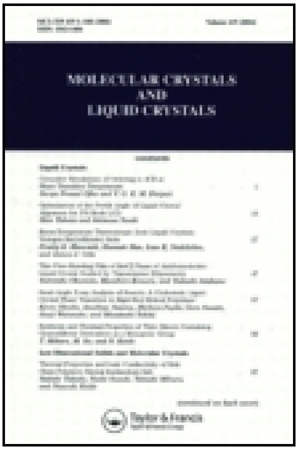


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Manipulating Spin System

Tadashi Sugawara [a]

[a] Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1, Komaba, Meguro, Tokyo, 153-8902, JAPAN

Version of record first published: 24 Sep 2006

To cite this article: Tadashi Sugawara (1999): Manipulating Spin System, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 257-273

To link to this article: http://dx.doi.org/10.1080/10587259908023324

Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 257-273
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Manipulating Spin System

TADASHI SUGAWARA

Department of Basic Science, Graduate School of Arts and Sciences,
The University of Tokyo, 3–8–1, Komaba, Meguro, Tokyo 153–8902, JAPAN

As a building block of organic conducting ferromagnets, TTF-based dimeric donors and spin-polarized TTF donors have been prepared. As an extension of the spin-polarized donor, spin-polarized polyradical donors which afford high spin cation polyradicals upon one-electron oxidation are documented. An idea to realize a manipulating spin system composed of hyper-structured spin-polarized donors is also introduced.

Keywords: cross-cyclophane type TTF donor; nitronyl nitroxide; spin-polarized donor; TTF-based radical donor; organic ferromagnetic metal

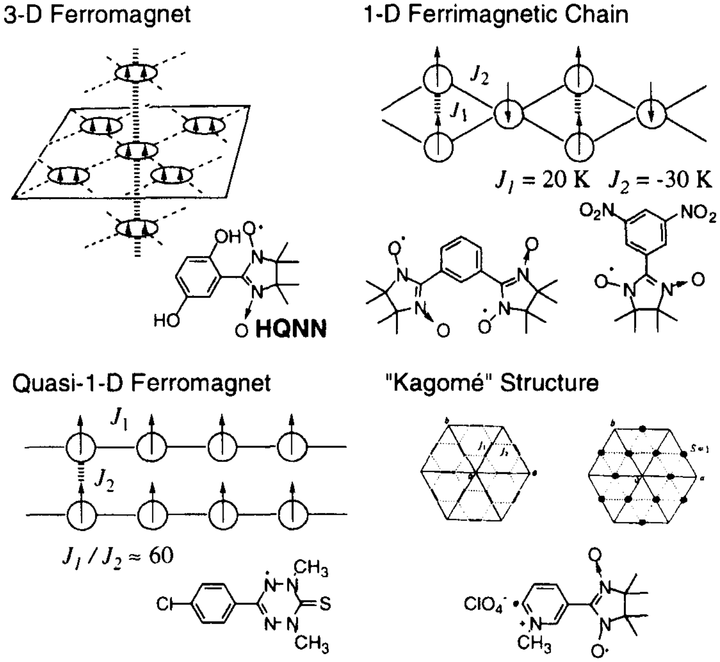
INTRODUCTION

Recent progress in constructing a quantum well or a quantum dot made of semiconductors, such as gallium-arsenide for example, enables to decrease the size of diameters less than 500 nm. When the size becomes that small, its electronic structure becomes quantized to have discrete energy levels just like that of a molecule. It is also found that an orbital-filling with electrons in the quantum dot obeys Hund's rule. Accordingly, such a quantum dot can be regarded as a superatom. If the dots are located closely enough to be electronically communicative, an array of quantum dots may be regarded as a supermolecule. People now are much interested in the spin-polarized phenomenon to be observed in these quantum structures.[1]

Along this line, chemistry of π-conjugated molecules, in fact, has advanced far ahead. One can synthesize a number of π-conjugated molecules of various topologies and even introduce a spin-carrying carbon atom into the π-conjugated molecule at a desired position.

High spin molecules, *e.g.*, poly(*meta*-phenylenemethylene), were found to be generated in use of a carbenic carbon atom as a spin source and a *meta*-phenylene unit as a ferromagnetic coupler.[2] A ferromagnetic coupling in poly(*meta*-phenylenemethylene) is derived from the spin-polarization along the π-conjugated chain. As seen from this example, high spin species, of which spin quantum number exceeds those of transition metal ions or even rare earth ones can be synthesized based on the appropriately designed π-topology.[3] A number of high-spin polyradicals or polycarbenes have been prepared by now.[4]

High spin molecular assemblies were also obtained as shown in Figure 1. A nitronyl nitroxide group or a verdazyl group carries an unpaired electron


3-D Ferromagnet

1-D Ferrimagnetic Chain

Quasi-1-D Ferromagnet

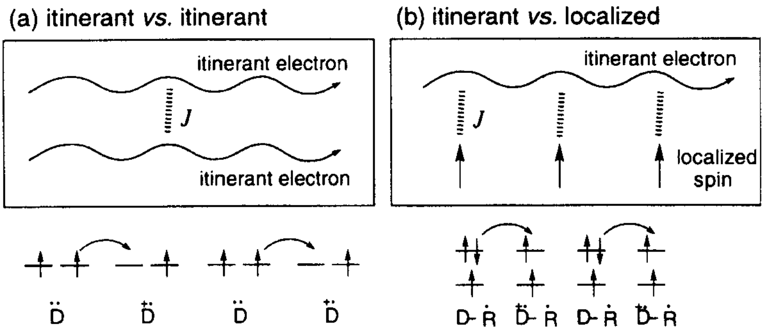
"Kagomé" Structure

FIGURE 1 Molecular spin systems composed of open-shell molecules with an orientation controlling site.

and the other part of the molecule, such as a *para*-hydroxyquinonyl,[5] *meta*-dinitrophenyl,[6] *para*-chlorophenyl[7] or 3-pyridinium group,[8] plays a big role of assembling organic radicals in such a way as to manifest a prominent magnetic property.[9]

Strategies to construct static spin systems have almost been established. Now it is required to realize novel spin systems such that their magnetic properties can be controlled by external stimuli. In this respect, it is promising to study the magnetism of electrons of an itinerant character.[10]

There are two approaches for achieving organic conducting ferromagnets (Figure 2). One is to construct a molecular assembly which carries ferromagnetically coupled conduction electrons.[11] The other is to assemble donor radicals into a columnar stacking with a mixed-valent state in which conduction electrons are exchange-coupled with localized spins.[12]

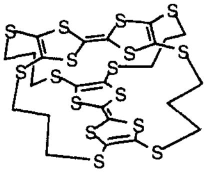

(a) itinerant *vs.* itinerant

(b) itinerant *vs.* localized

FIGURE 2 Magnetism of electrons with itinerant character.

As a first approach, we propose here a TTF-based dimeric donor[13] in which two equivalent donor units are constrained in a cyclophane type geometry.[14] When two π-radicals are connected with an alkyl chain, two types of interactions are expected. They are *through-space* and *through-bond* interactions. Whereas *through-space* interaction usually leads to an antiferromagnetic coupling, *through-bond* interaction depends on the number of carbon atoms. Odd numbers of carbon atoms cause ferromagnetic interaction, while even ones are antiferromagnetic.

Recently we prepared a *cross*-cyclophane type twin donor (**CPTD**) in which two TTF units are connected by four trimethylenedithio chains. Here, the *through-bond* interaction is considered to be ferromagnetic and the antiferromagnetic *through-space* interaction is expected to be negligibly small, since two donor units as fixed by longer alkyl chains in an orthogonal orientation.


CPTD

Another approach for organic ferromagnetic metals where localized spins are aligned by itinerant electrons has been explored as well. We prepared spin-polarized donors in which a donor unit and a radical unit are connected by cross-conjugation as powerful building blocks in this respect.[15]

This paper describes these two approaches refering the model compounds synthesized for this purpose. The spin-polarized polyradicals, of which spin multiplicities may be switchable by redox processes, are also proposed.

EXPERIMENTALS

Preparation of materials were reported in detail elsewhere.[14, 15]

X-ray data were collected by a Rigaku AFC-7R four-circle diffractometer or RAXIS-IV imaging plate diffractometer, using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). Data collection at low temperatures were performed using a cold nitrogen-flow equipment. For obtaining a single crystal of the low-temperature phase, the cold nitrogen was flown to the crystal from a fixed-direction, and the crystal was cooled gently for 50 hours. The structures were solved by a direct method (teXsan SIR92) and were refined for sulfur and bromine atoms with anisotropic temperature factors and other non–hydrogen atoms with isotropic ones by a full matrix least–squares method. The coordinates of hydrogen atoms were recalculated after an each refinement cycle with the isotropic temperature factor.

The electrical conductivity was measured by a two or four probe method, using gold paste for attaching gold wires (ϕ 25 μm) to a sample.

Magnetic susceptibility measurements were performed on a Quantum

Design MPMS SQUID magnetometer/susceptometer or an Oxford Faraday-type magnetic balance system.

ESR measurements were performed on a JEOL JES-RE2X spectrometer equipped with an Air Products LTR-3 liquid helium transfer system and a Scientific Instruments 3700 digital temperature indicator/controller. The temperature close to the sample was measured separately with an Advantest TR2114H digital multi-thermometer with a gold-iron thermocouple. Temperature calibration was performed by a Lake Shore GR-200B-1500 monitoring Ge resistance thermometer. Microwave frequency was measured with an ADVANTEST TR5212 counter, and resonance field values were measured with the aid of an Echo Electronics ES-FC5 NMR field meter.

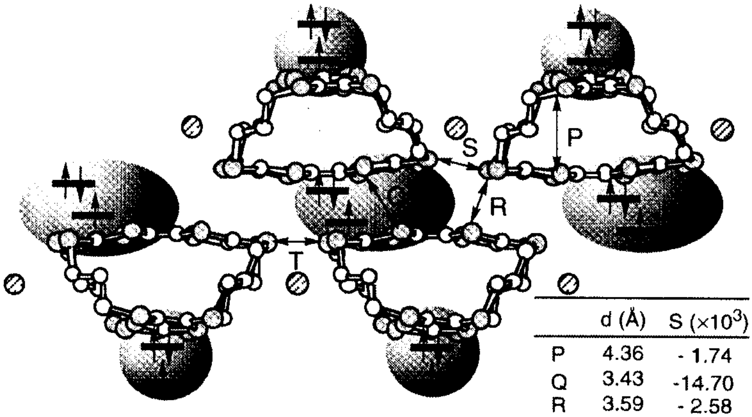
RESULTS AND DISCUSSION

1) Design and preparation of conducting organic magnets

a) Molecular conductor composed of a cross-cyclophane TTF donor with ferromagnetic intermolecular interaction

The *cross*-cyclophane type TTF derivative (**CPTD**) afforded an ion-radical salt, **CPTD**·Br·TCE_2 (TCE=1,1,2-trichloroethane), by electrocrystallization in 1,1,2-trichloroethane in the presence of tetra-*n*-butylammonium bromide. An X-ray crystallographic analysis of the salt (space group: $P4_1$) reveals that cation radicals of **CPTD** are arranged in a *face-to-face* manner as shown in Figure 3 along the *a*- and *b*-axes, although the long molecular axes are shifted by one half. Incidentally, two axes are equivalent according to the symmetry of the crystal structure. Inside the cavity created by surrounding donors, a bromide ion and two solvent molecules of 1,1,2-trichloroethane are incorporated per one donor molecule.

The conductivity of the salt measured by a two-probe method was 1.0×10^{-4} S•cm^{-1} along the *a*- or *b*-axis and 5.5×10^{-5} S•cm^{-1} along the *c*-axis. Judged from the overlap integrals shown in Figure 3, the highest possibility of finding an unpaired electron was recognized in an overlapping region of two intermolecular donor planes. Temperature dependence of the conductivity



	d (Å)	S (×10^3)
P	4.36	- 1.74
Q	3.43	-14.70
R	3.59	- 2.58
S	3.47	0.16
T	3.44	0.26

FIGURE 3 Crystal structure of **CPTD**·Br·TCE$_2$.
[Crystal data: *Tetragonal*, Space group: $P4_1$, a = 12.3395(5), c = 29.6494(8) Å, V = 4514.5098Å^3, Z = 4, D_{calc} = 1.724 g•cm^{-1}, R = 0.050]

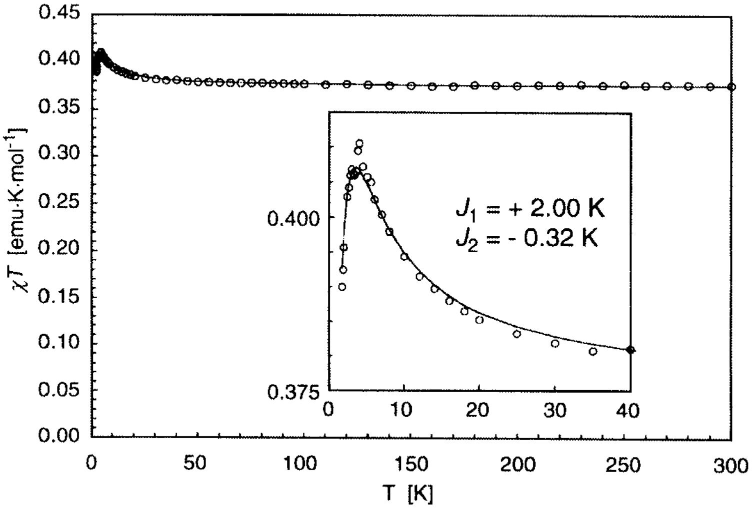
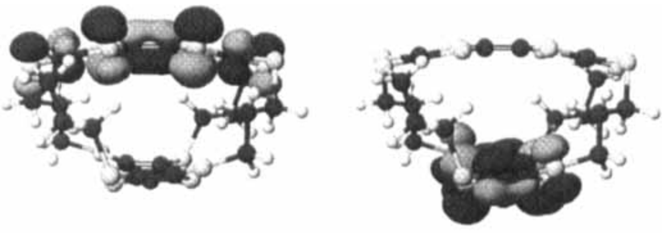


FIGURE 4 χT vs. T plot of **CPTD**·Br·TCE$_2$.

indicated that the salt is a semiconductor, and the activation energy was estimated to be 0.54 eV.

Magnetic property of the single crystal of the salt was measured by SQUID with increasing temperature from 2 K to 300 K (Figure 4). The χT value is 0.375 emu•K•mol^{-1} at room temperature, indicating that each donor molecule carries one unpaired electron when the molecular weight was estimated from the elemental analysis. The temperature dependence of the χT value shows a ferromagnetic interaction of J = +2.0 K, although a small antiferromagnetic interaction (J = -0.3 K) was observed at lower temperatures.

The observed results can be rationalized by the MO calculation. The shape of SOMOs of dication-diradical of **CPTD** was calculated by the PM3/UHF method as shown in Figure 5. The energy levels of two SOMOs are practically the same, and they have small coefficients at the middle carbon of bridging chains. The ferromagnetic interaction is, thus, caused by the spin-polarization mechanism. Namely two SOMOs spin-polarize the low-lying MO of which coefficients are localized on the alkyl chains.



SOMO-1 SOMO-2

FIGURE 5 SOMOs of dication-diradical of **CPTD**.

Since the unpaired electrons have a high chance to reside in-between two donor planes which are overlapped intermolecularly, the donor **CPTD** is sandwiched by two unpaired electrons in the HOMO-SOMO interacting sites. The intermolecular ferromagnetic interaction, therefore, can be ascribed to the intramolecular ferromagnetic coupling of **CPTD** through the spin-polarization along the trimethylenedithio chains (Figure 6).

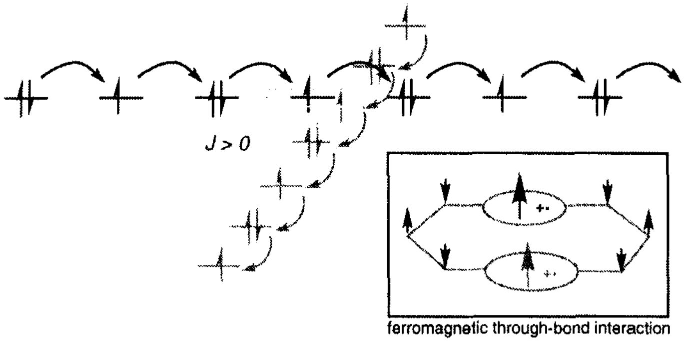


FIGURE 6 Schematic drawing of conduction mechanism and magnetic interaction in **CPTD**·Br·TCE$_2$.

Although a degree of the ferromagnetic coupling in **CPTD**·Br·TCE$_2$ is weak, the coexistence of conductivity and magnetism in the ion-radical salt observed here is of great significance in designing an organic ferromagnetic metal.

b) Reversible change of conducting and magnetic properties of ion radical salts of cross-cyclophane donor CPTD

When magnetic susceptibility was measured by a Faraday-type magnetic balance at a slower cooling rate (0.16 K/min), the χT value was found to decrease abruptly at *ca.* 160 K to 0.21 emu•K•mol^{-1} which is about one half of the original one (Figure 7). With warming the sample, the χT value recovered to the original one at *ca.* 180 K. The result suggests the presence of a high temperature phase and a low temperature one. The interconversion between two phases was found to be reversible, exhibiting a hysteretic behavior. On the other hand, when the sample was super-cooled, the χT value is kept constant at the value of the high temperature phase as described in the last section.

The conductivity was also found to change coupled with the structural phase transition reversibly. Interestingly, the conductivity of the low temperature phase is one order higher than that of the high temperature one.

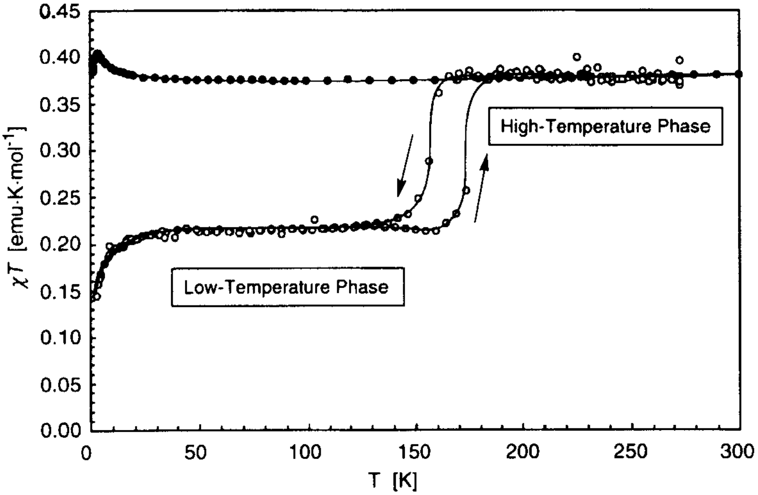
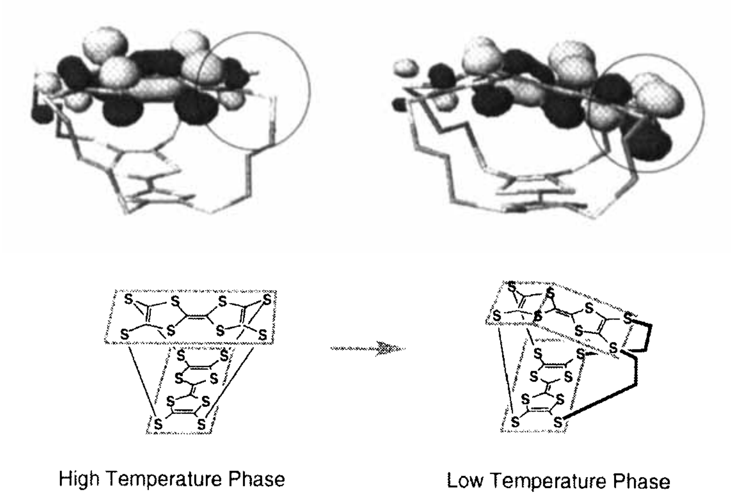


FIGURE 7 Hysteretic behavior observed in the χT vs. T plot of **CPTD**·Br·TCE$_2$.

The transition temperature was sensitive to the external pressures applied. And the transition temperature shifted to the higher temperature side with increasing the external pressure (*e.g.* 255 K / 3 kbar; 280 K / 5 kbar).

The crystal structure of the low temperature phase was also determined. The symmetry of the space group decreases from $P4_1$ to $P2_1$. The arrangement of the ion-radical species in the low temperature phase is not significantly different from that of the high temperature one. The conformation of the donor unit of **CPTD**, however, changed drastically as shown in Figure 8. The long axis of the deformed donor unit is arranged only along the one of the two axes, *e.g.* *b*-axis. Whereas the conformation of the donor unit along the other axis is kept unchanged.

The driving force of the structural phase transition may be explained as follows. At the low temperature phase, dynamic disorder of the incorporated solvent molecules is suppressed. Since the effetive volume of the solvent molecules in the cavity becomes smaller, the conformation of the donor molecule is considered to change so as to fill the void created by the shrinkage of the cavity.



High Temperature Phase

Low Temperature Phase

FIGURE 8 Distribution of coefficients of SOMOs of dication-diradical of **CPTD** at high and low temperature phases.
[Crystal data of the low temperature phase: *Monoclinic*, Space group: $P2_1$, a = 12.314(5), b = 29.33(1), c = 12.211(5) Å, β = 90.29(3), V = 4410(3) Å^3, Z = 4, D_{calc} = 1.765 g•cm^{-1}, R = 0.191]

According to the MO analysis, the coefficient of the sulfur atoms directly attached to the TTF skeleton are negligibly small in the high temperature phase, but they become considerably large when the conformation around the C-S bond changes coupled with the deformation of the donor in the low temperature phase (Figure 8). The increase of the coefficients at the sulfur atoms constructs an efficient conduction path along the *b* axis. Therefore, the unpaired electrons along this axis were strongly coupled antiferromagnetically. This may be the reason for the decrease of the magnetic susceptibility by half in the low temperature phase.

The interconversion between two phases with different mangetic susceptibilities may be compared with a spin-crossover phenomenon of transition metal complexes with high spin and low spin states. It is to be noted that the magnetic interconversion of this ion-radical salt is not originated from the different spin states of the donor molecule, but from a change of the number of paramagnetic species coupled with the structural transition.

c) Preparation of spin-polarized TTF donors as a building block of orgnaic ferromagnetic metal

Let us consider a donor radical in which a stable radical site is connected with a donor site through a cross conjugation. As a prototype of such a donor radical, we designed a nitronyl nitroxide derivative (**DMANN**) substituted by a dimethylamino group (Figure 9).

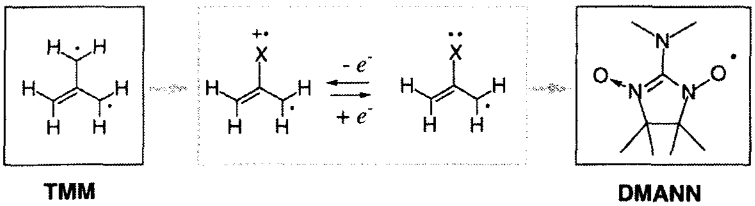


FIGURE 9 Design of a spin-polarized donor: Dimethylaminonitronyl nitroxide.

When **DMANN** is singly oxidized, the resultant cation diradical is considered to exist as a ground state triplet species. The origin of the ferromagnetic spin coupling in **DMANN**$^{+\bullet}$ can be rationalized as follows. While coefficients of one of the SOMOs are restricted only on the NN site, those of the other, which is generated from HOMO upon one-electron oxidation, spread over to the donor site, sharing coefficients even on the radical site. The electronic feature of **DMANN**$^{+\bullet}$ is exactly the same as that of trimethylenemethane (**TMM**), although the degeneracy of SOMOs is removed in **DMANN**.

When this donor radical is oxidized by iodine, an ESR spectrum of the singly oxidized species shows a distinct triplet signal with zero-field parameters of $|D| = 0.0276\ \mathrm{cm}^{-1}$, $|E| = 0.0016\ \mathrm{cm}^{-1}$. The temperature dependence of the triplet signal obeys Curie law. The result reveals that the cation-diradical has the ground triplet spin multiplicity. *If the electrons in HOMO of a donor* radical is spin-polarized sufficiently by the unpaired electron in SOMO, one-electron oxidation of the donor radical should afford a ground state triplet

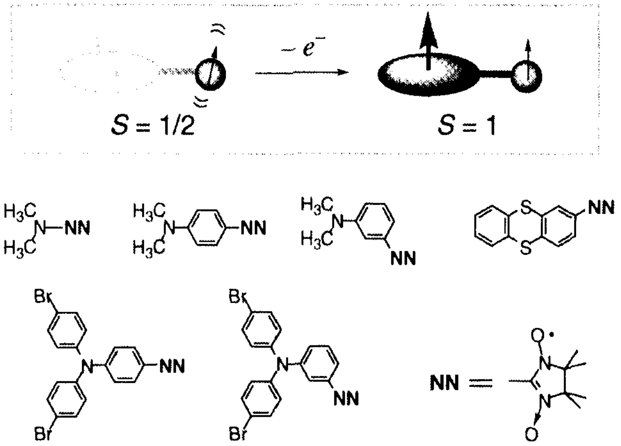


FIGURE 10 Spin-polarized donors which afford triplet cation diradicals upon one-electron oxidation.

cation diradical. Such a type of donor radicals can be designated as a spin-polarized donor. Spin-polarized donors which have been synthesized so far are summarized in Figure 10.

When spin-polarized donors are stacked and partially doped, they are expected to form a conduction column. Since two spins generated in the singly oxidized species are coupled ferromagnetically, the electron to be transferred is of a β spin, which align all the unpaired electron to α. This mechanism of the spin ordering is called a double exchange mechanism and is found to be operating in some of transition metal oxides which exhibit both metallic conductivity and ferromagnetism.

For constructing such a conducting ferromangnet, a donor part was replaced with a TTF skeleton in order to guarantee a columnar stacking of a mixed valence state. We synthesized several TTF-based donor radicals for this purpose (Figure 11). For instance, **TTF-PN** was oxidized by iodine in DMSO at room temperature, and a triplet ESR spectrum ($|D| = 0.0255\ \mathrm{cm}^{-1}$, $|E| = 0.0023\ \mathrm{cm}^{-1}$) was measured in a glassy matrix at 5 K. The temperature dependence of the intensity of the triplet signal obeys Curie law, suggesting that the triplet is the ground state of the resultant cation-diradical. In order to

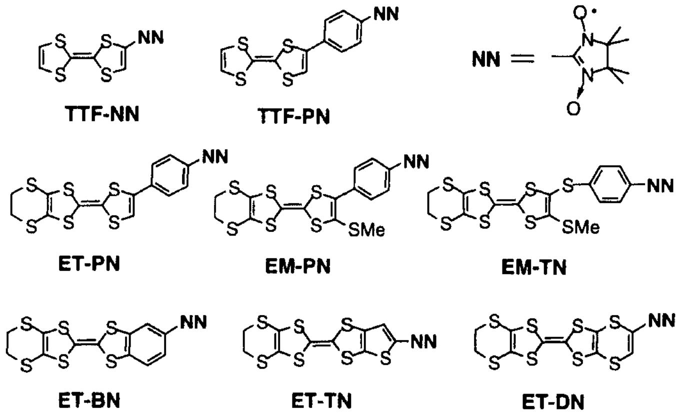


FIGURE 11 TTF-based donor radicals.

increase the kinetic stability of the singly oxidized species, a methylthio group was introduced to the vinylic carbon atom to afford **EM-PN**. The synthetic route of **EM-PN** is shown in Figure 12. In fact the kinetic stability of the cation-diradical of **EM-PN** was found to be appreciably increased.

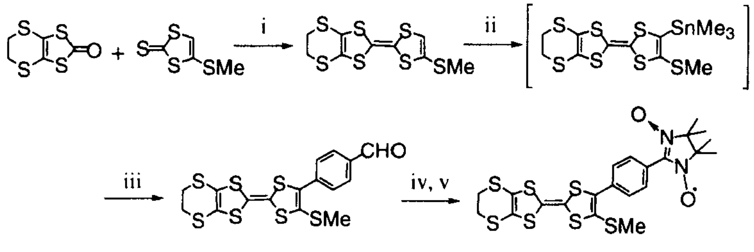


FIGURE 12 Synthetic route of **EM-PN**.
(i) $P(OEt)_3$, 110°C, 4 h, 60 %; (ii) (1) LDA/THF, -70°C, (2) Me_3SnCl, -70°C; (iii) IPhCHO, $Pd(PPh_3)_4$, toluene-1M Na_2CO_3aq., reflux 30 h, 56 %; (iv) $(C(CH_3)_2(NHOH))_2$, CH_2Cl_2-Hexane, reflux 40 h, 94 %; (v) PbO_2, K_2CO_3, THF, 4 h, 83 %.

Single crystals of radical ion salts of the spin-polarized donors are considered to be obtained when a molecular shape of the donor radical becomes more or less symmetrical. For this purpose a new donor radical (**ET-TN**) in which a thienyl ring is fused with the donor core was also synthesized in order to introduce a radical group along the long molecular axis.

2) Generation of high spin species derived from spin-polarized polyradicals

As an extension of the spin-polarized donor, we designed a spin-polarized polyradical donor as depicted in Figure 13. Since these radical units are coupled loosely in the neutral state, the unpaired electrons behave paramagnetically. However, once the core unit is singly oxidized, the generated unpaired electron delocalizes over the entire molecule, aligning these fluctuating local spins to the same direction, giving rise to a high spin species. The point here is that one can generate high spin species by removing only one electron.

Thianthrene or *N,N*-tetraphenyl-*para*-phenylenediamine is used as an oxidizable core for the diradical, and NN groups are introduced into the aromatic rings. In a neutral state, the diradical shows a doublet signal, suggesting that the magnetic interaction between NN groups are negligibly

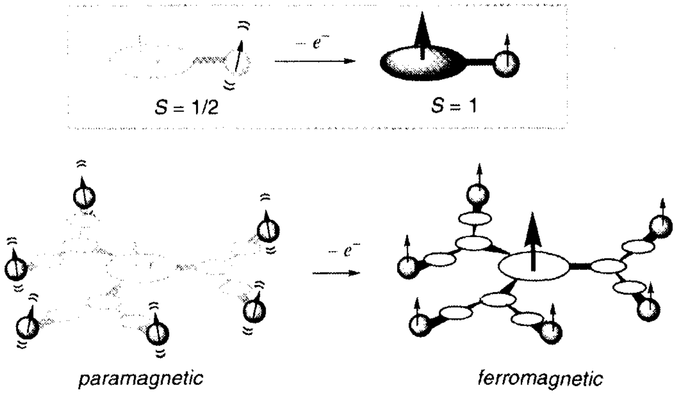


FIGURE 13 Generation of high-spin species by one-electron oxidation.

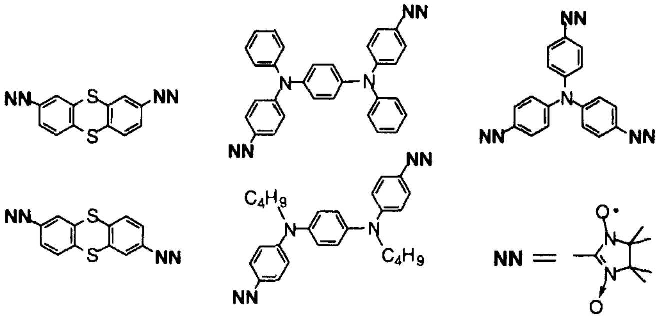


FIGURE 14 Spin-polarized polyradical donors.

small, because the NN group is substituted with the donor site at the nodal carbon (so called "disjoint" connection). When the donor part is oxidized, carbon atoms at the foot of the NN groups become active carbon atoms. Then, the spins on the radical sites start to communicate with the π-delocalizing spin to afford a quartet signal. The Curie plot suggests that the quartet is the ground state for the cation triradical. The triradical with a triphenylamine skeleton also provided the corresponding result.

PROSPECT OF MANIPULATING ORGANIC SPIN SYSTEM

Lastly, prospect of organic spin system will be mentioned. Some time ago, Carter proposed a concept of molecular devices.[16] His idea was thought to be impractical at that time. A rapid progress in the instrumental techniques, such as spin-polarized STM or magnetic force microscopy, enables to detect magnetized micro-domains efficiently. If an organic high spin molecule itself becomes a magnetic micro-domain, the resolution of the information storage should be enhanced tremendously.

Since a concept of spin-polarized polyradical donors has been established, hyper-structured spin-polarized donors are planned to be synthesized, because such donors are considered to be observed by scanning probe microscopy (SPM) and the change of spin-multiplicities may be differentiated from the images with an atomic-resolution. In such a case, hyper-structured spin-polarized donors may be regarded as molecular spin devices.

Acknowledgments

This work was partly supported by CREST from Japan Science and Technology Corporation (JST).

References

[1] S. Tarucha, D.G. Austing, T. Honda, R.J. van der Hage, L.P. Kouwenhoven, *Phys. Rev. Lett.*, **77,** 3613 (1996).

[2] a) K. Itoh, ***Chem. Phys. Lett.,*** **1,** 235 (1967); b) E. Wasserman, R.W. Murray, W.A. Yanger, A.M. Trozzolo, G. Smolinsky, *J. Am. Chem. Soc.*, **89,** 5076 (1967).

[3] a) T. Sugawara, S. Bandow, K. Kimura, H. Iwamura, K. Itoh, *J. Am. Chem. Soc.*, **106,** 6449 (1984); b) T. Sugawara, S. Bandow, K. Kimura, H. Iwamura, K. Itoh, *J. Am. Chem. Soc.*, **108,** 368 (1986).

[4] a) A. Rajca, J. Wongsriratanakul, S. Rajca, R. Cerny, *Angew. Chem. Int. Ed.*, **37,** 1229 (1998); b) R.J. Bushby, D. Gooding, *J. Chem. Soc., Perkin Trans.* **2, 1998,** 1069; c) K. Matsuda, N. Nakamura, K. Inoue, N. Koga, H. Iwamura, *Bull. Chem. Soc. Jpn.*, **69,** 1483 (1996).

[5] a) T. Sugawara, M.M. Matsushita, A. Izuoka, N. Wada, N. Takeda, M. Ishikawa, *J. Chem. Soc., Chem. Commun.*, **1994,** 1723; b) M.M. Matsushita, A. Izuoka, T. Sugawara, T. Kobayashi, N. Wada, N. Takeda, M. Ishikawa, *J. Am. Chem. Soc.*, **119,** 4369 (1997).

[6] a) A. Izuoka, M. Fukada, T. Sugawara, M. Sakai, S. Bandow, *Chem. Lett.*, **1992,** 1627; b) A. Izuoka, M. Fukada, T. Sugawara, *Mol. Cryst. Liq. Cryst.*, **232,** 103 (1993); c) A. Izuoka, M. Fukada, R. Kumai, M. Itakura, S. Hikami, T. Sugawara, *J. Am. Chem. Soc.*, **116,** 2609 (1994); d) D. Shiomi, M. Nishizawa, K. Sato, T. Takui, K. Itoh, H. Sakurai, A. Izuoka, T. Sugawara, *J. Phys. Chem. B,* **101,** 3342 (1997).

[7] a) K. Mukai, K. Konishi, K. Nedachi, K. Takeda, *J. Phys. Chem.*, **100,**9658 (1996); b) K. Takeda, K. Konishi, K. Nedachi, K. Mukai, *Phys. Rev. Lett.*, **74,** 1673 (1995).

[8] K. Awaga, T. Okuno, A. Yamaguchi, M. Hasegawa, T. Inabe, Y. Maruyama, N. Wada, *Phys. Rev. B,* **49,** 3975 (1994).

[9] a) M. Kinoshita, P. Turek, M. Tamura, K. Nozawa, D. Shiomi, Y. Nakazawa, M. Ishikawa, M. Takahashi, K. Awaga, T. Inabe, Y. Maruyama, *Chem. Lett.*, **1991,** 1225; b) R. Chiarelli, M.A. Novak, A. Rassat, J.L. Tholence, *Nature,* **363,**147 (1993); c) T. Nogami, T. Ishida, H. Tsuboi, H. Yoshikawa, H. Yamamoto, M. Yasui, F. Iwasaki, H. Iwamura, N. Takeda, M. Ishikawa, *Chem. Lett.*, **1995,** 635; d) J. Cirujeda, M. Mas, E. Molins, F.L. Panthou, J. Laugier, J.G. Park, C. Paulsen, P. Rey, C. Rovira, J. Veciana, *J. Chem. Soc., Chem. Commun.,*1995, 709; e) K. Mukai, K. Konishi, K. Nedachi, K. Takeda, *J. Magn. Magn. Mater.*, **140–144,** 1449 (1995); f) A. Caneschi, F. Ferraro, D. Gatteschi, A. Lirzin, M.A. Novak, E. Rentschler, R. Sessoli, *Adv. Mater.*, **7,** 476 (1995).

[10] T.J. Lepage, R. Breslow, ***J. Am. Chem. Soc.,*** **109,** 6412 (1987).

[11] E. Dormann, M. Nowak, K.A. Williams, R.O. Angus Jr., F. Wudl, *J. Am. Chem. Soc.*, **109,** 2594 (1987).

[12] a) K. Yamaguchi, H. Nishimoto, T. Fueno, T. Nogami, Y. Shirota, *Chem. Phys. Lett.*, **166,** 408 (1990); b) K. Yamaguchi, M. Okumura, T. Fueno, K. Nakasuji, *Synth. Metals,* **41,** 3631 (1991).

[13] a) A. Izuoka, R. Kumai, T. Sugawara, *Chem. Lett.*, **1992,** 285; b) A. Izuoka, R. Kumai, T. Tachikawa, T. Sugawara, *Mol. Cryst. Liq. Cryst.*, **218,** 213 (1992); c) T. Tachikawa,

A. Izuoka, R. Kumai, T. Sugawara, Y. Sugawara, *Solid State Commun.*, **82,** 19 (1992); d) T. Tachikawa, A. Izuoka, T. Sugawara, *Solid State Commun.*, **88,** 207 (1993); e) R. Kumai, K. Ozawa, G. Ono, T. Tachikawa, A. Izuoka, T. Sugawara, *Mol. Cryst. Liq. Cryst.*, **255,** 17 (1994).

[14] a) J. Tanabe, T. Kudo, M. Okamoto, Y. Kawada, G. Ono, A. Izuoka, T. Sugawara, *Chem. Lett.*, **1995,** 579; b) J. Tanabe, G. Ono, A. Izuoka, T. Sugawara, T. Kudo, T. Saito, M. Okamoto, Y. Kawada, *Mol. Cryst. Liq. Cryst.*, **296,** 61 (1997); c) A. Izuoka, J. Tanabe, T. Sugawara, Y. Kawada, R. Kumai, A. Asamitsu, Y. Tokura, *Mol. Cryst. Liq. Cryst.*, **306,** 265 (1997).

[15] a) R. Kumai, M.M. Matsushita, A. Izuoka, T. Sugawara, *J. Am. Chem. Soc.*, **116,** 4523 (1994); b) R. Kumai, H. Sakurai, A. Izuoka, T. Sugawara, *Mol. Cryst. Liq. Cryst.*, **279,** 133 (1996); c) H. Sakurai, R. Kumai, A. Izuoka, T. Sugawara, *Chem. Lett.*, **1996,** 879; d) H. Sakurai, A. Izuoka, T. Sugawara, *Mol. Cryst. Liq. Cryst.*, **306,** 415 (1997).

[16] F. Carter, *Molecular Electronic Devices* (Marcel Dekker, New York, 1980).