Electronic Supplementary Information

Title: Novel thermotropic gels composed of only ions

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General procedure for [P_{4444}][amino acid] ionic liquid synthesis

An [P_{4444}][OH] aqueous solution(40 %, from Hokko Chemical Co. Ltd, 26 ml) was added dropwise to a slightly excess amino acid(0.045 mol). After gentle mixing for 10 min, water was gradually evaporated at 50 °C with rotary evaporator. To this reaction mixture were added 60 ml of acetonitrile and 40 ml of methanol. Then the mixture was stirred vigorously for 30-60 min, depending on amino acid species. Free amino acid was insoluble in this mixed solvent. The mixture was then filtered to remove excess amino acid. Filtration was repeated together with washing for a few times. Filtrate was evaporated to remove solvents at room temperature. The product was dried *in vacuo* for 1 day at 70 °C. Structure of AAILs was confirmed by ^{1}H NMR spectroscopy (JEOL α-500). TMS was used as an inner reference for their ^{1}H-NMR measurements.

^{1}H-NMR spectra for the solid and liquid phase of [P_{4444}][Val] + [bmim][Tf_2N]

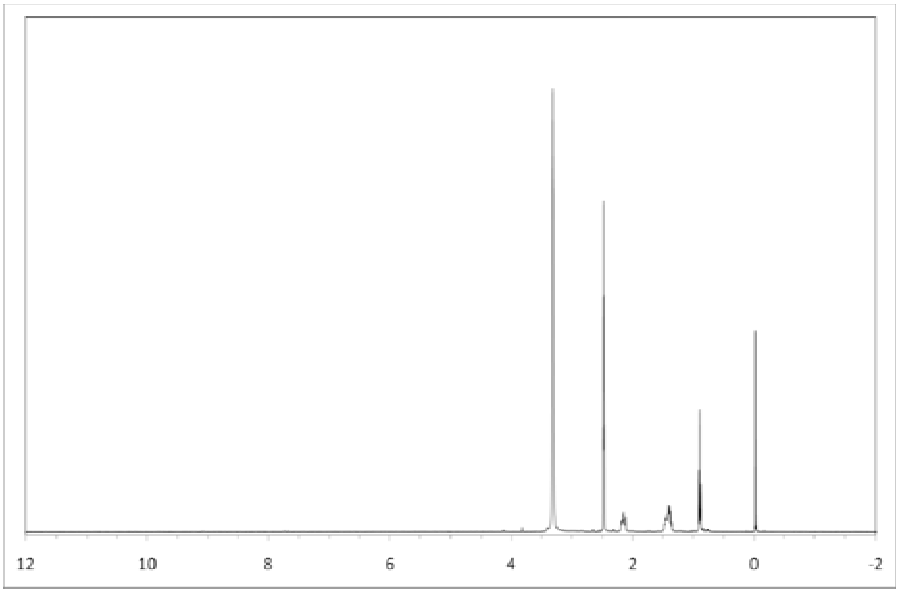

Fig. S1 ^{1}H-NMR spectra for the solid phase of [P_{4444}][Val] + [bmim][Tf_2N] mixture.

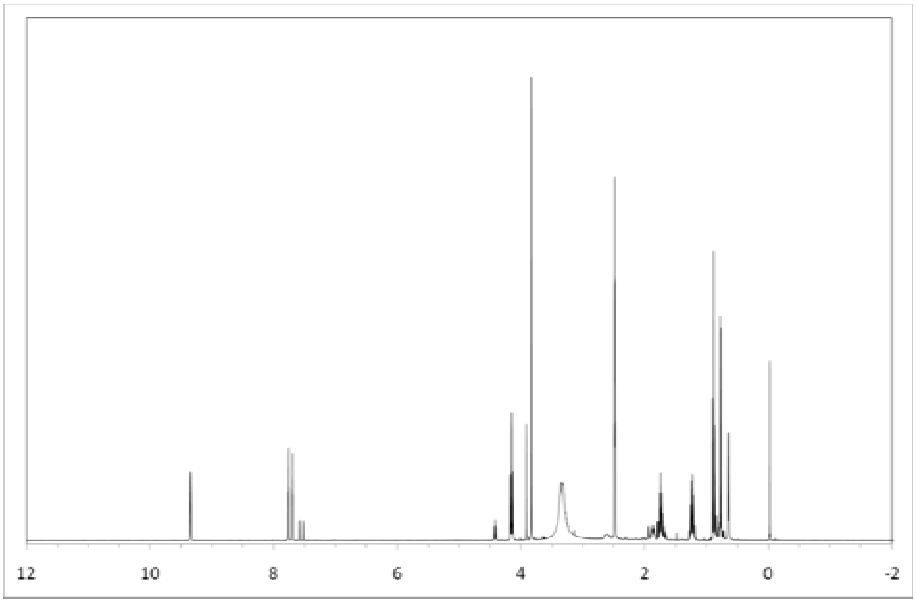

Fig. S2 ^{1}H-NMR spectra for the liquid phase of $[P_{4444}][Val]$ + $[bmim][Tf_2N]$ mixture.

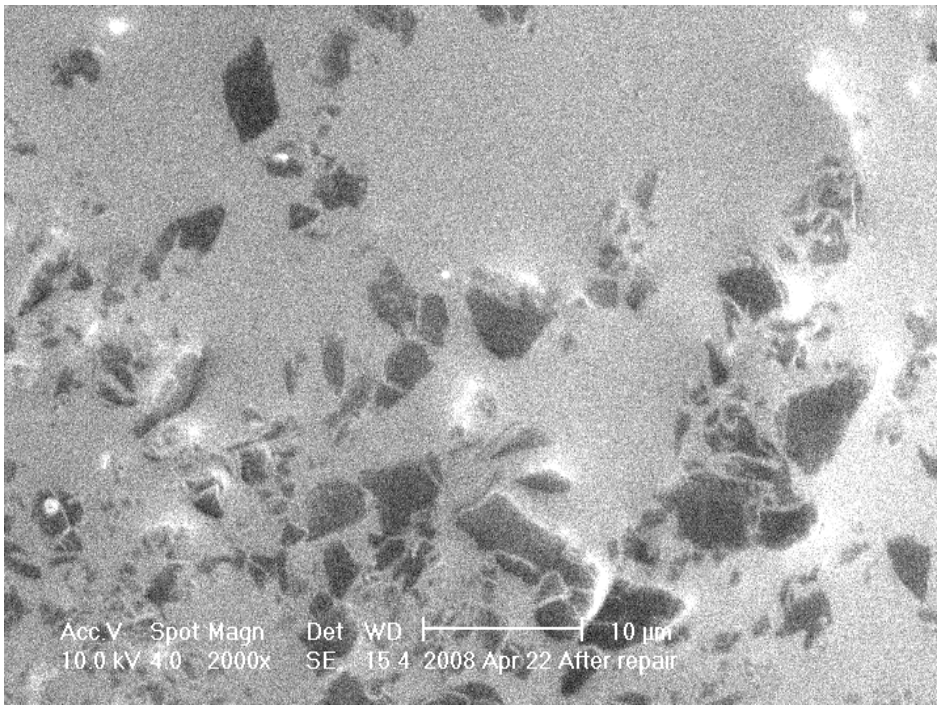

Fig. S3 SEM image of $[P_{4444}][Val]$ + $[bmim][Tf_2N]$ mixture.
Insoluble $[P_{4444}][Tf_2N]$ formed dispersion colloids in the mixture.