# Synthesis of Tetrabutylphosphonium Carboxylate Ionic Liquids and its Catalytic Activities for the Alcoholysis Reaction of Propylene Oxide

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## Supporting Information

Four CAILs $[P_{4444}][CA]$ had been synthesized via simple acid-base neutralization reactions, and all the yields of such CAILs were more than 80%. $^1$H NMR (Bruker DPX-300), FT-IR spectra (Thermo Nicolet 870) and thermogravimetry (PerkinElmer Diamond TG/DTA) characterization for each $[P_{4444}][CA]$ synthesized. In addition, an Anton Paar densimeter (model DMA4500) and cone-plate viscometer (Brookfield DV II+ Pro) were used to measure the densities and viscosities, respectively. The precision of the density apparatus was ± 0.001 g·cm$^{-3}$, which was also calibrated with dry air before each series of measurements. The attaining thermal equilibrium time in the viscometer was about 30 min, and the uncertainties were estimated to be ± 5.5 %. Conductivity was determined by a conductivity meter (DDJS-308A, Shanghai Leici Company) with a DJS-1C electrode. The uncertainty of the conductivity data was ±

3 %.

**[$P_{4444}$][For].** $^1$H NMR (300 MHz, $CDCl_3$) δ: 0.94 (12H, m, ($CH_3CH_2CH_2CH_2$)$_4$P), 1.42-1.67 (16H, m, ($CH_3CH_2CH_2CH_2$)$_4$P), 2.40 (8H, t, ($CH_3CH_2CH_2CH_2$)$_4$P), 8.92 (1H, s, *H*COO). (Yield 87% based on the amount of [$P_{4444}$]Br).

**[$P_{4444}$][Ace].** $^1$H NMR (300 MHz, $CDCl_3$) δ: 0.97 (12H, m, ($CH_3CH_2CH_2CH_2$)$_4$P), 1.52 (16H, m, ($CH_3CH_2CH_2CH_2$)$_4$P), 2.45 (8H, t, ($CH_3CH_2CH_2CH_2$)$_4$P), 1.96 (3H, s, $CH_3$COO). (Yield 86% based on the amount of [$P_{4444}$]Br).

**[$P_{4444}$][Prop].** $^1$H NMR (300 MHz, $CDCl_3$) δ: 0.97 (12H, m, ($CH_3CH_2CH_2CH_2$)$_4$P), 1.52 (16H, m, ($CH_3CH_2CH_2CH_2$)$_4$P), 2.46 (8H, t, ($CH_3CH_2CH_2CH_2$)$_4$P), 1.09-1.13 (3H, t, $CH_3CH_2$COO), 2.18-2.20 (2H, q, $CH_3CH_2$COO). (Yield 86% based on the amount of [$P_{4444}$]Br).

**[$P_{4444}$][Buty].** $^1$H NMR (300 MHz, $CDCl_3$) δ: 0.91-0.97 (15H, m, ($CH_3CH_2CH_2CH_2$)$_4$P, $CH_3CH_2CH_2$COO), 1.52 (16H, m, ($CH_3CH_2CH_2CH_2$)$_4$P), 2.45 (8H, m, ($CH_3CH_2CH_2CH_2$)$_4$P), 1.62-1.65 (2H, q, $CH_3CH_2CH_2$COO), 2.14-2.17 (2H, t, $CH_3CH_2CH_2$COO). (Yield 84% based on the amount of [$P_{4444}$]Br).

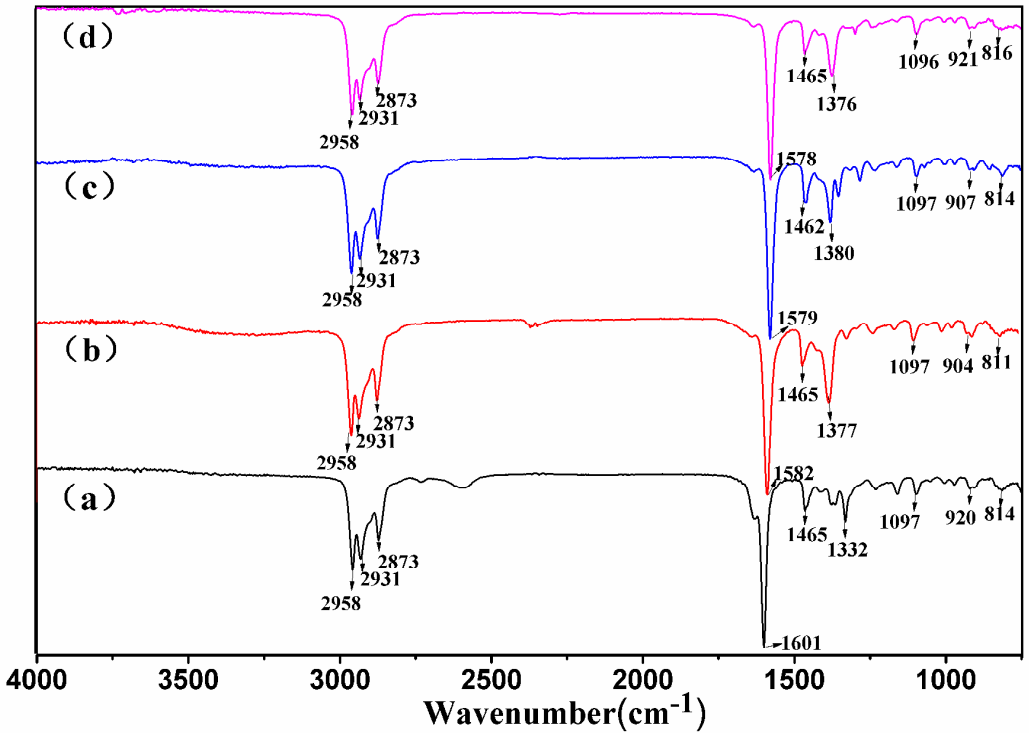


**Fig. S1.** FT-IR spectra of (a) [$P_{4444}$][For], (b) [$P_{4444}$][Ace], (c) [$P_{4444}$][Pro], (d) [$P_{4444}$][Buty].

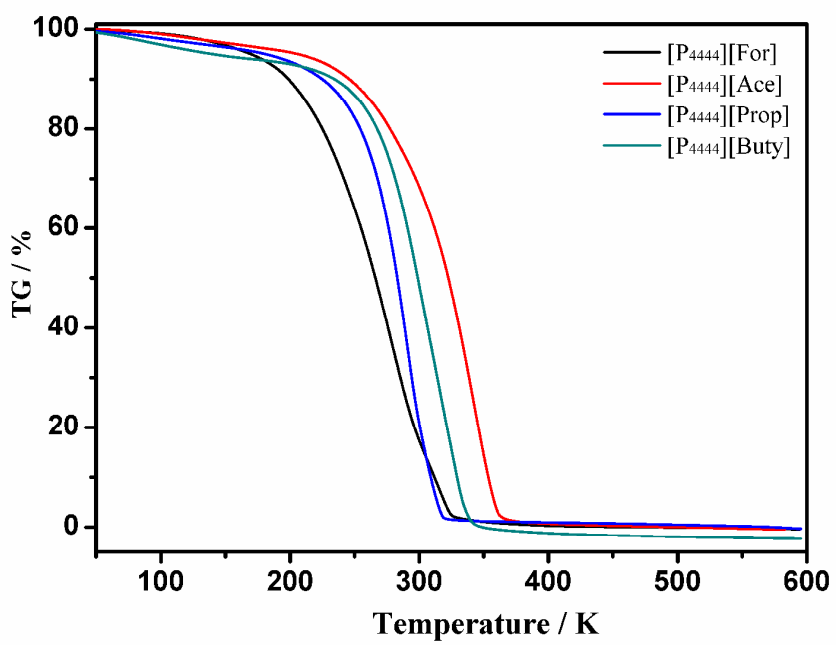


**Fig. S2.** TGA curves for [$P_{4444}$][CA] ILs.

**Table S1.** Density, viscosity, and conductivity for $[P_{4444}][CA]$ ILs at 25 °C.

| Ionic liquids | Density ($g \cdot cm^{-3}$) | Viscosity (mPa·s) | Conductivity ($\mu s \cdot cm^{-1}$) |
|---|---|---|---|
| $[P_{4444}][For]$ | 0.93713 | 459.6 | 74.1 |
| $[P_{4444}][Ace]$ | 0.93792 | 267.0 | 150.2 |
| $[P_{4444}][Prop]$ | 0.92869 | 245.6 | 200.1 |
| $[P_{4444}][Buty]$ | 0.93366 | 43.2 | 156.5 |