

## Electronic Supplementary Information

Title: Addition of suitably-designed zwitterion improves the saturated water content of hydrophobic ionic liquids

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### Preparation of zwitterions and an ionic liquid

All zwitterions (ZIs) and an ionic liquid (IL) in this study were synthesised as reported previously.<sup>1,2</sup>

C<sub>1</sub>Im3S: 3-(1-Methyl-3-imidazolium)propanesulfonate was obtained by refluxing 1-methylimidazole with 1,3-propanesultone in acetone under dry nitrogen at room temperature for 24 h. The insoluble ZI was separated by filtration. The product was washed with acetone several times. The resultant product was obtained as a white powder.

<sup>1</sup>H-NMR (400MHz, D<sub>2</sub>O, δ/ppm relative to TMS): 2.32 (2H, m, *J* = 14.7, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>), 2.92 (2H, t, *J* = 7.3, N-(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>), 3.90 (3H, s, N-CH<sub>3</sub>), 4.37 (2H, t, *J* = 14.2, N-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>), 7.46 (1H, s, imidazolium), 7.53 (1H, s, imidazolium), 8.76 (1H, s, imidazolium)

Elemental analysis calcd (%): C 41.16, H 5.92, N 13.72; found: C 41.64, H 6.09, N 13.86

C<sub>2</sub>Im3S: 3-(1-Ethyl-3-imidazolium)propanesulfonate was obtained by refluxing 1-ethylimidazole with 1,3-propanesultone in acetone under dry nitrogen at room temperature for 24 h. The insoluble ZI was separated by filtration. The product was washed with acetone several times. The resultant product was obtained as a white powder.

<sup>1</sup>H-NMR (400MHz, D<sub>2</sub>O, δ/ppm relative to TMS): 1.51 (3H, t, *J* = 11.4, N-CH<sub>2</sub>CH<sub>3</sub>), 2.33 (2H, m, *J* = 23.4, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>), 2.93 (2H, t, *J* = 11.9, N-(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>), 4.24 (2H, m, *J* = 17.8, N-CH<sub>2</sub>CH<sub>3</sub>), 4.37 (2H, t, *J* = 11.4, N-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>), 7.54 (2H, s, imidazolium), 8.83 (1H, s, imidazolium)

Elemental analysis calcd (%): C 44.02, H 6.46, N 12.83; found: C 44.15, H 6.69, N 12.82

C<sub>1,1</sub>Im3S: 3-(1,2-Dimethyl-3-imidazolium)propanesulfonate was obtained by refluxing 1,2-dimethylimidazole with 1,3-propanesultone in acetone under dry nitrogen at room temperature for 24 h. The insoluble ZI was separated by filtration. The product was washed with acetone several times. The resultant product was obtained as a white powder.

<sup>1</sup>H-NMR (400MHz, D<sub>2</sub>O, δ/ppm relative to TMS): 2.25 (2H, m, *J* = 29.3, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>), 2.60 (3H, s, N-C(CH<sub>3</sub>)-N), 2.92 (2H, t, *J* = 27.5, N-(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>), 3.76 (3H, s, N-CH<sub>3</sub>), 4.28 (2H, t, *J* = 14.7, N-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>), 7.33 (1H, s, imidazolium), 7.39 (1H, s, imidazolium)

C<sub>4</sub>Im3S: 3-(1-Butyl-3-imidazolium)propanesulfonate was obtained by refluxing 1-butylimidazole with 1,3-propanesultone in acetone under dry nitrogen at room temperature for 24 h. The insoluble ZI was separated by filtration. The product was washed with acetone several times. The resultant product was obtained as a white powder.

<sup>1</sup>H-NMR (400MHz, D<sub>2</sub>O, δ/ppm relative to TMS): 0.99 (3H, t, *J* = 14.6, N-(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.38 (2H, m, *J* = 22.5, N-(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.88 (2H, m, *J* = 14.6, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.33 (2H, m, *J* = 14.2, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>), 2.81 (2H, t, *J* = 13.8, N-(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>), 4.23 (2H, t, *J* = 14.7, N-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 4.43 (2H, t, *J* = 14.2, N-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>SO<sub>3</sub>), 7.66 (1H, s, imidazolium), 7.70 (1H, s, imidazolium), 9.04 (1H, s, imidazolium)

Elemental analysis calcd (%): C 48.76, H 7.37, N 11.37; found: C 49.37, H 7.62, N 11.43

[C<sub>4</sub>mim][Br]: 1-Butyl-3-methylimidazolium bromide was obtained by refluxing 1-methylimidazole with 1-bromobutane in acetonitrile under dry nitrogen at room temperature for 24 h. After acetonitrile was evaporated, the product was purified with diethyl ether several times. The resultant product was obtained as a white powder.

<sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>, δ/ppm relative to TMS): 0.96 (3H, t, *J* = 14.6, N-(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.39 (2H, m, *J* = 37.6, N-(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.92 (2H, m, *J* = 30.2, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 4.14 (3H, s, N-CH<sub>3</sub>), 4.36 (2H, t, *J* = 14.7, N-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 7.61 (1H, s, imidazolium), 7.73 (1H, s, imidazolium), 10.25 (1H, s, imidazolium)

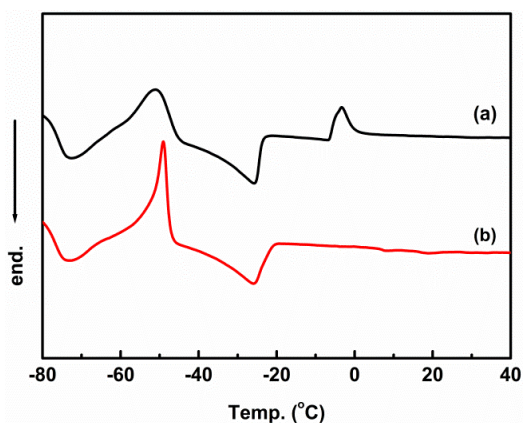
[C<sub>4</sub>mim][Tf<sub>2</sub>N]: 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide was obtained by reflexing 1-butyl-3-methylimidazolium bromide with lithium bis(trifluoromethanesulfonyl)imide in water under dry nitrogen at room temperature for 24 h. The product was purified with water several times. The resultant product was obtained as a clear solution.

<sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>, δ/ppm relative to TMS): 0.96 (3H, t, *J* = 15.1, N-(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.36 (2H, m, *J* = 37.1, N-(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.85 (2H, m, *J* = 30.2, N-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.93 (3H, s, N-CH<sub>3</sub>), 4.17 (2H, t, *J* = 15.1, N-CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 7.27 (1H, s, imidazolium), 7.31 (1H, s, imidazolium), 8.73 (1H, s, imidazolium)

## Measurement

Chemical structures were confirmed by <sup>1</sup>H NMR spectroscopy (JEOL α-400 NMR spectrometer). Water content of hydrophobic ionic liquid was determined by Karl-Fischer titration method (Kyoto Electronics; MKC-520N). The Raman spectra were obtained on a Jasco NRS-1000 spectrometer

with a Kaiser Optical holographic notch-plus filter and a liquid N<sub>2</sub>-cooled charge-coupled device (CCD) detector. Data were accumulated for 150 s with spectral resolution of 4.0 cm<sup>-1</sup>. The excitation source was a Coherent Innova 90C Kr laser with a 20 mW beam at a 413.1 nm excitation wavelength. Spectra were collected on samples in bulk condition at room temperature by use of a backscattering geometry. The peak frequencies were calibrated relative to an indene standard and are accurate to ±1 cm<sup>-1</sup>. The DSC measurement was performed with a DSC-6220 (Seiko Instruments Inc.) at a heating rate of 5 °C min<sup>-1</sup> and temperature range -100 °C to +50 °C.



**Fig. S1** DSC trace of C<sub>4</sub>Im3S/water mixture (black line, a), and [C<sub>4</sub>mim][Tf<sub>2</sub>N]/C<sub>4</sub>Im3S/water mixture (red line, b).

As seen in Fig. S1, the endothermic peak derived from freezing bound water was also observed in the mixture of [C<sub>4</sub>mim][Tf<sub>2</sub>N]/C<sub>4</sub>Im3S/water.

## References

- <sup>1</sup> M. Yoshizawa, A. Narita and H. Ohno, *Aust. J. Chem.*, 2004, **57**, 139
- <sup>2</sup> M. Yoshizawa and H. Ohno, *Chem. Commun.*, 2004, 1828.