Electronic Supplementary Information

Nano-biphasic ionic liquid systems composed of hydrophobic phosphonium salts and a hydrophilic ammonium salt

Satomi Taguchi, Takahiro Ichikawa, Takashi Kato and Hiroyuki Ohno*

Preparation of zwitterions and an ionic liquid

All chemical reagents and solvents were obtained from commercial sources and used without purification. The structure of the zwitterions and the ionic liquid were determined by ^{1}H NMR (α-400, JEOL). The molecular weights were examined by ESI-MS.

Synthesis of sulphobutyl-tri-n-hexylphosphonium betaine. To a solution of tri-n-hexylphosphine (22.0 g, 76.8 mmol) in toluene (40 mL) was added a solution of 1,4-butanesultone (12.5 g, 91.8mmol) in toluene with stirring at room temperature. The solution was heated and stirred at 140 °C for 36 h during which time a crude product was gradually obtained as a white precipitate. The resultant precipitate was collected via vacuum filtration, rinsed with diethyl ether. The crude material was further purified by recrystallisation from ethyl acetate (200 mL), to give 23.6g(73%) as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$, δ /ppm relative to TMS): 0.89 (t, *J* = 6.9 Hz, 9H), 1.31 (m, 12H), 1.49 (m, broad, 12H), 1.76 (m, 2H), 2.00 (m, 2H), 2.22 (m, 6H), 2.46 (m, 2H), 2.86 (t, *J* = 7.3 Hz, 2H). ESI–TOF–MS: Calculated for $C_{22}H_{47}O_3PS$ $[M + Na]^+$: m/z = 445.64; Found: 446.24. Elemental analysis: Calculated for $C_{22}H_{47}O_3PS$: C, 62.52; H, 11.21; O, 11.36; P, 7.33; S, 7.59. Found: C, 61.75; H, 11.52; N, 0.

Synthesis of sulphobutyl-tri-n-octylphosphonium betaine. Titled compound was prepared using same procedure described for sulphobutyl-tri-n-hexylphosphonium betaine.

^{1}H NMR (400 MHz, $CDCl_3$, δ /ppm relative to TMS): 0.89 (t, *J* = 6.8 Hz, 9H), 1.31 (m, 24H), 1.49 (m, 12H), 1.76 (m, 2H), 2.00 (m,2H), 2.20 (m, 6H), 2.45 (m, 2H), 2.87 (t, *J* = 7.8 Hz, 2H). ESI–TOF–MS: Calculated for $C_{28}H_{59}O_3PS$ $[M + Na]^+$: m/z = 529.80; Found: 529.24. Elemental analysis: Calculated for $C_{28}H_{59}O_3PS$: C, 66.36; H, 11.73; O,9.47; P, 6.11; S, 6.33. Found: C, 66.32; H, 12.06; N, 0.

Synthesis of tris(2-hydroxyethyl)methylammonium bis(trifluoromethanesulfonyl)imide (**2**). A solution of tris(2-hydroxyethyl)methylammoniummethylsulfate (12.0 g, 43.6 mmol) in water (200ml) was passed through a column filled with anion exchange resin (Amberlite IR-78) to give a solution of tris(2-hydroxyethyl)methylammonium hydroxide. To the resultant solution was dropwise added a solution of bis(trifluoromethanesulfonyl)imidic acid (13.5 g, 47.9 mmol) in water (20 ml) over a period of 30 min, and the resulting solution was stirred for 2 h at room temperature. The reaction mixture was evaporated under reduced pressure. The crude material was dissolved in acetone (100 ml) and then passed through a short column filled with active alumina (20 ml). The acetone was removed by evaporation and the resulting liquid was dried under vacuum at 60 °C for 12 h. The resultant product was obtained as a colorless liquid.

^{1}H NMR (400MHz, DMSO, δ/ppm relative to TMS): 3.15 (s, 3H), 3.53 (t, *J* = 10.6 Hz, 6H), 3.85 (s, 6H), 5.24 (s, 3H). Elemental analysis: Calculated for $C_9H_{18}F_6N_2O_7S_2$: C, 24.33; H, 4.08; F, 25.65; N, 6.30; O, 25.20; S, 14.43. Found: C, 23.94; H, 3.88; N; 6.40.

Measurement

The thermal property of the materials were examined by differential scanning calorimetry (DSC, DSC6220, Seiko Instruments) from −100 to 250°C at a heating/cooling rate of 10 °C/min. An Olympus BX51 optical polarising microscope equipped with a Lincam hot-stage was used to examine thermal phase behaviour of the materials. Wide-angle X-ray diffraction (WAXD) patterns were obtained using a Rigaku RINT-2500 diffractometer with Cu Kα radiation. The ionic conductivity was measured with an impedance analyzer (Schlumberger, Solartron 1260) using a Programmable Temperature Controller TXN-700; the heating rate was 2 °C/min. The comb-shaped gold electrodes (Fig. S5) were used to measure ionic conductivity parallel to the substrate.

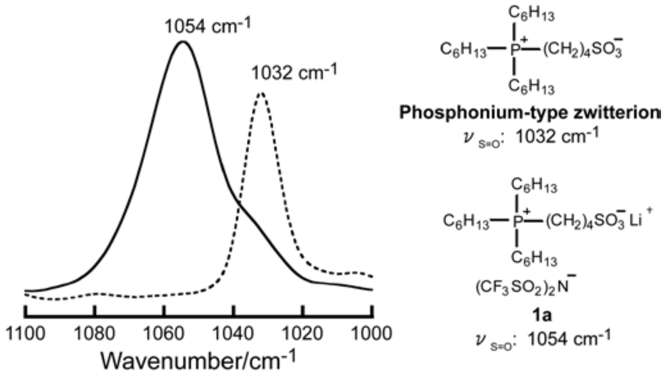

Fig.S1 IR spectra of the phosphonium-type-zwitterion (n = 6) (dotted line) and its complex with equimolar $LiTf_2N$ (complex **1a**) (solid line) at room temperature.

The phosphonium-type-zwitterion shows the stretching vibration band of the sulfonate group at 1054 cm^{-1}. Upon the addition of equimolar lithium bis(trifluoromethanesulfonyl)imide ($LiTf_2N$), the $\nu_{S=O}$ shifts to 1032 cm^{-1}. This shift is attributed to the formation of preferential electrostatic interaction between the sulfonate anion and lithium cation.

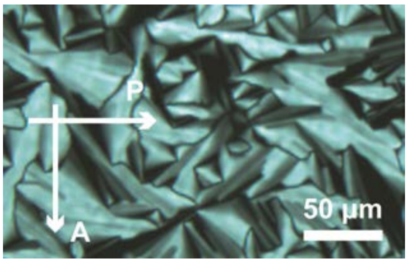

Fig. S2 Polarising optical microscopic image for **1a**/**2** mixture (mole fraction 0.3 for **2**) at room temperature. Directions: A, analyser; P, polariser.

Mixtures of **1a** and **2** show birefringence under polarising optical microscopic observation depending on the composition of the two components while they possess fluidity. For example, a fan-like birefringence is observed for **1a**/**2** mixture (mole fraction 0.3 for **2**) (Fig. S2), which is indicative of the formation of a columnar liquid-crystalline structure.

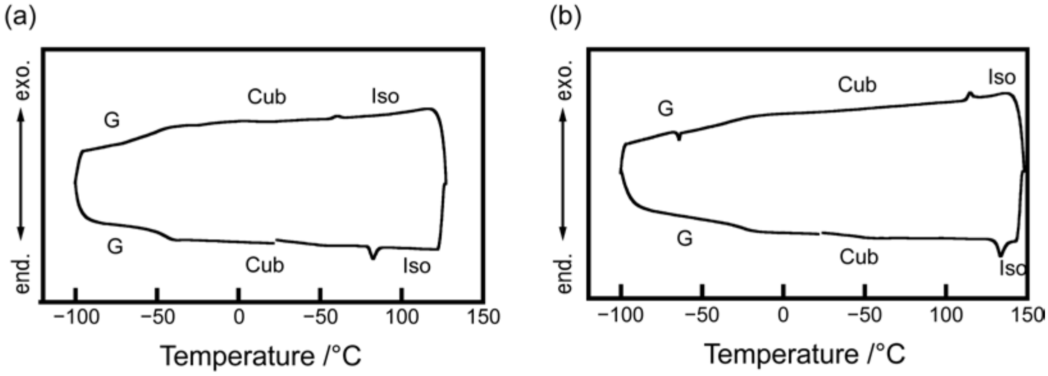

Fig. S3 DSC thermograms of (a) **1a**/**2** mixture (mole fraction 0.2 for **2**) and (b) **1b**/**2** mixture (mole fraction 0.2 for **2**).

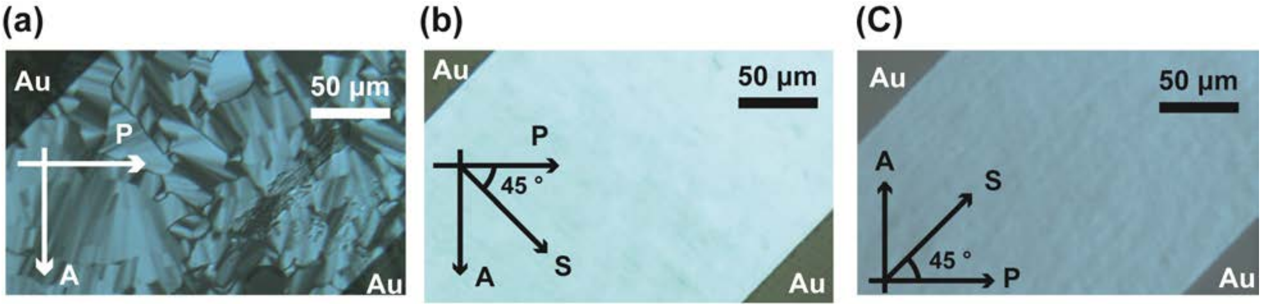

Fig. S4 Polarising optical microscopic images for **1b**/**2** mixture (mole fraction 0.37 for **2**): (a) before shearing; (b) after shearing the sample parallel to the electric field, (c) after shearing the sample perpendicular to the electric field. The mechanical shearing makes column axis in the hydrophilic IL domains aligns to the shearing direction. Directions: A, analyser; P, polariser; S, shearing.

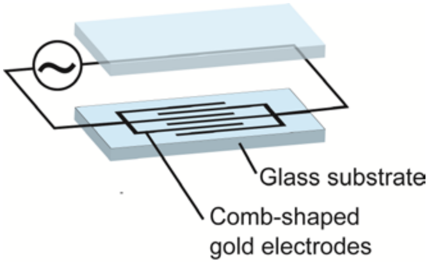

Fig. S5 Illustration of glass cell with comb-shaped gold electrodes for the ion conduction measurements.