Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Simple synthesis of tetra-*n*-butylphosphonium benzimidazolate/benzimidazole mixture as a thermally stable proton conductor

Yuki Tsuji, Tomonobu Mizumo, and Hiroyuki Ohno*

Preparation of ionic liquids and mixture with benzimidazole

Aqueous solution of $[P_{4444}][OH]$ (a donation from Hokko Chemical) and reagent grade BzIm (Tokyo Chemical Industry Co., Ltd.) were used without further purification. Equimolar amounts of $[P_{4444}][OH]$ and BzIm were mixed slowly in methanol under an atmosphere of nitrogen and stirred on an ice bath, so as to prepare the tetra-*n*-butylphosphonium benzimidazolate ($[P_{4444}][BzIm]$) after drying (Scheme 1). A similar process was used to prepare the $[P_{4444}][BzIm]/(BzIm)_x$ mixture (x=0.2-3.0) with differing BzIm fractions in order to analyze the proton conductive property. The water content of these mixtures was analysed using a Karl−Fischer moisture titrator (MKS−210, Kyoto Electronics Manufacturing Co.).

Characterization

The structure of $[P_{4444}][BzIm]$ and of the $[P_{4444}][BzIm]/(BzIm)_x$ mixture was confirmed by ^{1}H−NMR measurement. The NMR charts for BzIm and $[P_{4444}][BzIm]$ is shown in Fig. S1. The shifts of proton peaks strongly suggest the formation of salts.

● BzIm (400MHz, d_6−DMSO)
δ=7.2 (t, 2H)、7.59 (t, 2H), 8.21 (s, 1H)
● $[P_{4444}][BzIm]$ (x=0) (400MHz,d_6−DMSO)
δ= 0.91 (t, 3H), 1.42 (m, 4H), 2.17 (t, 3H), 6.67 (t, 2H), 7.28 (t 2H), 7.61(s, 1H)
● $[P_{4444}][BzIm]/(BzIm)_{0.2}$ (400MHz, d_6−DMSO)
δ= 0.91 (t, 3H), 1.41 (m, 4H), 2.15 (t, 3H), 6.76 (t, 2H), 7.33 (t 2H), 7.73(s, 1H)
● $[P_{4444}][BzIm]/(BzIm)_{0.5}$ (400MHz, d_6−DMSO)
δ= 0.90 (t, 3H), 1.42 (m, 4H), 2.17 (t, 3H), 6.82 (t, 2H), 7.39 (t 2H), 7.82(s, 1H)
● $[P_{4444}][BzIm]/(BzIm)_{1.0}$ (400MHz, d_6−DMSO)
δ= 0.91 (t, 3H), 1.41 (m, 4H), 2.13 (t, 3H), 6.92 (t, 2H), 7.44 (t 2H), 7.94(s, 1H)
● $[P_{4444}][BzIm]/(BzIm)_{2.0}$ (400MHz, d_6−DMSO)
δ= 0.90 (t, 3H), 1.38 (m, 4H), 2.13 (t, 3H), 7.03 (t, 2H), 7.52 (t 2H), 8.10(s, 1H)
● $[P_{4444}][BzIm]/(BzIm)_{3.0}$ (400MHz, d_6−DMSO)
δ= 0.91 (t, 3H), 1.42 (m, 4H), 2.15 (t, 3H), 7.06 (t, 2H), 7.52 (t 2H), 8.09(s, 1H)

Elemental analysis: calcd for $C_{23}H_{41}N_6P_3$ 1/3 H_2O: C:72.21; H:10.98; N:7.32. Found C:72.54; H:11.19; N:7.11. This $[P_{4444}][BzIm]$ salt is very hygroscopic and is quite difficult to get a stable data. The elemental analysis gives the data for the $[P_{4444}][BzIm]$ containing small amount of water.

Conductivity and measurements

The thermal properties of these samples were studied by differential scanning calorimetry (DSC: Seiko Instruments, DSC-120) and by thermogravimetric analysis (TG/DTA: Seiko Instruments, TGDTA-220). The viscosity of the samples was measured by a Brookfield viscometer, DV-1+.

Ionic conductivity was measured by the AC impedance method using a Schlumberger Solartron 1260 impedance/gain-phase analyzer. The impedance of the samples was measured from 10Hz to 1MHz with temperature scanning at 2 °C min^{-1} from 10 °C to 120 °C. Chronoamperometric measurements were also made to confirm the proton conduction in the $[P_{4444}][BzIm]/(BzIm)_x$ mixture. A steady-state current should be observed as a result of the electrolytic reduction of protons transported in the matrix.

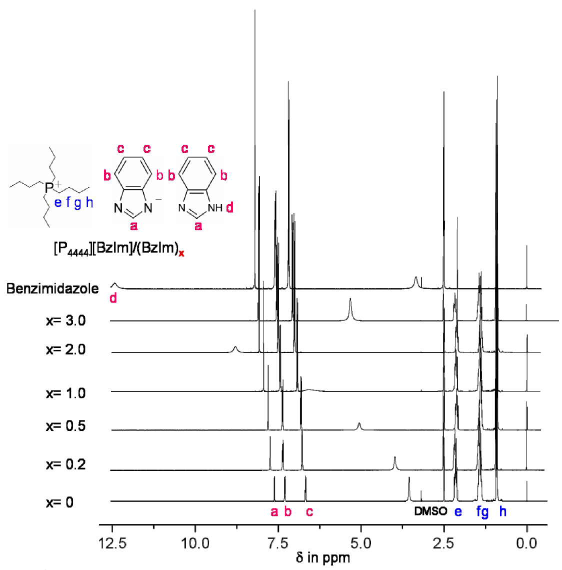

Fig. S1 ^{1}H-NMR charts of benzimidazole and mixtures with salts.