Electric Supplementary Information (ESI)

Phosphonium phosphonate-type zwitterion/water mixed systems showing variable hydrogen bonding ability as a function of temperature

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Experimental section

1. Preparation of zwitterions

i) Materials and instruments

Tri-*n*-hexylphosphine, tri-*n*-octylphosphine, and diethyl 2-bromoethylphosphonate were purchased from Tokyo Chemical Industry Co., Ltd. (TCI), and used as received. Amberlite® IRN-78 was purchased from SPELCO. The measurements of ^{1}H-NMR spectra were carried out on JEOL ECX-400. Electrospray ionization-time-of-flight-mass (ESI-TOF-MAS) spectrometry was made on JEOL JMS-T100LC. Elemental analysis was performed by Elementar vario EL III. The amount of water was confirmed by Karl Fischer coulometric titration (Kyoto Electronics MKC-510N). The differential scanning calorimetry (DSC) measurements were carried out using DSC-6200 (SEIKO Instruments) at a scanning rate for both heating and cooling of 2.5 °C mim^{-1} in the temperature range -120 °C to 200 °C. The thermogravimetric analysis (TGA) was made on SEIKO TG/DTA 220 instrument with heating rate of 10 ºCmim^{-1} from 25 °C to 500 °C under nitrogen gas. Visible spectrum was measured using Shimadzu UV 2450.

ii) Preparation procedures

As general procedures to give ZIs, preparation of [P8C2P] was described as follows. To tri-*n*-octylphosphin (32.15 g, 0.11 mol) in *n*-hexane (100 ml), diethyl 2-bromoethylphosphonate (25 g, 0.10 mol) in *n*-hexane (100 ml) was added dropwise under nitrogen gas atmosphere. The reaction solution was stirred under reflux for 48 h. After removal of *n*-hexane, the resulting liquid was washed repeatedly with *n*-hexane to give [P8C2P]Br (48.26 g, yield: 89%).

[P8C2P]Br (40 g) was dissolved in ethanol/water (2/1 (v/v)) (500 ml); and the resulting solution was passed through the column filled with anion exchange resin (Amberlite$^{®}$ IRN-78) (200 ml). After stirring the resulting solution at room temperature for 24 h, ethanol and water was removed by evaporation to give [P8C2P]. Crude [P8C2P] was purified by recrystallization from ethyl acetate repeatedly. [P8C2P] was dried under reduced pressure at 80 °C for 12 h to give [P8C2P] as white solid (22 g, yield: 69%). Chemical structure of [P8C2P] was confirmed with ^{1}H-NMR spectra, MS spectra, and elemental analysis. [P6C2P] was prepared as the same procedure using tri-*n*-hexylphosphine instead of tri-*n*-octylphosphine.

Chemical structures of ZIs [P8C2P] and [P6C2P] were confirmed by ^{1}H-NMR, ESI-TOF-MS spectra, and elemental analysis.

[P8C2P]: ^{1}H-NMR (400 MHz; $CDCl_3$; Me_4Si) $\delta = 0.88$ (9H, t, $J = 6.9$ Hz, $CH_2CH_2C\mathit{H_3}$), 1.23-1.32 (27H, m, $(C\mathit{H_2})_4CH_3$, $POCH_2C\mathit{H_3}$), 1.50 (12H, m, $(C\mathit{H_2})_2CH_2$), 1.70-1.82 (2H, m, $POC\mathit{H_2}CH_3$), 2.36-2.29 (6H, m, $PC\mathit{H_2}CH_2$), 2.50 (2H, tt, $J = 12.4$, 5.6 Hz, $PC\mathit{H_2}CH_2P$), 3.99-3.92 (2H, m, $PCH_2C\mathit{H_2}P$). ESI-TOF-MS: Calcd for $C_{28}H_{60}O_3P_2$ [M+H]+: m/z = 507.41; Found: 504.41. Elemental analysis: Calcd for $C_{28}H_{60}O_3P_2$: C, 66.37; H, 11.93; O, 9.47; P, 12.23 Found: C, 66.07; H, 11.91; N, 0.

[P6C2P]: ^{1}H-NMR (400 MHz; $CDCl_3$; Me_4Si) $\delta = 0.90$ (9H, t, J = 6.9 Hz, $CH_2CH_2C\mathit{H_3}$), 1.25 (3H, t, J = 7.1 Hz, $POCH_2C\mathit{H_3}$), 1.31 (12H, m, $(C\mathit{H_2})_2CH_3$), 1.52 (12H, m, $PCH_2(C\mathit{H_2})_2CH_2$), 1.84-1.72 (2H, m $POC\mathit{H_2}CH_3$), 2.36-2.28 (6H, m, $PC\mathit{H_2}(CH_2)_2CH_2$), 2.49 (2H, ddd, $J = 21.5$, 11.4, 6.4 Hz, $PC\mathit{H_2}CH_2P$), 3.93-4.00 (2H, m, $PCH_2C\mathit{H_2}P$). ESI-TOF-MS: Calcd for $C_{22}H_{48}O_3P_2$ [M+H]+: m/z =423.32; Found: 423.31. Elemental analysis: Calcd for $C_{22}H_{48}O_3P_2$: C, 62.53; H, 11.45; O, 11.36; P, 14.66 Found: C, 61.87; H, 11.27; N, 0.

2. Estimation of Kamlet-Taft parameters

The Kamlet-Taft parameters of ZI-water mixed systems were determined as follows. Spectroscopic grade solvatochromic dyes, (2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)-phenolate (Reichardt's dye #33) (from Fluka), 4-nitroaniline (from Tokyo Chemical Ind. Co., Ltd), and *N,N-diethyl-4-nitroaniline* (from Kanto Chem.), were used as received. We mixed probe dyes directly with ZI-rich phase after phase separation and gently stirred the resulting mixture, to give dye solutions. To prevent dye aggregation, the dye concentration in any series of ILs was chosen to be low but sufficient to allow an absorbance greater than 0.15.

These dye solutions were placed in quartz cells with an optical path length of 1mm. The temperature of the quartz cell was maintained at 25 °C. Once the maximum absorption wavelength (λ_{max}) was determined, the Kamlet-Taft parameters (α: hydrogen-bonding acidity, β: hydrogen-bonding basicity, and π^*: dipolarity) were calculated from the following equations:

$$\nu_{(\mathrm{dye})} = 1/(\lambda_{\mathrm{max(dye)}} \times 10^{-4})$$

$$E_{\mathrm{T}}(30) = 0.9986(28592/\lambda_{\mathrm{max(Reichardt's\ dye\ \#33)}}) - 8.6878$$

$$\pi^* = 0.314(27.52 - \nu_{(N,N\text{-diethyl-4-nitroaniline})})$$

$$\alpha = 0.0649E_{\mathrm{T}}(30) - 2.03 - 0.72\pi^*$$

$$\beta = (1.035\nu_{(N,N\text{-diethyl-4-nitroaniline})} + 2.64 - \nu_{(\text{4-nitroaniline})})/2.80$$

3. Determination of the phase transition temperature of ZI/water mixtures and the water content of ZI-rich phases

We added MilliQ water to the [P8C2P] in amounts ranging from 1 to 50 (by mol/mol). The mixture was cooled to 0 °C and then gradually heated in a water bath equipped with a digital thermometer (Fine Thermo F002DN). The lowest temperature at which the mixture went cloudy (the cloud point) was recorded as the phase transition temperature (T_{c}). To determine the water content of ZI-rich phase, we stored the ZI/water mixtures at each temperature (above T_{c}) until these mixtures undergo obvious phase separation. The water content of the IL-rich phase was determined by the Karl-Fischer moisture titration method.

4. Characterisation of ZIs (NMR, MS, DSC, and TGA data)

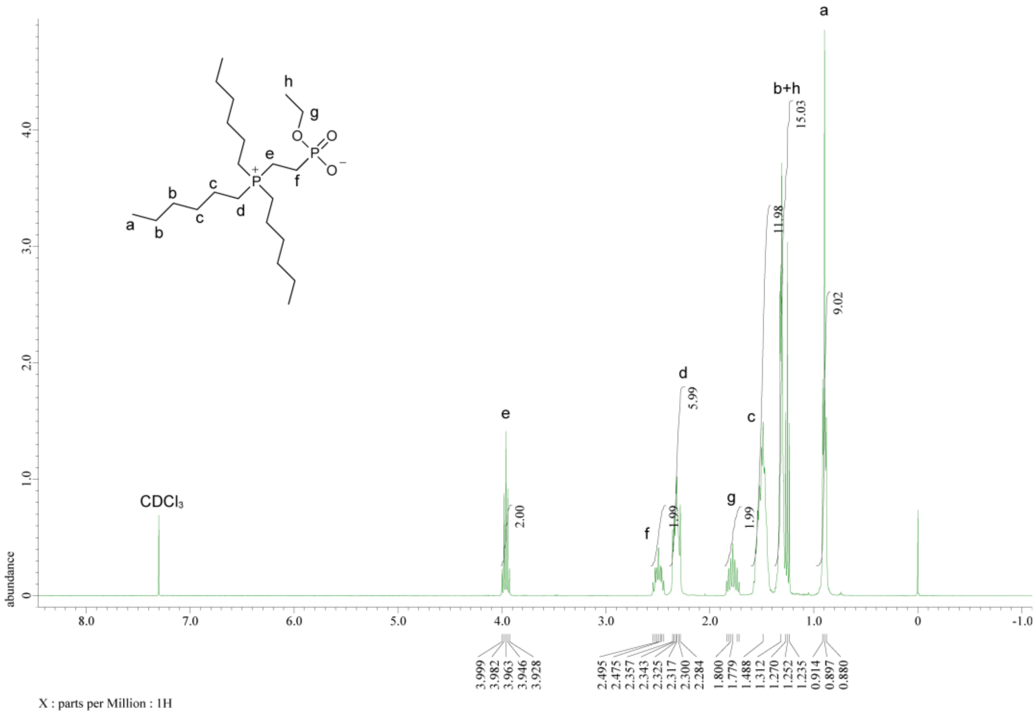

Fig. S1 NMR chart of [P6C2P]

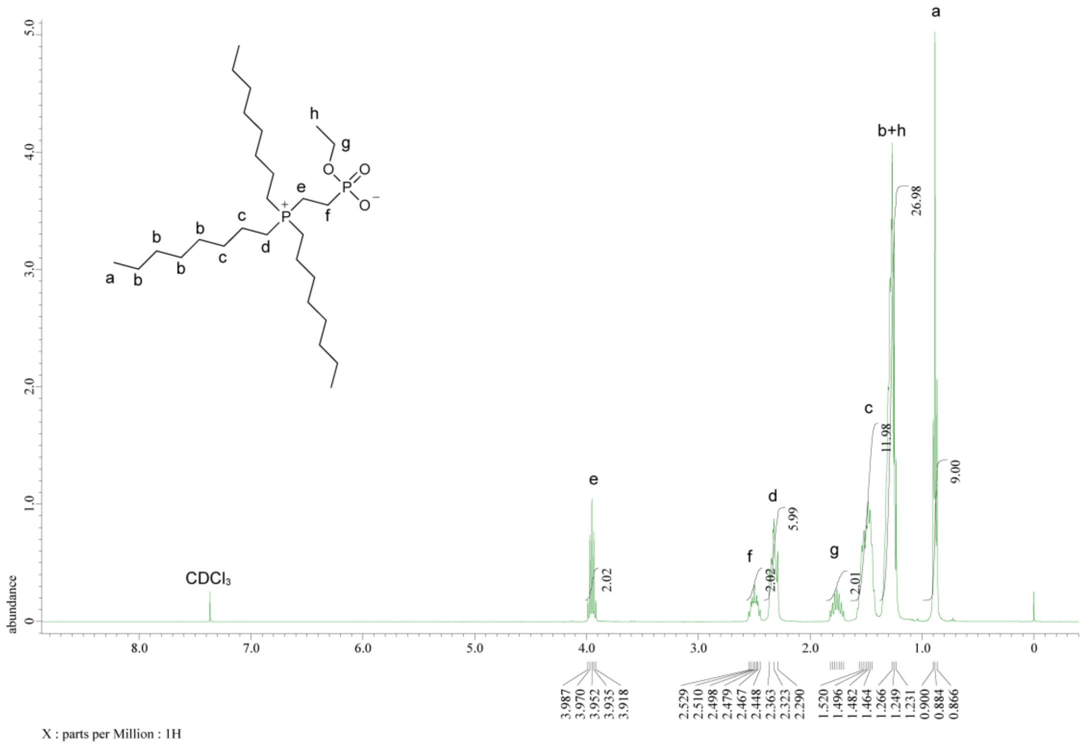

Fig. S2 NMR chart of [P8C2P]

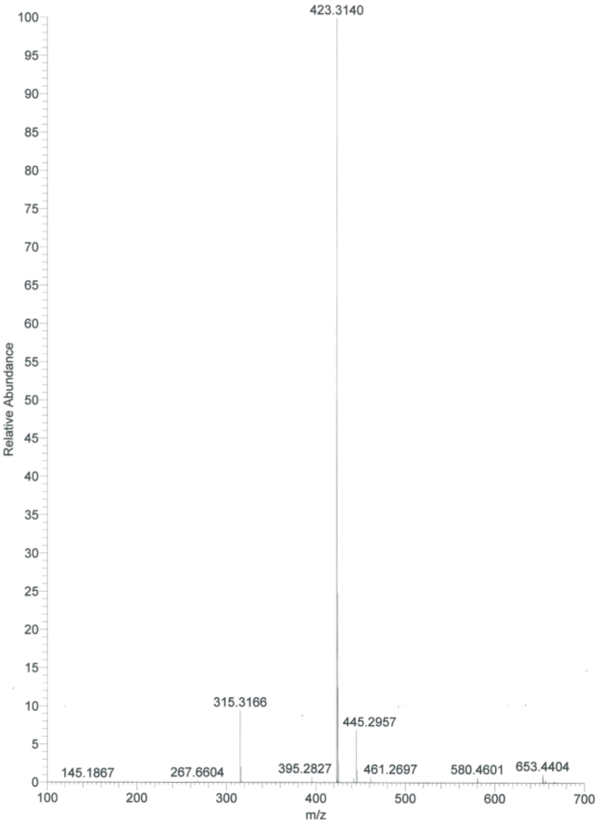

Fig. S3 MS spectrum of [P6C2P]

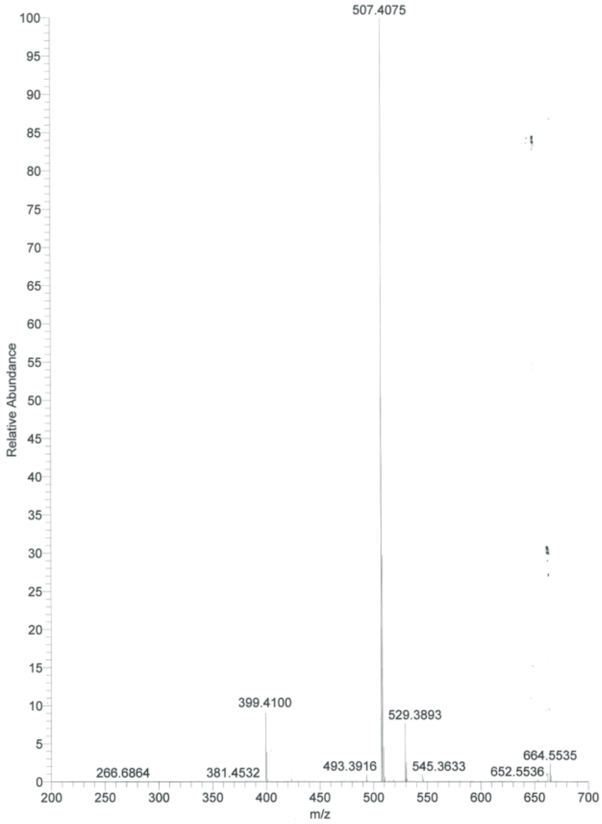

Fig. S4 MS spectrum of [P8C2P]

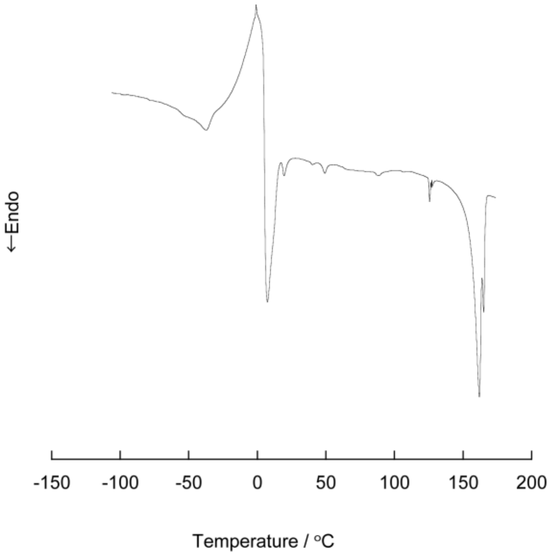

Fig. S5 DSC plot of [P6C2P]

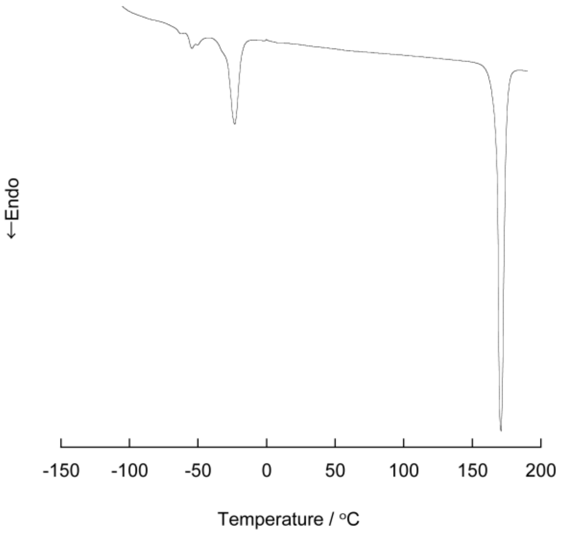

Fig. S6 DSC plot of [P8C2P]

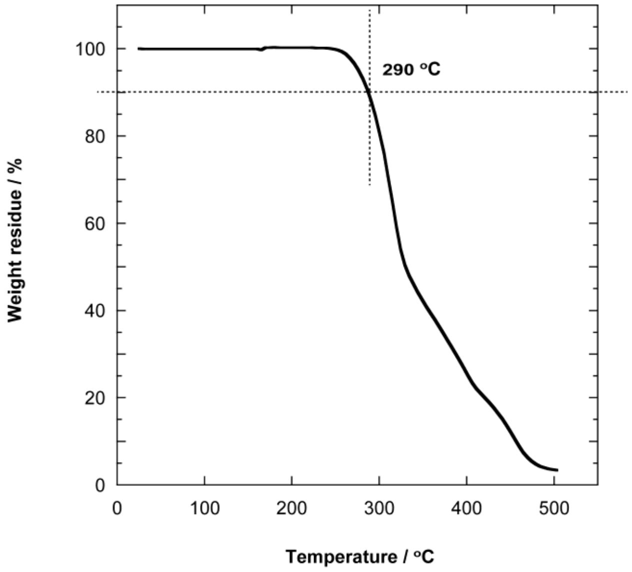

Fig. S7 TGA curve of [P6C2P]

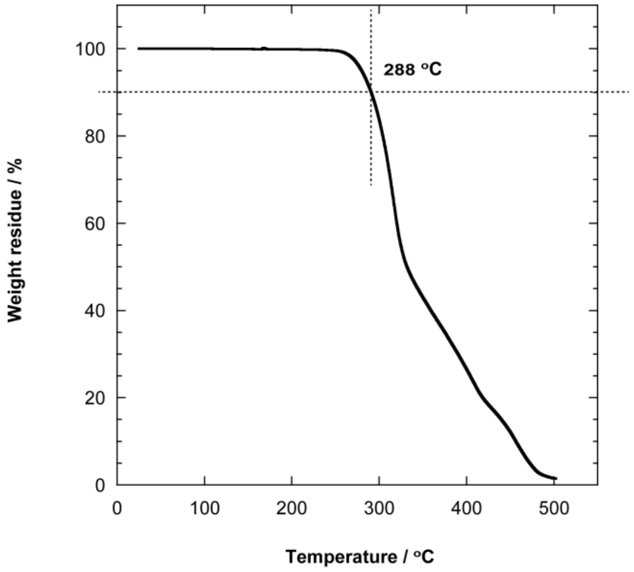

Fig. S8 TGA curve of [P8C2P]