

## Approach to a Single-Component Ferrimagnetism by Organic Radical Crystals

Yuko Hosokoshi,<sup>\*,†</sup> Keiichi Katoh,<sup>†</sup> Yasuhiro Nakazawa,<sup>‡</sup>  
Hiroki Nakano,<sup>§</sup> and Katsuya Inoue<sup>\*,†</sup>

Institute for Molecular Science  
Nishigonaka 38 Myodaiji  
Okazaki 444-8585, Japan

Research Center for Molecular Thermodynamics  
Faculty of Science, Osaka University  
Machikaneyama 1-1

Toyonaka-city, 560-0043 Osaka, Japan

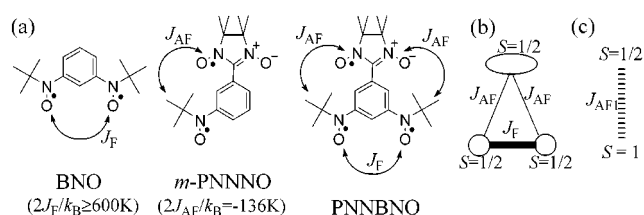
Department of Applied Physics, The University of Tokyo  
Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan

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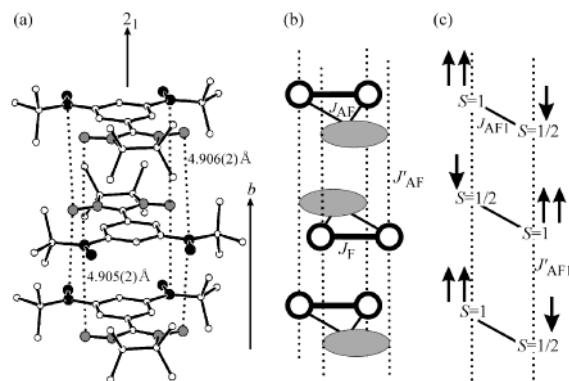
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In the past decades, the magnetism of molecule-based material has drawn much interest. After the discovery of the organic ferromagnet in 1991,<sup>1</sup> search for an organic ferrimagnet attracts great interest and is considered as one of today's challenging targets in material science. Although a number of ferrimagnets are realized in inorganic–organic hybrid systems,<sup>2</sup> a genuine organic ferrimagnet has not yet been realized. In 1980s, ferrimagnetism is proposed as an effective strategy to give organic materials spontaneous magnetizations by the alternant arrangement of two kinds of organic radicals having different spin-multiplicities.<sup>3</sup> All of the reported ferrimagnets include at least two magnetic components: bimetallic compounds or metal complexes with organic radicals. To achieve this challenging subject of an organic ferrimagnet from a different viewpoint, we propose here a single-component strategy: utilizing a triradical including an  $S = 1$  and an  $S = 1/2$  unit within a molecule and connecting the  $S = 1$  and  $S = 1/2$  units by intra- and intermolecular antiferromagnetic interactions. Our new strategy to use a single component has the advantages of the ease of controlling the crystal structure and the good crystallinity for quality and size.

Here we design a novel organic triradical of 2-[3',5'-bis(*N*-tert-butylaminoxyl)phenyl]-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-oxide, abbreviated as PNNBNO. The PNNBNO molecule includes three  $S = 1/2$  spins: two *N*-tert-butyl aminoxyls (*t*BuNO's) and a nitronyl nitroxide (NN). For the *m*-phenylene linkage of the two *t*BuNO's or of the *t*BuNO and the NN, we can expect the ferro- or antiferromagnetic exchange coupling, respectively, according to the well-established guideline for the sign of the intramolecular exchange interactions between the unpaired electrons.<sup>4</sup> In fact, the related biradical BNO is known



**Figure 1.** (a) Molecular structures of PNNBNO and related biradicals. (b) Schematic illustration of the magnetic model of a PNNBNO molecule. (c) Extreme limit of the model (b) when  $J_F \rightarrow \infty$ .



**Figure 2.** (a) Uniform chain structure in PNNBNO crystals. (b) Schematic illustration of the chain structure. A PNNBNO molecule is represented by the same definition used in Figure 1(b).  $J_{AF}$  is intermolecular antiferromagnetic interactions. (c) Ferrimagnetic ladder structure in the extreme limit when  $J_F \rightarrow \infty$ .

to possess a large ferromagnetic intramolecular interaction of  $2J_F/k_B \geq 600$  K.<sup>5</sup> Below the room temperature, a BNO molecule behaves almost as an  $S = 1$  species. The intramolecular exchange coupling in the biradical *m*-PNNNO is antiferromagnetic and estimated to be  $2J_{AF}/k_B = -136$  K.<sup>6</sup> Thus, the magnetic exchange coupling scheme in a PNNBNO molecule is drawn in Figure 1b. At low temperature, a PNNBNO molecule behaves as the pair of an  $S = 1/2$  and  $S = 1$  which is shown in Figure 1c.

The synthesis of PNNBNO was carried out basically following the conventional method<sup>7</sup> and purified by column chromatography on silica gel with a mixture of diethyl ether and hexane (1:1). Recrystallization from the mixed solvent of diethyl ether and hexane (2:1) yielded single crystals.<sup>8</sup>

A PNNBNO molecule is planar lying on a mirror plane. Molecules stack along the *b* axis in the “head-to-tail” fashion: the NN is situated on the two *t*BuNO's, and vice versa. The oxygen atoms of the NN and the nitrogen atoms of the *t*BuNO's come close to each other by distances of  $O1 \cdots N3$  4.905(2) or  $O2 \cdots N4$  4.906(2) Å. (Figure 2a) The intermolecular interactions for these contacts should be antiferromagnetic, since a significant overlap between the molecular orbitals of unpaired electrons is expected.<sup>9</sup> The schematic illustrations of the chain and of the magnetic interactions are shown in Figure 2, b and c. The alternant

\* Corresponding author. E-mail: yhoso@ims.ac.jp, kino@ims.ac.jp.

† Institute for Molecular Science.

‡ Research Center of Molecular Thermodynamics, Osaka University.

§ Tokyo University.

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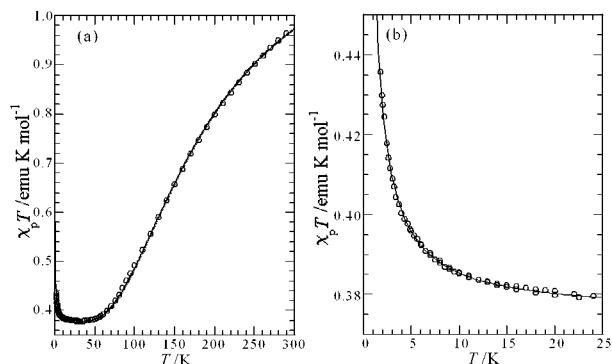
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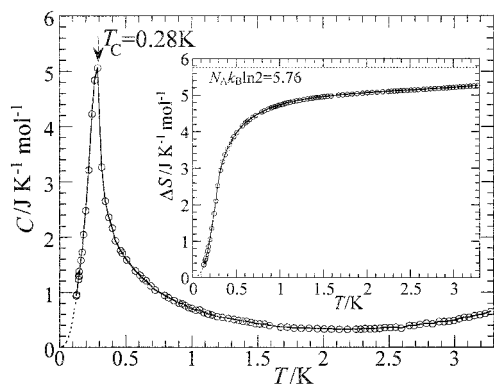
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(8) PNNBNO ( $C_{21}H_{33}N_4O_4$ ): Anal. Calcd: C, 62.20; H, 8.20; N, 13.82. Found: C, 61.86; H, 8.32; N, 13.84. HRMS  $m/z$  calcd: 405.2502, found: 405.2513. Mp 130.8–133.7 °C. Crystal data. (A dark green crystal,  $T = 296$  K): MW = 405.52, orthorhombic, *Pnma*,  $a = 11.652(1)$  Å,  $b = 9.6117(9)$  Å,  $c = 20.605(2)$  Å,  $V = 2307.6(3)$  Å<sup>3</sup>, and  $D_{\text{calc}} = 1.167$  gcm<sup>-3</sup> for  $Z = 4$ . Mo K $\alpha$  graphite monochromated,  $R(F) = 0.080$  and  $R_w(F^2) = 0.076$  for 1514 observed reflections ( $I > 3.0\sigma(I)$ ) and 163 variables. GOF = 0.24.

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**Figure 3.** (a) Temperature dependence of  $\chi_p T$  of PNNBNO using randomly oriented crystals. Solid curve represents the calculation. (b) Low-temperature part.

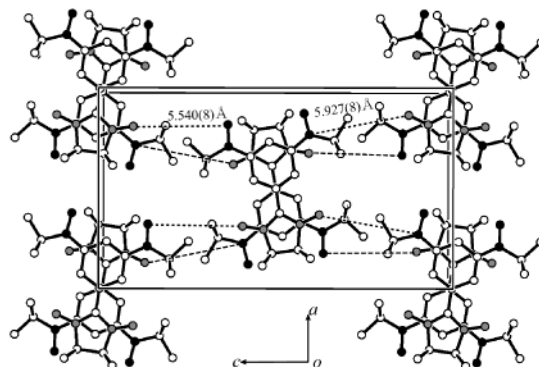


**Figure 4.** Temperature dependence of heat capacity of PNNBNO. (Inset: estimated entropy change.)

array of the  $S = 1/2$  (NN) and the  $S = 1$  unit (*t*BuNO's with *m*-phenylene linkage) is formed in the fashion of a two-leg ladder. It is considered that a ferrimagnetic ladder, with rungs of intramolecular antiferromagnetic interactions and legs of intermolecular antiferromagnetic interactions between the  $S = 1/2$  and the  $S = 1$ , is formed along the *b* axis.

The temperature dependence of the product of the paramagnetic susceptibility ( $\chi_p$ ) and temperature ( $T$ ),  $\chi_p T$  ( $\propto \mu_{\text{eff}}^2$ , square of the effective magnetic moment), is shown in Figure 3. The  $\chi_p T$  value decreases with decreasing  $T$ , reaching a constant value (0.375 emu K mol<sup>-1</sup>) with the temperature range of 20–50 K, and then increases below 20 K. The stationary value within 20–50 K agrees well with the expectation of the formation of 1 mol of  $S = 1/2$  species. The increase of  $\chi_p T$  below 20 K means the development of the effective ferromagnetic interactions induced by the antiferromagnetic coupling between the  $S = 1/2$  and the  $S = 1$  species. It is evident that intermolecular antiferromagnetic exchange coupling between the  $S = 1/2$  and  $S = 1$  unit exists, because without intermolecular interaction, the values of  $\chi_p T$  should approach the constant value with decreasing  $T$ . We analyze the observed data using the numerical calculations based on the structure shown in Figure 2b. Exact diagonalizations of the model with even length up to 12 spins of  $S = 1/2$  are performed to calculate the susceptibility.<sup>10</sup> The solid curve in Figure 3 represents the calculation using the parameter set of  $2J_F/k_B = 860$  K,  $2J_{AF}/k_B = -216$  K, and  $2J'_{AF}/k_B = -0.6$  K, which well reproduces the observed data.<sup>11</sup> The increase of  $\chi_p T$  below 20 K is intrinsic

(10) The Hamiltonian used is:  $H = -2J_F \sum_i (S_{3i-2} \cdot S_{3i-1}) - 2J_{AF} \sum_i (S_{3i-2} \cdot S_{3i} + S_{3i-1} \cdot S_{3i}) - 2J'_{AF} \sum_i (S_{3i} \cdot S_{3(i+1)-1} + S_{3i} \cdot S_{3(i+1)-2} + S_{3i-1} \cdot S_{3(i+1)} + S_{3i-2} \cdot S_{3(i+1)})$ .



**Figure 5.** Crystal structure of PNNBNO viewed along the *b* axis.

feature of this material. The saturation ratio of magnetizations against  $H/T$  also increases as decreasing  $T$ .

Figure 4 shows the temperature dependence of the heat capacity of PNNBNO measured by the thermal relaxation technique. The  $\lambda$ -shaped peak is observed at 0.28 K. The total magnetic entropy gain ( $\Delta S$ ) obtained by the integration of  $C/T$  with  $T$  is shown in the inset of Figure 4. The extrapolation of low-temperature part is performed using the simple assumption based on the spin-wave model. The estimated value of  $\Delta S$  at 3.3 K reaches 91% of  $N_A k_B \ln 2$ , which is the theoretical expectation for the total magnetic entropy of 1 mol of  $S = 1/2$  species. It is evident that the effective  $S = 1/2$  species (ferrimagnetic spins) undergo a magnetic phase transition at 0.28 K.

The occurrence of the phase transition suggests the three-dimensional (3D) nature of this material in the even lower-temperature region. The crystal structure projected onto the *ac* plane is shown in Figure 5. Each molecule is surrounded by four neighboring molecules with the contacts between the oxygen atom of NN ( $S = 1/2$ ) and the NO groups of *t*BuNO's ( $S = 1$ ): O1...O4 5.540(8) Å, O1...N4 5.701(8) Å, O2...N3 5.927(8) Å, O2...O3 6.136(7) Å. Thus, each ladder is surrounded by four neighboring ladders with the alternant alignment of the  $S = 1/2$  and  $S = 1$ . Therefore, the crystal structure of PNNBNO includes the 3D ferrimagnetic network of the  $S = 1/2$  and  $S = 1$ .

In conclusion, we have succeeded in synthesizing the first example of a genuine organic ferrimagnetic material having well-defined chemical and crystal structure. This material undergoes the 3D phase transition at 0.28 K. The advantage of utilizing organic molecules is demonstrated aiming to a single component ferrimagnet.

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**Supporting Information Available:** Tables of crystal data, structure solution and refinement, atomic coordinates, bond length, and angles, and anisotropic thermal parameters for PNNBNO (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(11) The calculated curves using  $2J_F/k_B \geq 860$  K are indistinguishable up to 300 K;  $2J_F/k_B = 860$  K is the lowest limit to fit the observed data below 300 K. The behavior above 50 K reflects the intramolecular excitations and that below 50 K corresponds to the intermolecular ones. The values of  $J_{AF}$  and  $J'_{AF}$  are uniquely determined. The magnitude of the exchange coupling within a PNNBNO molecule is enhanced compared with BNO and/or *m*-PNNNO, probably due to the planarity of the PNNBNO molecule. See also ref 9.