Supporting Information

Alkoxy chains in ionic liquid anions; Effect of introducing ether oxygen into perfluoroalkylborate in physical and thermal properties

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1.1. *General*

^{1}H, ^{19}F, and ^{11}B NMR spectra were recorded on a JEOL ECA-500 FT-NMR spectrometer operating at 500.2, 470.6 and 160.5 MHz, respectively. FAB-MS were measured on a JEOL JMS-HX110/110A spectrometer. Elemental analysis (C, H and N) was carried out by the Center for Organic Elemental Microanalysis of Kyoto University.

1.2. Phase transition

Calorimetric measurements were performed on a differential scanning calorimeter (Perkin-Elmer Pyris 1 equipped with a liquid nitrogen cooling unit). The temperature calibration was performed with the following standard samples: *n*-pentane (melting point: -132.66 ºC), cyclohexane (solid-solid transition: -87.06 ºC; melting point: 6.54 ºC), *n*-decane (melting point: -29.64 ºC), benzoic acid (melting point: 122.37 ºC), and indium (melting point: 156.6 ºC) used as reference. An average weight of 5-10 mg of each sample was hermetically sealed in an aluminum pan in a dry chamber (Daikin, dew point <-50 ºC), and then heated and cooled, both at a rate of 10 ºC min^{-1}, under a flow of helium gas. Temperature range was -150 ºC ~ T_m + 20 ºC. The glass transition temperature (T_g, onset of the heat capacity change), and melting point (T_m, onset of the endothermic peak), where appropriate, was recorded on heating in the second heating/cooling cycle for each salt.

1.3. Measurements of the density, viscosity, and conductivity

The following measurements for the room-temperature liquid salts were carried out in a dry chamber (Daikin, HRG-50 A, dew point <-50 ºC). The density (ρ) was determined from the weight of 0.5 ml soaked up with an electric pipette at 25 ºC. The density data in Table 1 is the average value from three measurements of each ILs. The reported value for the density is the average of three measurements. The dynamic viscosity (η) was examined by a programmable viscometer (Brookfield, LVDV-III+) at 25ºC. The conductivity (κ) measurements were carried out using a computer-controlled Schlumberger Solartron 1260 impedance/gain-phase analyzer with a frequency range from 1 Hz to 1 MHz. Impedance data were analyzed by the complex impedance method. The measurement of the samples was carried out in a commercially available conductivity cell with platinum black electrode cells (Radiometer Analytical, CDC749, cell constant: 1.9 cm^{-1}).

1.4 Diffusion coefficient

Diffusion coefficients (D_H^{obs}, D_F^{obs}) of the ionic species were measured using the pulsed gradient spin−echo NMR (PGSE-NMR) technique with a JNM-ECP300W spectrometer. The D_H^{obs} and the D_F^{obs} were individually determined by the observation of the ^{1}H nuclei (300.5 MHz) in cation species and the ^{19}F nuclei (282.7 MHz) in the anion species. In all measurements, the diffusion time was fixed at 50 ms.

2. *Synthesis*

All materials used are commercially available and were used without further purification.

2.1. *K[$CF_3OCF_2CF_2BF_3$]*

To a stirred solution of $CF_3OCF_2CF_2I$ (15.8 g, 50.7 mmol) in anhydrous Et_2O (300 ml) was added dropwise PhMgBr (3.0M in Et_2O, 17.5 ml) for 1h at -78℃ under N_2 atmosphere. After stirring for 1.5 h at -78℃, $B(OCH_3)_3$ (6.2 g, 60 mmol) was added for 10 min. The mixture was stirred continuously for 2 h at -78℃ and subsequently warmed to room temperature for 2 h The resulted suspension poured to the pre-cooled solution (0℃) of 48 % aq. HF (100 ml) and vigorously stirred overnight. After saturation KF at 0℃, the ether phase was separated and the water phase was extracted Et_2O. The combined ether portions were treated with aq. $KHCO_3$ and dried. The solvents removed *in vacuo*. Recrystallization from MeOH/$CHCl_3$ gave the product. (7.7 g, 52.0 %)

^{19}F NMR (CD_3OD, $CFCl_3$, 470.6 MHz) δ –54.9 (t, J = 10.8 Hz, 3F, CF_3), -88.4 (s, 2F, OCF_2), -136.4 (q, J = 19.5 Hz, 2F, $OCF_2\boldsymbol{CF_2}$), -154.3 (q, J = 40.0 Hz, 3F, BF_3); ^{11}B NMR (CD_3OD, H_3BO_3, 160.5 MHz) δ -19.8 (m, 1B); MS m/z (%) 253 (100) $[CF_3OCF_2CF_2BF_3]^-$, 545 (100) $[2M-K]^-$; Anal Calcd. for $C_3F_{10}OBK$: C,12.34; Found : C, 12.09.

2.2. *EMI [$CF_3OCF_2CF_2BF_3$]*

To a stirred solution of K[$CF_3OCF_2CF_2BF_3$] (1.10 g, 3.8 mmol) in water (35 ml) was added 1-ethyl-3-methylimidazolium chloride (EMICl) (0.54 g, 3.7 mmol) at room temperature. The mixture was stirred for an additional 6 h. The bottom layer was separated, dissolved in CH_2Cl_2. The CH_2Cl_2 phase was separated and the water phase was extracted CH_2Cl_2. The combined CH_2Cl_2 was washed with water. After evaporation, the liquid obtained at 80℃ and 0.02 Torr for 24h. (0.90 g, 67.2 %)

^{1}H NMR (CD_3OD, TMS, 500.2 MHz) δ 1.54 (t, J = 7.5 Hz, 3H, $CH_2\boldsymbol{CH_3}$), 3.93 (s, 3H, N-CH_3), 4.26 (q, J = 7.5 Hz, 2H, $\boldsymbol{CH_2}CH_3$), 7.52 (s, 1H, imidazole 4-H), 7.59 (s, 1H, imidazole-C5), 8.82 (s, 1H, imidazole 2-H); ^{19}F NMR (CD_3OD, $CFCl_3$, 470.6 MHz) δ –54.7 (t, J = 11.1 Hz, 3F, CF_3), -88.3 (s, 2F, OCF_2), -136.4 (m, 2F, $OCF_2\boldsymbol{CF_2}$), -154.1 (q, J = 40.0 Hz, 3F, BF_3); ^{11}B NMR (CD_3OD H_3BO_3, 160.5 MHz) δ -19.8 (m, 1B) ; MS m/z (%) 111 (100) $[EMI]^+$, 253 (100) $[CF_3OCF_2CF_2BF_3]^-$; Anal Calcd. for $C_9H_{11}N_2F_{10}OB$: C,29.70; H, 3.05; N,7.70; Found : C, 29.60; H, 3.04; N, 8.00

2.3. *DEME[$CF_3OCF_2CF_2BF_3$]*(0.36 g, 65.5 %)

^{1}H NMR (CD_3OD, TMS, 500.2 MHz) δ 1.34 (t, J = 7.3 Hz, 6H, -$CH_2\boldsymbol{CH_3}$), 3.04 (s, 3H, N-CH_3), 3.39 (s, 3H, -OCH_3), 3.43 (q, J = 7.3 Hz, 4H, -$\boldsymbol{CH_2}CH_3$), 3.51 (t, J = 4.5

Hz, 2H, N-$\boldsymbol{CH_2}CH_2O$-), 3.79 (m, *2*H, N-$CH_2\boldsymbol{CH_2}O$-); ^{19}F NMR (CD_3OD, $CFCl_3$, 470.6 MHz) δ –54.7 (m, 3F, CF_3), -88.2 (s, 2F, OCF_2), -136.1 (q, *J* = 18.2 Hz, 2F, , $OCF_2\boldsymbol{CF_2}$), -153.5 (q, *J* = 40.0 Hz, 3F, BF_3); ^{11}B NMR (CD_3OD H_3BO_3, 160.5 MHz) δ -19.6 (m, 1B); MS m/z (%) 146 (100) $[DEME]^+$, 253 (100) $[CF_3OCF_2CF_2BF_3]^-$; Anal Calcd. for $C_{11}H_{20}NF_{10}O_2B$: C,33.11; H, 5.05; N,3.51; Found : C, 33.11; H, 4.76; N, 3.78.

2.4. $\boldsymbol{N_{1224}[CF_3OCF_2CF_2BF_3]}$(1.25 g, 82.9 %)

^1H NMR (CD_3OD, TMS, 500.2 MHz) δ 1.02 (t, *J* = 7.5 Hz, 3H, -$CH_2CH_2CH_2\boldsymbol{CH_3}$), 1.31-1.34 (m, 6H, N-$CH_2\boldsymbol{CH_3}$), 1.39-1.46 (m, 2H, -$CH_2CH_2\boldsymbol{CH_2}CH_3$) 1.67-1.73 (m, 2H, -$CH_2\boldsymbol{CH_2}CH_2CH_3$), 2.97 (s, 3H, N-$CH_3$), 3.21-3.24 (m, *2*H, -$\boldsymbol{CH_2}CH_2CH_2CH_3$), 3.35 (q, *J* = 7.3 Hz, 4H, N-$\boldsymbol{CH_2}CH_3$); ^{19}F NMR (CD_3OD, $CFCl_3$, 470.6 MHz) δ –54.9 (m, 3F, CF_3), -88.3 (s, 2F, -OCF_2), -136.1 (q, *J* = 18.2 Hz, 2F, -$OCF_2\boldsymbol{CF_2}$), -153.7 (q, *J* = 40.0 Hz, 3F, BF_3); ^{11}B NMR (CD_3OD H_3BO_3, 160.5 MHz) δ -19.7 (m, 1B); MS m/z (%) 144 (100) $[N_{1224}]^+$, 253 (100) $[CF_3OCF_2CF_2BF_3]^-$; Anal Calcd. for $C_{12}H_{22}NF_{10}OB$: C,36.30; H, 5.58; N,3.53; Found : C, 36.12; H, 5.84; N, 3.46.

2.5. $\boldsymbol{P13[CF_3OCF_2CF_2BF_3]}$(0.95 g, 49.9 %)

^1H NMR (CD_3OD, TMS, 500.2 MHz) δ 1.03 (t, *J* = 7.5 Hz, 3H, -$CH_2CH_2\boldsymbol{CH_3}$), 1.79-1.90 (m, 2H, -$CH_2\boldsymbol{CH_2}CH_3$), 2.24 (m, 4H, pyrrolidine 3-H and 4-H), 3.04 (s, 3H, N-CH_3), 3.29 (m, 2H, -$\boldsymbol{CH_2}CH_2CH_3$), 3.46-3.55 (m, 4H, pyrrolidine 2-H and 5-H); ^{19}F NMR (CD_3OD, $CFCl_3$, 470.6 MHz) δ –54.9 (m, 3F, CF_3), -88.3 (s, 2F, -OCF_2), -136.1 (q, *J* = 19.9 Hz, 2F, -$OCF_2\boldsymbol{CF_2}$), -153.7 (q, *J* = 41.7 Hz, 3F, BF_3); ^{11}B NMR (CD_3OD H_3BO_3, 160.5 MHz) δ -19.2(m, 1B); MS m/z (%) 128 (100) $[P_{13}]^+$, 253 (100) $[CF_3OCF_2CF_2BF_3]^-$; Anal Calcd. for $C_{11}H_{18}NF_{10}OB$: C,34.67; H, 4.76; N,3.68; Found : C, 34.47; H, 4.73; N, 3.67.