Characterization of the Chiral Paramagnetic Multispin System Built on a Cyclotriphosphazene Scaffold

Satoshi Shimono,[†] Rui Tamura,*[†,††] Naohiko Ikuma,[††] Hiroki Takahashi,[†] Naoko Sakai,[†] and Jun Yamauchi[†††]
[†]*Graduate School of Human & Environmental Studies, Kyoto University, Kyoto, 606-8501*
[††]*Graduate School of Global Environmental Studies, Kyoto University, Kyoto, 606-8501*
[†††]*Graduate School of Science, Kyoto University, Kyoto, 606-8501*

Chiral nitroxide–cyclotriphosphazene hybrid compounds such as 2,2-dinitroxide (**1a**), 2,2,4,4-tetranitroxide (**2a**), and 2,2,4,4,6,6-hexanitroxide (**3a**) have been prepared to examine the potentiality for the use of the cyclotriphosphazene framework as a molecular scaffold for elaborating robust, chiral paramagnetic multispin systems. EPR spectroscopic studies of these compounds in solution and in frozen solvent matrixes indicate the existence of appreciable intramolecular electron-exchange interactions between two or three neighboring radical moieties disposed on the same side of the cyclotriphosphazene ring. Their bulk paramagnetic properties have also been characterized by magnetic susceptibility measurements.
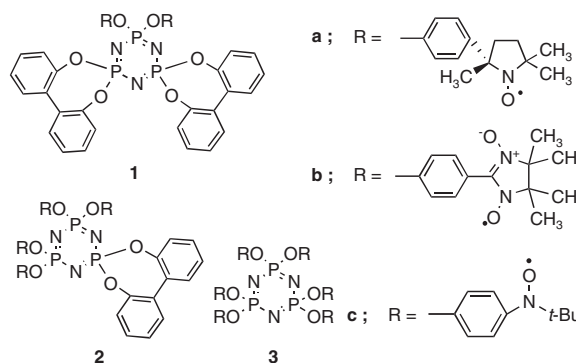
Cyclotriphosphazene is a unique inorganic compound which can serve as a molecular scaffold by incorporating various organic functional groups into the cyclic –P=N– backbone, making possible the preparation of various organic-inorganic hybrid compounds directed toward the development of new functional materials such as liquid crystals and polymers.[1,2]

With a view to obtaining chiral and achiral liquid-crystalline cyclotriphosphazenes with paramagnetic susceptibility anisotropy, which is necessary for the orientation of paramagnetic liquid crystals by weak magnetic fields,[3] we have investigated the possibility of elaboration of chiral and achiral multispin system on the cyclotriphosphazene scaffold so that intramolucular electron-exchange interactions enough to generate overall paramagnetic susceptibility anisotropy occur.[4] In this paper, we describe the preparation of chiral and achiral nitroxide–cyclotriphosphazene hybrid compounds **1–3** (Figure 1) and their magnetic properties disclosed by means of X-band EPR spectroscopy in solution and in frozen solvent matrixes, magnetic susceptibility measurements in the solid states, and X-ray crystallographic analysis.

Enantiomerically enriched hybrid compound (*S*)-**1a**–(*S*)-**3a** were successfully synthesized in 30–37% isolated yields by the reaction of (2*S*)-2,5,5-trimethyl-2-(4-hydroxyphenyl)pyrrolidine-1-oxide (88% ee)[5] with appropriate chlorocyclotriphosphazene derivatives such as $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$, $[N_3P_3Cl_4(O_2C_{12}H_8)]$, and $N_3P_3Cl_6$ in the presence of NaH in THF,[6] followed by purification by flash column chromatography on silica gel eluting with hexane/ethyl acetate (Figure 1). As for the achiral hybrid compounds, only nitronyl nitroxide derivative **1b** was isolated by a similar synthetic procedure, but more substituted **2b** and **3b** and *t*-butyl nitroxide derivatives **1c**–**3c** were too labile to be isolated. It is noteworthy that obtained (*S*)-**1a**–(*S*)-**3a** were extremely thermally-stable up to as high as 189–235 °C (Table 1).

Figure 1. Structural formula of chiral and achiral nitroxide-cyclotriphosphazene hybrid compounds.

The magnetic susceptibility of (*S*)-**1a**–(*S*)-**3a** and **1b** was measured in the temperature range from 2 K to 300 K using a SQUID susceptometer at an applied field of 0.5 T. As far as the bulk magnetic properties are concerned, all solid materials of (*S*)-**1a**–(*S*)-**3a** and **1b** showed weak antiferromagnetic interactions below 20 K. The Curie constants and Weiss temperatures are given in Table 1. The constant χT value between 20 and 300 K for each of (*S*)-**1a**–(*S*)-**3a** corresponds to the total amount of free $S = 1/2$ spins with *g*-factor of 2.0 (e.g., Figure 3b), indicating that their radical purity is satisfactory and that the intra- and inter-molecular exchange interactions are much smaller than the thermal energy $k_B T$ of 20 K. Slightly low Curie constant was noted for **1b**, indicating the decreased radical purity.

Thus, (*S*)-**1a**–(*S*)-**3a** turned out to be the good model compounds for the systematic studies on chiral nitroxide-cyclotriphosphazene hybrid compounds owing to their thermal stability.

The EPR spectra of (*S*)-**1a**–(*S*)-**3a** were measured at 298 K in MeTHF. No coupling with a phosphorous atom was observed in all EPR spectra of the degassed and diluted solutions (ca. 10^{-4} M) at 298 K or lower temperatures. The spectrum of (*S*)-**1a** shows that the electron-exchange interaction ($|J|$) between radical fragments is close to the hyperfine coupling constant

Table 1. Magnetic, thermal and optical properties of **1–3**

Compound	C^a /emu K mol^{-1}	θ^b/K	D. P.^{c}/°C	$[\alpha]_D^{24\,d}$
(*S*)-**1a**	0.75	−0.78	235.7	−6.00 (*c* 0.0563)
1b	0.68	−0.37	198.2	—
(*S*)-**2a**	1.54	−1.21	192.8	−7.43 (*c* 0.0887)
(*S*)-**3a**	2.25	−0.92	189.1	−13.0 (*c* 0.0540)

^{a}Curie constant. ^{b}Weiss temperature. ^{c}Decomposition point determined by TG analysis. ^{d}Measured in THF.
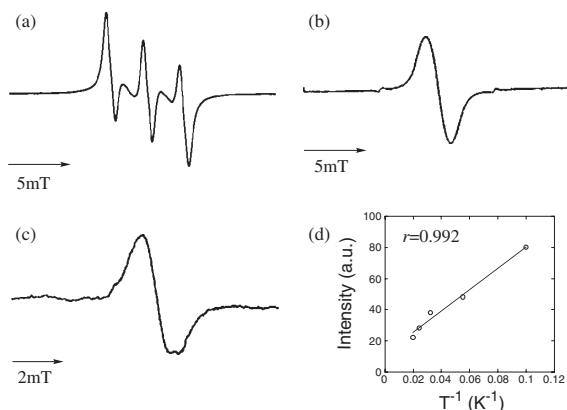
Figure 2. EPR spectra of (a) (*S*)-**1a** in THF at 298 K, (b) (*S*)-**2a** in 2-MeTHF at 298 K, (c) (*S*)-**3a** in 2-MeTHF at 298 K, and (d) Curie plot of the $\Delta m_s = \pm 2$ signal intensities of (*S*)-**3a** with the inverse of the temperature from 10 to 50 K.

(a_N), while the EPR spectra of (*S*)-**2a** and (*S*)-**3a** display a broad signal ($\Delta H_{pp} = 1.8$ and 1.5 mT, respectively) by intramolecular exchange interactions ($|J| \gg a_N$) among four or six NO radical groups (Figures 2b and 2c).

Further evidence of intramolecular electron-exchange interactions between NO radicals was given by the observation of broad singlet signals ($\Delta H_{pp} = 3.4$ and 2.8 mT at 75 K) in 2-MeTHF glassy solutions of (*S*)-**2a** and (*S*)-**3a**, respectively, at low temperatures corresponding to the $\Delta m_s = \pm 2$ forbidden transition. The signal intensities are in proportion to the inverse of the absolute temperatures according to the Curie's law in the low temperature range (Figure 2d), suggesting the presence of a multiplet or nearly degenerate singlet-multiplet ground state.

Thus, EPR spectroscopic studies microscopically showed the existence of appreciable intramolecular electron-exchange interactions ($|J| \gg a_N$) between two or three neighboring radical groups disposed on the same side of the cyclotriphosphazene ring at ambient temperature, although the macroscopic magnetic
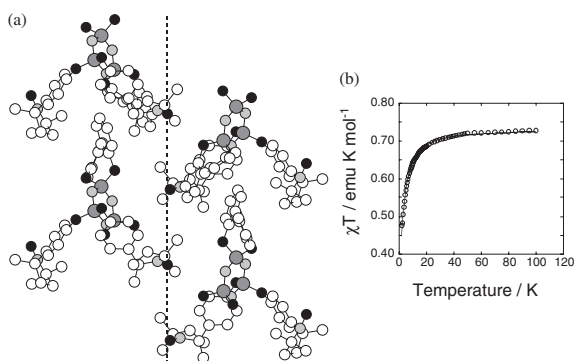

Figure 3. (a) Crystal structure of (*S*)-**1a** viewed down the *c* axis. The carbon, nitrogen, oxygen, and phosphorus atoms are represented by open, crosshatched, closed, and grid circles, respectively. All hydrogen atoms and one of two biphenyl groups are omitted for the sake of clarity. (b) χT vs. *T* plot for (*S*)-**1a** measured between 2 and 100 K at an applied field of 0.5 T. The circles represent the χT values of the polycrystalline sample, while the solid line indicates a theoretical curve.

susceptibility measurements indicated that the exchange interactions are small ($|J| \ll k_B T$ of 20 K).

The X-ray crystallographic analysis of the single crystal of (*S*)-**1a** obtained by recrystallization from CH_2Cl_2/Et_2O indicates that one of the two NO groups of a molecule interacts with the two nearest NO groups (both O⋯O distances: 5.734 Å) in two adjacent molecules to give a 1-D chain of NO groups while the other NO group is isolated (Figure 3a).[7] In contrast, the intramolecular O⋯O distance (13.349 Å) is too long to effect an appreciable magnetic interaction, as confirmed by the EPR studies described above.

In accordance with this crystal structure, the magnetic behavior of (*S*)-**1a** can be best fitted to a one-dimensional regular Heisenberg-linear chain model of S = 1/2 with $|J|/k_B$ of 2.4 K and 97.5% radical purity (Figure 3b).[8] Therefore, it has been suggested that the observed antiferromagnetic behaviors for all of them in the solid states may be ascribed to the intermolecular origin.

References and Notes

1   a) K. Inoue and T. Itaya, *Bull. Chem. Soc. Jpn.*, **74**, 1381 (2001). b) H. R. Allcock, "Chemistry and application of polyphosphazenes," Wiley-Interscience, Hoboken, New Jersey (2003).
2   a) K. Moriya, H. Mizusaki, M. Kato, T. Suzuki, S. Yano, M. Kajiwara, and K. Tashiro, *Chem. Mater.*, **9**, 255 (1997). b) H. R. Allcock and C. Kim, *Macromolecules*, **22**, 2596 (1989).
3   N. Ikuma, R. Tamura, S. Shimono, N. Kawame, O. Tamada, N. Sakai, J. Yamauchi, and Y. Yamamoto, *Angew. Chem., Int. Ed.*, in press.
4   For the organic radical-cyclotriphosphazene hybrid compounds, see; a) G. A. Carriedo, F. J. Garcia-Alonso, P. Gomez-Elipe, E. Brillas, and L. Julia, *J. Org. Chem.*, **69**, 99 (2004). b) T. M. Barclay, R. G. Hicks, A. S. Ichimura, and G. W. Patenaude, *Can. J. Chem.*, **80**, 1501 (2002). c) G. A. Carriedo, F. J. Garcia-Alonso, P. Gomez-Elipe, E. Brillas, and L. Julia, *Org. Lett.*, **3**, 1625 (2001). d) T. Terazono, R. C. Haddon, S. L. Mayo, S. V. Chichester, and J. H. Marshall, *J. Am. Chem. Soc.*, **107**, 7585 (1985).
5   N. Ikuma, R. Tamura, S. Shimono, N. Kawame, O. Tamada, N. Sakai, J. Yamauchi, and Y. Yamamoto, *Mendeleev Commun.*, **2003**, 109.
6   G. A. Carriedo, L. Fernandez-Catuxo, F. J. Garcia-Alonso, P. Gomez-Elipe, and P. A. Gonzalez, *Macromolecules*, **29**, 5320 (1996).
7   Crystallographic data: for (*S*)-**1a**; $C_{50}H_{50}N_5O_8P_3$, fw = 941.90, monoclinic, space group $P2_1$ (#4), $a = 13.9687(3)$, $b = 11.3822(2)$, $c = 16.1455(5)$ Å, $\beta = 110.8350(9)°$, $V = 2399.18(10)$ Å, $T = 298$ K, $Z = 2$, $D_{calcd} = 1.304$ g/cm^3, $2\theta = 55.0°$, Mo Kα ($\lambda = 0.71069$ Å), $\alpha = 1.83$ cm^{-1}, $R = 0.057$, $R_w = 0.068$ ($I > 3\sigma(I)$) for 5739 observed reflections. CCDC-217205 contains the supplementary crystallographic data for this paper.
8   Following equation was used; $\chi_m T = [(Ng^2\mu_B^2/k_B)(A + Bx + Cx^2)/(1 + Dx + Ex^2 + Fx^3) + 0.375]\alpha$, where *x* is $|J|/k_B T$ and α denotes the radical purity of the sample. A to F are the coefficients given in the reference, J. W. Hall, W. E. Marsh, R. R. Weller, and W. E. Hatfield, *Inorg. Chem.*, **20**, 1033 (1981).