Review

Organic-synthetic and supramolecular approaches to free radical-based magnets

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Abstract: Two approaches have been pursued to construct bulk magnets by ordering spins of unpaired 2p-electrons of organic free radicals. One is an intermolecular approach based on the crystal design of stable radicals. The other consists of intramolecular alignment of spins in polyradicals having many unpaired electron. The two approaches progressed complementarily to establish unprecedented molecule-based magnets. The second approach by our research group developed polyradicals, polycarbenes and their supramolecular assemblies with metal ions into permanent magnets, thereby deepening the understanding of chemical bonds and opening a new horizon of developing new magnets with other functionality.

Key words: Polyradicals; polycarbenes; supramolecular assembly; molecule-based magnets; heterospin systems; photomagnets.

Background. Organic free radicals are accepted as reactive intermediates for various chemical reactions. Some of them that are generated by reactions with molecular oxygen trigger the deterioration of usable materials and produce species responsible for aging and mutagenicity in the human body. Thus, most research work is focused on the chemistry of how to control the disappearance of free radicals. We became interested in challenging this scientific common sense and succeeded in stabilizing them, assembling their unpaired electrons in high concentration, aligning in parallel their spins that are the smallest units of magnetism, and achieving supramolecular magnets consisting of free radicals.

Chemical bonds are formed by antiparallel pairing of electron spins between two adjacent atoms. This is a direct consequence of Pauli exclusion principle that no two electrons in an atom can have identical quantum numbers. In spite of this general rule, there are two classes of simple organic molecules that are exceptional and have two unpaired electrons with parallel spins. They are the Schlenk hydrocarbon having degenerate non-bonding π orbitals and diphenylcarbene **LC1** carrying orthogonal sp²-hybridized and π orbitals at the divalent carbon atom. Hund's rule dictates that, when filling a set of degenerate orbitals, the lowest energy configuration is that which maximizes the number of electrons with the same spin, e.g., triplet ground states.^{1),2)} In 1967 mphenylenedicarbenes LC2 in which the above two structural features are combined into one molecule was found to have a quintet ground state.^{2),3)} Whereas Mataga presented the idea of constructing the higher analogues with higher spin states as prototypes for organic ferromagnets, the subject had remained untouched for some 15 years before we took it up in the early eighties on the basis of physical and synthetic organic chemistry.²⁾



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Design and synthesis of superparamagnetic polycarbenes.

Design: Natural extension of the *m*-phenylenedicarbene was to linear tetra- and pentacarbene (**LC4** and **LC5**) for which we first synthesized precursor tetrakis(diazo) and pentakis(diazo) compounds, respectively. The polycarbenes were kinetically unstable under ambient conditions and therefore generated by photolysis and analyzed *in situ* at cryogenic temperature in the absence of air (Eq. [1]).

EPR fine structures of the polycarbenes revealed that **LC4** and **LC5** have nonet (S = 4, D = 0.0316, E =0.0039 cm⁻¹, g = 2.002) and undecet (S = 5, D = $-0.0168, E = 0.0036 \text{ cm}^{-1}, g = 2.002)$ ground states, respectively.^{3),4)} In addition to this spectroscopic method, magnetic susceptibility measurements were carried out on these high spin species by photolyzing the precursor diazo compounds diluted in solid solutions in the sample cell placed in a Faraday magnetic balance. Later measurements were also carried out in a SQUID susceptometer/magnetomer. The measured magnetization values at various dc fields and temperature agreed well with the theoretical Brillouin functions for the theoretical S values. Thus, Sugawara et al. obtained for the first time paramagnetic hydrocarbons that have ground-state spins and therefore magnetic moments greater than those of d⁵ transition metal ions, e.g., Mn²⁺ and Fe^{3+} and f^7 lanthanide e.g., Gd^{3+5} .

The linear structure can in principle be extended to poly(*m*-phenylenecarbene)s $LC\infty$. In practice, however, there are two intrinsic drawbacks in the linear structure: vulnerability to chemical defects that could cut off the cross-conjugation along the main chain and facile thermal excitation to the lower spin states. Thus, any magnetic linear chain including **LCn** is predicted to exhibit no spontaneous magnetization at finite temperature. These difficulties would be overcome by employing polycarbenes in which a large number of the triplet carbene centers are joined ferromagnetically to form twoand three-dimensional structures. Thus we arrived at network structure **POLYC** as a goal of the strongly magnetic super-high-spin polycarbenes.⁶⁾ It was easier said than done. With no synthetic strategy conceivable for the network polymer structures, we were obliged to study the unit structures contained in **POLYC**.

Synthetic routes to branched-chain, cyclic and dendritic polydiazo compounds were explored and the polycarbenes generated therefrom were confirmed to have really the expected high-spin ground states. The dendritic structure is known in physics as a Bethe lattice



on which Ising spins are calculated to show a phase transition at finite temperature.

Synthesis: The construction of the skeleton of the polyketones was a focal point of the synthetic strategy. The linear skeleton of pentaketone, for example, was constructed by combining the readily available m-benzylbenzaldehyde and bis(m-bromophenyl-methane). Noting that the branching point has a 1,3,5-triaroylbenzene unit, we optimized and elucidated the mechanism of the Michael addition-type cyclotrimerization reaction of aryl ethynyl ketones. These reactions were employed not only to effect homocyclotrimerization but also to produce asymmetric 1,3,5-triaroylbenzenes. Thus, extension to a dendritic structure such as dodecaketone was made on the basis of Fréchet's convergent approach. Mixed cyclotrimerization of the ethynyl ketones followed by deprotection and second homo cyclotrimerization gave the expected structure as shown in Scheme 1.

A cyclic hexaketone was synthesized *via* a calix[6]arene derivative. All the ketones were fully characterized by ¹H, ¹³C NMR, IR, and mass spectroscopy. HH-COSY NMR spectroscopy was firmly in support of their structures.

The ketones were converted to the corresponding hydrazones. The oxidation reaction with yellow mercury(II) oxide was carried out in the dark and monitored by thin-layer chromatography (TLC) on alumina. The



diazo compounds were purified by column chromatography on alumina (activity IV) in the dark. The IR spectra of the polydiazo compounds showed absorptions at 2040-60 cm⁻¹ characteristic of the diazo groups. The UVvis spectra revealed absorption maxima at 520 nm attributable to the n- π * transitions. The molar absorptivities (ε) were 950 and 1660 for nona- and dodecadiazo compounds, values nearly nine and twelve times as large as that of diphenyldiazomethane, indicating that the molecules had nine and twelve cross-conjugated diazo groups.

Magnetization of photoproducts: Photolysis was carried out at 2 K in the sample compartment of a Faraday magnetic balance. The light ($400 < \lambda < 500$ nm) from a Xe lamp treated with a combination of a bandpass filter and a cold mirror was introduced through a quartz light guide installed for irradiation of the precursor. After the photolysis, the field dependence of the magnetization of the photoproduct was measured *in situ* in the dark. The plots of the magnetization vs. the temperature-normalized magnetic field (*H*/*T*) due to the polycarbenes were analyzed in terms of Eq. [2]:

$$M = Ng\mu_{\rm B}SB_{\rm S}(x)$$
 [2]

where *N* is the number of the molecules, *S* is the spin quantum number, $\mu_{\rm B}$ is the Bohr magneton, *g* is the Landé *g*-factor, and $B_{\rm S}(x)$ is the Brillouin function. Since these carbenes are hydrocarbons and have only light elements, the orbital angular momentum should be negligible and *S* can be used for total angular momentum



Fig. 1. The observed magnetization data for hexa- and nonacarbenes in reference to theoretical curves represented by Brillouin functions for various *S* values.

in Eq. [2].

The data for the nonacarbene **DC9** showed saturation of magnetization at a field lower than 1 T, demonstrating that an unconventionally high spin species was generated (Fig. 1). The formation of the nonadecet ground state species was supported by best-fitting the observed data to the theoretical curve with S = 9. This material showed neither spontaneous magnetization nor hysteresis and therefore was concluded to be a paramagnetic species with exceptionally large Landé magnetic moment, the highest spin ever reported for a welldefined organic molecule. Cyclic hexacarbene CC6 derived from a calixarene has a tridecet (S = 6) ground state. However, the expected high spin species were not necessarily obtained upon photolysis of dendritic analogues due to intramolecular dimerization and/or azine formation.

An independent approach was employed more recently by Rajca who obtained polyradicals having average S of several hundreds based on the condensation of the calixarene-type trityl radicals. By studying the temperature and frequency dependence of ac susceptibilities, some of the polymers were found to behave as spin glasses.⁷⁾

Magnetic interaction between high-spin molecules: In the spectroscopic and bulk magnetic measurements, it was always necessary to isolate each molecule of the polydiazo compounds in host crystals or solid solutions so that the unimolecular magnetic properties might not be smeared by mostly antiferromagnetic intermolecular interactions. This is easily understood if we take into account not only the dipolar interaction but also the exchange interaction due to the overlap of the orbitals containing unpaired electrons between the neighboring molecules. A radical recombination reaction takes place in an extreme case.

In 1963 McConnell had proposed that such an interaction could become ferromagnetic i.e., the spins might align parallel between two interacting free-radical molecules, when the two approaching orbitals are orthogonal to each other.⁸⁾ We studied the stacking interaction of two diphenylcarbene molecules by preparing isomeric [2.2]paracyclophanes **PCC** in which each *p*-phenylene ring had a phenylcarbene unit as a substituent. In effect, the isomers had two diphenylcarbene units modeled to overlap at one of the two benzene rings with the rotation of 60, 120 and 180 degrees. The isomers were shown to have quintet, singlet, and quintet ground states, respectively, offering the first experimental verification of the McConnell's theory serving as a basis for the crystal design.⁹⁾



Whereas we developed sound molecular chemistry of polyradicals in general and polycarbenes in particular, we noted that magnetism is not molecular properties but bulk properties of an assembly of spins for which the following three essential conditions have to be met for realizing spontaneous magnetization at $T_c > 0$.

- 1) Assemblage of a number of unpaired electrons in high density.
- 2) Operation of a strong coupling mechanism among the spins.
- 3) Exercise of conditions 1) and 2) in two- and three-dimensions in meso- and macroscopic scale.

Supramolecular approaches to metalaminoxyl radical hybrid spin magnets. Since it was difficult to satisfy the above three conditions within the framework of polycarbenes, we turned to supramolecular approaches to the construction of high-dimensional network structures by using magnetic metal ions as bridging units for organic free radicals serving as ligands. Such coordination bonds are considerably weaker than conventional covalent bonds and the products are formed under thermodynamic rather than kinetic control.

Polyaminoxyl radicals: Aminoxyl radicals can be made stable at room temperature under air by kinetic stabilization with bulky substituents such as *t*-butyl groups and thermodynamic stabilization with additional resonance. The unpaired electron resides on the antibonding p* orbital in aminoxyl radicals and the spin density at the nitrogen and oxygen atoms are roughly equal (Eq. [3]).



Aminoxyl radicals were the first purely organic ferromagnets ever discovered in the early nineties. The above three conditions for molecular-based magnets appear to be realized by special arrangement of the radical molecules in crystals,¹⁰⁾ although $T_{\rm C}$ is quite low (< 1.4 K) due to weak intermolecular exchange interaction.

Inoue and Ishida synthesized a series of bis- and tris(aminoxyl) radicals (BR and TR) that have two and three radical centers placed in the 1,3- and 1,3,5-positions on an aromatic ring (see formula attached to Table I).¹¹⁾ Triplet and quartet states were found by the temperature dependence of their magnetic susceptibilities to be ground states and often energetically well separated from lower spin states. Since the intramolecular magnetic interaction is dictated by the spin polarization of the π electrons on the cross-conjugated aromatic ring, the two or three radical centers have to be placed as close as possible for stronger ferromagnetic interaction. When the exchange coupling parameters J is defined by the Heisenberg Hamiltonian (Eq. [4]) for the energies of the interacting spins Sa and Sb at sites a and b, we note that insertion of an additional phenylene ring between any two aminoxyl radical centers reduces the strength of the interaction by an order of magnitude.

$$H = -2JSa \cdot Sb$$
[4]

In order to simulate d^5 Mn(II) and Fe(III) ions by a single organic molecule, we had to synthesize such a complicated organic pentaradical **PR** carrying additional

substituents for stabilization.¹²⁾



Table I. The magnitude of the intraligand exchange coupling $(J_{\text{intra}} \text{ in unit of K}; 1 \text{ K} = 1.987 \text{ cal mol}^{-1})$ in bis- and tris(aminoxyl)s (**BR** and **TR**)¹¹⁾







Fig. 2. Schematic presentation of the formation of a 1D chain of the complex from 3d metal ions and coordinatively doubly unsaturated biradicals and the spin alignment therein.

relatively strong Lewis-acidic metal centers such as metal anhydrous halides, perchlorates, hexafluoroacetylacetonates (hfac), and halogenated carboxylates.

Inoue *et al.* advanced a strategy of constructing hybrid spin magnets on the basis of the idea that, depending on the number and geometrical disposition of the aminoxyl oxygen atoms in the **BR** and **TR**, extended one-dimensional (1D) chain, two-dimensional (2D) network and three-dimensional (3D) parallel-crosses structures would be obtained by spontaneous formation of the coordination bonds with magnetic metal ions. Then the organic 2p and metallic 3d spins would couple strongly throughout the extended structures. Since the exchange coupling between the ligands and the directly attached metal ions is expected to be antiferromagnetic $\{J(\text{coordination}) \ll 0\}$ and the 2p and 3d spins tend to cancel each other out, a residual spin would be established for the repeating units (Fig. 2) to give antiferro-, meta-, or ferromagnet depending on the nature of the additional interchain interaction.

Preparation of the 3d transition metal poly(aminoxyl) radical complexes:¹¹⁾ A representative example is the preparation of black needles of $[Mn(hfac)_{2} \cdot BR1_{H}]$ from a deep brown solution of anhydrous $[Mn(hfac)_2]$ and **BR1_H** in *n*-heptane. The reaction was preferably carried out in inert atmosphere and anhydrous conditions, often in a refrigerator to give crystals on standing. Excess of either one of the components may give complexes of different composition. For example, reaction [Mn(hfac)₂] the of with tris(aminoxyl) TR4 was complex; while an equimolar mixture in ether containing *n*-hexane at -10 °C gave black blocks of 1:1 complex $[{Mn(hfac)_2} \cdot \mathbf{TR4}] \cdot n$ -C₆H₁₄, a mixture containing [Mn(hfac)₂] in 1.7 molar excess in n-heptane-ether gave black blocks of 3:2 complex $[{Mn(hfac)_2}_3 \cdot \mathbf{TR4}_2]$ in ten days at 0 °C.



Fig. 3. Crystal structure showing a unit cell of $[{Mn(II)(hfac)_2}_3 \cdot TR1_2] \cdot n \cdot C_7H_{16}$.

X-ray crystal and molecular structures of the **complexes:**¹¹⁾ X-ray crystallographic analyses revealed that almost all the Mn(II) ions have the octahedral coordination with four oxygen atoms of two hfac anions and two aminoxyl oxygen atoms from two different di- or triradical molecules either in cis or trans configuration. [Mn(II)(hfac)₂·BR1_H]. The *cis*-coordinated complex gave rise to 1D polymeric chains that are isotactic with respect to the Δ and Λ chirality of the octahedral Mn(II) centers as all units of the same chirality reside on a given chain and folded like an α -helix of peptides to make either a right-handed or left-handed helix with a pitch corresponding to two $[Mn(hfac)_2 \cdot BR1_H]$ units. Since a second isotactic chain lying along the crystal b axis has chirality opposite to the first one, there is no net chirality exhibited by the crystals themselves.

 $[{Mn(II)(hfac)_2}_3 \cdot TR1_2] \cdot n - C_7 H_{16}$. Six triadical molecules and six *trans*-coordinated Mn(II) ions make a large hexagon from which a honeycomb network is constructed by sharing the edges of the hexagon (Fig. 3). A disordered *n*-heptane molecule is contained in each hexagonal cavity. The 2D network sheets form a graphite-like layered structure with a mean interlayer distance of 3.58 Å. The adjacent layers are slid in the ab plane by a length of the edge of the hexagon from the superimposable disposition. As a result, any middle benzene ring of **TR1** stacks with the corresponding ring on the next layer rotated by 60° along the C_3 axis.

Note that the 2D sheet is equivalent in connectivity of spins to the polycarbene network **POLYC** proposed in the previous section. In place of spin S = 1 residing on each edge of the hexagonal polycarbene network, we now have the manganese(II) ion and aminoxyl radicals couple antiferromagnetically as described below to give S = 5/2 - 1/2 - 1/2 = 3/2. Otherwise, the correspondence between the two series is quite good.

[{ $Mn(II)(hfac)_{2}_{3} \cdot TR4_{2}$]. Two terminal aminoxyl groups in triradical **TR4** are attached to two different manganese ions in *trans* configuration to form a 1D zigzag chain in the bc-plane of the crystal as in the 1:1 complex [{ $Mn(II)(hfac)_{2}$ } $\cdot TR4$] $\cdot n$ -C₆H₁₄]. The central N, Ndiarylaminoxyl unit in **TR4** is in chiral C_2 conformation and the R and S configurations alternate along the chain to make it syndiotactic. The central aminoxyl group in **TR4** on one chain is used to link its oxygen with that in the adjacent chains extended in the b/–c diagonal direction through a third Mn(II) ion in a *cis*-octahedral position. The mean intersecting angle of the two chains is 54.4 °, establishing a parallel crosses-shaped 3D polymeric network.

Magnetic susceptibility and magnetization of metal complexes:¹¹⁾ Magnetic data of the heterospin complexes were determined on a Quantum Design MPMS2 SQUID susceptometer unless otherwise stated. High-field data (H > 10000 Oe) were obtained on an Oxford Instruments Faraday magnetic balance system



Fig. 4. Anisotropic magnetization data for a single crystalline sample of [{Mn(hfac)₂]₃ · **TR4**₂] at 5 Oe.

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with a 7 T superconducting magnet. The results were analyzed on the basis of their crystal structures described above.

1D complex $[Mn(II)(hfac)_2 \cdot BR1_H]$, a metamagnet. Temperature dependence of molar paramagnetic susceptibility χ_{mol} (for the formal unit structure) at 5000 Oe followed a Curie-Weiss relation which was analyzed on a model of ferromagnetic chain $(2J/k_{\rm B} = 23 \text{ K})$ consisting of pseudo-spins S = 3/2 formed by two aminoxyl groups from two different ligand molecules bridged by a Mn(II) ion. The $\chi_{mol}T$ values increased steadily, reached a maximum at 8.5 K, and then decreased with decreasing temperature. The zero-field cooled (ZFC) magnetization measured at 0.5 Oe after cooling down without field showed also a sharp cusp at 5.5 K, suggesting the development of a higher order antiferromagnetic interaction $(2J/k_{\rm B} = -0.018 \text{ K})$. The magnetization at 1.8 K revealed metamagnetic behavior ($T_{\rm C}$ = 5.5 K).

2D complex $[{Mn(hfac)_2}_3 \cdot TR1_2] \cdot n \cdot C_7 H_{16}$ with T_C of 3.4 K. $\chi_{mol}T$ vs. T plots at 5000 Oe gave a minimum of 6.7 $\mu_{\rm B}$ at ca. 115 K in good agreement with a model in which the interaction between the directly attached Mn(II) and the aminoxyl group is antiferromagnetic $(J_{\rm coord} < 0)$ and the three spins within a ligand molecule are not yet aligned. Then $\chi_{\mathrm{mol}}T$ values increased with decreasing temperature and showed a maximum at 2.5 K. When the measurement was carried out at 1 Oe, magnetization values showed a sharp rise at $T_{\rm c} = 3.4$ K below which the spontaneous magnetization due to transition to a bulk magnet was observed. The magnetization reached nearly 9 $\mu_{\rm B}$ (theoretical $M_{\rm sat} = 9 \,\mu_{\rm B} = 5/2 \times 3 3/2 \times 2 = 9/2$). A hysteresis loop at 2 K consisted of a remnant magnetization of 53.9 emu G mol⁻¹ and the coercive field of 3.8 Oe.

The observed $T_{\rm c}$ to the ordered state was not so high as expected from the perfect 2D network sheet structure with ferro- $(J_{\rm intra} > 0)$ and antiferromagnetic $(J_{\rm coord} < 0)$ coupling together with the ferromagnetic stacking of the layers. The result is ascribed to a weak intramolecular coupling $(J_{\rm intra} = 6.8 \text{ K})$ among the three aminoxyl units in the ligand **TR1** molecule. Trisaminoxyl radical **TR2** that has stronger ferromagnetic interaction (see Table I) gave black blocks of $[{\rm Mn}({\rm hfac})_2\}_3 \cdot {\rm TR2}_2]$ that has indeed a higher $T_{\rm c}$ value of 9.3 K.

3D [{**Mn(II)(hfac)**₂}₃ · **TR4**₂] with High $T_{\rm c}$ of 46 K. As the temperature was lowered, $\mu_{\rm eff}$ value of 8.31 $\mu_{\rm B}$ at 300 K under 5000 Oe increased monotonically. The lack of a minimum at lower temperature, the room temperature $\mu_{\rm eff}$ value suggests the operation of a strong antiferromagnetic coupling ($J_{\rm coord}/k_{\rm B} < -300$ K) between the Mn(II) ion and the aminoxyl radical in [{Mn(hfac)₂}₃ · **TR4**₂] and the onset of an intramolecular ferromagnetic coupling ($J_{\rm intra}/k_{\rm B} \sim 300$ K) at 300 K. The behavior in the low-temperature range is qualitatively consistent with the three-dimensional, ferromagnetically coupled network of S = 3/2 spins consisting of the S(1/2) - S(5/2) - S(1/2) units.

When single а crystalline sample of $[{Mn(hfac)_2}_3 \cdot \mathbf{TR4}_2]$ was cooled within the field of 5 Oe, the field-cooled (FC) magnetization showed an abrupt rise at $T_{\rm C}$ = 46 K (Fig. 4). The field dependence of the magnetization at 5 K showed two important features. First, the magnetization rose sharply at low field, reached a value of ca. 9 $\mu_{\rm B}$ (50000 emu G mol⁻¹) at 220 Oe and became saturated. The saturation value is in good agreement with a theoretical $M_{\rm sat}$ of 9 $\mu_{\rm B}$ (5/2 \times 3 – 3/2 \times 2 = 9/2) expected for the antiferromagnetic ordering between the d⁵ Mn(II) ion and S = 3/2 triradical **TR4**. Secondly, a conspicuous magnetocrystalline anisotropy was found in which the easy axis of magnetization lie along the c axis of the crystal lattice and the hard axis lies perpendicular to it (Fig. 4). It was noted that a coercive field of 18 Oe was not dependent on temperature below 46 K.

Supramolecular approaches to metal-carbene hybrid spin magnets.¹³⁾ Koga advanced the idea of combining the photochemical generation of triplet carbene centers from the precursor diazo compounds (see Eq. [1]) with the formation of extended network structures on the basis of metal-pyridine complexation. Calorimetric and spectrometric studies show that the formation constant of the 1:1 complex of [Cu(hfac)₂] with pyridine is 7.0×10^5 M⁻¹ and greater than those with aminoxyls by two orders of magnitude. The straightforward candidate for such photoresponsive magnetic coupler proved to be diazodi(4-pyridyl)methane (Py,D) for coordinatively doubly unsaturated metal ions (Eq. [5]). Dilute paramagnetic metal complexes $[M(II)(hfac)_{2} \cdot \mathbf{Py}_{2}\mathbf{D}]$ would be formed and give the corresponding hybrid-spin magnet by photolysis.



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One dimensional structure:

 $[Mn(II)(hfac)_2 \cdot Py_2D]$ and $[Cu(II)(hfac)_2 \cdot Py_2D]$. When [Mn(hfac)₂] was allowed to react with equimolar amounts of **Py₂D**, two kinds of crystals **a** and **b** of 1:1 complex $[Mn(hfac)_2 \cdot Py_2D]$ were obtained depending on the solvents used for recrystallization. The X-ray crystal structure analysis revealed that two pyridyl nitrogen atoms from two different Py₂D molecules are coordinated to an octahedral Mn(II) ion in cis and trans configurations, respectively. In complex **a**, the chain is isotactic with respect to the chirality of both the C_2 molecules of Py_2D and the octahedral Mn(II) center. Like an α -helix of peptides or single-stranded DNA, the one-dimensional chain is folded to make a helix with a pitch corresponding to two $[Mn(hfac)_2 \cdot \mathbf{Py}_2\mathbf{D}]$ units. In crystal **b**, zig-zag infinite chains are formed.¹⁴⁾ [Cu(hfac)₂] also gave two complexes **a** and **b** of $[Cu(hfac)_2 \cdot \mathbf{Py}_2\mathbf{D}]$.

The magnetic properties of $[Mn(II)(hfac)_2 \cdot Py_2D]$ and $[Cu(II)(hfac)_2 \cdot Py_2D]$ before and after irradiation: The temperature dependences of $\chi_{mol}T$ values for microcrystalline samples (ca. 0.6 mg) of $[M(hfac)_2 \cdot Py_2D]$ investigated before and after irradiation are shown in Fig. 5.

Before irradiation, the $\chi_{\rm mol}T$ values of $[Mn(hfac)_2 \cdot \mathbf{Py}_2\mathbf{D}]$ and $[Cu(hfac)_2 \cdot \mathbf{Py}_2\mathbf{D}]$ were nearly constant at 4.14 and 0.42 $\text{emu} \cdot \text{K} \cdot \text{mol}^{-1}$ in whole temperature range, indicating that the d electron spins of the metal (II) ions are magnetically isolated. When irradiated with Ar ion laser ($\lambda = 517$ nm), a striking difference in the temperature dependence of $\chi_{mol}T$ values was observed below 230 K between the Mn(II) and Cu(II) complexes. On cooling from 240 K, $\chi_{mol}T$ values of Mn(II) complexes **a** and **b** gradually decreased to a shallow minimum at ca. 80 K, and then increased sharply. On the other hand, $\chi_{mol}T$ values of Cu(II) complexes **a** and **b** increased monotonically and reached maxima at 14 and 3.0 K, respectively, and started to decrease somewhat towards 2 K.

The data for the Mn(II) complexes were analyzed theoretically on the basis of a ferrimagnetic chain model consisting of S = 5/2 classical and S = 2/2 quantum spins by a method originally developed by Bonner and



Fig. 5. Temperature dependence of $\chi_{mol}T$ for complexes **a** and **b** of [M(hfac)₂ · **Py**₂**D**], : before irradiation, and : after irradiation of **a** and **b**, and **x** : after leaving the samples at 300 K.¹⁴

Fischer and modified by Drillon *et al.* to give the best-fit data in Table II. In order to improve the fits, interchain interaction z_j was taken into account by a molecular field. The minima in the χT vs T plots were well reproduced.

A similar theory has been applied to the analysis of the magnetic data of photogenerated S = 1/2 and S = 2/2Heisenberg ferromagnetic chain of Cu(II) complex for T > 4 K, giving $J/k_{\rm B} = +66.8$ K as the exchange interaction between the Cu(II) ions and the attached di(4pyridyl)carbene centers. The maximum $\chi_{\rm mol}T$ values correspond to average correlation lengths of ca. 6 units at 15 K for **a** and ca. 15 units at 3 K for **b** along the chains. These correlation lengths should be taken as minimum estimates since they are not free from saturation at 0.5 kOe employed for the measurement and antiferromagnetic interchain interaction.¹⁵

The contrasting results that the magnetic interactions are antiferro- and ferromagnetic in the Mn(II) and Cu(II) complexes, respectively are explained by the difference in the magnetic orbitals of metal ions; d_{xy} , d_{yz} , d_{xz} , d_{x^2,y^2} , and d_{z^2} for Mn(II) ion and d_{x^2,y^2} for Cu(II) ion. In the former, some of the d-orbitals, e.g., d_{xz} orbital, containing the unpaired electron can overlap with the π orbital at the nitrogen atom of the ligand, while, in the

Table II. Parameters characterizing the ferromagnetic chains of $[Mn(hfac)_2 \cdot Py_2D]^{14}$

complex	$(J/k_{\rm B})/{ m K}$	g	$z_{\rm j}/{ m K}$	Scale	Correlation length
		(assumed)		factor	of $S = 3/2$ unit
a (cis)	-34.8 ± 0.8	2.00	0.51 ± 0.02	0.81 ± 0.01	186 (5 K)
b (trans)	-24.4 ± 0.5	2.00	0.049 ± 0.004	0.88 ± 0.01	218 (1.9 K)

latter, the $d_{x^2\cdot y^2}$ orbital is orthogonal to the ligand orbital.

Abrupt changes in the $\chi_{mol}T$ values were observed at above 230 K where they traced the horizontal line before irradiation. Subsequent measurements of the $\chi_{mol}T$ values at 2-300 K of the same samples left at 300 K for an hour showed temperature independent horizontal lines overlapped with those before irradiation. The decrease and temperature independence of $\chi_{mol}T$ were interpreted in terms of a loss of the generated carbene centers by chemical reactions. Still the observed stability of the carbene centers is novel and most probably due to kinetic protection in the stiff crystal lattice of the metal complex in both the Mn(II) and Cu(II) complex.

The success in the construction of the extended 1Dspin systems proved that our supramolecular strategy overcame the limitations in organic synthetic approaches to photomagnetic \mathbf{LC}_{∞} and encouraged the construction of the 2D and/or 3D network structures.

Attempts at 2D- and/or 3D-spin networks in frozen solutions: For this purpose, the number of pyridyl ligating sites in **Py₂D** had to be increased as we proceeded from BR1 to TR4. We therefore designed tripyridyl-tridiazo- and tetrapyridyl-pentadiazo compounds $\mathbf{Py}_{3}\mathbf{D}$ and $\mathbf{Py}_{4}\mathbf{D}$, respectively, as new photomagnetic coupling units. They were prepared by standard methods, characterized to have the correct chemical structures and gave the polycarbenes with S = 6/2 and 10/2 ground states, respectively, after photolysis. Although it was difficult to make good single crystals of the complexes with any of [M(hfac)₂]s for X-ray analyses, $\chi_{\rm mol}T$ value of 143 emu·Oe·mol⁻¹ 20 K for $[{Cu(hfac)_2}_3 \cdot \mathbf{Py_3D_2}]$ after photolysis in 20 mM frozen solution suggested the formation of a tetramer. Whereas a weak hysteresis of M with respect to H was observed with the coercive force and the remnant magnetization of ca. 2 Oe and 6.3×10^3 emu Oe mol⁻¹, respectively, the temperature dependence of ac susceptibility $\chi'_{\rm mol}$ and $\chi''_{\rm mol}$ gave $\Delta T_{\rm f}/T_{\rm f}(0)\Delta \log \omega = 0.04$ suggesting that the magnetic behavior is not due to a ferromagnet but a spin glass.¹⁶⁾



Concluding remarks and prognosis.¹⁷⁾ Since the antiparallel pairing of electron spins constitutes the principle of chemical bonds in molecular systems, our findings described here served as its antithesis and contributed to the deeper understanding of chemical bonds and the development of molecular materials exhibiting novel physical properties.

The molecule-based magnets would not replace conventional magnets that are based on iron, cobalt, nickel and some lanthanides. Instead, the new magnets should be evaluated by their additional functions such as the responses to light, pressure, electric current, pH, etc. for advanced materials. The carbene-based magnets generated by photolysis of the precursor diazo compounds mean that only the irradiated part of these materials becomes a magnet in contrast with the conventional photomagnetic recording devices that utilize the light-induced heat for phase transitions of the magnetic materials, and therefore generate write-only magnetic recording elements of the sharper area and higher density.

In this connection, we consider the following three pieces of discovery as worthy of mention. One is a prototype of rewritable memory elements based on the photochromic control of the exchange coupling between the separated spins of two Ullman's nitronylaminoxyl radical units by Matsuda and Irie.¹⁸⁾ A second topic is Koga's mixed ligand complex of $Co(p-Tolsal)_2$ with two molecules of trisdiazomonopyridine ligand that became a single-molecule magnet (SMM) having $H_{\rm C} = 10$ kOe and k_d $= 1.7 \times 10^{-4} \text{ sec}^{-1}$ at 2 K upon uv-irradiation.¹⁹ The slow relaxation for the reorientation of spins is due to the double-well energy potential in which the positive and negative M_s quantum levels are separated by an activation barrier $\Delta/k_{\rm B}$ corresponding to $|D|S^2$ where D (< 0) and Sare an axial zero-field splitting parameter and a total spin quantum number, respectively,²⁰⁾ and the high barrier is attained by S = 13/2. SMMs are of great interest in the rapidly developing area of nanoscience and technology because they have <10 nm-size and exhibit the onset of quantum size effect. A third topic is a chiral magnet.²¹⁾ Many self-assembled metal-radical magnets described in this paper contained helical chains, but, since there was no intrinsic chirality both in the coordinatively unsaturated metal ions and ligands, their crystals as a whole were achiral; the unit cell contained an enantiomeric pair. Inoue and his coworkers prepared biradicals **BR1** that carried chiral substituents R at the position 5 on the benzene ring. When these chiral radicals were used as ligands for metal ions, they formed chiral crystals that underwent transition to ferrimagnets. They not only showed huge magnetic circular dichroism but its sign changed drastically at the transition temperature. Since reading out of the recorded bits on the photomagnetic discs is conventionally made by the Kerr effect of the polarized light, any increase in the magnitude of the effect should increase the sensitivity of the reading-out, thus contributing to the down-sizing of the photomagnetic memory elements. Inoue further made pale-green needles of $[Cr(CN)_6][Mn(S)-pnH(H_2O)](H_2O)$ that have a chiral crystal structure and $T_{\rm c}$ = 38 K. Since they are mostly transparent to visible light, such materials are expected to show interesting photophysical behavior such as isolators in optoelectronics. Even with the current $T_{\rm c}$ of all these materials, they will already be usable in the area of superconducting electronics.

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Profile

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