Molecules to Materials

3. Molecular Magnetic Materials

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Molecular materials represent an area of fruitful interaction between synthetic chemistry, solid state physics and materials science. This article discusses the development of magnetic materials based on metal complexes, organometallic compounds and organic radicals.

Introduction

Previous articles of this series were on:
1. Design and fabrication of functional molecular solids, Vol.3, April 1998.
2. Liquid crystals and molecular conductors, Vol.3, May 1998.

In Part 1 of this series of articles the historical background of the development of molecular materials was presented. The subtle interactions exploited in their design and the various methods of fabrication were reviewed. Part 2 provided an overview of liquid crystals and molecular semiconductors, conductors and superconductors. In the present article we focus attention on molecular magnetic materials.

We outline the early development of magnetic materials based on coordination polymers and molecular systems in which metal ions serve as the source of the magnetic moment. The intense research efforts that followed to develop magnetic materials based on organic radicals are reviewed.

Molecule-based Magnetic Materials

Please Note in part 2.
1) Page 17 last line was inadvertently omitted, the same is given below: '... 6.3×10^5 Scm^{-1} and 2.2×106 Scm^{-1}. However, at lower ...'

2) Figure 5: The structure on the right is TTF$^+ \cdot$ (and not TTF^{+-}).

3) Figure 6: Real 'unpaired e$^-$' instead of unpaired $^-$e.

For centuries after the discovery of the naturally occurring magnet, Fe_3O_4, most of the magnets that were fabricated and used were based on the compounds and alloys of elements such as iron, cobalt, nickel and gadolinium which are themselves ferromagnetic in their bulk state (*Box 1*). Therefore the idea of designing and fabricating a ferromagnetic solid starting with simple paramagnetic units and controlling its magnetism using synthetic manipulations, emerged as a fascinating problem. Naturally, the initial attempts in this direction were based on paramagnetic

## Box 1. Paramagnetism, Ferromagnetism, Antiferromagnetism and Ferrimagnetism

Atoms, ions, molecules and solids having unpaired electrons when brought under the influence of a magnetic field, develop a net magnetisation (alignment of the spins) and are attracted into the field. Such materials are described as paramagnetic. In the absence of unpaired electrons, paramagnetism can still show up if the nucleus has a spin; however, nuclear paramagnetism is usually much weaker than electron paramagnetism. Systems having only paired electrons are described as diamagnetic and these are repelled from a magnetic field. Most organic molecules are diamagnetic. Metal ions such as Mn^{2+} and Cu^{2+} and their complexes, organic free and ion radicals and molecules such as O_2 and NO are good examples of paramagnetic systems. Paramagnetism is characterised by the magnetic susceptibility, χ, the variation of the magnetisation with respect to the applied magnetic field. The paramagnetic susceptibility varies inversely with the temperature and this behaviour is known as the *Curie law*.

PARAMAGNET   FERROMAGNET   ANTIFERROMAGNET
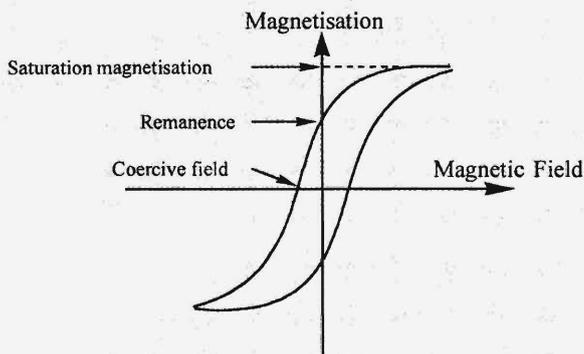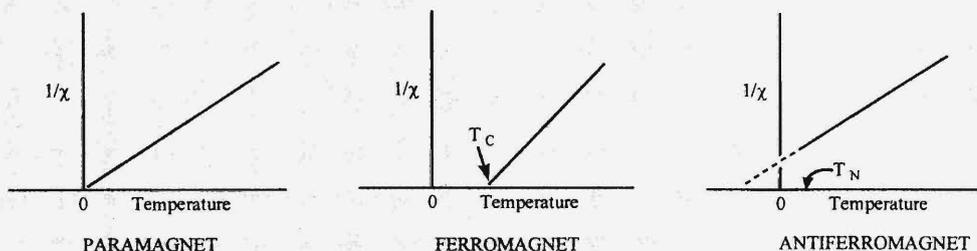
HYSTERESIS IN A FERROMAGNET

In some materials such as iron, cobalt and nickel the spins can remain aligned parallel, even in the absence of an external magnetic field. This is possible due to an internal field arising as a result of a cooperative interaction between the spins. Such materials having a spontaneous magnetisation are referred to as ferromagnets. It can also happen that the internal field causes each spin to align antiparallel with respect to its nearest neighbours. Such a phenomenon is called anti-ferromagnetism. Famous examples of antiferromagnets are metal compounds such as MnO, MnF_2 and NiO. Ferrimagnetism is a special case of antiferromagnetism, where the neighbouring spins which are aligned antiparallel are of unequal magnitude so that a total cancellation of the magnetic moments does not occur. The best example of a ferrimagnet is the mineral 'magnetite' (Fe_3O_4). At certain characteristic temperatures, ferro, antiferro and ferrimagnets undergo phase transition to the paramagnetic state. This temperature in the case of a ferromagnet is referred to as the *Curie temperature*. In the paramagnetic regime of ferromagnetic materials, the susceptibility rise with lowering temperature is stronger than in the case of simple Curie paramagnets. In the paramagnetic regime of antiferromagnets (*i.e.* above its phase transition temperature, namely the Néel temperature, T_N), the susceptibility increase on lowering temperature is weaker than in paramagnets. Several other kinds of complex magnetic orderings are possible in solids.

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When a ferromagnet is subjected to an increasing magnetic field, the magnetisation increases and reaches a constant value known as the saturation magnetisation. If the applied field is then reversed, the magnetisation decreases but does not become zero when the applied field is reduced to zero. The magnetisation at zero field is called *remanence*. The reversed magnetic field required to bring the magnetisation back to zero is known as the *coercive field*. This nonreversible behaviour of the magnetisation against the applied magnetic field is termed *hysteresis* and is an important characterisation of a ferromagnet. The magnitude of the spontaneous magnetisation, remanence and coercive field determine the type of application that a ferromagnet can be put to.

metal ions as the spin centres. The basic idea is to build chains or sheets of these metal ions with appropriate bridging ligands so that the desired magnetic interactions between the ions could be achieved. The magnetic coupling between the metal ion spins is often controlled by what is known as the 'superexchange interaction', in which the spins communicate through the intervening ligand orbitals. Hence the nature of the participating ligand orbitals and their orientation with respect to the metal orbitals are crucial. The metal ion – ligand – metal ion angles and metal ion – metal ion distances play a decisive role in determining the nature of spin interactions. Impressive success was achieved in this area leading to the fabrication of a variety of metal coordination polymers with interesting magnetic properties; an example is the ferromagnetic Cu(II) chain polymer shown in *Figure 1*. Research on these materials has also provided

Figure 1. Examples of ferromagnetic and ferrimagnetic coordination polymers.

Ferromagnetic Cu(II) chains

$R = C_6H_{11}$

Ferrimagnetic Cu(II)-Mn(II) chain
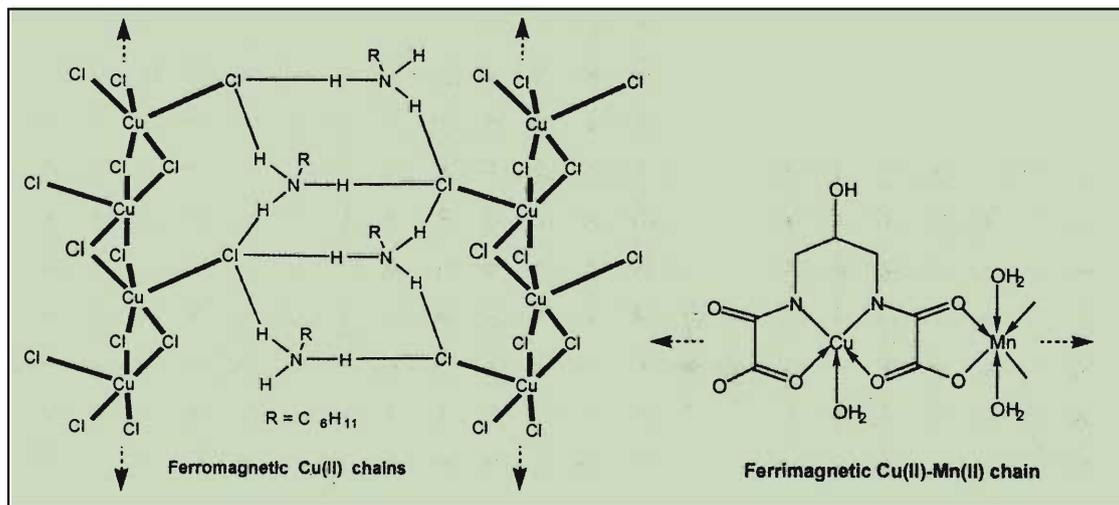
a sound understanding of the fundamental principles of magnetic interactions in low-dimensional lattices.

The dominant tendency towards antiferromagnetic coupling of spins arising from the bonding interaction between orbitals is a serious problem in the design of ferromagnetic materials. However, this inherent antiferromagnetic interaction has been exploited by designing ferrimagnetic polymers based on systems such as the mixed Mn-Cu complexes (*Figure 1*) wherein the Mn^{2+} and Cu^{2+} ions bear respectively 5/2 and 1/2 spins.
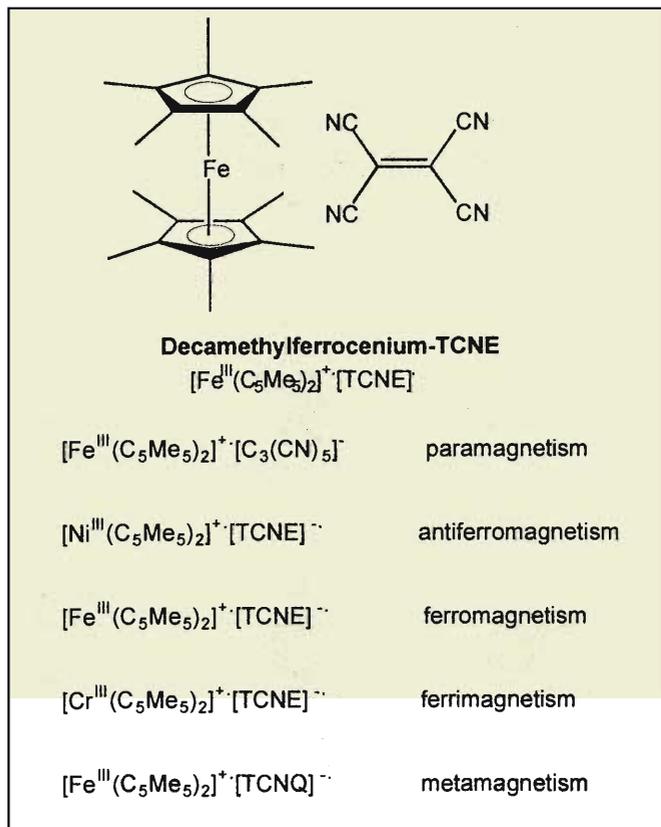
In all these systems the spin is resident on a metal ion centre which is not amenable to chemical modifications. Any fine-tuning of the magnetism is based on the modifications of the bridging ligands or counterions. Simultaneously with the development of these magnetic materials based on coordination polymers, theoretical ideas were mooted which suggested the possibility of designing ferromagnetic interactions between molecular spin systems; the basic spin units would be organic free radicals or molecular ion radicals or even paramagnetic organometallic systems. The first success in this direction was the discovery of a ferromagnetic phase transition at about 4.8 K in the charge transfer complex, decamethylferrocenium-TCNE (*Figure 2*). This could be considered the first molecule-based magnetic material. The versatility of molecular materials is demonstrated by the profound changes in the magnetic properties effected by alterations of the components in this charge transfer complex (*Figure 2*). The latest in this class of materials is the TCNE complex of vanadium containing molecules of the solvent, dichloromethane ($V(TCNE)_x.yCH_2Cl_2$). This compound is found to be ferromagnetic at ambient temperatures; however, it is handicapped by extreme chemical reactivity and the consequent need to preserve it under inert atmosphere. The origin of ferromagnetism in these materials has been a subject of considerable debate. The contribution of high spin charge transfer excited states was considered important in the mechanisms proposed initially. It has been argued later that the direct interaction of spin densities between the radical

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The first success in the design of molecule based magnets was the discovery of a ferromagnetic phase transition at about 4.8 K in the charge transfer complex, decamethyl-ferrocenium - TCNE.

Decamethylferrocenium-TCNE
$[Fe^{III}(C_5Me_5)_2]^{+\cdot}[TCNE]^{\overline{}}$

$[Fe^{III}(C_5Me_5)_2]^{+\cdot}[C_3(CN)_5]^{-}$	paramagnetism
$[Ni^{III}(C_5Me_5)_2]^{+\cdot}[TCNE]^{\cdot\cdot}$	antiferromagnetism
$[Fe^{III}(C_5Me_5)_2]^{+\cdot}[TCNE]^{\cdot\cdot}$	ferromagnetism
$[Cr^{III}(C_5Me_5)_2]^{+\cdot}[TCNE]^{\cdot\cdot}$	ferrimagnetism
$[Fe^{III}(C_5Me_5)_2]^{+\cdot}[TCNQ]^{\cdot\cdot}$	metamagnetism

components is more significant. We discuss the latter mechanism in the following section.

Organic Magnetic Materials

Fabrication of a completely metal-free ferromagnet continued to be a challenge for materials chemists. Since purely organic radicals are not difficult to come by (*Figure 3*), the focus of the effort is to attain a ferromagnetic coupling of these spins in the solid state. Unlike in metal-based systems where the unpaired electron spin is largely confined to the metal ion centre, in molecular spin systems the unpaired electron is delocalised over the various atoms that constitute the molecule (compare with the discussion of charge distribution in Part 1 of this series). The contribution of each atomic site to the total spin is called the spin density at that site; these spin densities can be positive

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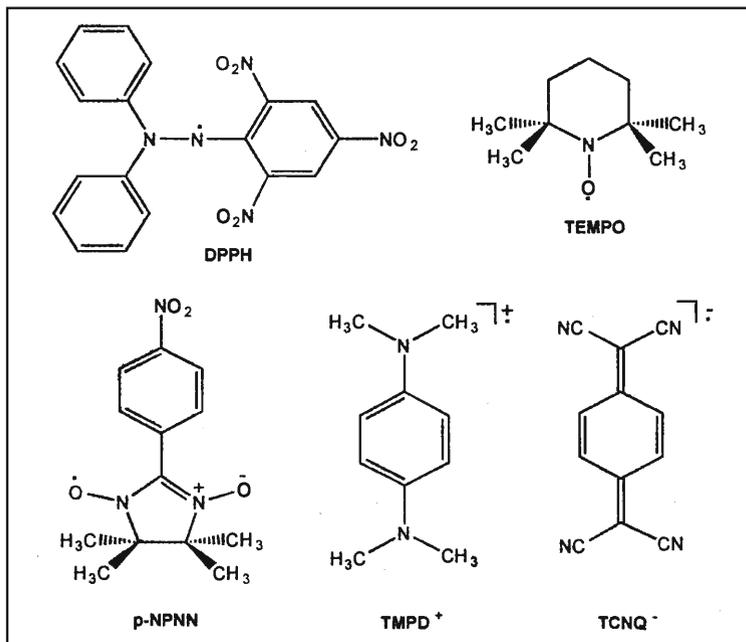
Figure 3. Examples of stable organic radicals, neutral and ionic.

or negative. As noted earlier, bonding tendencies between orbitals lead to preferential antiferromagnetic coupling of spins. One of the ideas proposed to obtain ferromagnetic spin coupling between molecular spin systems was to achieve a packing of the molecules in such a way that the regions of positive spin densities on one molecule would be in close contact with regions of negative spin densities on the neighbour and *vice versa*. This would make the products of spin densities on one radical with the spin densities on the second radical predominantly negative, which in turn coupled with the inherent negative exchange interactions lead to an effectively positive or ferromagnetic spin coupling.

The following is a fine experimental demonstration of how molecular design influences the nature of spin coupling between neighbouring radicals as dictated by the above principle. *p*-Nitrophenyldiphenylverdazyl (NPDV in *Figure 4*) is a stable radical that shows antiferromagnetic spin interactions at low temperatures as seen from the dip of the χT value. When an extra phenyl group is substituted on the verdazyl moiety to make NPTV, the low temperature spin interactions do a *volte-face* and become ferromagnetic. This interesting phenomenon

One proposal to obtain ferromagnetic coupling between molecular spin systems is to 'engineer' the packing of the molecules such that regions of positive spin densities of one molecule are close to regions of negative spin densities of its neighbours and vice versa.

Figure 4. Ferro and anti-ferromagnetic interactions in verdazyl based radicals.

Schematic plots of χT (magnetic susceptibility × temperature) vs. temperature.
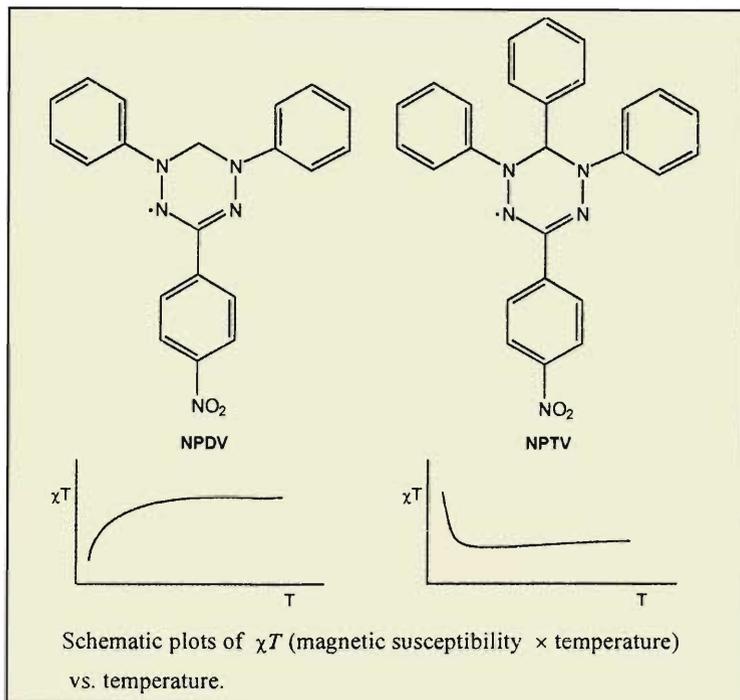
may be explained on the basis of the spin density interaction model. In the crystals of NPDV, the adjacent radicals have regions of the same spin densities in close proximity. The extra phenyl group in NPTV creates a steric hindrance that causes one molecule to slip with respect to its neighbour so that regions of opposite spin densities on the neighbouring radicals come close together. Thus the mode of spin coupling is antiferromagnetic in NPDV and ferromagnetic in NPTV. Though ferromagnetic spin interaction is obtained in NPTV, this crystal does not undergo a phase transition to a ferromagnetically ordered state. The idea of spin density interaction was successfully implemented in crystals of the stable radical, p-nitrophenylnitronylnitroxide (p-NPNN in *Figure 3*) which undergoes phase transition to a ferromagnetically ordered state below 1K. Though the Curie temperature is extremely low, this material provided the first example of a ferromagnet based on a purely organic molecule containing only C, H, N and O atoms. Several related systems based on the nitronylnitroxide radical are found to become ferromagnetic at similar low temperatures.

Crystals of p-NPNN below 1K provided the first example of a ferromagnet based on a purely organic molecule containing only C, H, N and O atoms.
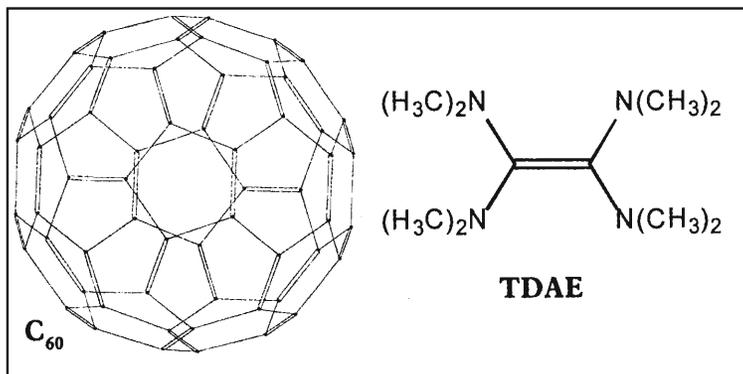
Another interesting case of an organic ferromagnet is based on, by now familiar, buckminsterfullerene (recall the C_{60} based superconductors mentioned in Part 2 of this series). The charge transfer complex between the powerful electron donor TDAE and C_{60} (*Figure 5*) was found to undergo a phase transition to a ferromagnetic state at about 16K. The resulting magnetic material is found to have small coercive fields and is termed a soft ferromagnet. Like the K-doped fullerene superconductors, this material also is plagued by extreme chemical reactivity.

There have been extensive efforts to realise experimentally, ferromagnetic spin interactions in organic oligo and polyradicals. A simple connectivity principle can·be used to visualise the magnetic interactions. If radical sites occur at locations separated by an odd number of π-electrons on a conjugated polymer, the resulting spin polarisation along the conjugation pathway should lead to a ferromagnetic alignment of the spins at the radical sites; when the sites are separated by an even number of electrons, the magnetic coupling will be antiferromagnetic (*Figure 6*). Basic entropy considerations show that long range ordering is

Figure 6. Representation of spin polarisation leading to ferro and antiferro-magnetic spin coupling in polyradical fragments.
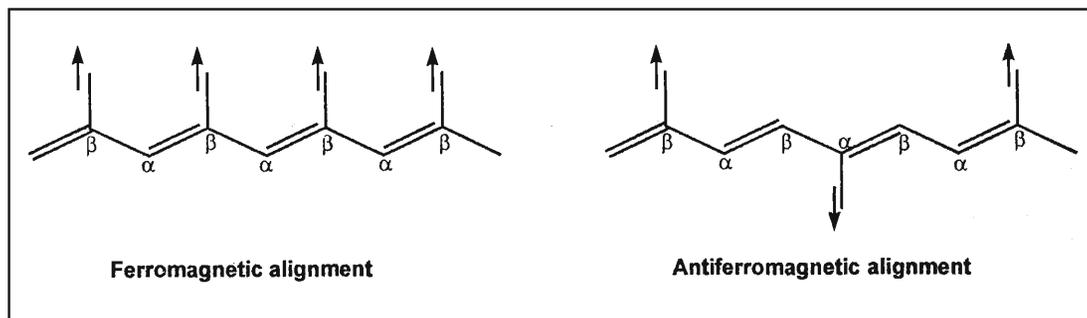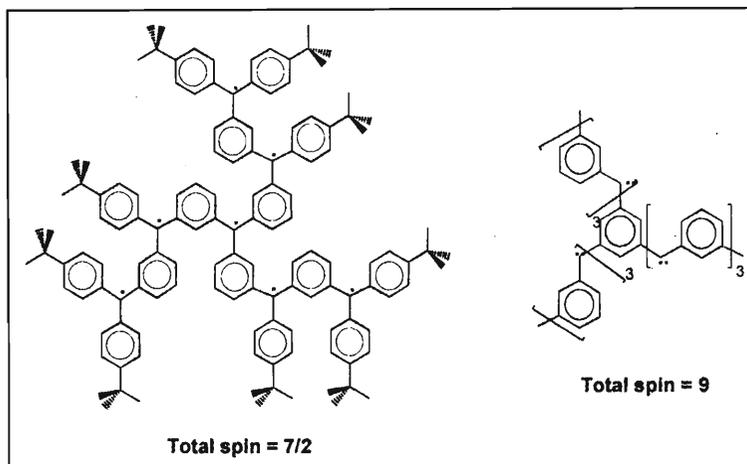

Ferromagnetic alignment   Antiferromagnetic alignment

Total spin = 9

Total spin = 7/2

impossible at finite temperatures in one-dimensional systems; taking cognisance of this, ferromagnetic materials may be designed based on π-conjugated two-dimensional networks with appropriately placed radical sites. These ideas have been discussed at the theoretical level in several different ways and extensive experimental work has been carried out. Even tentative claims of the synthesis of polymeric ferromagnets have been made and disproved later. Success has been limited to achieving small spin clusters based on some carefully designed and synthesised compounds; some interesting examples of high spin oligoradicals reported in the literature are provided in *Figure 7*. A well characterised organic polymer ferromagnet is yet to be realised. One of the major problems with organic polyradicals is the high chemical reactivity that results in extensive loss of the spin centres. Investigation of composite systems containing paramagnetic metal ion spin sites and stable organic radicals like nitrosyl molecules is becoming increasingly popular.

The promise of realising magnets based on materials such as organic polymers and organic charge transfer complexes continues to fascinate materials chemists. These novel materials would provide valuable insight into the mechanism of spin interactions between electrons in *s* and *p* orbitals on light atoms. Combination of the mechanical properties of polymers and magnetism would be invaluable in several device applications.

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Concluding Remarks

We have made a brief survey of the development of molecule-based magnetic materials. Once again the focus has been on the basic philosophy of optimisations at the molecular level leading to the control of bulk material properties. The unifying theme of how the assembly of the molecular units determines the material attributes is underscored throughout. In the case of magnetism, this has to do with the interaction of the spin densities of adjacent radicals. In the next part of the series, we will consider potential non-linear optical applications of molecules and polymeric systems.

Suggested Reading

O Kahn. *Molecular Magnetism*. VCH. New York, 1993.

Combination of the mechanical properties of polymers and magnetism would be invaluable in several device applications.

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I seriously say to you that business or job as an engineer is not the thing for me. It is totally foreign to my nature and radically opposed to my temperament and opinions. Physics is my line. I know I shall do great things here. For, each man can do best and excel in only that thing of which he is passionately fond, in which he believes, as I do, that he has the ability to do it, that he is in fact born and destined to do it. My success will not depend on what A or B thinks of me. My success will be what I make of my work. Besides, India is not a land where science cannot be carried on ... I am burning with a desire to do physics. I will and must do it some time. It is my only ambition. I have no desire to be a 'successful' man or the head of a big firm. There are intelligent people who like that and let them do it. I hear you saying 'But you are not Socrates or Einstein'. No – and that is what Berlioz's father said to Berlioz. Berlioz who is now accepted as one of the world's greatest geniuses and France's greatest musician. How can anybody else know at what time what one will do, if there is nothing to show. ... It is no use saying to Beethoven 'You must be a scientist for it is a great thing', when he did not care two hoots for science; or to Socrates 'Be an engineer; it is the work of an intelligent man'. It is not in the nature of things. I therefore earnestly implore you to let me do physics.

Homi J Bhabha in a letter to his father, 1928.