Electronic Supplementary Information

Title: Dual stimuli-responsive phase transition of ionic liquid/water mixture

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Synthesis of tetrabutylphosphonium N-trifluoromethanesulfonyl leucine ([P_{4444}][Tf-Leu])

[P_{4444}][Tf-Leu] was synthesized and purified using the procedure reported previously.[1] *N*-trifluoromethanesulfonyl leucine methyl ester was synthesized by a reaction of trifluoromethanesulfonic anhydride with leucine methyl ester. The leucine methyl ester was suspended in dry dichloromethane, and bimolar triethylamine was then added under gentle stirring. A solution of trifluoromethanesulfonic anhydride was added to the mixture under dry N_2 atmosphere at -78 °C. The resulting product was extracted to the diethyl ether and purified on silica gel ($MeOH/CHCl_3$ = 1:5) to provide *N*-trifluoromethanesulfonyl leucine methyl ester. Resulting trifluoromethanesulfonylated leucine methyl ester was treated with 1.0 N NaOH solution at 0 °C for 10 h to hydrolyze the methyl ester group, and the sodium ions were removed by passing through a column filled with proton-exchange resign (Amberlite IRN 77). The product was washed with hexane to give *N*-trifluoromethanesulfonyl leucine. Tetrabutylphosphonium cation ([P_{4444}]) was coupled with the *N*-trifluoromethanesulfonyl leucine to form the IL. Aqueous solution of [P_{4444}][OH] was mixed with a slightly less amount of trifluoromethanesulfonyl leucine, and the product was extracted with chloroform. After evaporation, the product was dried in vacuo for at least 24 h at 70 °C. The structure of the IL was confirmed by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm relative to TMS): 0.94(m, J = 44.9, 18H, CH_2CH_3), 1.39(m, J = 185.1, 18H, CH_2CH_3), 1.88(m, J = 27.0, 1H, CH_2CH_3), 2.26(m, J = 29.3, 8H, PCH_2), 3.67(q, J = 12.8, 1H, NCH).

Reference

1 K. Fukumoto, H. Ohno, *Angew. Chem. Int. Ed.*, 2007, **46**, 1852.

^{13}NMR measurement of [P_{4444}][Tf-Leu]/water mixture

^{13}NMR spectroscopy for [P_{4444}][Tf-Leu]/water mixture was measured using a double NMR tube technique. [P_{4444}][Tf-Leu] was mixed with pure water to reach the water content of 31.4 wt%. The mixture was put into the inner tube, and the outer tube was filled with D_2O containing sodium 3-trimethylsilyl propanesulfonate (DSS) as an internal standard. ^{13}C NMR spectrum was obtained by either JEOL JNM-ECX400 or JEOL JNM-ECX500.

Chemical shift change of carboxylic acid group on Tf-Leu after mixing with water

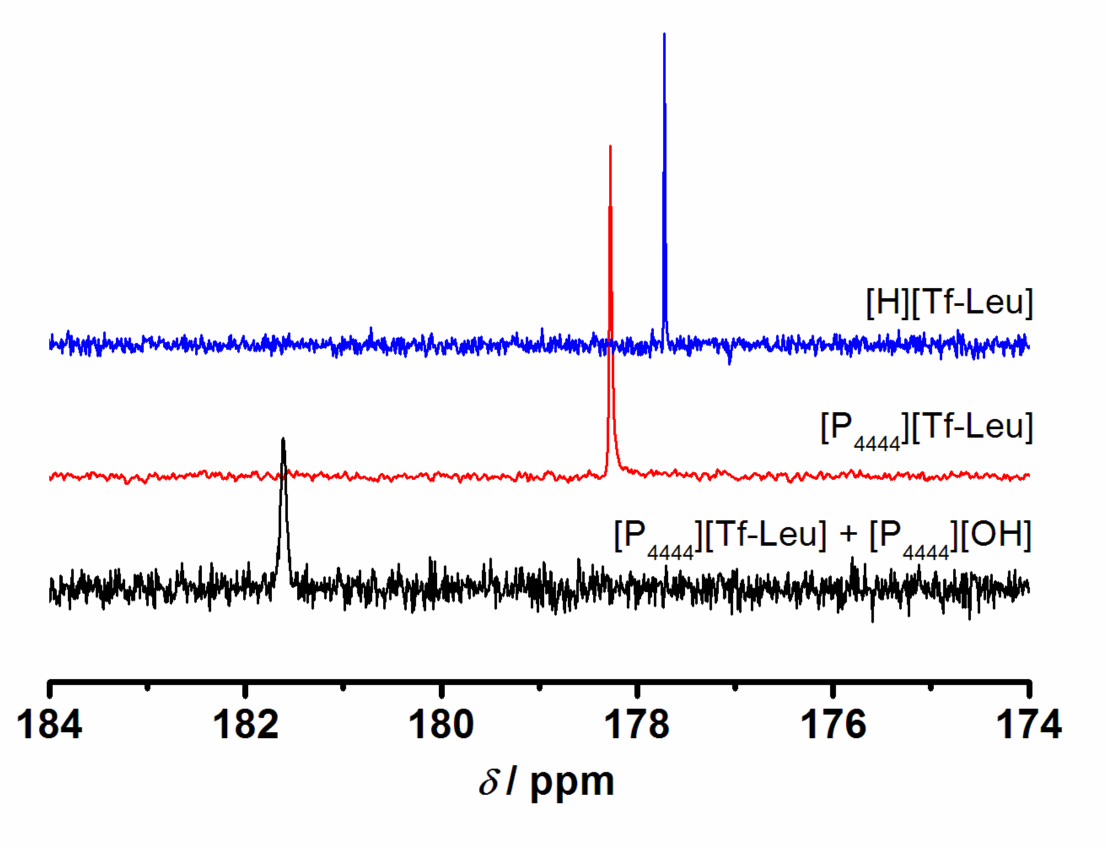

Fig. S1 ^{13}C NMR spectrum of free carboxylic group on [Tf-Leu] anion after mixing with water. Blue; [H][Tf-Leu], red; [P_{4444}][Tf-Leu], and black; [P_{4444}][Tf-Leu]/[P_{4444}][OH] mixture at 25 °C.

Chemical shift change of carboxylic acid group on Tf-Leu anion for $[P_{4444}]$[Tf-Leu] after bubbling CO_2 gas

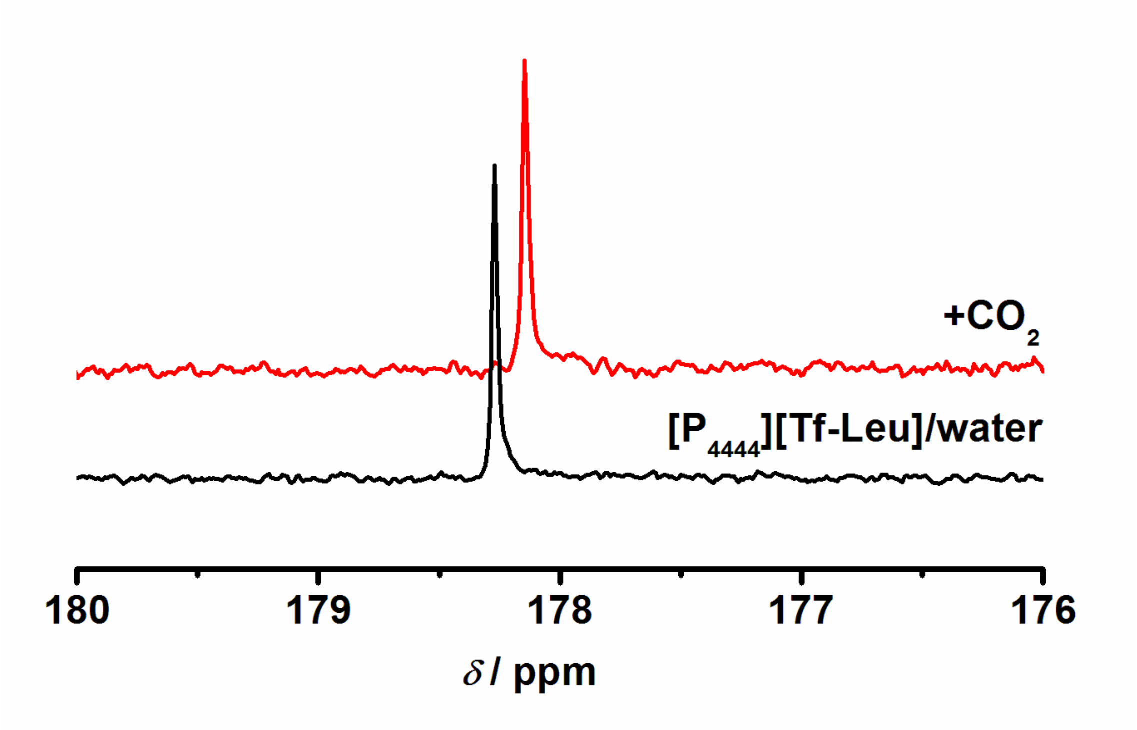

Fig. S2 ^{13}C NMR spectrum of $[P_{4444}]$[Tf-Leu]/water mixture before and after CO_2 bubbling at 25 °C.