Organic Paramagnetic Ionic Liquids Based on Anion Containing 2,2,6,6-Tetramethyl-1-piperidinyloxyl Radical Moiety

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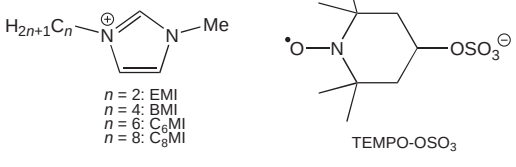
A series of genuine organic paramagnetic ionic liquids were prepared utilizing 2,2,6,6-tetramethyl-1-piperidinyloxyl-4-sulfate (TEMPO-OSO_3) anion with $S = 1/2$ radical spin. Their static susceptibilities and EPR spectra can be explained in terms of the paramagnetic spins on the TEMPO radical moieties, although they have much low fluidities and ionic conductivities.

The potential applications of organic radicals in molecular spintronic devices have stimulated efforts to develop benign stable and magnetically active molecules.[1] The first organic neutral radical was reported more than a century ago by Gomberg, who synthesized a stable and persistent free radical triphenylmethyl.[2] Most organic neutral radicals in existence are composed of thiazolyl or nitroxide moiety, such as 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA) with room-temperature (RT) magnetic bistability,[3] weak-ferromagnet 1,2,3,5-dithiadiazolyl radical β-NCC_6F_4CNSSN with a rather high critical temperature ($T_c = 35.5$ K),[4] and the first organic paramagnetic liquid (t-$Bu)_2NO$.[5] Of particular note is that some heterocyclic thiazyl radicals form an exclusive class of compounds which are essentially paramagnetic in the liquid state, developed by Passmore and his co-workers.[6] Recently, we have prepared RT molten salts (ionic liquids) composed of 1-alkyl-3-methylimidazolium cations (Scheme 1) and magnetically active inorganic $Fe^{III}X_4$ (X: Cl and Br) anions, which exhibit not only paramagnetic behavior (5.7–5.9 μ_B) but also high ionic conductivity ($<2.0 \times 10^{-2}$ S cm^{-1} at 25 °C).[7] Our particular interest is currently centered on the exploration of genuine organic paramagnetic ionic liquids. Herein, we report the preparation, characterization, and properties of a series of ionic liquids based on 2,2,6,6-tetramethyl-1-piperidinyloxyl-4-sulfate (TEMPO-OSO_3, see Scheme 1) anions with $S = 1/2$ radical spin and 1-alkyl-3-methylimidazolium cations with different alkyl chain lengths, i.e., ethyl (EMI, **1**), n-butyl (BMI, **2**), n-hexyl (C_6MI, **3**), and n-octyl (C_8MI, **4**).[8]

Na[TEMPO-OSO_3]·H_2O was synthesized according to the literature procedure[9] and recrystallized from acetone (53% yield). The salts **1**–**4** were prepared by the metathesis of appropriate 1-alkyl-3-methylimidazolium chloride and Na[TEMPO-OSO_3]·H_2O in dry acetone, washed by ethyl acetate/water and/or chloroform/water, and dried under vacuum at 40 °C for 1 day. Whereas **1** is reddish crystalline solid, the salts **2**–**4** are reddish highly viscous liquid.[10] No trace of Cl and Na was detected for energy-dispersive X-ray spectroscopy (EDS).



Scheme 1. Chemicals in text.

Table 1. Several characteristic values of **1**–**4**[a]

	cation	T_g /°C	T_m /°C	T_d /°C	σ (70 °C) /S cm^{-1}	μ_{eff} (70 °C) /μ_B
1	EMI	−22[b]	57	ca. 200	2.0×10^{-4}	1.72
2	BMI	−27	—[c]	ca. 230	1.4×10^{-4}	1.73
3	C_6MI	−27	—[c]	ca. 220	7.8×10^{-5}	1.68
4	C_8MI	−31	—[c]	ca. 210	4.4×10^{-5}	1.61

[a]T_g, glass-transition temperature; T_m, melting temperature; T_d, decomposition temperature; σ, ionic conductivity; μ_{eff}, effective magnetic moment. [b]Detected by rapid cooling (−30 °C min^{-1}). [c]Not observed.

Thermal data, as determined by DSC trace on heating process, of **1**–**4** are summarized in Table 1. Crystalline **1** shows a melting event at 57 °C, and the rapid cooling results in a glass forming with a transition at −22 °C. On the other hand, none of liquids **2**–**4** crystallize on cooling, but show a glass transition far below RT. All the salts decompose at 200–230 °C, implying a liquid range over 140 °C. It seems that the observed high T_g values are a reflection of the high cohesive ability of the TEMPO moiety.

Because of their low fluidities and conductivities, in relation to the high T_g, the viscosity and impedance measurements are available only at high temperatures. Viscosities of **1**–**4** show the Arrhenius-type temperature dependence, although the values are more than 400 cP even at 70 °C. On heating, ionic conductivity (σ) of **1** rapidly increases up to 64 °C through melting, and it then becomes relatively temperature-insensitive. The σ value at 70 °C substantially exceeds the values of **2**–**4**, namely the ionic conductivity in the liquid state decreases as the alkyl chain in the cations elongates (Table 1).

Whereas the salts **1**–**4** exhibit a broad Lorentzian-shaped EPR signal at $g = 2.0067$–2.0068 in their neat condition, three distinct signals associated with ^{14}N hyperfine splitting ($a_N = 1.60$ mT) were observed in a 10^{-3} M chloroform solution

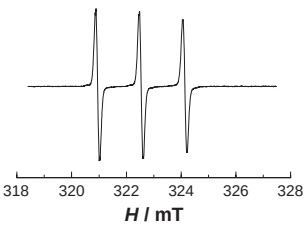


Figure 1. EPR spectrum of **4** in a 10^{-3} M chloroform solution at RT.

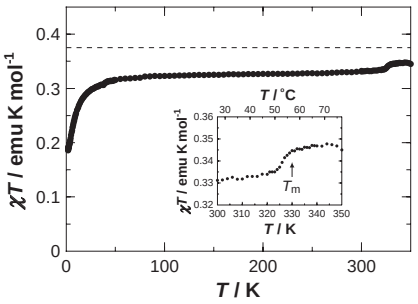


Figure 2. Temperature dependence of χT for **1** in an applied field of 0.1 T on heating process. The dotted line indicates the value expected for uncorrelated $S = 1/2$ spin system (0.375 emu K mol^{-1}). The inset is the enlargement for the melting event range. An arrow indicates the melting temperature (T_m).

(Figure 1 for **4**). These observations give us firm evidence of an existence of radical species on TEMPO moiety.[11] In the neat condition, the EPR linewidth (ΔH_{pp}) steadily reduces as the alkyl chain in the cations shortens in going from **4** (1.62 mT) to **1** (1.14 mT). This trend is presumably associated with the exchange narrowing, since the molar concentration is anticipated to be higher in the present salts with shorter alkyl chain, as the case of the FeX_4 (X: Cl and Br) salts.[7d]

Static susceptibility (χ) measurements under an applied magnetic field of 0.1 T revealed that all the present salts exhibit paramagnetic behavior at RT. Their effective magnetic moments (μ_{eff}) at 70 °C were estimated as values in the range of 1.61–1.73 μ_B, which resemble closely that expected for a paramagnetic $S = 1/2$ state (spin only value is 1.73 μ_B). Figure 2 shows the temperature dependence of χT for **1**. On cooling from RT, the χT value remains almost constant down to ca. 50 K through solidification, where it begins to fall due to the antiferromagnetic interactions between TEMPO radicals. There is no propensity for long-range magnetic ordering down to 1.9 K, and the temperature dependency below RT can be fit well to the Curie–Weiss expression $\chi = C(T - \theta)^{-1}$, with Curie constant ($C$) of 0.351 emu K mol^{-1} and Weiss temperature (θ) of −4.3 K. All the salts in this study show similar temperature dependency below RT, but the χT of **1** is outstanding for its abrupt upturn of ca. 0.02 emu K mol^{-1} just above its T_m (inset of Figure 2). Such behavior is markedly different from our earlier works on paramagnetic ionic liquids [EMI][FeX_4] (X: Cl and Br),[7c,7d] whose χT values show a pronounced drop at around their T_m on heating process. The source of the opposite χT change remains very unclear to us, but it is more likely that a certain fraction of TEMPO radicals in solid are magnetically correlated in ways that lead to a diminished magnetic moment, since, on melting, the χT value approaches that expected for uncorrelated $S = 1/2$ spin system.

In summary, we prepared the first well-characterized genuine organic paramagnetic ionic liquids based on an anion containing TEMPO radical moiety. At RT, the BMI, C_6MI, and C_8MI salts are in a liquid form, whereas the EMI cation with a shorter alkyl chain gives a crystalline salt with a melting event at 57 °C.

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10 **1**: Reddish crystalline solid (95% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.39 (t, 3H, $J = 7.0$ Hz, CH_3CH$_2$), 3.90 (s, 3H, CH$_3$), 4.17 (q, 2H, $J = 7.0$ Hz, CH$_3$CH_2), 7.66 (s, 1H, CH), 7.74 (s, 1H, CH), 9.06 (s, 1H, NCHN). Calcd for $C_{15}H_{28}N_3O_5S$: C, 49.70; H, 7.79; N, 11.59; S, 8.85; Cl, 0.00%. Found: C, 49.27; H, 7.83; N, 11.38; S, 8.69; Cl, 0.00%. **2**: Reddish viscous liquid (72% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.89 (s, 3H, CH$_2$CH$_2$CH$_2$CH_3), 1.24 (s, 2H, CH$_2$CH$_2$CH_2CH$_3$), 1.75 (s, 2H, CH$_2$CH_2CH$_2$CH$_3$), 3.83 (s, 3H, CH$_3$), 4.15 (t, 2H, CH_2CH$_2$CH$_2$CH$_3$), 7.69 (s, 1H, CH), 7.75 (s, 1H, CH), 9.09 (s, 1H, NCHN). Calcd for $C_{17}H_{32}N_3O_5S$: C, 52.29; H, 8.26; N, 10.76; S, 8.21; Cl, 0.00%. Found: C, 51.49; H, 8.40; N, 10.57; S, 8.26; Cl, 0.00%. **3**: Reddish viscous liquid (76% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.86 (s, 3H, CH$_2$CH$_2$(CH$_2$)$_3$CH_3), 1.26 (s, 6H, CH$_2$CH$_2$(CH_2)$_3$CH$_3$), 1.77 (s, 2H, CH$_2$CH_2(CH$_2$)$_3$CH$_3$), 3.83 (s, 3H, CH$_3$), 4.14 (s, 2H, CH_2CH$_2$(CH$_2$)$_3$CH$_3$), 7.69 (s, 1H, CH), 7.75 (s, 1H, CH), 9.09 (s, 1H, NCHN). Calcd for $C_{19}H_{36}N_3O_5S$: C, 54.52; H, 8.67; N, 10.04; S, 7.66; Cl, 0.00%. Found: C, 54.00; H, 8.61; N, 9.93; S, 7.92; Cl, 0.00%. **4**: Reddish viscous liquid (85% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 0.86 (s, 3H, CH$_2$CH$_2$(CH$_2$)$_5$CH_3), 1.25 (s, 10H, CH$_2$CH$_2$(CH_2)$_5$CH$_3$), 1.78 (s, 2H, CH$_2$CH_2(CH$_2$)$_5$CH$_3$), 3.84 (s, 3H, CH$_3$), 4.14 (s, 2H, CH_2CH$_2$(CH$_2$)$_5$CH$_3$), 7.68 (s, 1H, CH), 7.75 (s, 1H, CH), 9.09 (s, NCHN). Calcd for $C_{21}H_{40}N_3O_5S$: C, 56.47; H, 9.03; N, 9.41; S, 7.18; Cl, 0.00%. Found: C, 56.25; H, 9.09; N, 9.27; S, 7.30; Cl, 0.00%.

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