Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Magnetism: Present and Future

Tadashi Sugawara [a] & Akira Izuoka [a]

[a] Department of Pure & Applied Sciences, Graduate School of Arts & Sciences The University of Tokyo, 3-8-1 Komaba, Meguro, Tokyo, 153, Japan

Version of record first published: 04 Oct 2006

To cite this article: Tadashi Sugawara & Akira Izuoka (1997): Molecular Magnetism: Present and Future, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 305:1, 41-54

To link to this article: http://dx.doi.org/10.1080/10587259708045045

Mol. Cryst. Liq. Cryst., 1997, Vol. 305, pp. 41–54
Reprints available directly from the publisher
Photocopying permitted by license only

MOLECULAR MAGNETISM: PRESENT AND FUTURE

TADASHI SUGAWARA* AND AKIRA IZUOKA
Department of Pure & Applied Sciences, Graduate School of Arts & Sciences
The University of Tokyo, 3-8-1 Komaba, Meguro, Tokyo 153, Japan

Abstract Organic functional molecules equipped with an *orientation controlling site* are found to construct an organic self-assembly exhibiting prominent magnetic properties. Typical examples are a one-dimensional organic ferrimagnetic spin system, a hydrogen-bonded organic ferromagnet, and an approach to high spin charge transfer complexes. Dynamical spin systems respondent to external stimuli are also described.

I. Introduction

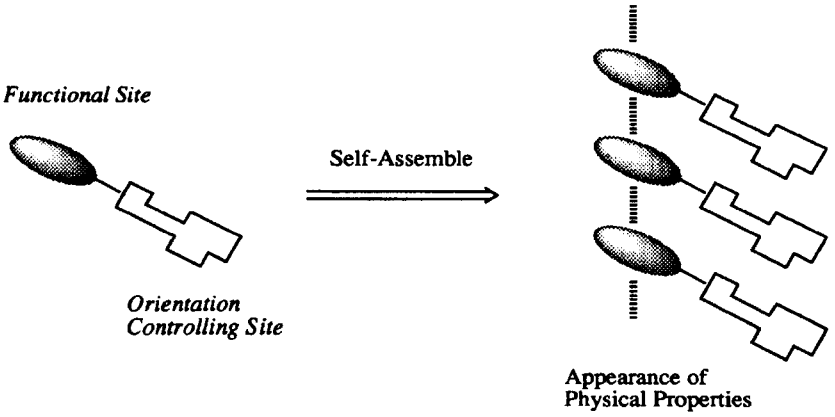
Molecular magnetism is a young research area which has grown rapidly in these two decades.[1] We are now at such a promoted stage as we could not have imagined at that time. An advantage of molecular magnetism is that we can design and prepare spin sources at the molecular level. The origin of molecular magnetism may be traced back to the discovery of a quintet dicarbene by Itoh[2] and Wasserman,[3] and the theoretical proposal of possible ferromagnetic states of hydrocarbons by Mataga.[4] High spin states of poly-*meta*-phenylmethylene (**PMPM**) are realized by a combination of π-topology and a positive exchange interaction at carbenic carbon atoms. For instance, a spin quantum number of the tetracarbene already exceeded those of transition metals, including Fe(III), and Gd(III).[5] Extended systems of such polycarbenes have been reported in both one-dimensional and two-dimensional series.[6] Since magnetism is a property of the bulk nature, one has to take account of intermolecular magnetic interactions among open-shell molecules. In this respect ferromagnetic interaction found in the galvinoxyl crystal was of great significance.[7] Meanwhile cyclophane dicarbenes were synthesized as a model compound for understanding intermolecular magnetic interactions of organic radicals.[8] Magnetic interaction of cyclophane dicarbenes with various relative orientations is an experimental proof for the McConnell's mechanism. These experimental results are the background of a discovery of the first genuine organic ferromagnet by Kinoshita *et al.*[9]

In this paper the authors first describe a couple of important spin systems which were constructed based on the idea of self-assembling of open-shell molecules by virtue of an *orientation controlling site*. And then, some recent attempts are also mentioned concerning

the dynamic spin systems which can be controlled by means of photo-irradiation, transportation of electrons, or modulation of crystal lattices.

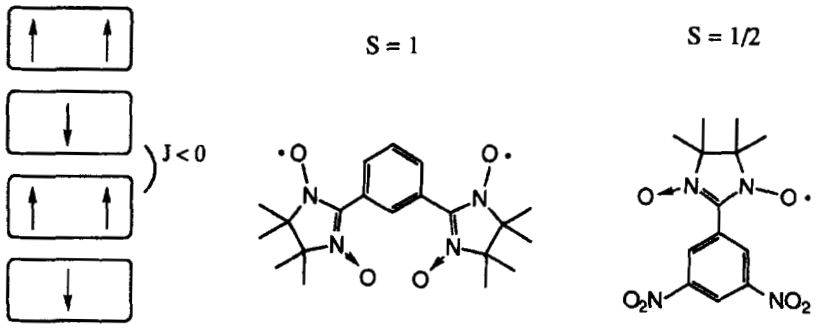
II. Self-organized molecular assemblies of open-shell molecules exhibiting prominent magnetic properties

Establishment of methodology of designing crystal structures exhibiting prominent physical properties is of great significance in materials science. Here we have proposed a method of controlling the structure of a molecular assembly, using a functional molecule equipped with a *functional site* and an *orientation controlling site*. The latter site plays a role of arranging functional molecules in a proper manner in order to manifest the desired magnetic properties by means of intermolecular electrostatic interactions, hydrogen bonds, or charge transfer interactions *etc.* Functional molecules then self-assemble by themselves to create a highly ordered molecular architecture of intriguing physical properties.



1) Crystal designing ferrimagnet

We planned to apply such an idea to construct an organic ferrimagnet, utilizing antiferromagnetic interactions, which are frequently observed between organic radicals. The designed ferrimagnet consists of a ground state triplet diradical, *m*-phenylene-bis(nitronyl nitroxide) (**PBNN**),[10] and a monoradical, *m*-dinitrophenyl nitronyl nitroxide (**DNPN**), where two nitro groups operate as *orientation controlling sites*. Since both nitro groups and nitronyl nitroxide groups are charge polarized, an electrostatic interaction is supposed to exert between them. Mixed-stack crystals of the monoradical and the diradical were obtained as black rods (**PBNN·DNPN·**C_6H_6) from a benzene solution by slow evaporation of the solvent.[11] The two kinds of radical molecules are stacked alternately to form a columnar structure along the *c* axis as presented in Figure 1. As a result of the electrostatic interaction between the nitro groups of the monoradical and the



nitronyl nitroxide groups of the diradical, the distances between them being in the range of 3.18-3.38 Å. This geometrical features should lead to antiferromagnetic interactions of reasonable strength between the triplet diradical and the doublet monoradical. The spin system can be regarded as a one-dimensional ferrimagnetic system, because an intercolumnar distance is as remote as 11.5 Å. The spin system was theoretically analyzed using a Heisenberg Hamiltonian, with parameters for an intramolecular ferromagnetic coupling (J_1) and an intermolecular antiferromagnetic coupling (J_2) between the diradical and the monoradical as shown in Figure 2. A theoretical value of χT was evaluated by diagonalization of the Heisenberg Hamiltonian for a six-spin configuration with a periodic

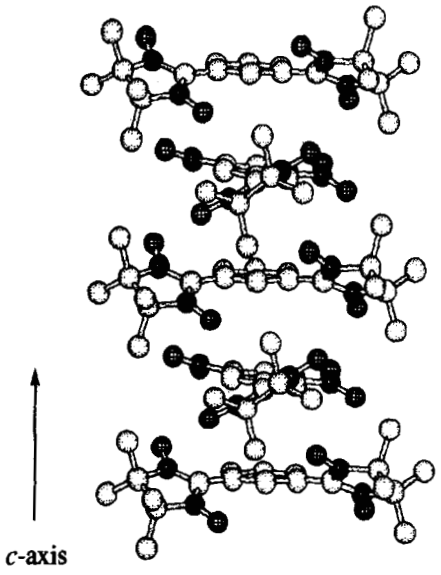


FIGURE 1 Mixed stacking of diradical **PBNN** and monoradical **DNPN** in the crystal.

boundary condition. The experimental values of the χT *vs.* T plot were well reproduced by J_1/k_B = +20 K and J_2/k_B = -30 K.

The ferrimagnetic spin system is unique from the view point of the competing magnetic interaction between the intramolecular ferro- and the intermolecular antiferromagnetic couplings of the same order[12]. Although the size of a ferrimagnetic domain increases with lowering temperatures, the domain size can not extend large enough, because the magnitude of ferro- and antiferromagnetic interactions are weak compared with thermal fluctuation. Thus the net spins, which appeared as the difference between oppositely ordered domains, are supposed to behave paramagnetically. This magnetic behavior is in sharp contrast to one-dimensional *metal to metal* or *metal to radical* ferrimagnetic systems,[13] where an extremely large ferromagnetic coupling is guaranteed by electron spins in d orbitals of metal ions.

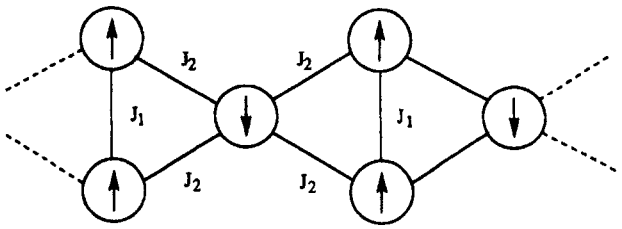


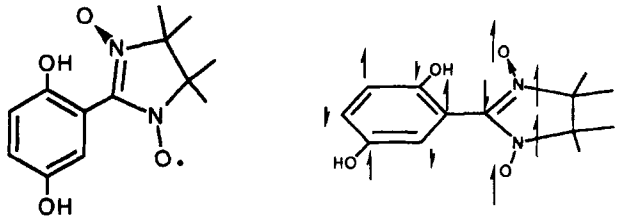
FIGURE 2 Magnetic model of a one-dimensional ferrimagnetic system.

2) Organic ferromagnet of a hydrogen-bonded crystal

Hydrogen bond has drawn much attention from an aspect of constructing a molecular self-assembly.[14] If hydrogen bond plays a role not only of organizing organic molecules but also of a spin coupler which transmits spin polarization intermolecularly, a hydrogen-bonded molecular assembly may manifest prominent magnetic properties[15].

Thus we designed and prepared nitronyl nitroxide derivative (**HQNN**) substituted with *p*-hydroquinone as an *orientation controlling site*. It may be advantageous to estimate the spin distribution of **HQNN** by the semi-empirical molecular orbital calculation (MOPAC MNDO-PM3/UHF method). The oxygen and nitrogen atoms of the nitronyl nitroxide (NN) groups have large positive spin densities, suggesting that the unpaired electron is mostly localized at these sites. While the positive and the negative spin densities distribute alternately over the benzene ring. The hydroxy groups of **HQNN** are spin polarized in the same sign as those of the *ipso*-carbon atom of the benzene ring. Namely, the hydroxy group at the *ortho*-position is spin polarized negatively, whereas that of the *meta*-position

is polarized positively. Contrastingly, methyl hydrogens are all negatively polarized due to a through-bond mechanism.



HQNN

HQNN was found to afford two phases of crystals. In the α-phase crystal, in particular, the phenolic hydroxy group at the *ortho*-position not only forms a strong intramolecular hydrogen bond with the nitroxide group (O···O distance of 2.51 Å), but also forms a bifurcated hydrogen bond with a facing **HQNN** to afford a hydrogen-bonded dimer, the O···O distance between the phenolic oxygen and the nitroxide oxygen being 3.00 Å. This hydroxy group also participates in an intermolecular hydrogen bond with the hydroxy group at the *meta*- position of the translated molecule along the *c* axis with a distance of 2.75 Å (Figure 3), resulting in the intermolecular hydrogen bond along the *c* axis. A similar one-dimensional chain runs in parallel to the former chain with symmetry of inversion between facing molecules. These doubly hydrogen-bonded chains are arranged in a herringbone-type structure as depicted in Figure 4.

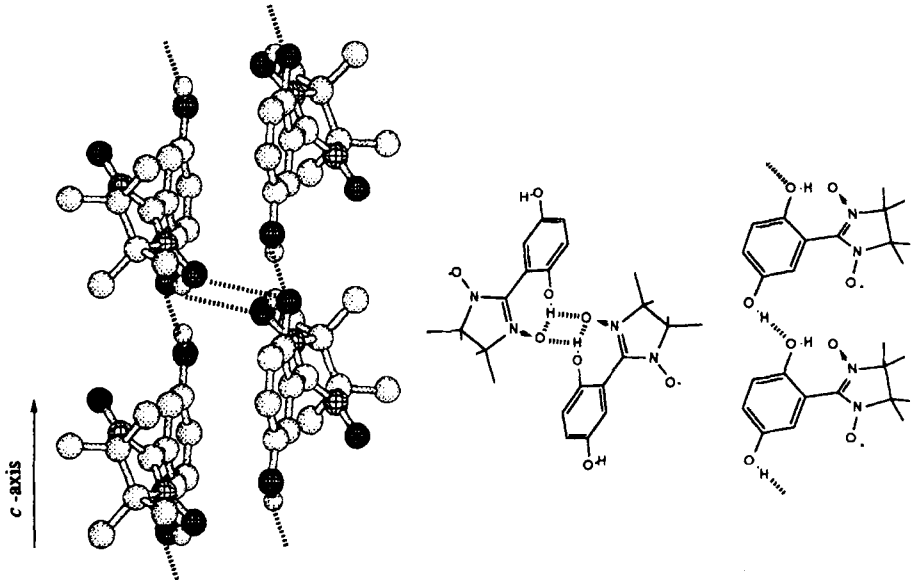


FIGURE 3 Double one-dimensional hydrogen-bonded chains connected by the bifurcated hydrogen bonds.

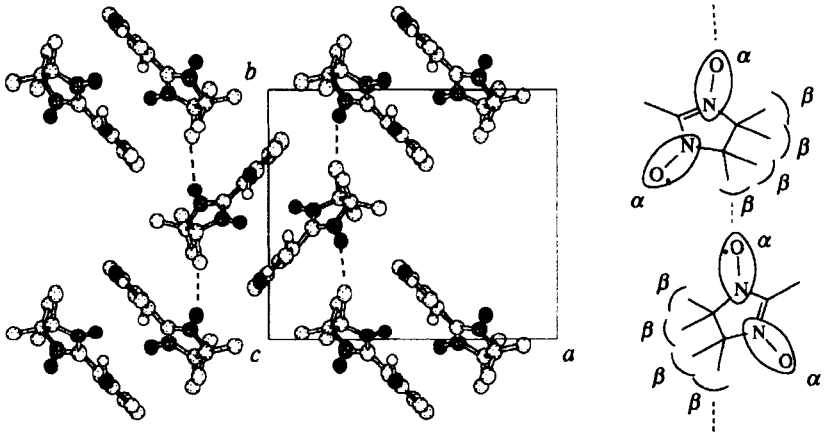


FIGURE 4 Herringbone-type structure of the double hydrogen-bonded chains viewed normal to the *ab* plane. Dotted lines indicate the NO···HC contacts.

The magnetic susceptibility of the polycrystalline sample of α-**HQNN** was analyzed by the S-T model ($J/k_B = 0.95$ K) with a positive Weiss temperature of $\theta = +0.44$ K. The ac susceptibility of α-**HQNN** increased rapidly around 0.5 K, suggesting that a phase transition to the ferromagnetic phase occurred at this temperature. Since the estimated saturation value of the magnetization was very close to the theoretical one ($1\ \mu_B \cdot mol^{-1}$), the phase transition could be regarded as a bulk transition. It also showed a hysteretic behavior, although a coercive force was less than 20 Oe. From the heat capacity data, the spin system of α-**HQNN** turns out to be expressed by the three-dimensional Heisenberg model with a number of the nearest neighbors of $z = 6$ (Figure 5).

The magnetic property of **HQNN** was found to be consistent with the crystal structure. First, the dimeric interaction with the ferromagnetic coupling can be assigned to the hydrogen-bonded face-to-face dimer formed through the bifurcated hydrogen bond. Since this bifurcated hydrogen bond brings two facing **HQNN** molecules closer, the intermolecular distance between the oxygen atoms of NN groups is as short as 3.16 Å. Although such a close location usually causes the antiferromagnetic interaction between NN groups, the experimental result suggests the presence of ferromagnetic interaction even at this site. Thus one might consider that the ferromagnetic interaction through the hydrogen bond predominates over the antiferromagnetic through space NO···ON interaction.[16] Second, the spin polarization should be transmitted ferromagnetically along the one-dimensional hydrogen-bonded chain, because the signs of the spin densities of these sites are opposite. Third, it is also to be noted that the oxygen atom of the NN group

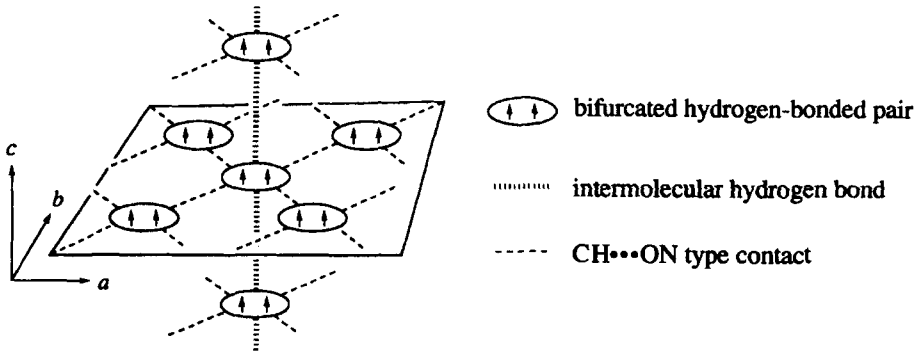


FIGURE 5 Three-dimensional Heisenberg model of **HQNN**.

is closely located to a hydrogen atom (2.74 Å) of the methyl group of the adjacent molecule. Since the methyl hydrogens are supposed to have the negative spin densities, the CH•••ON interaction should increase the dimensionality of the ferromagnetic interactions in crystal.

Although the crystal design of organic ferromagnets is extremely difficult at the present stage, utility of hydrogen bond as a *ferromagnetic coupler* is considered to be one of the promising methods in this respect, because crystal structure based on the hydrogen bond is somewhat predictable. Thus it may be applicable widely to control the molecular arrangement of open-shell molecules.

3) An approach to high spin molecular assembly utilizing charge transfer interaction

Mixed stacking of donors and acceptors is one of the basic assembling patterns of molecular conductors based on charge transfer interaction. If the charge transfer interaction plays a role of not only arranging the constituent molecules in a proper manner, but also aligning electron spins ferromagnetically, it may be powerful to introduce charge transfer interaction into the molecular assembly of open-shell molecules for constructing organic ferromagnets.

McConnell proposed a possibility of ferromagnetic charge transfer complexes composed of a triplet donor and an acceptor.[17] Charge transfer interaction from such a donor to an acceptor should induce a contribution of the cation radical of the donor and an anion radical of the acceptor, resulting in a ferromagnetic spin alignment in the charge transfer complex (Figure 6a). Attempts to realize ferromagnetic charge transfer complexes, using symmetrical donors ($\geq C_{3v}$) possessing degenerated HOMOs, have been unsuccessful,[18] because the degeneracy of HOMOs was removed by the Jahn-Teller distortion.[19]

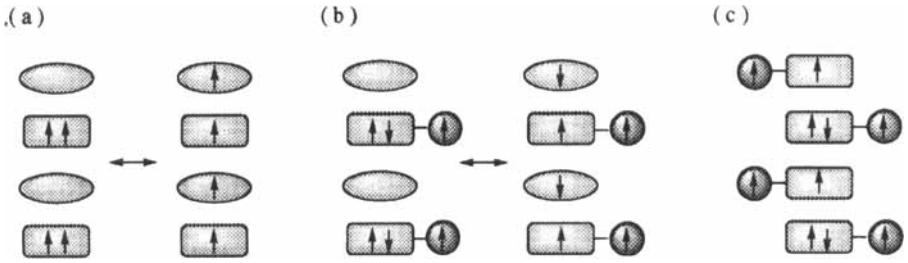


FIGURE 6 Ferromagnetic spin alignment of charge transfer complexes and ion radical salts. (a) McConnell's model. (b) Yamaguchi's model. (c) Modified Wudl's model.

Recently we have reported novel open-shell donors which are composed of a π-donor site and a π radical site, two of the π-systems being cross-conjugated. These open-shell donors are found to afford a ground state triplet cation diradical through one-electron oxidation (Figure 7). Since the high spin state of the cation diradical does not originate from the degeneracy of HOMOs based on the molecular symmetry, but from spin polarization between a localized spin on the radical site and a π spin on the donor site, the ground triplet state of the cation diradical does not suffer from Jahn-Teller effect.[20] Thus the charge transfer complexes obtained by these open-shell donors may be appropriate to realize a ferromagnetic spin alignment (Figure 6b).[21]

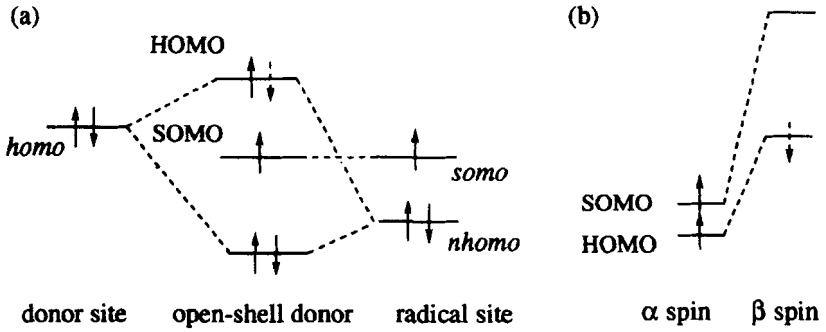
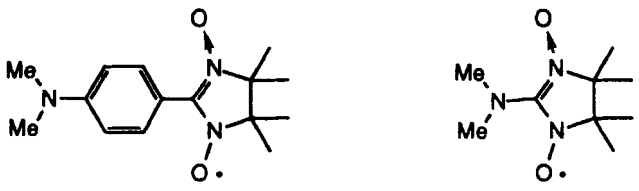


FIGURE 7 Electronic structure of an open-shell donor. (a) Perturbational MO description. (b) UHF-MO description.



Among open-shell donors so far developed, *p-N,N*-dimethylaminophenyl nitronyl nitroxide (**APNN**) was found to afford single crystals of a charge transfer complex with chloranil from a benzene solution.[22] An absorption spectrum of the complex in a KBr disk showed a broad peak at around 900 nm, assignable to the charge transfer band. The complex, however, is considered to be almost neutral, judged from the difference between redox potentials of the donor ($E_{1/2}^{ox}$ = 0.64 V) and the acceptor ($E_{1/2}^{red}$ = 0.11 V), and also from the IR spectral data. An X-ray crystallographic analysis revealed the crystal structure of the complex. As expected, **APNN** and chloranil form a columnar structure of the mixed-stack. The dimethylaminophenyl ring and the quinone ring of chloranil are

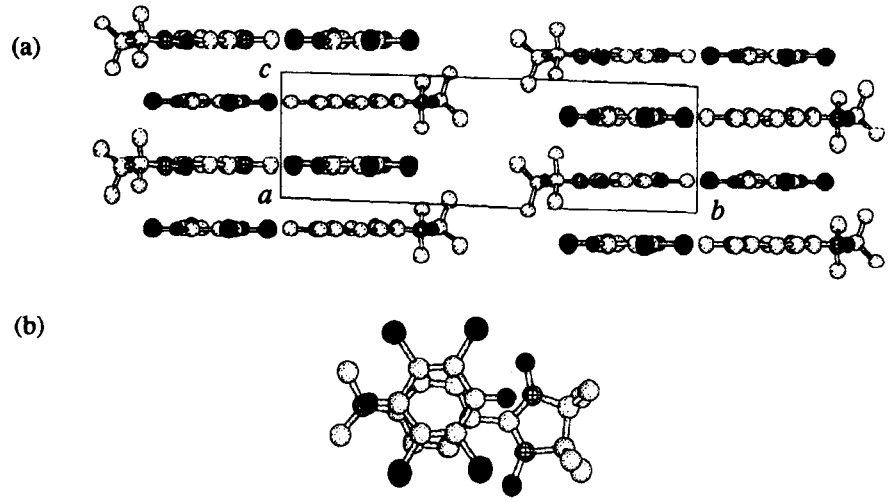


FIGURE 7 (a) Mixed stack of DMANN and chloranil in the charge transfer complex. (b) Overlap between DMANN and chloranil.

parallel, and the interplanar distance being 4.3 Å. The structure suggests that HOMO of the donor and LUMO of the acceptor are overlapped exactly in phase. A benzene molecule is incorporated within a cavity created by methyl groups of the nitronyl nitroxide moieties of the facing **APNN** s. The temperature dependence of the magnetic susceptibility revealed that the complex was basically a paramagnet, exhibiting a weak antiferromagnetic intermolecular interaction (θ = -0.5 K). This **APNN**-chloranil crystal is the first charge transfer complex composed of open-shell donors of which structure has been revealed.

Since **APNN** was proved to afford the ground state triplet cation diradicals, the complex may be considered to satisfy the requirement for the ferromagnetic charge transfer complex. The complex, however, did not exhibit any ferromagnetic interactions. This may be because the degree of charge transfer is not enough to cause a sufficient

contribution of the charge-transferred state into its electronic structure. Then a new charge transfer complex was prepared, using stronger open-shell donor and stronger acceptor: N,N-dimethylamino nitronyl nitroxide (**DMANN**) ($E_{1/2}^{ox}$ = 0.53 V) and **DDQ** ($E_{1/2}^{red}$ = 0.59 V). The complex turned out to be an ion radical salt, judged from the difference between redox potentials and the IR spectrum of the complex. The complex, however, exhibited also a paramagnetic behavior with weak antiferromagnetic interaction (θ = -1 K).

When the above experimental results were examined cautiously, the following requirement may be pointed out. In order to achieve ferrimagnetic spin alignments through charge transfer interaction, the degree of intramolecular ferromagnetic coupling within the open-shell donor (J_1) should be significantly large compared with the intermolecular antiferromagnetic coupling (J_2). Otherwise, one should construct a mixed stack of a ground state triplet donor and its cation radical as an acceptor, in other words, a segregated column of donor with mixed valency (Figure 6c).[23] Since a complex in the latter case is supposed to show metallic conductivity, a ferromagnetic alignment of local spins on the radical site may be achieved through RKKY mechanism.

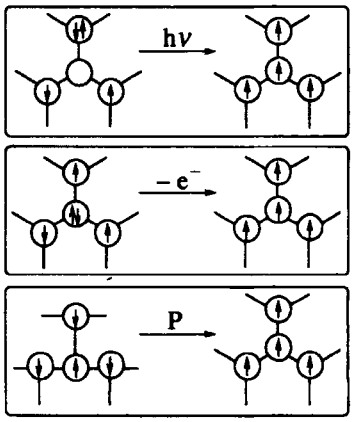
III. Dynamical spin systems correspondent with external stimuli

As describe above, many unconventional spin systems are now available by organizing open-shell molecules. A next stage of advancement of molecular magnetism is to construct dynamical spin systems which can be controlled by means of photo-irradiation, electron attachment or detachment, transportation of electrons, or modulation of crystal lattices. Development of such dynamical systems can be achieved by taking advantage of molecular spin system in which flexible organic molecules carry electron spins. Some of the preliminary results, which fall into this category, will be presented here.

1) Photochemical control

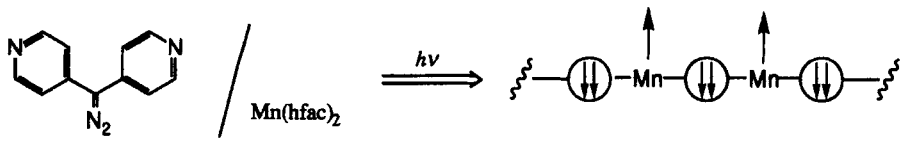
2) Electronic control

3) Lattice control



1) Photochemical modulation

When 1,3-bis(α-diazobenzyl)benzene was photolyzed in host crystals of benzophenone or in a rigid glass at cryogenic temperatures, the quintet signals due to *m*-phenylenebis(phenylmethylene) (*m*-**PBPM**) were observed immediately after UV irradiation. The rate of formation of the quintet signals shows a linear dependence on the light intensity. It was concluded from these findings that the quintet species is formed through the one-photon process.[24] The one-photon mechanism was explained by the efficient intramolecular energy migration, which occurs coupled with elimination of nitrogen, between *meta*- jointed diazo chromophores. Intermolecular counterpart of the similar phenomenon was observed in the photolysis of crystals of bis(4-methoxyphenyl)diazomethane.[25] Recently Koga *et al.* found that irradiation of polymeric complex of bis(4-pyridyl)diazomethane with $Mn(hfac)_2$ afforded high spin species (unit number > 30) efficiently.[26] Reversible photo-magnetization systems should be explored in the near future.



2) Electronic modulation

An anion radical and a cation radical of the quintet dicarbene (*m*-**PBPM**) have been prepared by γ-radiolysis in glassy 2-methyl-THF or in freon matrix, respectively. The ground state spin multiplicity was changed to doublet in both cases of electron attachment (formation of anion radical) and detachment (formation of cation radical).[27] We have generated tricarbene incorporated in a triphenylamine skeleton. Whereas the spin multiplicity of the neutral tricarbene was triplet, that of the anion radical was 3/2 (Figure 8).[28] The change of spin multiplicities of high spin carbenes should be rationalized in detail based on the characteristics of their electronic structure.

Construction of organic ferromagnetic metals is the most challenging target in molecular magnetism. One of the approaches using open-shell donors is described in II-3 in this text. As another approach, utility of a π-conjugated backbone of a conductive polymer has become into consideration. Polypyrroles carrying a stable radical as a pendant group are supposed to show a high spin state when they are doped chemically or electrochemically.[29] The research along this line is in progress in these laboratories.

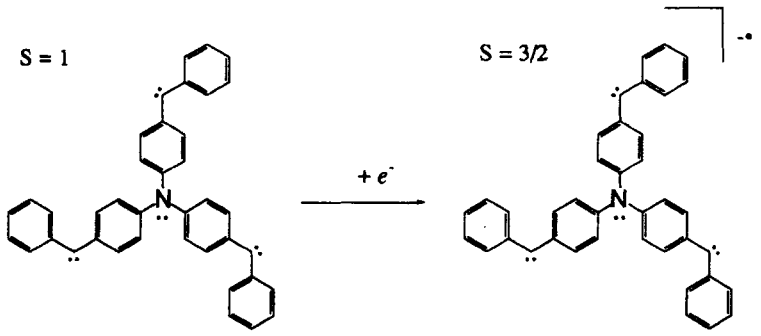
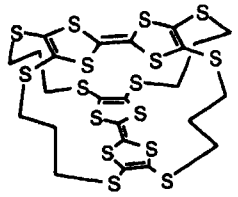


FIGURE 8 Change of ground state spin multiplicity of tricarbene upon electron attachment.

3) Lattice modulation

In order to switch magnetic properties of a molecular spin system through modulation of an external environment, in particular, of a crystal lattices, it is inevitable for a constituent molecule or a molecular assembly to have bistable states.

We have designed a cross-cyclophane twin donor (*X*-**CPTD**), in which long axes of two TTF units are fixed in an orthogonal orientation.[30] There are two electronic configurations for the doubly oxidized state of *X*-**CPTD**: one is a closed-shell singlet



X-**CPTD**

dication and the other is a triplet dication diradical. This donor afforded ion-radical salts through a galvanostatic electrocrystallization in 1,1,2-trichloroethane (TCE) in the presence of tetra-*n*-butylammonium bromide as a supporting electrolyte. The chemical composition of the salt was determined by elemental analysis to be *X*-**CPTD** :Br:TCE = 1:1:2.

Although the χT value of the salt was 0.375 emu·K·mol^{-1} at room temperature, it decreased abruptly, and kept constant in the temperature range of 160 - 300 K. The reduced value of 0.21 emu·K·mol^{-1} was about one half of the original one. With warming the sample, the χT value recovered to the original one. The result suggests the presence of a high temperature phase and a low temperature one for the salt. The interconversion between these two phases was found to be reversible, exhibiting a hysteretic behavior. When the sample was supercooled and the magnetic susceptibility was measured with

increasing temperature, the χT value showed that of the high temperature phase in the temperature range of 30 - 300 K.[31] This interconversion was revealed to be coupled with a structural transition based on the thermal analysis. Thus the sudden decrease of the magnetic susceptibility may be explained in terms of a strong antiferromagnetic coupling induced by the dimerization among donors. The magnetic interconversion observed in this ion radical salt has to be elucidated in detail, considering the dual contribution of electronic configurations of the doubly oxidized state.

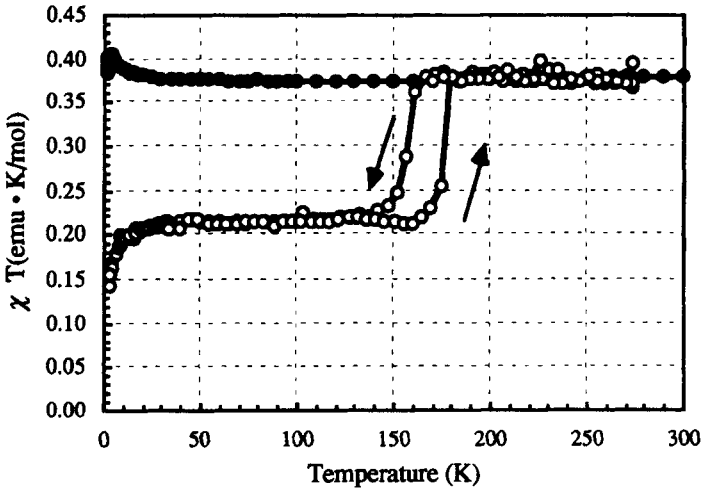


FIGURE 9 The χT *vs.* T plot of ion radical salts of *X*-**CPTD** . White circles indicate the reversible temperature dependence of the χT value observed in a slow cooling-and-warming cycle. Black circles indicate the temperature dependence of χT value for the super-cooled sample.

REFERENCES

1. (a) J. S. Miller and A. J. Epstein, Angew. Chem. Int. Ed. Engl., 33, 385 (1994); (b) A. Rajca, Chem. Rev., 94, 871 (1994); (c) C. Kollmar and O. Kahn, Acc. Chem. Res., 26, 259 (1993).
2. K. Itoh, Chem. Phys. Lett., 1, 235 (1967).
3. E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, G. Smolinsky, J. Am. Chem. Soc., 89, 5076 (1967).
4. N. Mataga, Theor. Chim. Acta, 10, 372 (1968).
5. T. Sugawara, S. Bandow, K. Kimura, H. Iwamura, K. Itoh, J. Am. Chem. Soc., 108, 368 (1986)
6. K. Matsuda, N. Nakamura, K. Inoue, N. Koga, and H. Iwamura, Bull. Chem. Soc. Jpn., 69, 1483 (1996), and references therein.
7. (a) K. Mukai, Bull. Chem. Soc. Jpn., 42, 40 (1969); (b) K. Awaga, T. Sugano,

M. Kinoshita, J. Chem. Phys., 85, 2211 (1986).
8. A. Izuoka, S. Murata, T. Sugawara, H. Iwamura, J. Am. Chem. Soc., 109, 2631 (1987).
9. M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe, and Y. Maruyama, Chem. Lett., 1991, 1225.
10. A. Izuoka, M. Fukada, and T. Sugawara, Mol. Cryst. Liq. Cryst., 232, 103 (1993).
11. (a) A. Izuoka, M. Fukada, R. Kumai, M. Itakura, S. Hikami, and T. Sugawara, J. Am. Chem. Soc., 116, 2609 (1994); (b) A. Izuoka, R. Kumai, and T. Sugawara, Adv. Mater., 7, 672 (1995).
12. D. Shiomi, M. Nishizawa, K. Sato, T. Takui, K.Itoh, H. Sakurai, A. Izuoka, and T. Sugawara, Mol. Cryst. Liq. Cryst., 278, 279 (1996).
13. (a) C. Kollmar, M. Couty, O. Kahn, J. Am. Chem. Soc., 113, 7994 (1991); (b) A. Caneschi, D. Gatteschi, P. Rey, Acc. Chem. Res., 22, 392 (1989).
14. M. C. Etter, Acc. Chem. Res., 23, 120 (1990).
15. (a) T. Sugawara, M. M. Matsushita, A. Izuoka, N. Wada, N. Takeda, and M. Ishikawa, J. Chem. Soc., Chem. Commun., 1994, 1723; (b) J. Cirujeda, M Mas, E. Molins, F. L. Panthou, J. Laugier, J. G. Park, C. Paulsen, P. Rey, C. Rovira, and J. Veciana, J. Chem. Soc., Chem. Commun., 1995, 709.
16. (a) M. M. Matsushita, A. Izuoka, and T. Sugawara, Mol. Cryst. Liq. Cryst., 279, 139-144 (1996); (b) A. Oda, T. Kawakami, S. Takeda, W. Mori, M. M. Matsushita, A. Izuoka, T. Sugawara, K. Yamaguchi, in this proceedings.
17. H. McConnell, Proc. R. A. Welch Found. Conf. Chem. Res., 11, 144 (1968).
18. J. Thomaides, P. Maslak and R. Breslow, J. Am. Chem. Soc., 110, 3970 (1988).
19. J. S. Miller, D. A. Dixon, J. C. Calabrese, C. Vazquez, P. J. Krusic, M. D. Ward, E. Wasserman and R. L. Harlow, J. Am. Chem. Soc., 112, 381 (1990).
20. (a) R. Kumai, H. Sakurai, A. Izuoka and T. Sugawara, Mol. Cryst. Liq. Cryst., 279, 133 (1996); (b) H. Sakurai, R. Kumai, A. Izuoka and T. Sugawara, Chem. Lett., in press.
21. H. Sakurai, A. Izuoka and T. Sugawara, in this proceedings.
22. H. Sakurai, A. Izuoka and T. Sugawara, unpublished data.
23. E. Dormann, M. J. Nowak, K. A. Williams, R. O. Angus, Jr., F. Wudl, J. Am. Chem. Soc., 109, 2594 (1987).
24. K. Itoh, H. Konishi, and N. Mataga, J. Chem. Phys., 48, 4789 (1968).
25. T. Sugawara, H. Tukada, A. Izuoka, S. Murata, and H. Iwamura, J. Am. Chem. Soc., 108, 4272 (1986).
26. H. Iwamura, T. Hayamizu, K. Inoue, N. Koga, in this proceedings.
27. (a) M. Matsushita, T. Nakamura, T. Momose, T. Shida, Y. Teki, T. Takui, T. Kinoshita, and K. Itoh, Bull. Chem. Soc. Jpn., 66, 1333 (1993); (b) M. Matsushita, T. Momose, T. Shida, Y. Teki, T. Takui, and K. Itoh, J. Am. Chem. Soc., 112, 4700 (1990).
28. T. Nakamura, T. Momose, T. Shida, K. Sato, S. Nakazawa, T. Kinoshita, T. Takui, K. Itoh, T. Okuno, A. Izuoka, T. Sugawara, J. Am. Chem. Soc., to be published.
29. J. Nakazaki, M. M. Matsushita, A. Izuoka, and T. Sugawara, in this proceedings.
30. J. Tanabe, T. Kudo, M. Okamoto, Y. Kawada, G. Ono, A. Izuoka, and T. Sugawara, Chem. Lett., 1995, 579.
31. A. Izuoka, J. Tanabe, T. Sugawara, Y. Kawada, R. Kumai, A. Asamitsu, and Y. Tokura, in this proceedings.