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Electric, Electrochemical and Magnetic Properties of Novel Ionic-Liquid Nitroxides, and Their Use as an EPR Spin Probe

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Electronic Supplementary Information

Estimation of the Diameters of Cations

First, the moment of inertia (I) (Eqn (S1)) of cations of **1b** and **4**-**7** were calculated (Eqn (S2),(S3)) using each coordinate (x_i) (Eqn (S4)) and atomic weight (m_i) of atom i in the optimized molecular structure,[1] which was obtained by the Monte Carlo method using the Merck Molecular Force Field (MMFF), followed by an AM1 semi-empirical calculation using PC Spartan'02 (Figure S4). Next, the diagonalization of I gave I' ($I_a < I_b < I_c$) (Eqn (S5)). By using the principal axes of inertia (I_a, I_b, I_c), diameters a, b and c were calculated as molecular lengths along with the principal axes of inertia (Eqn (S6)-(S8)) and a diameter d was calculated as a geometric mean of a, b and c (Eqn (S9)).

$$I = \begin{bmatrix} I_{11} & I_{12} & I_{13} \\ I_{21} & I_{22} & I_{23} \\ I_{31} & I_{32} & I_{33} \end{bmatrix} \tag{S1}$$

$$I_{jj} = \sum_{i} \sum_{k \neq j} m_i x_{ik}^2 \tag{S2}$$

$$I_{jk} = -\sum_{i} m_i x_{ij} x_{ik} \qquad (j \neq k) \tag{S3}$$

$$x_i = \begin{pmatrix} x_{i1} \\ x_{i2} \\ x_{i3} \end{pmatrix} \tag{S4}$$

$$I' = \begin{bmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{bmatrix} \tag{S5}$$

$$a = \left[\frac{10}{M}(I_b + I_c - I_a)\right]^{1/2} \tag{S6}$$

$$b = \left[\frac{10}{M}(I_c + I_a - I_b)\right]^{1/2} \quad \text{(S7)}$$

$$c = \left[\frac{10}{M}(I_a + I_b - I_c)\right]^{1/2} \quad \text{(S8)}$$

$$a' = \sqrt[3]{abc} \quad \text{(S9)}$$

1. Y. Uchida, R. Tamura, N. Ikuma, S. Shimono, J. Yamauchi, Y. Shimbo, H. Takezoe, Y. Aoki and H. Nohira, *J. Mater. Chem.*, 2009, **19**, 415–418.

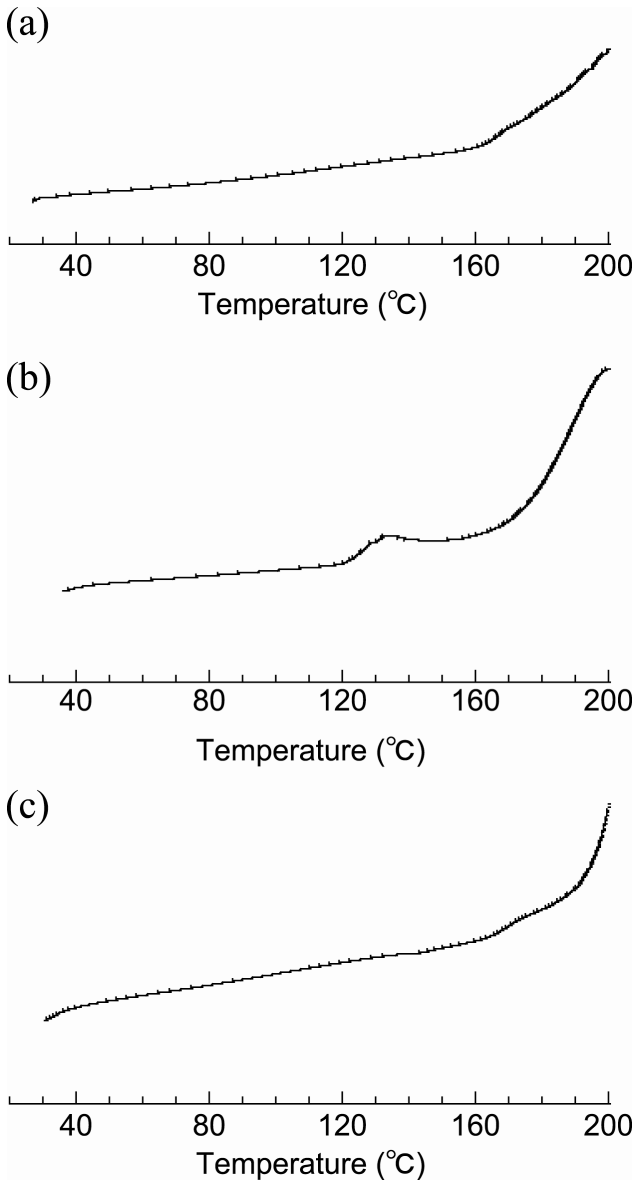

Fig. S1 DSC curves of (a) (±)-**1b**, (b) (±)-**1c** and (c) (±)-**1d.**

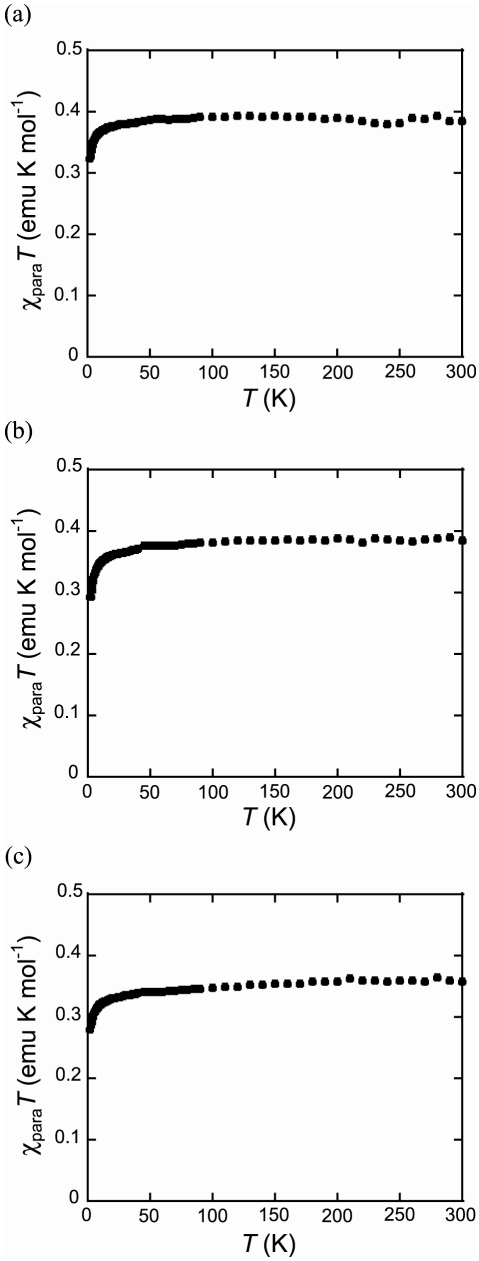

Fig. S2 Temperature dependence of $\chi_{para}T$ for (a) (±)-**1b**, (b) (±)-**1c** and (c) (±)-**1d** at a field of 0.5 T on the heating process between 2 and 300 K.

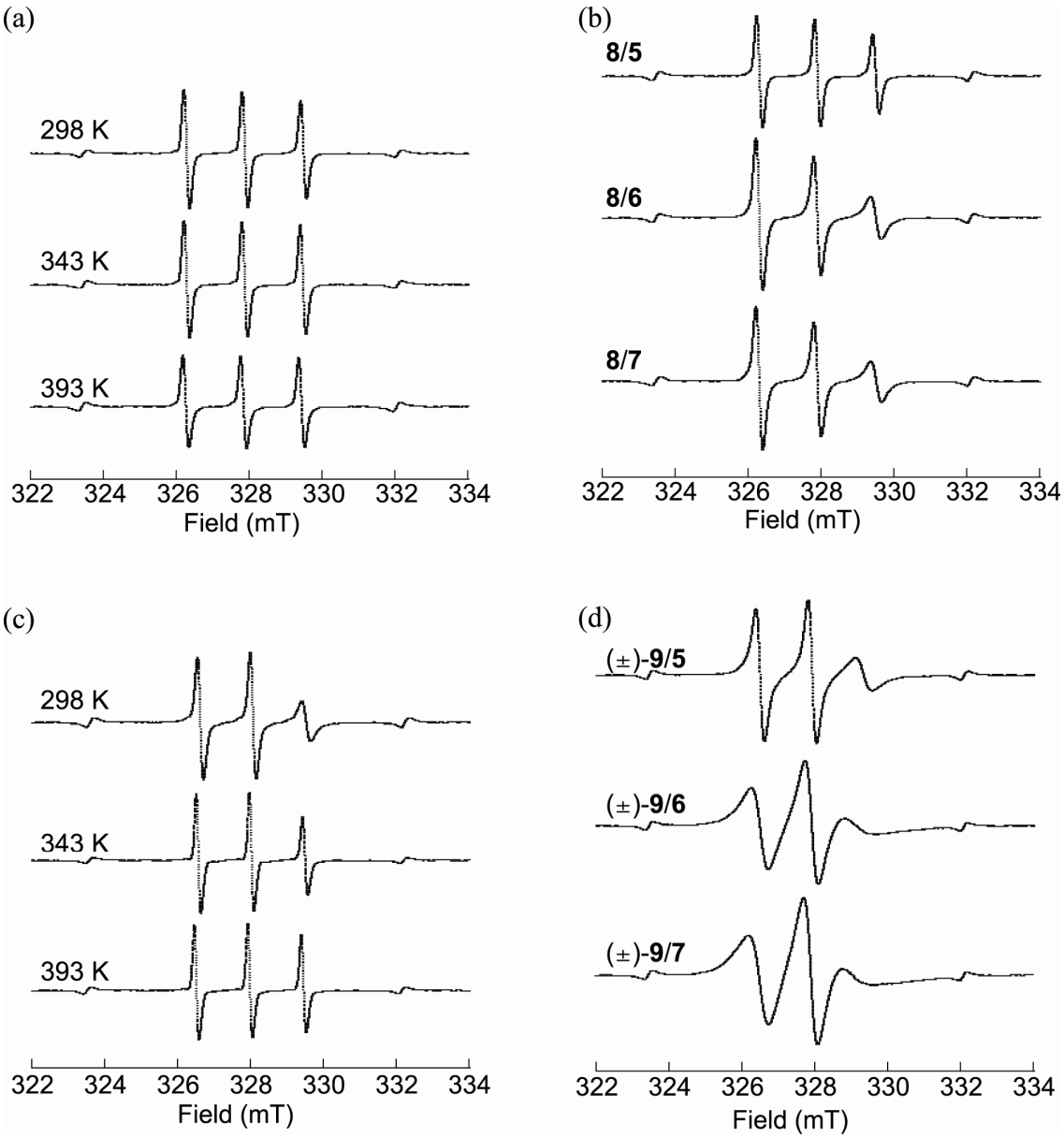

Fig. S3 EPR spectra of **8** (1 mM) (a) in ionic liquid **4** at 298, 343, and 393 K, and (b) in ionic liquids **5**-**7** at 298 K, and EPR spectra of (±)-**9** (1 mM) (c) in ionic liquid **4** at 298, 343, and 393 K, and (d) in ionic liquids **5**-**7** at 298 K. The small signals of the standard Mn^{2+}/MgO were observed at 323 and 332 mT.

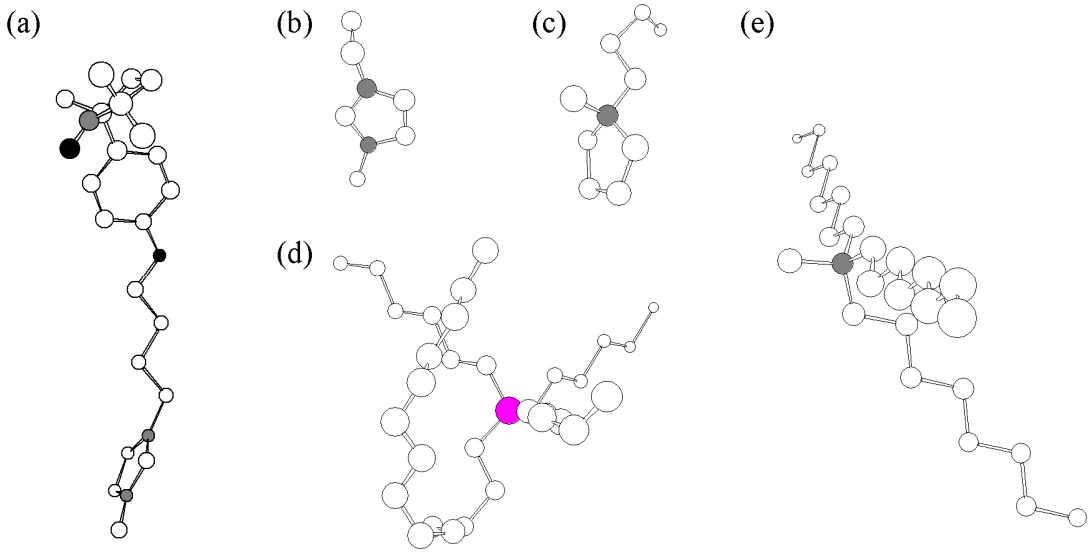

Fig. S4 The molecular conformations of the cations of (a) **1**, (b) **4**, (c) **5**, (d) **6**, and (e) **7** optimized by the unrestricted AM1 method (PC Spartan'02). Carbon, nitrogen, oxygen, and phosphorus atoms are denoted by white, gray, black, and pink circles, respectively. Hydrogen atoms are omitted.