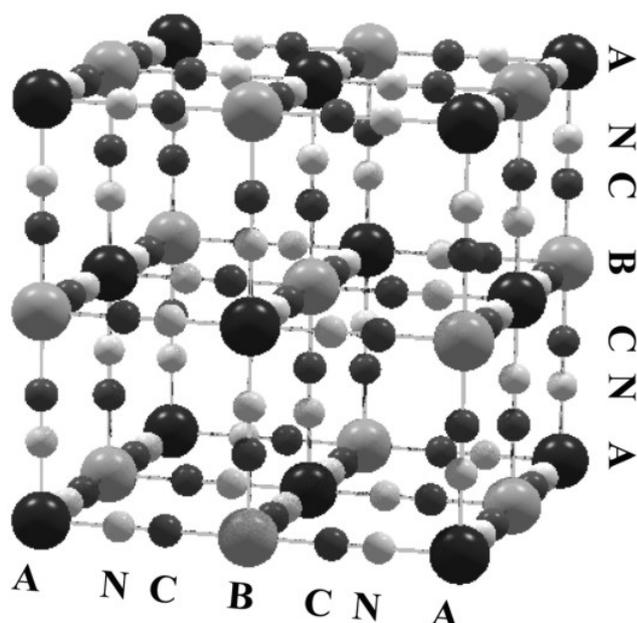


Figure 6. *FCC* structure of Prussian Blue analogues, $A[B(CN)_6]_x \cdot zH_2O$. For clarity, H and O atoms are not shown.

cationic sites, making it difficult to grow single crystals or to study any magnetic anisotropy. In the PBAs, $A_m[B(CN)_6]_n \cdot zH_2O$ with $m > n$, the $[B(CN)_6]$ vacancies, which maintain the required charge neutrality, and partial occupancies of the non-coordinated water molecules constitute the main structural defects. As the magnetic properties of a compound depend on its crystal structure, the study of defects and disorders ought to be carried out systematically for proper understanding of the possible correlation between the structural defects and magnetic ordering. Substitution of Ru at Ni-site introduces a substitutional disorder in $Ru_xNi_{3-3x/2}[Cr(CN)_6]_2 \cdot zH_2O$ compounds. The effect of Ru^{3+} ion substitution on the structural defects/disorders in this system has been studied by us (Kumar *et al* 2007) employing X-ray diffraction, IR spectroscopy, d.c. magnetization and neutron diffraction. The influence on T_c with increasing substitution of Ru can be explained on the extent of the structural disorder, and this disorder itself was estimated by us from the Reverse Monte Carlo treatment of the observed neutron diffraction patterns.

We have demonstrated that one can grow crystals of Prussian Blue Analogues (NiHCF, CoHCF) at the air-water interface using a surfactant (octadecylamine) monolayer as a template (Choudhury *et al* 2002, 2003; Bagkar *et al* 2006a). The AFM image of the crystalline film of cobalt-hexacyanoferrate grown over three days showed a granular structure (grain size, ~ 200 nm). SQUID magnetometry on nanocrystals of nickel hexacyanoferrate (NiHCF) transferred as a monolayer showed that they were magnetic below 20 K. Sodium hexametaphosphate (HMP) stabilized nickel hexacyanoferrate

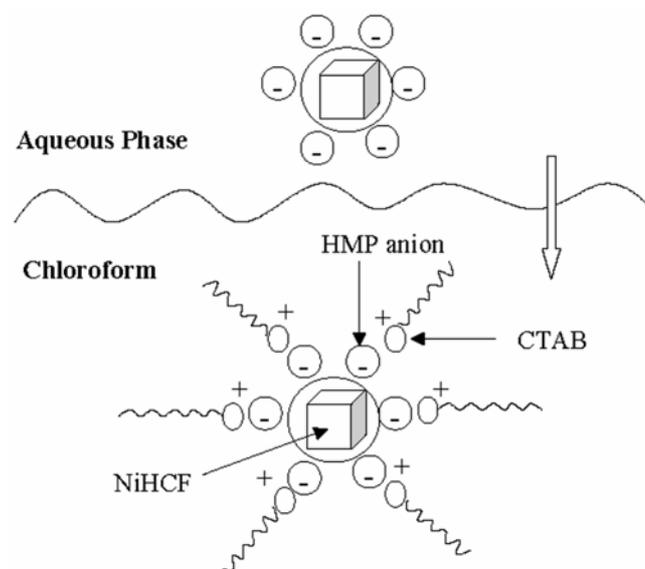


Figure 7. Schematic representation of extraction of NiHCF nanoparticles from the aqueous phase to the organic phase. Reproduced from Bagkar *et al* (2004), with permission of The Royal Society of Chemistry (copyright).

(NiHCF) nanoparticles were prepared in aqueous solution and were successfully extracted into an organic phase (figure 7) using cetyltrimethylammonium bromide (CTAB) as the surfactant (Bagkar *et al* 2004). Potassium ion sensing action was demonstrated by us by employing cyclic voltammetry and impedance measurements on NiHCF–DODA films (DODA: dioctadecyl dimethylammonium bromide) (Bagkar *et al* 2006b). We have also used the double-stranded CT–DNA as a template to self-assemble crystals of nickel hexacyanoferrate, $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2 \cdot 14\text{H}_2\text{O}$, with an average diameter of 400 nm. As a function of temperature, the morphology of NiHCF crystals can change and they self-assemble into linear ropes, spheres, and dendritic structures (Bagkar *et al* 2008).

An increase in the surface to volume ratio, due to a reduction in particle size, and inter-particle interactions play an important role in deciding the magnetic properties of nanoparticle systems. We have compared the observed magnetic behaviour of $\text{Fe}[\text{Fe}(\text{CN})_6 \cdot x\text{H}_2\text{O}]$ nanoparticles (mean diameter ~ 50 nm) prepared using a water-in-oil microemulsion technique, with that of its bulk counterpart. A magnetic ordering temperature, T_C of 13.0 K was estimated from the magnetization data, which is low compared to that for the bulk polycrystalline sample, $T_C = 17.4$ K, and suggests the presence of a weak surface spin disorder in the ferromagnetically ordered cores of nanoparticles, the surface spin-disorder causing a spin glass behaviour (Mukadam *et al* 2008).

4.1 Negative magnetization and pole-reversal

A crossover of the field-cooled magnetization from positive to negative below the magnetic ordering temperature is a unique feature exhibited by molecular multi-cation ferrimagnets (Chavan *et al* 1996; Mathoniere *et al* 1996); and by Prussian Blue Analogues (Ohkoshi *et al* 1999). We have recently provided the first neutron magnetic structure evidence towards the microscopic understanding of the negative magnetization phenomenon in the PBA, $\text{Cu}_{0.73}\text{Mn}_{0.77}[\text{Fe}(\text{CN})_6] \cdot z\text{H}_2\text{O}$ ($T_C = 17.9$ K). The Reverse Monte Carlo analysis, combined with the Rietveld refinement technique shows an antiferromagnetic ordering of Mn moments with respect to the Cu as well as the Fe moments (Kumar *et al* 2008). Apart from temperature-dependent pole-reversal it also exhibited reversible (bipolar) switching of magnetization under low magnetic fields, which leads to the reversal of magnetic entropy change (ΔS_m), causing a bipolar magneto-caloric effect (MCE), i.e. both positive and negative MCEs below the magnetic ordering temperature. These novel phenomena related to pole reversal could find applications in novel devices such as magnetic memory, thermomagnetic switches, and magnetic cooling/heating based constant temperature baths.

Apart from the fact that a molecule is the ultimate unit for data-storage, the design of molecular magnets has

also opened the doors for the unique possibility of designing poly-functional materials, at the molecular level such as those exhibiting ferromagnetic behaviour and second-order optical nonlinearity (Benard *et al* 2000), or, liquid crystallinity and magnetism (Binnemans *et al* 2000). In collaboration with Prof. Inoue's group from Japan, we designed a three-dimensional chiral, transparent ferrimagnet, $\text{K}_{0.4}[\text{Cr}(\text{CN})_6][\text{Mn}(\text{S}-pn)(\text{S}-pn)\text{H}_{0.6}]$ with $T_C = 53$ K, where (S)-pn stands for (S)-1,2-diaminopropane (Inoue *et al* 2001), and there have been many additions to this class of bi-functional magnets, since.

4.2 Hepta/octacyanates

An alternate strategy adopted by us to grow single crystals of cyanometallates was to employ the heptacyanate anion $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ as a precursor because its pentagonal bipyramidal coordination sphere is incompatible with a cubic lattice. Reaction of Mn^{II} ions with the heptacyanate $[\text{Mo}^{\text{III}}(\text{CN})_7]^{4-}$ precursor led to lowering of symmetry and high values of Curie temperatures ($T_C = 51$ K) arising from a ferromagnetic interaction between the low spin Mo^{3+} and the high spin Mn^{2+} through the $\text{Mo}^{\text{III}}\text{--C--N--Mn}^{\text{II}}$ bridges. The use of a macrocycle reduced the symmetry further by imposing hepta-coordination on Mn^{II} ion, too, but a low T_C (3K) for the compound $[\text{Mn}^{\text{II}}L]_6[\text{Mo}^{\text{III}}(\text{CN})_7][\text{Mo}^{\text{IV}}(\text{CN})_8]_2 \cdot 19.5\text{H}_2\text{O}$, where L is the macrocycle (figure 8), which was attributed to the existence of diamagnetic Mo^{4+} along certain --CN-- bridges, in addition to the paramagnetic Mo^{3+} (Sra *et al* 1999). We also demonstrated the use of octacyanometalates as versatile building blocks (Sra *et al* 2000). Ohkoshi *et al* (2006) reported reversible switching between paramagnetic and ferromagnetic states for $\text{Cu}_2[\text{Mo}^{\text{IV}}(\text{CN})_8] \cdot 8\text{H}_2\text{O}$ solid by irradiating it with visible lights, which is very encouraging. However, its T_C is low (25 K), and to be practically useful, the T_C value in the extended network must be raised to above room temperature.

5. Open-framework magnetic structures

Magnetic zeolitic structures offer excellent conditions to encapsulate different functional systems with conducting, optical, chiral and NLO properties, among others. It is desirable, therefore, to evolve a synergism of magnetic and nanoporous behaviour, together with the molecular characteristics of coordination polymers, as a new route to the development of multifunctional molecular materials. Veciana and co-workers (MasPOCH *et al* 2003, 2004) have fabricated a nanoporous molecular magnet, $\text{Cu}_3(\text{PTMTC})_2(\text{py})_6(\text{CH}_3\text{CH}_2\text{OH})_2(\text{H}_2\text{O})$, [PTMTC being a radical, viz. polychlorinated triphenylmethyl with three carboxylic groups] with reversible solvent-induced mechanical and magnetic properties. This compound has an open-framework structure, with very large pores (2.8–3.1 nm)

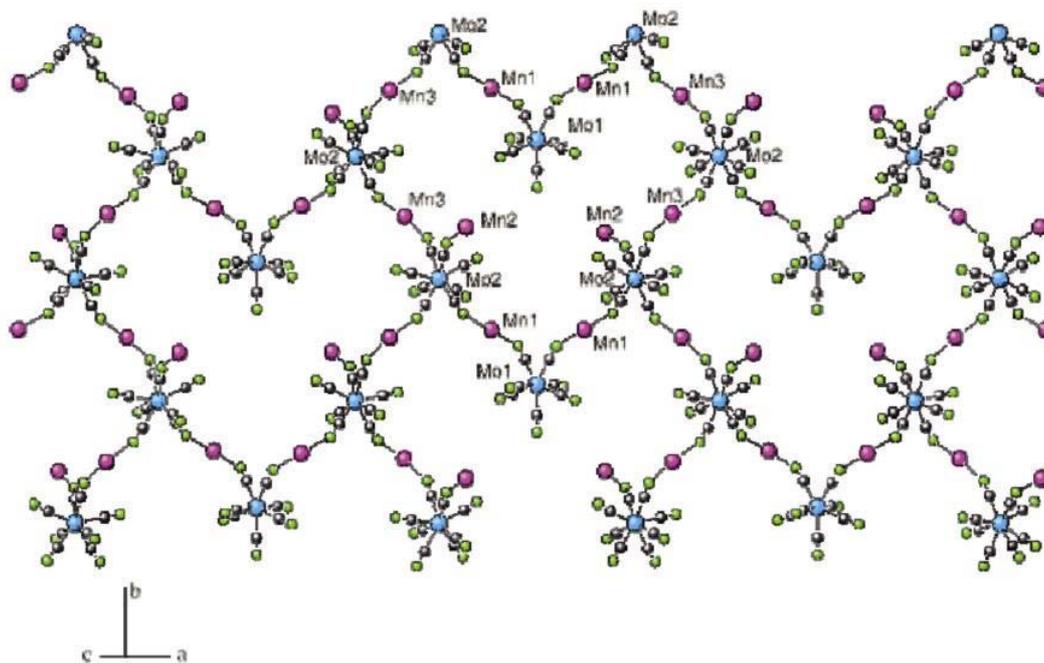


Figure 8. The compound $[\text{Mn}^{\text{II}}\text{L}]_6[\text{Mo}^{\text{III}}(\text{CN})_7][\text{Mo}^{\text{IV}}(\text{CN})_8]_2 \cdot 19 \cdot 5\text{H}_2\text{O}$, where L is a macrocycle. Reproduced from Sra *et al* (1999), with permission from Wiley-VCH Verlag GmbH & Co. KGaA (copyright).

and bulk magnetic ordering. Reversible behaviour has only been observed for ethanol and methanol, showing the selectivity of this sponge-like magnetic sensor.

6. Single molecule magnets

Synthesis activity in molecular magnets has recently led to the development of what are known as single molecule magnets (SMMs), such as $\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4$, with large spin ground state (e.g. $S = 10$). Crystals of SMMs function as collections of monodisperse nanomagnets, unlike other nanoscale magnetic materials which have size distribution. As magnetic aggregates, the SMMs are examples of 'zero-dimensional' systems, though essentially mesoscopic, and therefore, lie on the border between the classical and quantum regimes, serving as model systems to study new sources of magnetic phenomena including quantum tunneling, quantum coherence, QuBits, magnetocaloric effect, etc (Friedman *et al* 1996; Barbara and Gunther 1999; Leuenberger and Loss 2001). More recently, there is much interest also in what is known as single-chain magnets (SCM), which are ferromagnetic or ferrimagnetic chains, and mostly Ising systems. A typical example of SCMs is the cobalt(II)-organic radical polymer $\text{Co}(\text{hfac})_2\text{NITPhOMe}$, nicknamed 'CoPhOMe' (Bogani *et al* 2005). Relaxation in these isotropic ferromagnetic chains follow Glauber's dynamics, and no quantum tunneling is observed, unlike in SMMs. We have, however, studied slow magnetic relaxations in Mn(III)

tetra(*ortho*-fluorophenyl)porphyrin-tetracyanoethylene, an anisotropic Heisenberg chain compound consisting of ferrimagnetic chains, in which magnetic moments of Mn ion ($S = 2$) in the centre of a porphyrin disc and of a tetracyanoethylene radical ($s = 1/2$), are antiferromagnetically coupled (Balanda *et al* 2006).

7. Current scenario and future perspectives

Magnets fabricated from molecules are unique to magnetism. They exhibit all the phenomena observed in conventional transition-metal and rare earth-based magnets, and more, by exhibiting liquid crystallinity, chirality, low density, solubility, spin-crossover (Krober *et al* 1993), negative magnetization (Mathoniere *et al* 1994; Chavan *et al* 1996; Kumar *et al* 2008), photoinduced magnetization/switching due to their coloured nature (Hashimoto and Ohkoshi 1999; Sastry *et al* 1999; Pejakovic *et al* 2002), and possibility of modulation of their properties electrochemically, all of which are arising from their characteristic molecular nature. In this context, an exciting development is the fabrication of a tri-functional phenalenyl-based neutral radical, by Itkis *et al* (2002), which exhibits magneto-opto-electronic bistability with hysteresis loops centred near 335 K, thus opening the possibility for new type of electronic devices, where multiple physical channels can be used for writing, reading, and transferring information.

Some groups are attempting to utilize the high degree of directionality of hydrogen bonding between open-shell

molecules to obtain supramolecular self-organization aimed at achieving new molecular ferromagnets. There is also a substantial activity and progress in the development of spin-crossover compounds that exhibit magnetic bistability (Krober *et al* 1993; Fujita and Awaga 1999), which is at times accompanied by a change of colour, too. Then, there is a continuing quest for discovering new molecular materials which can exhibit long range magnetic order at room temperature (or even above), the earliest example of which was $V[TCNE]_{x,y}CH_2Cl_2$ ($x \sim 2$; $y \sim 1/2$), a disordered, amorphous magnet depicting a T_c of ~ 400 K, but extremely water/air sensitive (Zhang *et al* 1996). Jain *et al* (2007) recently reported the synthesis of three air-stable Ni_2A -based metal-organic magnets (T_c above room temperature), by reacting a metal (M) precursor complex *bis*(1,5-cyclooctadiene)nickel with organics $A = TCNE$ (tetracyanoethylene), TCNQ (7,7,8,8-tetracyanoquinodimethane) or DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone). A structural model for these materials is not available, though spectroscopic features suggested that the organic ligands are σ -bound to nickel. However, subsequent study by Miller and Pokhodnya (2007) has negated these findings, and proposed that the black powdery magnetic material made upon dissolution of $Ni(COD)_2$ in CH_2Cl_2 presumably consists of 'nano'- or bigger-sized particles of nickel metal, and lacks the 'organic' species which may entitle it to be called a molecular magnet.

Unique combination of tunability, processability, and other attributes of molecular lattices hold promise for molecule-based magnets for future applications, but much progress has to be made before that happens because of certain vexing issues like their air stability, degradability (in some cases) and processability, phenomena unique to molecular lattices. Perhaps, one has to learn more from the self-assembly processes of Nature, which synthesizes monodisperse nano-scale single-domain magnetite crystals in magnetotactic bacteria, which collectively behave as bar magnets, imparting the bacteria an ability to orient and migrate along geomagnetic field lines. These nanocrystals form in intracellular magnetic structures, called magnetosomes, via a biological mechanism that controls their biomineralization (Philipse and Mass 2002). Biogenic magnetite has also been detected in animals (honeybees, birds, salmon, newts, sea turtles, spiny lobsters etc), which use them to transduce geomagnetic field information to the nervous system for 'homing' action (Lohmann and Johnsen 2000).

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