Electronic Supplementary Information

Gelation of an amino acid ionic liquid by the addition of a phosphonium-type zwitterion

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Preparation of zwitterion, ionic liquid, and their mixtures

ZI: 1-(Trioctylphosphonio)butane-4-sulfonate was obtained by refluxing trioctylphosphine with 1,4-butanesultone in toluene at 140 ˚C for 36 h. After toluene was evaporated, the product was purified with diethyl ether three times. The crude compound was further purified by the recrystallization from ethyl acetate/ethanol mixture. The resultant product was obtained as a white powder in 77% yield.

^{1}H NMR($CDCl_3$, 400MHz): δ_H = 0.88 (9H, t, J = 13.76 Hz), 1.26 (24H, m, J = 31.92 Hz), 1.48 (12H, m. J = 4.12 Hz), 1.75 (2H, m, J = 31.16 Hz), 2.01 (2H, t, J = 29.32 Hz), 2.21 (6H, m, J = 28.44 Hz), 2.47 (2H, m, J = 30.24 Hz), 2.87 (2H, t, J = 14.68 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ_C = 13.99, 18.52, 18.99, 20.65, 21.73, 22.51, 26.59, 26.75, 28.88, 30.65, 30.78, 31.62, 50.10.

Elemental analysis for $C_{28}H_{59}O_3PS$ calcd: C, 66.36; H, 11.73; N, 0; O, 9.47; P, 6.11; S, 6.33. Found: C, 66.32; H, 12.06; N, 0.

[emim][Leu]: 1-Ethyl-3-methylimidazolium leucine was synthesised as reported previously. The [emim][Leu] was prepared by neutralisation of amino acid with 1-ethyl-3-methyl imidazolium hydroxide in dilute aqueous solution.[1]

Mixtures of ZI and [emim][Leu] were prepared by slow evaporation of the methanol solution of ZI and [emim][Leu], and the obtained mixtures were further dried at 60 ºC under vacuum for 24 h.

Measurement

Both ^{1}H and ^{13}C NMR spectra were recorded on a JEOL 400 spectrometer. Mixtures were loaded under a dry N_2 atmosphere into the internal chamber of a NMR coaxial capillary. The internal chamber was sealed by gas burner. The internal tube inserted a solution of DMSO-d_6 in the external chamber. The insert was sealed by gas burner. DSC measurements were performed on a DSC6220 (SEIKO Instrument Inc.) at a scanning rate of 5 ºC min^{-1}. X ray diffraction measurements were performed on a Smart Lab (Rigaku). Samples were loaded into 1 mm capillaries and sealed by bas burner to prevent water absorption. Ionic conductivity was measured by the AC impedance method

using a Schlumberger Solartron 1260 impedance/gain-phase analyzer. The impedance of the samples was measured from 10 Hz to 1 MHz with temperature scanning at 2 °C min^{-1} from 30 to 110 °C.

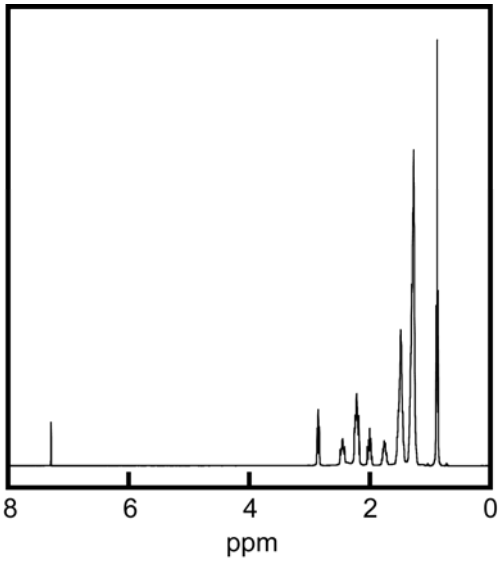

Fig. S1 ^{1}H NMR spectrum of ZI.

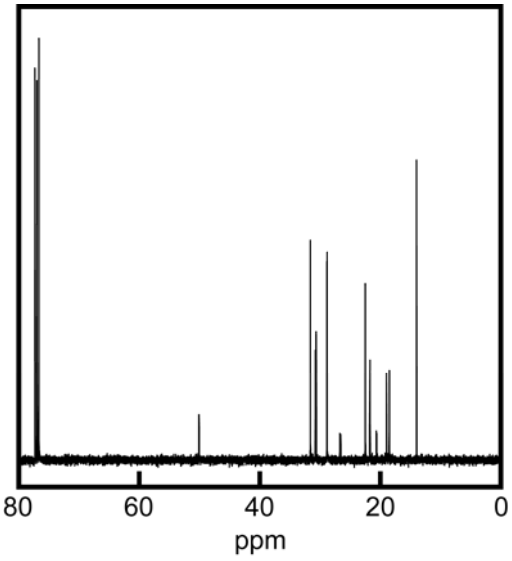

Fig. S2 ^{13}C NMR spectrum of ZI.

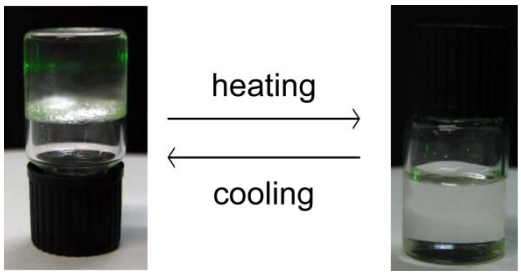

Fig. S3 Photograph of the Tyndall phenomenon for ZI/[emim][Leu] (1:3) mixture with green laser (532nm).

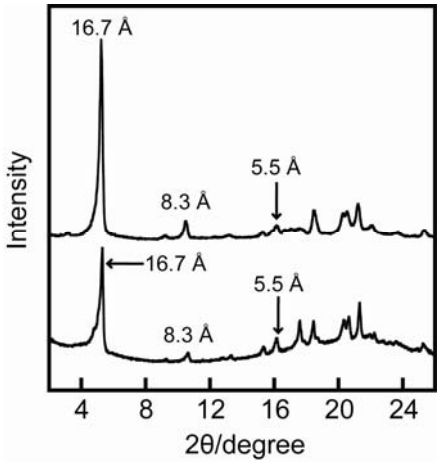

Fig. S4 X-ray diffraction patterns for: (a) ZI alone and (b) the ZI/[emim][Leu] (1:3) mixture at 25 ˚C.

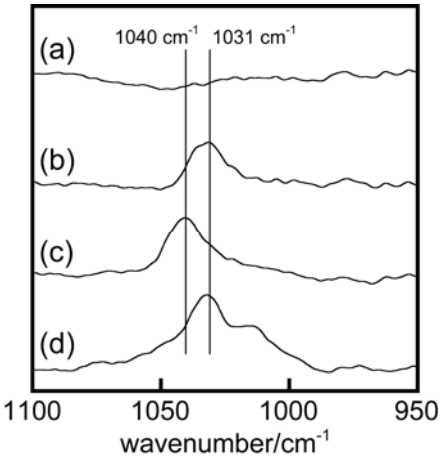

Fig. S5 IR spectra of ZI and [emim][Leu] mixture at room temperature. (a) [emim][Leu], (b) ZI/[emim][Leu] (1:1) mixture, (c) ZI, (d) imidazolium type zwitterion (1-methyl-3-(3-sulfopropyl)-imidazolium betaine).

Table 1 VFT parameters for ZI and ZI/[emim][Leu] mixture (1:3)

compound	T_0(K)	A(S/cm)	B(K)	Ea(keV)[a]	R^2
ZI	209	2.688	657	5.37	0.9995
ZI/[emim][Leu] (1:3)	198	0.516	654	5.34	0.9990

A:carrier ion number, B: activation energy [a] Ea = BØ 8.1674 (10^5 eV)

Reference

[1] K. Fukumoto, M. Yoshizawa and H. Ohno, *J. Am. Chem. Soc.*, 2005, **127**, 2398.