

Review Commentary

Principles of physical organic chemistry for molecular architecture and functions

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ABSTRACT: Application of the principles of physical organic chemistry to the construction of molecule-based magnets is discussed. Not only the magnetic structures of conventional magnets but also secondary and tertiary structures of biopolymers are instrumental in the molecular design. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: molecular architecture; molecule-based magnets; biopolymers

Chemists are builders by nature, master riggers of the atomic stuff. Single molecules of moderate complexity under their belt, they now long to move on to the construction of more elaborate structures.... Chemists have ingeniously designed small modular units of varying rigidity that can be assembled or assemble themselves, or that they wish would assemble, into larger, ordered structures of substantial complexity.

R. Hoffmann, *American Scientist* **82**, 308 (1994)

Since the establishment of physical organic chemistry in the 1950s, our understanding of the structures, physical properties, chemical reactivities and correlations among them of relatively small molecular entities has deepened considerably. It was the conviction of 20th century chemical scientists that macroscopic properties of molecular materials should be controlled by molecular and electronic structures of the constituent molecules. However, it is being increasingly accepted that some macroscopic properties cannot be represented by a sum of microscopic properties. Instead, some properties are more closely related to those of molecular assemblies on a mesoscopic scale. It is the organized molecular assemblies of these dimensions that are expected to develop most important and novel functions of molecular materials. A living organism, for example, forms proteins, nucleic acids and cells of mesoscopic scales to recognize other molecules and molecular assemblies, convert them selectively and perform the storage and transformation of biological energy and information. The construction of similar artificial molecular systems and the development of new properties and functions

unattainable by independent molecules will be two of the most important subjects of science and technology of the early 21st century.

In this short commentary, let me take, as an example, the application of the principles of physical organic chemistry to the construction of molecule-based magnets. Free radicals have been accepted as one of the key reactive intermediates and understanding their structures and reactivities has been a subject of physical organic chemistry. The unstable reactive intermediates have been stabilized on the basis of the principles of thermodynamic stabilization through conjugation and of steric protection to produce a number of stable free radicals. Free radical reactions that have been reputed to be too reactive and less selective have been tamed to develop reactions usable in modern synthetic strategies. These free radicals are paramagnetic while the ground electronic state of typical organic molecules is singlet, and as a result most organic compounds are diamagnetic. Strong and/or tunable magnetism is one of the last interesting properties yet to be exploited in organic materials. Thus, free radicals serve as a good starting point for developing magnetic organic materials.

Conventional magnets made of metals such as iron, cobalt and nickel, alloys, metal oxides and other inorganic compounds teach the instructive lesson that there are three conditions necessary for developing strong magnetism: (1) assemblage of d- and/or f-electron spins in high concentration, (2) operation of strong exchange interaction aligning the spins and (3) formation of a magnetic domain in which all the spins are ordered in a two- or three-dimensional network on a mesoscopic scale. Physical organic chemists who are ever engaged in free radical chemistry would be interested in simulating such molecular architecture having dimensional and

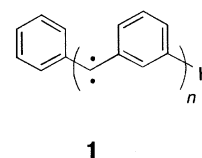
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electronic characteristics by using the 2p spins of free radicals. They would also sense that it would be useful to mimic the secondary and tertiary structures on a mesoscopic scale in peptides, nucleic acids, amylose, etc., to construct two- and/or three-dimensional molecular network architecture.

Two extreme approaches can be made towards this goal.¹ One is the exploration of a series of crystals of free radicals to find ones that have ferromagnetic intermolecular exchange coupling by chance or by crystal design. Otherwise any overlap of the two singly occupied orbitals stabilizes the antiparallel alignment of the spins (a singlet state) relative to the parallel alignment (a triplet state); a closed-shell dimer is formed in the extreme. Several purely organic crystalline ferromagnets were found in the early 1990s.² Recently, Togashi *et al.* investigated 165 kinds of 4-arylmethyleneamino-2,2,6,6-tetramethylpiperidin-1-yloxy to find that the NO \cdot ··aryl contact is a key to the development of intermolecular ferromagnetic interactions.³ Since the exchange interaction between free radical molecules in van der Waals contacts or hydrogen bonds is not strong, the ordering temperatures T_C (transition temperature from a paramagnet to a ferromagnet) of the spins of free radicals in crystal is limited to <1.5 K. It seems to be the charge and/or electron transfer interaction between donor and acceptor organic molecules in which T_C can become as high as 16 K or even room temperature.^{1d,e} However, in the tetrakis(dimethylamino)ethylene-C₆₀ complex⁴ and the neutral – radical anion mixed salt of tetrafluorotetracyanoquinodimethane⁵ the saturation magnetization values are only a few per cent of the theoretical values; only a limited domain of the solid materials appears to constitute a ferromagnet or the magnetization might be strongly canted.

Intramolecular exchange coupling between two unpaired electrons via π -covalent bonds can become stronger and of long range.⁶ Some diradicals are known to have ground triplet states that lie far below excited singlet states. This second approach relies on the

synthesis of high-spin polyradicals designed on the basis of molecular theories of how diradicals can have a triplet ground state.^{6a,b,e} Trimethylenemethane (TMM) and tetramethyleneethane (TME) are the simplest non-Kekulé alternant hydrocarbons for which Longuet-Higgins' rule dictates the occurrence of two non-bonding molecular orbitals (NBMO) that have zero π -bond energy and therefore both are diradicals. The two NBMOs, each of which is represented by a linear combination of the constituent 2p atomic orbitals, have atoms in common in TMM (non-disjoint), but can be confined to two different sets of atoms in TME (disjoint) (Fig. 1). Borden and Davidson^{6d} predicted in their perturbational MO theory that, while TMM should have a ground triplet state on the basis of Hund's rule, singlet and triplet states are nearly degenerate and higher order terms favor the singlet ground state for TME. The ground electronic states of non-disjoint and disjoint hydrocarbons have been discussed. It is noted that any non-Kekulé alternant hydrocarbons of extended π -conjugation may be regarded as a vinylog or phenylog of TMM or TME (including pentamethylenepropane). It is only the former that can have high-spin ground states.^{6e}



1

One-dimensional poly(*m*-phenylenecarbenes) (**1**) were proposed as the first prototype of organic ferromagnets and were investigated extensively for some time.⁷ However, in the one-dimensional array of spins, the first excited states in which the spins of the second half block flopped upside down to those of the first half are populated thermally, of lower-spin, multiply degenerate and, therefore, favored statistically; one-dimensional spins are regarded by statistical mechanics not to order at finite temperature. At least two-dimensional and preferably three-dimensional magnetic structures are

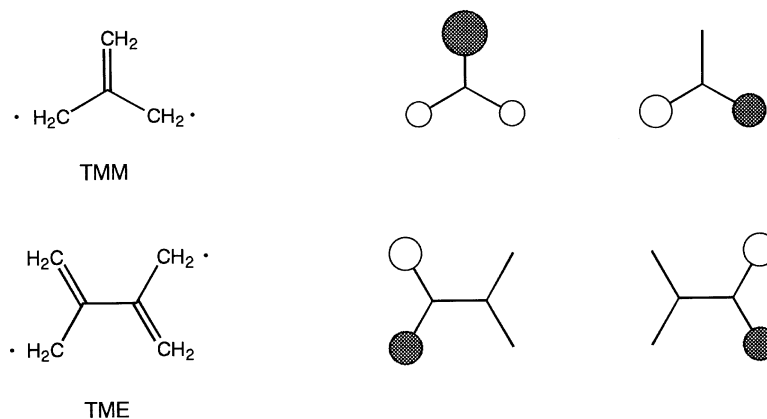
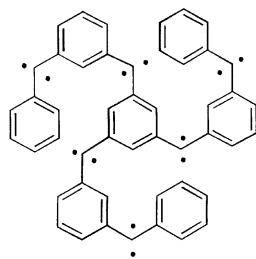


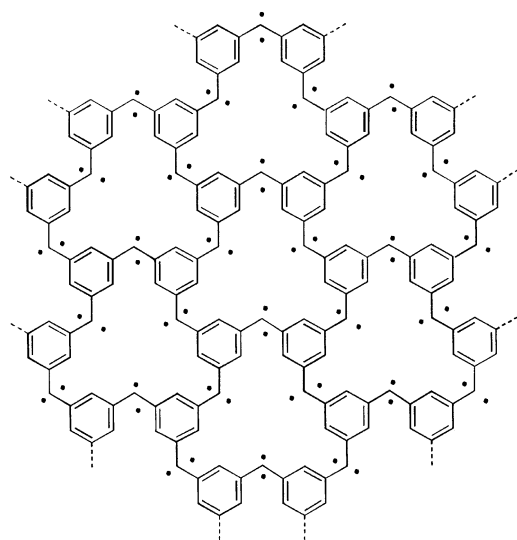
Figure 1. Sets of non-bonding MOs for TMM and TME.

required for stabilizing the high-spin ground states. Two-dimensional molecular systems have been proposed and surveyed. The highest spin ever reported for purely organic systems is only $S = 9$ for nonacarbenes higher



2

analogs of **2**.⁸ Highly branched dendritic structures including a dodecacarbene expected to give an $S = 12$ species have been prepared, but the observed spin states were lower than the theoretical values.^{8d} This observation is explained in terms of a facile interbranch recombination of the carbene centers, due to the congested and flexible structures. The most promising last candidate is a network structure (**3**).⁸ However, it is a most difficult



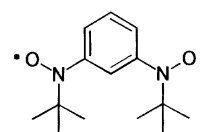
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target of modern synthetic organic chemistry to construct such network skeletons. Well-developed polymerization and condensation reactions are for chain structures that have one-dimensional connectivity: pseudo-two-dimensional ladder and dendritic polymers at best.

Self-assembly of free radical molecules into supramolecular structures relieves the difficulty associated with the construction of intricate covalent bonds. Organic radicals having basic coordinating sites have been employed together with magnetic metal ions to make polymer complexes containing organic 2p and metal 3d hybrid spins.⁹ When an organic free radical carries two ligating sites as in Ullman's nitronyl nitroxides, extended structures that are often chain polymers or macrocycles

are formed with coordinatively doubly unsaturated metal ions such as manganese(II) bis(hexafluoroacetylacetonate) as pioneered by Caneschi *et al.*^{9a} The exchange interaction between organic radicals and magnetic metal ions through coordination bonds can become strong, although the spins tend to align antiparallel next to each other and cancel each other out as in covalent bonds. Ferrimagnets due to the residual spins would be obtained if the magnitude of the spins of the ligand and metal ions is different. Depending on the nature of the additional interchain interactions, the chain polymers become antiferromagnets, metamagnets or ferri/ferromagnets.⁹

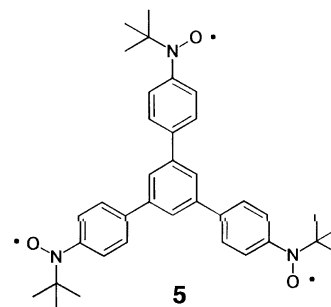
Modification and systematic extension of this design strategy of using the oxygen atoms of aminoxyl radicals as ligating sites have been achieved by employing the π -cross-conjugated triplet *m*-phenylenebis(*N-tert*-butylaminoxyl) diradical (**4**) and quartet tris(aminoxyl)



4

radicals having a defined geometrical arrangement of the ligating sites. With the aid of magnetic metal ions, these aminoxyl radicals have been assembled systematically into a one-dimensional (1D) chain (Fig. 2), two-dimensional (2D) network and three-dimensional (3D) parallel-crosses structures in which both the organic 2p and metallic 3d spins are ordered on the macroscopic scale.¹⁰

When three aminoxyl radical centers are placed in the trigonal configuration, the triradical **5** serves as a bridging



5

ligand to generate an extended polymer complex that have a honeycomb network structure (Fig. 3) and all the spins ordered at 3.4 K to become a magnet.¹⁰ This structure happens to be similar to the network polycarbene **3** which was difficult to make by organic synthesis. The only difference between the two is that whereas the polycarbene network contains spin $S = 1$ on each edge of the hexagon, the manganese(II) ion and aminoxyl radicals couple antiferromagnetically to give $S = 5/2 - 1/2 - 1/2 = 3/2$. Otherwise, the correspondence between the two series is fairly good.

Such a logical approach by self-assembly to the tailored extended systems has succeeded in generating

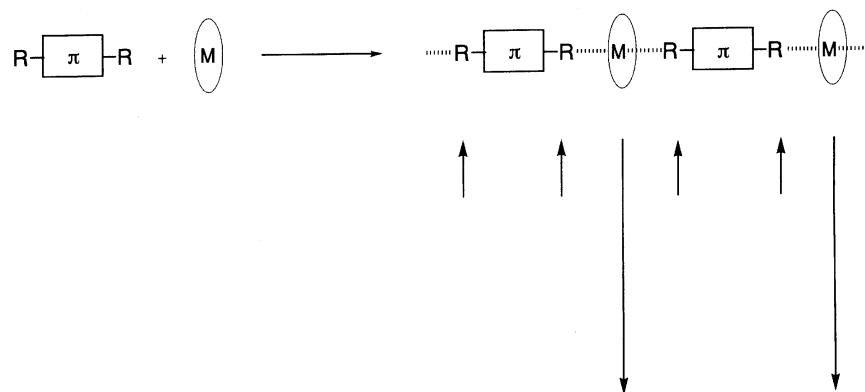


Figure 2. Schematic diagram of the formation of the polymer complex of a π -cross-conjugated triplet diradical carrying two ligating sites R as in *m*-phenylenebis(*N*-*tert*-butylaminoxyl) radical (**4**) with coordinatively doubly unsaturated metal ions M such as manganese(II) bis(hexafluoroacetylacetonate).¹⁰ The 2p spin-1/2 and 3d spin-5/2 are expected to align in an antiferromagnetic fashion as shown by arrows. Residual spins-3/2 are obtained per repeating unit.

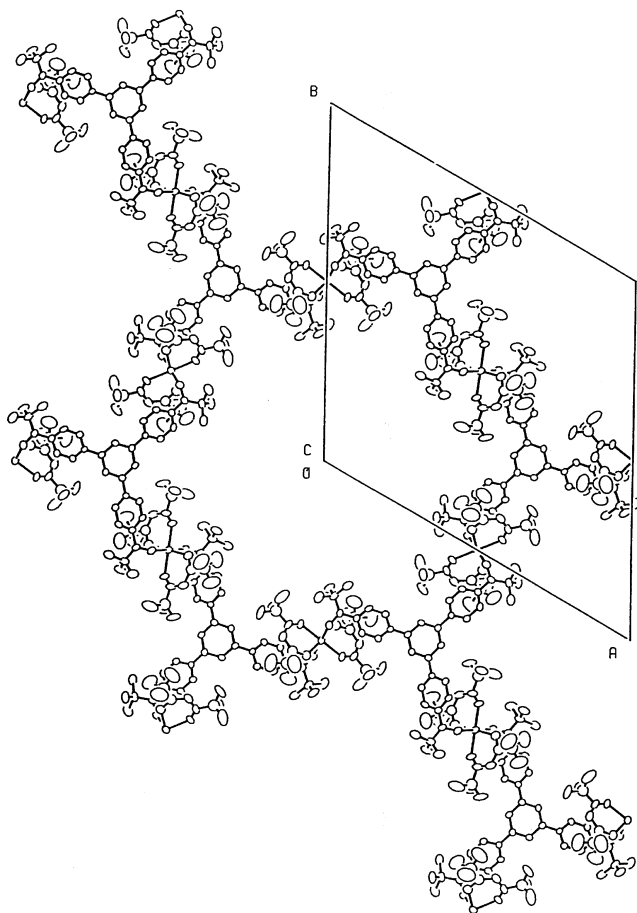
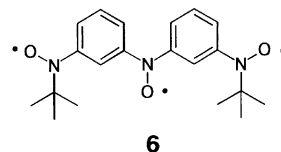


Figure 3. An x-ray two-dimensional honeycomb network structure made of Mn^{II}(hfac)₂ and trinitroxide radical **5** in a 3:2 ratio.

from the T-shaped tris(aminoxyl) radical **6** and Mn(II)



ions a three-dimensional parallel-crosses structure [Fig. 4(b)] reminiscent of that of the silicon sublattice [Fig. 4(a)] of natural Th₂Si. The crystals become a ferri/ferromagnet that has a critical temperature as high as 46 K.¹⁰

When the crystal structures are studied more carefully in a systematic manner, we find that dimensionality of the crystal structures in these heterospin magnets is closely related to the tacticity of the polymeric chains in which chirality is generated by a C₁ or C₂ configuration of the free radical ligand fixed in the crystal and the octahedrally *cis*-coordinated metal center.¹¹ While the isotactic polymeric chains remain 1D and have difficulty in making strong interchain interactions, the ligating sites are in-phase between the adjacent chains and 2D and/or 3D networks are formed by extending interchain connectivity in the syndiotactic chains.

This is exactly what Nature tells us. In polypeptides, DNA and amylose, α -amino acids, deoxyribose and D-glucose of the same chirality constitute isotactic chains. Interchain interaction is limited and leads to α -helix, its bundle, double helix or macrocycles. The β -sheet structure having extended interchain interactions is found under special conditions in polypeptides. Ghadiri *et al.* made unnatural cyclic peptides consisting of an alternat-

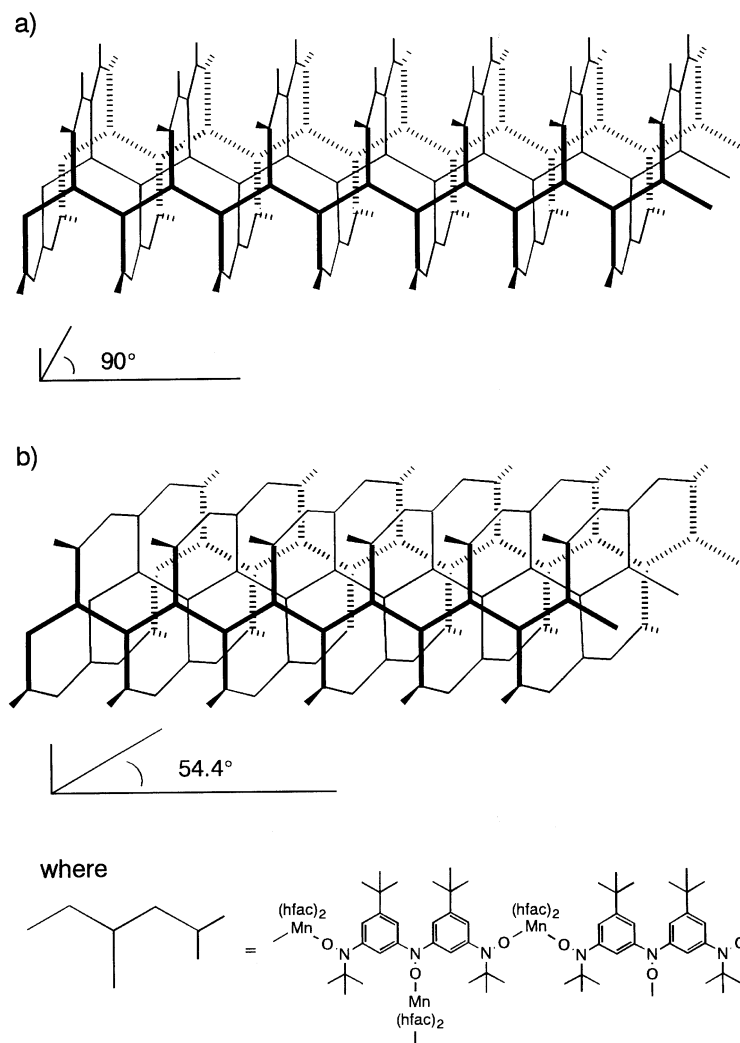


Figure 4. (a) A three-connected net for the Si sublattice of Th_2Si . (b) Schematic diagram of the x-ray three-dimensional parallel-crosses structure for a 3:2 complex of $\text{Mn}(\text{hfac})_2$ with trinitroxide radical **6** that undergoes transition to a magnet at 46 K.

ing array of D- and L-amino acids. As a consequence of matching of the phase for the hydrogen bonds, inter-ring interaction is favored, and peptide nanotubes are formed in the extreme.¹²

The ligands employed so far are conformationally labile and chiral only in the crystals. The right chirality of each ligand and the consequent tacticity have been selected during the self-assembling and crystallization processes. Furthermore, isotactic chains of opposite chirality cancel each other out and there is no net chirality exhibited by the bulk crystals. Ongoing studies should employ ligands stable with respect to chirality to dictate the dimension of the resulting metal complexes. Once such crystals have been obtained, they might become chiral magnets that would show interesting photophysical behavior.

Other molecular architecture on the nanometer scale is considered to exhibit various quantum size effects and

will be of use as new devices in the near future. A deeper understanding of what can be built and how to assemble molecules in ordered dimension will be provided by the existing and new principles of physical organic chemistry.

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