Electronic Supplementary Information

Detection of small differences in the hydrophilicity of ions using the LCST-type phase transition of ionic liquid/water mixture

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Preparation of ionic liquids

In this paper, a series of $[P_{4444}]^+$ -based and CF_3COO^- -based salts were used. $[P_{4444}]^+$ -based salts containing $[Tf_2N]^-$, $CF_3SO_3^-$, BF_4^- , were prepared by anion exchange reaction of $[P_{4444}]^+$ -based salts, aqueous solutions of the tetrabutylphosphonium hydroxide ($[P_{4444}]OH$: donated by Hokko Chem. Co.) was directly neutralized by the corresponding acids. $[C4pyr]CF_3COO$, $[N_{4444}]CF_3COO$, and $[P_{5555}]CF_3COO$ were synthesised by neutralizing trifluoroacetic acid and corresponding hydroxides. Three hydroxide solutions, [C4pyr]OH, $[N_{4444}]OH$, and $[P_{5555}]OH$, were prepared by passing [C4pyr]Br, $[N_{4444}]Br$, and $[P_{5555}]Br$ through a column filled with anion exchange resin (Amberlite IRN 78). $[C4mim]CF_3COO$ was obtained by refluxing 1-butylimidazole with methyl trifluoroacetate in toluene under dry nitrogen at 50 °C for 24 h. All salts were dried *in vacuo* for at least 24 h at 60 °C before experiments. The structure and purity of salts were confirmed by ¹H NMR and elemental analysis.

¹H NMR and elemental analysis data of the used materials

[P4444]CH3SO3 Tetrabutylphosphonium methanesulfonate

 $\delta_{\rm H}$ (400 MHz; DMSO; δ /ppm relative to TMS): 0.92 (12H, t, J = 13.8, CH₂CH₃), 1.38–1.47 (16H, m, CH₂CH₂CH₃), 2.15–2.22 (8H, m, P-CH₂), 2.29 (3H, s, S-CH₃).

Elemental analysis (%): Found: C, 55.06; H, 11.48; N, 0. C₁₇H₃₉O₃PS • H₂O calcd: C, 54.81; H, 11.09; N, 0.

[P₄₄₄₄]Cl Tetrabutylphosphonium chloride

 $\delta_{\rm H}$ (400 MHz; DMSO; δ /ppm relative to TMS): 0.92 (12H, t, J = 14.2, CH₂CH₃), 1.40–1.49 (16H, m, CH₂CH₂CH₃), 2.30 (8H, m, P-CH₂).

Elemental analysis (%): Found: C, 61.12; H, 13.03; N, 0. C₁₆H₃₆ClP • H₂O calcd: C, 61.42; H, 12.24; N, 0.

[P₄₄₄₄]Br Tetrabutylphosphonium bromide

 $\delta_{\rm H}$ (400 MHz; DMSO; δ /ppm relative to TMS): 0.98 (12H, t, J = 19.7, CH₂CH₃), 1.48–1.62 (16H, m, CH₂CH₂CH₃), 2.39-2.54 (8H, m, P-CH₂).

Elemental analysis (%): Found: C, 53.75; H, 10.37; N, 0. C₁₆H₃₆BrP • H₂O calcd: C, 53.76; H, 10.72; N, 0.

$[P_{4444}]$ [TsO] Tetrabutylphosphonium *p*-toluenesulfonate

 $\delta_{\rm H}$ (400 MHz; DMSO; δ /ppm relative to TMS): 0.93 (12H, t, J = 11.0, CH₂CH₃), 1.37–1.45 (16H, m, CH₂CH₂CH₃), 2.14–2.28 (8H, m, P-CH₂), 2.50 (3H, s, Ph-CH₃), 7.11 (2H, d, J = 5.96, Ph-H), 7.47 (2H, d, J = 5.48, Ph-H).

Elemental analysis (%): Found: C, 63.40; H, 10.24; N, 0. C₂₃H₄₃O₃PS • 0.25H₂O calcd: C, 63.49; H, 10.08; N 0.

[P₄₄₄₄]NO₃ Tetrabutylphosphonium nitrate

 $\delta_{\rm H}$ (400 MHz; DMSO; δ /ppm relative to TMS): 0.92 (12H, t, J = 12.4, CH₂CH₃), 1.40–1.46 (16H, m, CH₂CH₂CH₃), 2.21 (8H, m, P-CH₂).

Elemental analysis (%): Found: C, 59.31; H, 11.47; N, 4.27; C/N, 13.88. C₁₆H₃₆NO₃P calcd: C, 59.79; H, 11.29; N, 4.36; C/N, 13.71.

[P4444]CF3COO Tetrabutylphosphonium trifluoroacetate

 $\delta_{\rm H}$ (400 MHz; DMSO; δ /ppm relative to TMS): 0.92 (12H, t, J = 14.2, CH₂CH₃), 1.38–1.48 (16H, m, CH₂CH₂CH₃), 2.16–2.23 (8H, m, P-CH₂).

Elemental analysis (%): Found: C, 56.75; H, 10.19; N, 0. C₁₈H₃₆F₃O₂P • 0.5H₂O calcd: C, 56.68; H, 9.78; N, 0.

$[P_{4444}] BF_4 \ Tetrabutyl phosphonium \ tetrafluoroborate$

 $\delta_{\rm H}$ (400 MHz; CDCl₃; δ /ppm relative to TMS): 0.97 (12H, t, J = 13.7, CH₂CH₃), 1.51–1.53 (16H, m, CH₂CH₂CH₃), 2.14–2.21 (8H, m, P-CH₂).

Elemental analysis (%): Found: C, 55.47; H, 10.50; N, 0. C₁₆H₃₆BF₄P calcd: C, 55.50; H, 10.48; N, 0.

$[P_{4444}] CF_3 SO_3 \ Tetrabutyl phosphonium \ trifluoromethan esulfonate$

 $\delta_{\rm H}$ (400 MHz; DMSO; δ /ppm relative to TMS): 0.92 (12H, t, J = 14.2, CH₂CH₃), 1.38–1.48 (16H, m, CH₂CH₂CH₃), 2.14–2.22 (8H, m, P-CH₂).

Elemental analysis (%): Found: C, 50.02; H, 9.01; N, 0. C₁₇H₃₆F₃O₃PS calcd: C, 49.98; H, 8.88; N, 0.

$[P_{4444}] [Tf_2N] \ Tetrabutyl phosphonium \ bis(trifluoromethanesulfonyl) \ imide$

 $\delta_{\rm H}$ (400 MHz; DMSO; δ /ppm relative to TMS): 0.92 (12H, t, J = 13.8, CH₂CH₃), 1.38–1.47 (16H, m, CH₂CH₂CH₃), 2.14–2.21 (8H, m, P-CH₂).

Elemental analysis (%): Found: C, 40.07; H, 6.79; N, 2.43; C/N, 16.50. C₁₈H₃₆F₆NO₄PS₂ calcd: C, 40.07; H, 6.72; N, 2.60; C/N, 15.43.

[C4mim]CF₃COO 1-butyl-3-methylimidazolium trifluoroacetate

 $\delta_{\rm H}$ (400 MHz; CDCl₃; δ /ppm relative to TMS): 0.95 (3H, t, J = 24.3, CH₂CH₃), 1.27–1.41 (2H, m, CH₂CH₃), 1.80–1.92 (2H, m, NCH₂CH₂), 4.01 (3H, s, NCH₃), 4.20-4.30 (2H, m, NCH₂), 7.41-7.45 (1H, m, NCHCHN), 7.51-7.48 (1H, m, NCHCHN), 10.14-10.02 (1H, m, NCHN).

Elemental analysis (%): Found: C, 47.24; H, 6.39; N, 11.10; C/N, 4.26. C₁₀H₁₅F₃N₂O₂ calcd: C, 47.28; H, 6.03; N, 11.03; C/N, 4.29.

[C4pyr]CF₃COO 1-butylpyridinium trifluoroacetate

 $\delta_{\rm H}$ (400 MHz; CDCl₃; δ /ppm relative to TMS): 0.94 (3H, t, J = 21.5, CH₂CH₃), 1.29–1.47 (2H, m, CH₂CH₃), 1.94–2.08 (2H, m, NCH₂CH₂), 4.78-4.91 (2H, m, NCH₂), 8.02-8.17 (2H, m, NCHCH), 8.45-8.56 (1H, m, NCHCHCH), 9.41-9.52 (2H, m, NCH).

Elemental analysis (%): Found: C, 52.95; H, 6.31; N, 5.64; C/N, 9.39. C₁₁H₁₄F₃NO₂ calcd: C 53.01, H 5.66, N 5.62; C/N, 9.43.

[N4444]CF3COO Tetrabutylammonium trifluoroacetate

 $\delta_{\rm H}$ (400 MHz; CDCl₃; δ /ppm relative to TMS): 1.00 (12H, t, J = 14.8, CH₂CH₃), 1.40–1.45 (8H, m, CH₂CH₃),

1.60–1.68 (8H, m, NCH₂CH₂), 3.28 (8H, t, *J* = 17.2, NCH₂).

Elemental analysis (%): Found: C, 60.76; H, 10.84; N, 3.90; C/N, 15.58. C₁₈H₃₆F₃NO₂ calcd: C, 60.82; H, 10.21; N, 3.94; C/N, 15.43.

[P₅₅₅₅]CF₃COO Tetrapentylphosphonium trifluoroacetate

 $\delta_{\rm H}$ (400 MHz; DMSO; δ /ppm relative to TMS): 0.91 (12H, t, J = 14.0, CH₂CH₃), 1.33–1.56 (24H, m, CH₂CH₂CH₃), 2.30–2.33 (8H, m, P-CH₂).

Elemental analysis (%): Found: C, 61.01; H, 10.05; N, 0. C₂₂H₄₄F₃O₂P • 0.25H₂O calcd: C, 61.02; H, 10.36; N 0.

References

¹ Y. Kohno, H. Arai, S. Saita, and H. Ohno, Aust. J. Chem., 2011, 64, 1560-1567