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Single-Component Molecule-Based Ferrimagnetics

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The past decades have witnessed a rapid development of molecule-based magnetism.[1] More than 30 ferromagnets have been well-documented in genuinely organic molecule-based materials,[1] following the first organic ferromagnet *p*-NPNN.[2] In contrast, ferrimagnetic spin ordering resulting from an antiparallel coupling of different spin quantum numbers, e.g., $S = 1$ and $^1/_2$, has never been realized in organic molecular solids. Only a molecular complex of an $S = 1$ biradical and an $S = {}^1/_2$ radical has been reported,[3] which exhibits no long-range ordering. Construction of organic ferrimagnetics has been a challenging issue since the first theoretical proposal in 1979.[4] In this paper, we report a ferrimagnetic behavior in a genuinely organic material based on a novel approach of molecular designing proposed previously.[5a,b] Very recently, Hosokoshi et al.[6] have claimed to succeed in making for the first time a purely organic molecule-based ferrimagnet. Their molecular designing strategy[6] is seemingly the same as ours. From comparison of the electronic spin and crystal structures for the two model compounds, the nature of ferrimagnetic spin alignment in organic materials is discussed. A crucial question is raised about the molecule-based ferrimagnetism in connection with the mechanism for ferromagnetic spin alignment in assemblages of ordinary $S = {}^1/_2$ radicals.

As a purposive molecular designing for cocrystallizing distinct molecules in a solid state, we have proposed a strategy of "single-component ferrimagnetics":[5a,b] When a π-biradical with a triplet ($S = 1$) ground state and a π-radical with $S = {}^1/_2$ are connected by σ-bonds, additional intramolecular interactions through the σ-bonds, $J_1(\sigma)$ and $J_2(\sigma)$, in the resultant triradical are expected to be extremely small as compared with the ferromagnetic interaction, $J_3(\pi)$, in the $S = 1$ moiety (Figure 1). In such systems, the π-conjugation across the moieties is substantially truncated. Intermolecular π-orbital overlaps between an $S = 1$ moiety of one molecule and an $S = {}^1/_2$ moiety of the adjacent molecule mimic molecular complexation of π-biradicals and π-monoradicals. We have designed and synthesized a triradical **1** (Figure 1, left) from a phenol-substituted biradical **2**[5c] and a benzoic acid monoradical **3**[7] as a building block of "single-component ferrimagnetics". The phenol biradical **2** is known to have an intramolecular ferromagnetic interaction of $J_3(\pi)/k_B \sim 10$ K.[5c] The lower limit of the additional interactions, $|J_1(\sigma)|$ and $|J_2(\sigma)|$, of **1** has been estimated to be 10 mK from ^{14}N hyperfine splitting patterns of ESR spectra in solutions.[5a]

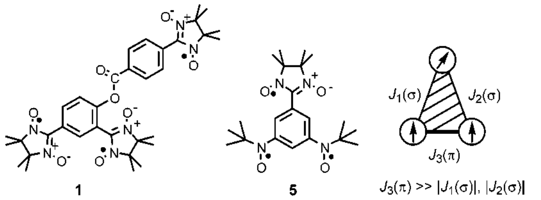

Figure 1. Triradicals **1** and **5** and the schematic drawing of the three-centered exchange coupled system. $J_1(\sigma)$ and $J_2(\sigma)$ show the weak interactions through the σ-bonds in **1**, while $J_3(\pi)$ denotes the ferromagnetic interaction through the π-conjugation of the *m*-phenylene-based biradical.

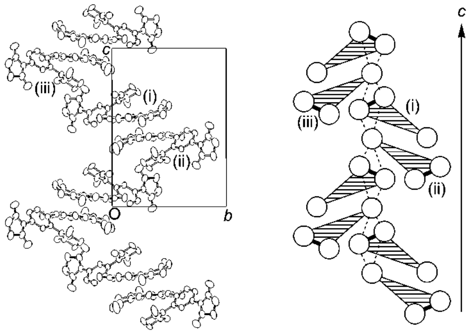

Figure 2. Left: Crystal structure of **1** projected onto the *bc* plane. Symmetry operations: (i) x, y, z; (ii) $^1/_2 - x, {}^1/_2 - y, -z$; (iii) $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$. Right: Schematic diagram for the chain along the *c*-axis. The dashed lines represent the intermolecular interactions along the chain.

In Figure 2 is depicted the crystal structure of **1**.[8] Intermolecular short contacts between the nitroxide groups with a large spin density are found between the $S = 1$ and $^1/_2$ moieties along the *c*-axis,[9] which predominate in the intermolecular interactions in the lattice. Thus, there is established an alternating chain of $S = 1$ and $^1/_2$ molecular units, as schematically shown in Figure 2.

Temperature dependence of paramagnetic susceptibility χ_p is shown in Figure 3. The χ_pT value increases as T lowers, indicating that the intramolecular ferromagnetic interaction in **2**[5c] is retained in **1**. The χ_pT value decreases below 10 K, which is attributed to intermolecular antiferromagnetic interactions along the chain. A minimum and upturn of χ_pT show up around 0.28 K. This behavior is characteristic of low-dimensional ferrimagnetic systems.[10,11] Thus, a ferrimagnetic spin alignment is achieved in the alternating chain of **1**. The triradical **1** is an example of single-component organic molecule-based substance exhibiting ferrimagnetic behavior.

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(8) Single crystals of **1** were obtained by recrystallization from ethyl acetate/hexane. Crystallographic data: $C_{34}H_{43}N_6O_8 \cdot C_6H_{14}$, $M = 749.93$, $0.2 \times 0.2 \times 0.9$ mm^3, Mo Kα, 293 K, monoclinic, space group $C2/c$, $a = 3.416(2)$ nm, $b = 1.2551(9)$ nm, $c = 1.777(3)$ nm, $\beta = 100.68(8)°$, $V = 7.486(13)$ nm^3, $Z = 8$, $D_{calc} = 1.331$ g cm^{-3}. $R(F^2) = 0.105$ for 3746 reflections ($I > 3\sigma(I)$) and 458 parameters. The crystals contain crystal solvent of hexane. The R value larger than 0.1 results from a positional disorder of hexane.

(9) The ORTEP diagrams for nearest-neighbor molecules and tables of interatomic distances are provided as Supporting Information.

(10) For examples of transition metal-based ferrimagnets, see: (a) Kahn, O.; Pei, Y.; Verdaguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782. (b) Caneschi, A.; Gatteschi, D.; Renard, J. P.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1989**, *28*, 1976. (c) Stumpf, H. O.; Ouahab, L.; Pei Y.; Bergerat, P.; Kahn, O. *J. Am. Chem. Soc.* **1994**, *116*, 3866.

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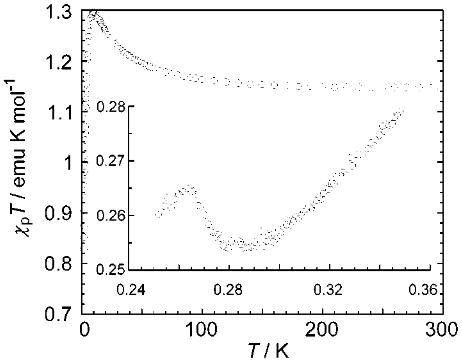

Figure 3. Temperature dependence of magnetic susceptibility χ_p of **1** measured on a SQUID magnetometer with $B = 0.1$ T in the $\chi_p T$ vs T plot. In the inset are shown the $\chi_p T$ values measured by an ac-bridge method ($B_{ac} = 0.01$ mT, $f = 15.9$ Hz).

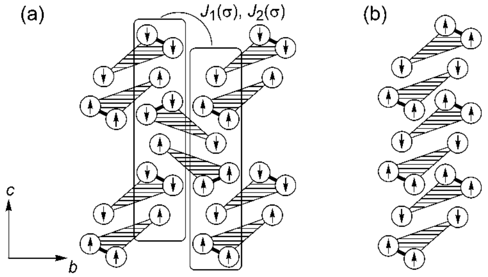

Figure 4. Schematic drawings of spin alignments at low temperatures: (a) The neighboring chains (the rectangles) of **1**. (b) The head-to-tail packing of the triradical **5**.

The $\chi_p T$ value decreases again below $T_{max} = 0.26$ K, as depicted in Figure 3. The decrease indicates an antiparallel alignment of the magnetizations from the short-range ordered ferrimagnetic chains.[12] If the weak intramolecular interactions $J_1(\sigma)$ and $J_2(\sigma)$ in **1** are ferromagnetic, they should bring about antiparallel alignment of magnetizations between the chains, as schematically shown in Figure 4a. The amplitude of the intramolecular interactions acting as the interchain interactions is estimated to be in the order of 10^2 mK from $T_{max} = 0.26$ K. The failure of a ferrimagnetic ordered state for **1** is ascribed to the weak intramolecular ferromagnetic interactions.

There have been reported two model compounds for organic ferrimagnets besides **1**; one is a molecular complex (**4**)[3a] of a biradical and a monoradical. The complex **4** has exhibited a minimum and upturn in $\chi_p T$ below 6 K.[3a,b] This is the first observation of ferrimagnetic behavior in purely organic materials. Although the complex **4** has exhibited no long-range ferrimagnetic ordering, it played a pilot role in uncovering a new category of organic magnetics. After the discovery of **4**, novel heterospin molecular assemblages have been sought, which should serve to clarify the intrinsic nature of ferrimagnetism in organic solids. The difficulty in cocrystallization, however, has prevented us from producing novel molecular assemblages. We have now been given a facile methodology in producing heterospin assemblages in a controllable manner by the single-component approach.

The other intriguing model compound is a triradical (**5**; Figure 1) by Hosokoshi et al.[6] possessing one ferromagnetic and two antiferromagnetic exchange couplings in the molecule, which is seemingly the same as our model. The triradical **5** is, however, distinguished from **1** by the fact that all three radical centers in **5** are π-conjugated. As a result, all three intramolecular exchange interactions in **5** fall within the same order of magnitude.[6] Consequently, at low temperature, the triradical **5** should behave as an $S = {}^1/_2$ monoradical.[13]

A molecular system composed of three open-shell moieties with one ferromagnetic and two antiferromagnetic interactions is regarded as a magnetic supramolecule with a resultant $S = {}^1/_2$ ground state.[14] The supramolecule should have totally positive spin densities at two ferromagnetically coupled moieties and a totally negative density at another moiety.[14] The adjacent supramolecules with $S = {}^1/_2$ should be coupled with each other by effectively ferromagnetic interactions, when local orbital overlaps are operative between the moieties with opposite signs of the spin densities.[14] Intermolecular π-orbital overlaps in the head-to-tail molecular packing for **5**[6] should bring about parallel alignment between the resultant $S = {}^1/_2$ spins on the supramolecules, i.e., on the molecules of **5**, as shown in Figure 4b. As for **1**, in the framework of the magnetic supramolecule, the couplings between the resultant $S = {}^1/_2$ spins are antiparallel, giving the ground-state spin alignment shown in Figure 4a.

Intermolecular ferromagnetic interactions between ordinary $S = {}^1/_2$ radicals have been understood in terms of the spin polarization effect in the $S = {}^1/_2$ molecules:[15] Intermolecular orbital overlaps between neighboring molecules at the atomic sites with opposite signs of spin densities give a totally ferromagnetic interaction between the molecules. Therefore, it is hard to distinguish a ferrimagnetic spin alignment between the $S = 1$ and ${}^1/_2$ moieties from a ferromagnetic alignment between the resultant $S = {}^1/_2$ spins,[14] which is exemplified in **5**. Some experimental evidence for the antiparallel alignment of the $S = 1$ site of one molecule of **5** and the $S = {}^1/_2$ site of the adjacent one is necessary, e.g., based on polarized neutron diffraction or magnetic field dependence of specific heat, to entitle the crystal of **5** to be a ferrimagnet.

The single-component ferrimagnet approach enables us to produce novel heterospin molecular assemblages, and it has raised a crucial question concerning the definition of ferrimagnetism occurring in assemblages of molecular components with different spins. The question is underlain by the very nature of multicenters and multicontactness in organic open-shell systems.[11] Further elaborate control for intra- and intermolecular interactions is necessary for a full understanding of ferrimagnetism in organic materials.

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Supporting Information Available: Crystallographic data (CIF) and ORTEP drawings (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] The $\chi_p T$ value at the low temperature is less than 0.375 emu K mol^{-1}, which is expected for 1 mol of $S = {}^1/_2$ as a result of the coupling of the adjacent biradical and the monoradical moieties. This reduced value of $\chi_p T$ is indicative of the interchain antiparallel coupling as well.

[13] In fact, the $\chi_p T$ of **5** decreased on lowering the temperature down to 0.375 emu K mol^{-1} (ref 6), which is expected for 1 mol of $S = {}^1/_2$ spin. On further lowering T, the $\chi_p T$ increased and exhibited a phase transition with an entropy change of $\Delta S = k_B \ln 2$ as expected for bulk transition of $S = {}^1/_2$ spins (ref 6).

[14] Spin polarization in the magnetic supramolecule with the resultant $S = {}^1/_2$ spin from antiparallel coupling of $S = 1$ and ${}^1/_2$ spins is discussed in terms of theoretical calculations of thermodynamic properties: Shiomi, D.; Sato, K.; Takui, T. *J. Phys. Chem. B.* Submitted for publication.

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