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

Yoshiaki Uchida, Shigeaki Oki, Rui Tamura,* Tatsunori Sakaguchi, Katsuaki Suzuki, Koichi Ishibashi and Jun Yamauchi

Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

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 ($\vec{x}_i$) (Eqn (S4)) and atomic weight ($m_i$) of atom $i$ in the optimized molecular structure, 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)).

\[
I = \begin{bmatrix}
I_{11} & I_{12} & I_{13} \\
I_{12} & I_{22} & I_{23} \\
I_{13} & I_{23} & I_{33}
\end{bmatrix}
\]

(S1)

\[
I_3 = \sum_i \sum_{h \neq i} \frac{m_i x_i^2 x_h^2}{d_{hi}^2}
\]

(S2)

\[
I_{jk} = -\sum_i \frac{m_i x_i^j x_i^k}{d_{hi}} \quad (j \neq k)
\]

(S3)

\[
\vec{x}_i = \begin{pmatrix}
x_i^1 \\
x_i^2 \\
x_i^3
\end{pmatrix}
\]

(S4)

\[
I' = \begin{bmatrix}
I_a & 0 & 0 \\
0 & I_b & 0 \\
0 & 0 & I_c
\end{bmatrix}
\]

(S5)

\[
d = \left( \frac{1}{3} \left( I_a + I_b - I_c \right) \right)^{1/2}
\]

(S6)
\[ b = \frac{10}{\sqrt{\lambda}} \left( I_L + I_S - I_L^2 \right)^{1/2} \]  
\[ c = \frac{10}{\sqrt{\lambda}} \left( I_L + I_S - I_L^2 \right)^{1/2} \]  
\[ d = \sqrt{abc} \]

Fig. S1  DSC curves of (a) (±)-1b, (b) (±)-1c and (c) (±)-1d.
**Fig. S2** Temperature dependence of $\chi_{\text{para}}T$ for (a) $(\pm)-1b$, (b) $(\pm)-1c$ and (c) $(\pm)-1d$ 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.