Electronic Supplementary Information

Facile preparation of hydroxide ion or proton conductive ionic liquids by mixing tetra-*n*-butylphosphonium hydroxide and benzimidazole

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Tetra-*n*-butylphosphonium hydroxide ([P_{4444}][OH]) was mixed with neutral benzimidazole to prepare tetra-*n*-butylphosphonium benzimidazolate ([P_{4444}][BzIm]). In case that the mixing ratio of [P_{4444}][OH] and benzimidazole is not 1:1, there are mixtures prepared for either hydroxide anion or proton conductive materials. The mixtures with different amount (x% in molar ratio) of benzimidazole were evaluated with their mixing ratio. Ionic conductivity of a series of mixtures with different x value was summarised in Fig. S−1 ($16.7 \leq x \leq 50.0$), and TG profiles of a series of mixtures with different x was summarized in Fig. S−2 ($x \geq 50.0$).

Elemental analysis of [P_{4444}][BzIm] salt (x= 50.0): calcd. for $C_{23}H_{41}N_6P_3$ 1/3 H_2O: C, 72.21; H, 10.98; N, 7.32. Found C72.54; H11.19; N7.11. This [P_{4444}][BzIm] salt (x= 50.0) is very hygroscopic and is quite difficult to get a stable data. The elemental analysis gives the data for the [P_{4444}][BzIm] (x= 50.0) containing a small amount of water. Since this was prepared by the neutralization of [P_{4444}][OH] with benzimidazole. This reaction produced equimolar amount of water, furthermore they are strongly bound onto the ions. Even after considerable drying, there are still some bound water molecules in the salts.

The structure of [P_{4444}][BzIm] (x=50.0), [P_{4444}][OH] and mixture of x=37.5 (benzimidazole /[P_{4444}][OH] mixtures with differing amounts of benzimidazole (x% in molar ratio)) were confirmed with ^{1}H−NMR measurements (400 MHz, D_2O, δ/ppm relative to TMS). [P_{4444}][BzIm] (x=50.0) : δ= 0.75 (t, 3H), 1.27 (m, 4H), 1.90 (t, 2H), 7.10(t, 2H), 7.51(t, 2H), 8.0(s, 1H). [P_{4444}][OH]: δ= 0.91 (m, 3H), 1.47 (m, 2H), 1.51 (m, 2H), 2.14 (m, 2H). Mixture x= 37.5: δ=0.91 (m, 3H), 1.44 (m, 4H), 1.77, 2.07 (m, 2H), 7.25 (t, 2H), 7.67(t, 2H), 8.12(s, 1H).

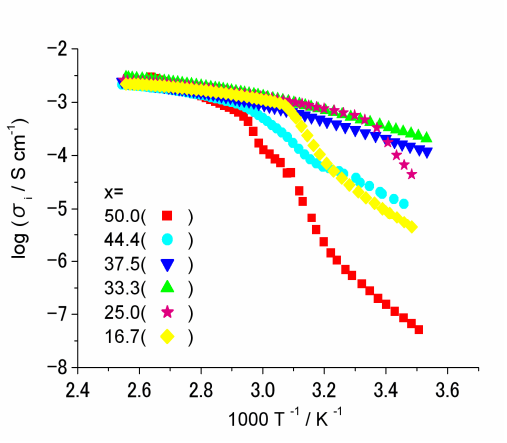

Fig. S−1 Arrhenius Plots of the ionic conductivity of a series of mixtures with different benzimidazole fraction (x).

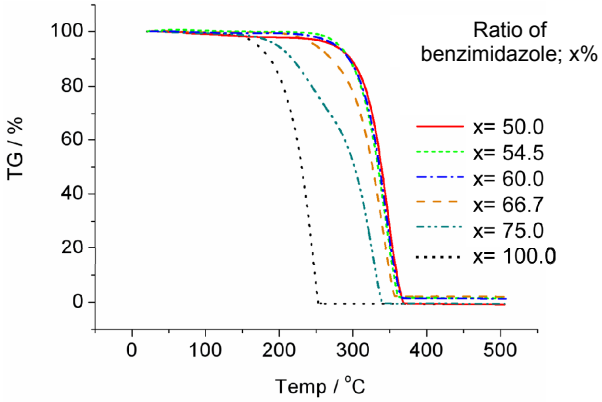

Fig. S−2 Thermogravimetric curves for a series of samples. The scan rate was 10°C min^{-1}.