Electronic Supplementary Information

Title: Introduction of hydrophilic groups onto *ortho*-position of benzoate anion lowers hydrophilicity of the corresponding ionic liquids

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Materials

Tetrabutylphosphonium hydroxide ($[P_{4444}]OH$) was donated from Hokko Chemical Industry Co. 2-hydroxybenzoic acid (H[Bz-*o*-OH]), 3-hydroxybenzoic acid (H[Bz-*m*-OH]), 4-hydroxybenzoic acid (H[Bz-*p*-OH]), phthalic acid (H[Bz-*o*-COOH]), isophthalic acid (H[Bz-*m*-COOH]), terephthalic acid (H[Bz-*p*-COOH]), 2-methoxybenzoic acid (H[Bz-*o*-OCH_3]), 2-aminobenzoic acid (H[Bz-*o*-NH_2]), 2-sulfobenzoic acid monoammonium salt (NH_4[Bz-*o*-SO_3]), and 3-sulfobenzoic acid monosodium salt (Na[Bz-*m*-SO_3]) were purchased from Tokyo Chemical Industry Co., Ltd. Benzoic acid (H[Bz]) and 4-sulfobenzoic acid monopotassium salt (K[Bz-*p*-SO_3]) was purchased from Wako Pure Chemical Industries, Ltd. All chemicals were used as received.

Preparation and characterisation of ionic liquids (ILs) in this study

$[P_{4444}]Cl$ was prepared by neutralisation of $[P_{4444}]OH$ and hydrochloric acid. ILs with [Bz-*o*-$SO_3]^-$, [Bz-*m*-$SO_3]^-$, and [Bz-*p*-$SO_3]^-$ as anions were prepared by anion exchange reaction of $[P_{4444}]Cl$ with the corresponding alkali metal salts in water, according to our previous report.[1] Other salts were prepared by neutralisation of $[P_{4444}]OH$ with the corresponding acids in water. The prepared ILs were extracted with dichloromethane and washed with water for several times. The dichloromethane layer was evaporated and the residual liquid was dried in vacuo for at least 24 h. Both chemical structure and purity of these salts were confirmed by ^1H NMR spectrometry

(JEOL ECX-400, 400 MHz) and elemental analysis (Elementar vario EL III).

[P_{4444}][Bz]: δ_H (400 MHz; DMSO; δ/ppm relative to TMS): 7.81-7.78 (m, 2H), 7.22-7.20 (m, 3H), 2.22-2.18 (m, 8H), 1.45-1.40 (m, 16H), 0.91 (t, J = 7.1 Hz, 12H). Found: C, 68.64; H, 11.35; N, 0. Calc. for $C_{23}H_{41}O_2P{\cdot}1.3H_2O$: C, 68.38; H, 10.88; N, 0%.

[P_{4444}][Bz-*o*-OH]: δ_H (400 MHz; $CDCl_3$; δ/ppm relative to TMS): 7.81 (d, J = 6.9 Hz, 1H), 7.09 (t, J = 7.3 Hz, 1H), 6.66-6.57 (m, 2H), 2.04 (s, 8H), 1.32 (s, 16H), 0.79 (s, 12H). Found: C, 68.52; H, 10.63; N, 0. Calc. for $C_{23}H_{41}O_3P{\cdot}0.3H_2O$: C, 68.73; H, 10.43; N, 0%.

[P_{4444}][Bz-*m*-OH]: δ_H (400 MHz; DMSO; δ/ppm relative to TMS): 9.13 (s, 1H), 7.21 (d, J = 23.5 Hz, 2H), 6.96 (s, 1H), 6.59 (s, 1H), 2.16 (s, 8H), 1.41 (s, 16H), 0.90 (s, 12H). Found: C, 68.19; H, 10.53; N, 0. Calc. for $C_{23}H_{41}O_3P{\cdot}0.5H_2O$: C, 68.12; H, 10.44; N, 0%.

[P_{4444}][Bz-*p*-OH]: δ_H (400 MHz; DMSO; δ/ppm relative to TMS): 7.63 (d, J = 6.9 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 2.19-2.13 (m, 8H), 1.48-1.35 (m, 16H), 0.90 (t, J = 7.2 Hz, 12H). Found: C, 68.1; H, 10.64; N, 0. Calc. for $C_{23}H_{41}O_3P{\cdot}0.5H_2O$: C, 68.12; H, 10.44; N, 0%.

[P_{4444}][Bz-*o*-COOH]: δ_H (400 MHz; $CDCl_3$; δ/ppm relative to TMS): 8.24 (t, J = 4.4 Hz, 2H), 7.42 (t, J = 4.4 Hz, 2H), 2.12 (s, 8H), 1.33-1.29 (m, 16H), 0.71 (t, J = 6.9 Hz, 12H). Found: C, 67.21; H, 9.758; N, 0. Calc. for $C_{24}H_{41}O_4P{\cdot}0.2H_2O$: C, 67.33; H, 9.746; N, 0%.

[P_{4444}][Bz-*m*-COOH]: δ_H (400 MHz; $CDCl_3$; δ/ppm relative to TMS): 8.38-8.37 (m, 2H), 7.53-7.45 (m, 2H), 2.28 (tt, J = 10.3, 4.1 Hz, 8H), 1.58-1.45 (m, 16H), 0.94 (t, J = 7.8 Hz, 12H). Found: C, 66.3; H, 10.06; N, 0. $C_{24}H_{41}O_4P{\cdot}0.5H_2O$: C, 66.49; H, 9.76; N, 0%.

$[P_{4444}]_2$[Bz-*p*-COO]: δ_H (400 MHz; DMSO; δ/ppm relative to TMS): 7.61 (s, 4H), 2.18 (dt, *J* = 15.7, 6.9 Hz, 16H), 1.48-1.35 (m, 32H), 0.90 (t, *J* = 7.2 Hz, 24H). Found: C, 66.73; H, 11.63; N, 0. Calc. for $C_{40}H_{76}O_4P_2{\cdot}2H_2O$: C, 66.45; H, 11.71; N, 0%.

$[P_{4444}]$[Bz-*o*-OCH_3]: δ_H (400 MHz; DMSO; δ/ppm relative to TMS): 7.00-6.95 (m, 2H), 6.75-6.67 (m, 2H), 3.62 (s, 3H), 2.20-2.13(m, 8H), 1.45-1.33(m, 16H), 0.88(t, *J* = 7.1, 12H). Found: C, 67.55; H, 10.56; N, 0. Calc. for $C_{24}H_{43}O_3P{\cdot}H_2O$: C, 67.26; H, 10.58; N, 0%.

$[P_{4444}]$[Bz-*o*-NH_2]: δ_H (400 MHz; DMSO; δ/ppm relative to TMS): 7.66 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.88-6.84 (1H, m), 6.44 (d, *J* = 7.8 Hz, 1H), 6.30 (t, *J* = 7.3 Hz, 1H), 2.22-2.15 (m, 8H), 1.40 (dt, *J* = 23.4, 8.9 Hz, 16H), 0.91 (t, *J* = 7.1 Hz, 12H). Found: C,67.03; H, 10.55; N, 3.34. Calc. for $C_{23}H_{42}NO_2P{\cdot}H_2O$: C, 66.79; H, 10.72; N, 3.39%.

$[P_{4444}]$[Bz-*o*-SO_3]: δ_H (400 MHz; DMSO; δ/ppm relative to TMS): 7.84 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 2.20-2.14 (m, 8H), 1.50-1.36 (m, 16H), 0.91 (t, *J* = 7.2 Hz, 12H). Found: C, 59.46; H, 9.055; N, 0. Calc. for $C_{23}H_{41}O_5PS{\cdot}0.1H_2O$: C, 59.74; H, 8.981; N, 0%.

$[P_{4444}]$[Bz-*m*-SO_3]: δ_H (400 MHz; DMSO; δ/ppm relative to TMS): 8.18 (t, *J* = 1.6 Hz, 1H), 7.86 (tt, *J* = 7.8, 1.6 Hz, 1H), 7.79 (tt, *J* = 7.6, 3.8 Hz, 1H), 7.43 (t, *J* = 9.6 Hz, 1H), 2.16 (dt, *J* = 15.3, 6.9 Hz, 8H), 1.41 (dtd, *J* = 31.4, 11.0, 6.5 Hz, 16H), 0.89 (t, *J* = 7.1 Hz, 12H). Found: C, 59.8; H, 9.205; N, 0. Calc. for $C_{23}H_{41}O_5PS$: C, 59.97; H, 8.972; N, 0%.

$[P_{4444}]$[Bz-*p*-SO_3]: δ_H (400 MHz; DMSO; δ/ppm relative to TMS):7.87 (d, *J* = 6.3 Hz, 2H), 7.65 (d, *J* = 4.0 Hz, 2H), 2.19-2.13 (m, 8H), 1.48-1.35 (m, 16H), 0.90 (t, *J* = 6.9 Hz, 12H). Found: C, 59.98; H, 9.016; N, 0. Calc. for $C_{23}H_{41}O_5PS$: C, 59.97; H, 8.972; N, 0%.

Thermal properties of ILs

Both melting point (T_m) and glass transition temperature (T_g) of the prepared ILs were measured by DSC measurement. The DSC measurement was performed with a DSC-6220 (Seiko Instruments Inc.) at a heating rate of 5 °C min^{-1}.

Determination of Hydrophilicity Index (HI) value

The prepared ILs were mixed with an equal weight of water (50 w/w%) and stirred vigorously. The phase behaviour of these IL/water mixtures were analysed after keeping the solution without perturbation at 60 °C until separated phases became clear. The water content of the separated IL phase was measured by Karl-Fischer titration method (Kyoto Electronics; MKC-520), and the number of water molecules per one ion pair was calculated and determined as HI.

Phase behaviour of [P_{4444}][Bz-*m*-COOH] with water at room temperature

[P_{4444}][Bz-*m*-COOH] showed liquid/liquid type phase separation with water at 60 °C. The hydrated [P_{4444}][Bz-*m*-COOH] phase, however, became gel-like solid phase when the mixture was cooled at room temperature as shown in Fig. S1.

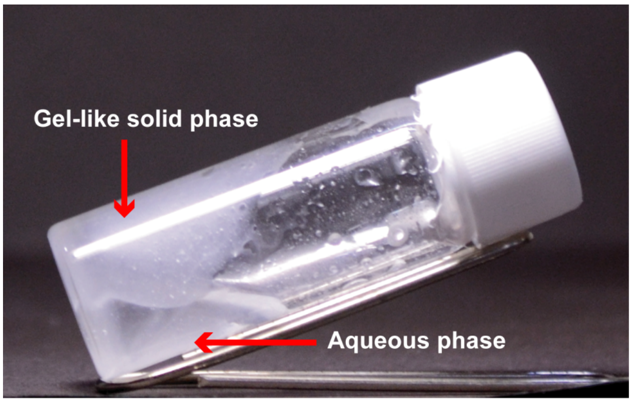

Fig. S1 Gel-like solid phase of [P_{4444}][Bz-*m*-COOH] after cooling at room temperature.

Effect of formula weight on the HI value

Fig. S2 shows the effect of introduced hydrophilic groups onto $[Bz]^-$. We compared the HI of prepared ILs in this study with that of other $[P_{4444}]^+$-type ILs reported previously, with different formula weight.

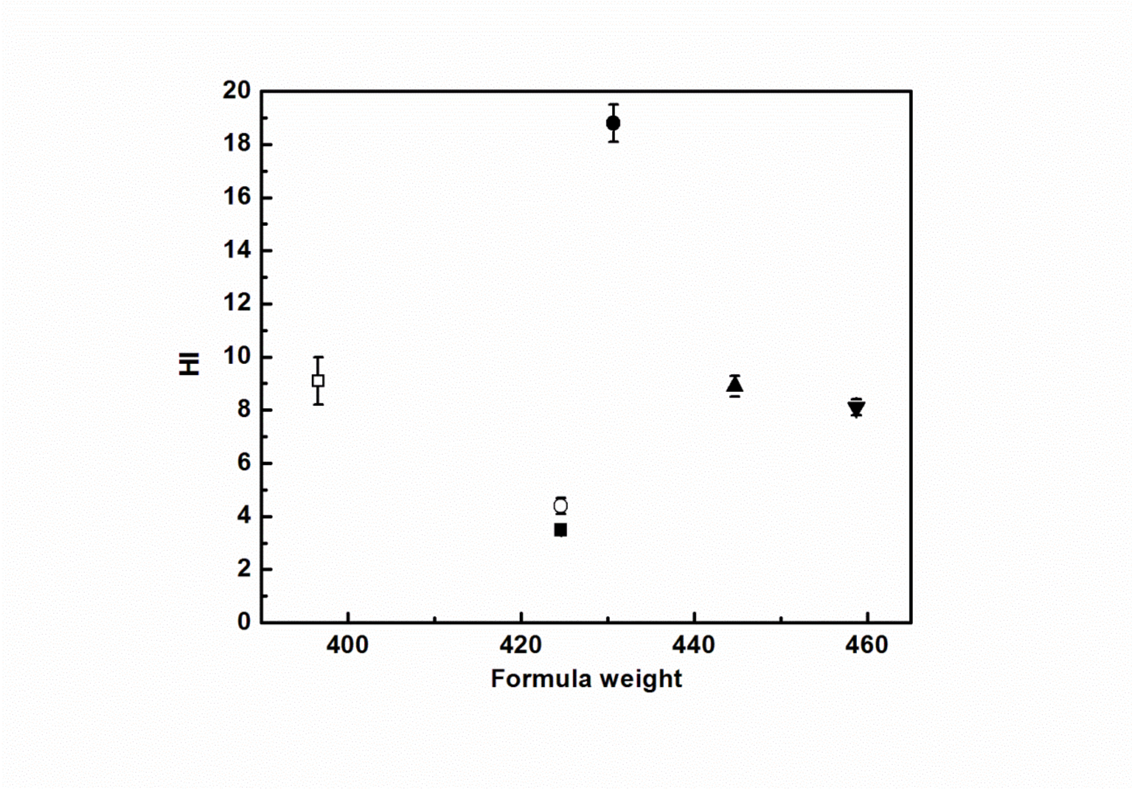

Fig. S2 The m_{water} value of prepared ILs as a function of formula weight; (□): $[P_{4444}]$[Bz-*o*-OH], (○): $[P_{4444}]$[Bz-*m*-COOH], (■): $[P_{4444}]$[Bz-*o*-COOH], (●): $[P_{4444}]$[TsO], (▲): $[P_{4444}]$[DMBS], (▼): $[P_{4444}]$[TMBS].

Crystallography

The crystal structure of [P_{4444}][Bz-*o*-OH] was determined by X-ray single-crystal analysis. [P_{4444}][Bz-*o*-OH] was successfully crystallised by adding a small amount of water to the salt and leaving the mixture at room temperature without a perturbation. X-ray diffraction data was collected using Rigaku R-AXIS RAPID system.[2] The structure was solved by direct methods and refined with a full-matrix least-squares technique with the SIR2008 and SHELXL program package, respectively. The non-hydrogen atoms were refined with anisotropic thermal parameters. All the hydrogen atom, except for that of the hydroxyl group, were located at idealized positions and subsequently treated as a riding model with fixed thermal parameters (U_{iso} = 1.2 U_{eq} for the atoms to which they are bonded). The hydrogen atom bonded to hydroxyl oxygen (O1) was found in the difference Fourier map and could be accurately refined with O-H distance of 0.964 Å. The C22 atoms in [P_{4444}]$^+$; was shown to be disordered at two positions. The occupancy of C22a and C22b were found to be 0.63 and 0.37, respectively during the refinement.

Table S1 Crystal data for [P_{4444}][Bz-*o*-OH]

Formula	$C_{23}H_{41}O_3P$
Formula weight	396.53
Temperature (K)	193
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	9.9732(2)
b (Å)	15.1013(3)
c (Å)	16.2700(3)
b (°)	102.662(1)
V (Å^3)	2390.80(8)
Z	4
r_{calc} (gcm^{-3})	1.102
m_{CuKa}(mm^{-1})	1.154

Reflections measured /independent reflections (R_{int})	43847/4363 (0.0170)
R_{sig}	0.0070
Completeness	0.999
R_1/wR_2 (I > 2 □)	0.0670/0.1952
R_1/wR_2 (all data)	0.0701/0.1982
Goodness-of-fit on F^2	1.149
Restraints	44
Parameters	257
Residue	0.476/-0.442

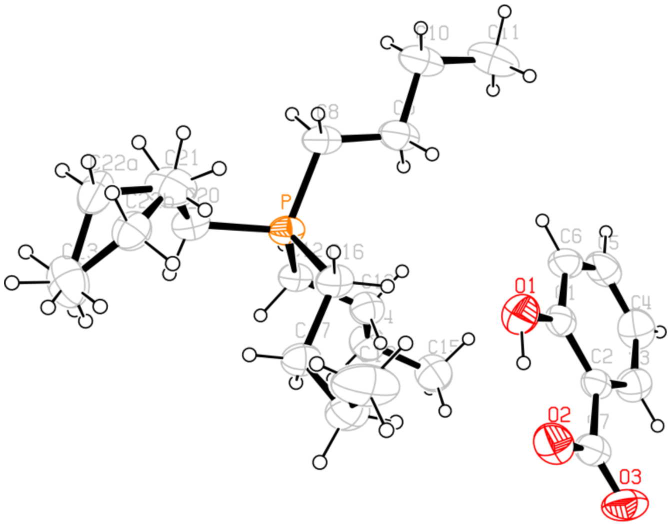

Fig. S3 Crystal structure of [P_{4444}][Bz-*o*-OH]; Orange: phosphorus, grey: carbon, white: hydrogen, red: oxygen.

The distance and angle between hydrogen atom of hydroxyl group and oxygen atom of carboxylate anion of [P$_{4444}$][Bz-*o*-OH] was measured with Mercury 3.1. In the case of [P$_{4444}$][Bz-*o*-OH], the distance and the angle were found to be 1.507 Å and 163.09°. This shows that the hydrogen atom of OH group was located closer to oxygen atom compared to salicylic acid[3], making the angle more collinear. The obtained result suggests that proton sharing seen in [P$_{4444}$][Bz-*o*-OH] is regarded to be distorted hydrogen bonding, and the distorted hydrogen bonding lowers the number of water molecules bound to [P$_{4444}$][Bz-*o*-OH].

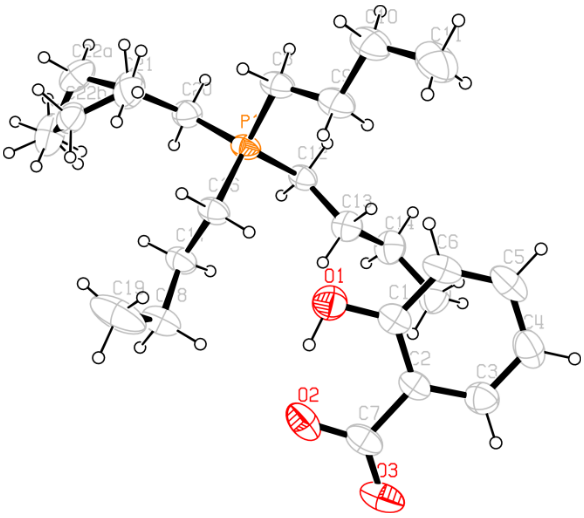

Fig. S4 Distorted hydrogen bonding between hydrogen atom of hydroxyl group and oxygen atom of carboxylate anion of [P$_{4444}$][Bz-*o*-OH]; Orange: phosphorus, grey: carbon, white: hydrogen, red: oxygen.

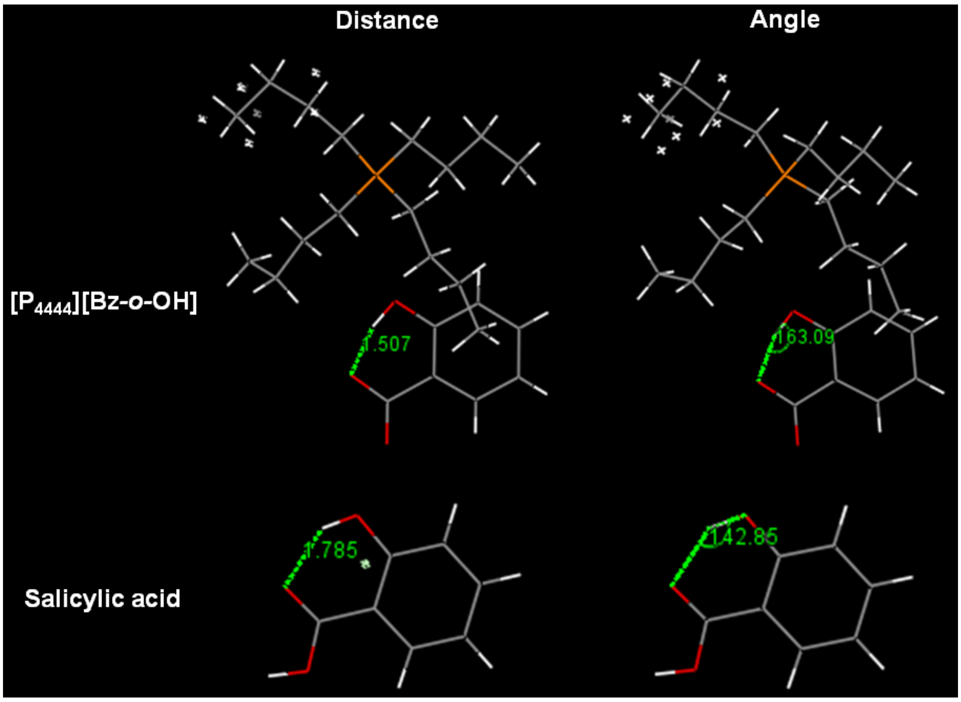

Fig. S5 Distance and angle of distorted hydrogen bonding of [P_{4444}][Bz-*o*-OH] and that of intramolecular hydrogen bonding of salicylic acid.

Phase behaviour of ILs with sulfonic acid group onto *ortho*-position of $[Bz]^-$

Table S2 shows thermal properties of ILs, prepared by introduction of sulfonic acid group onto *ortho*-position of $[Bz]^-$, and phase behaviour of mixtures of the ILs and water. The phase behaviour of the ILs prepared in this study with water was analysed at 60 °C to compare other ILs shown in Table 1.

Table S2 Thermal properties of ILs and phase behaviour of mixtures of ILs and water.

ILs	T_m (°C)	T_g (°C)	Phase behaviour[c]	HI[c]
$[P_{4444}][Bz\text{-}o\text{-}SO_3]$	–[a]	−52	L	1.1±0.02
$[P_{4444}][Bz\text{-}m\text{-}SO_3]$	78	−17	L	6.5±0.4
$[P_{4444}][Bz\text{-}p\text{-}SO_3]$	119	–[a]	S	–[b]

L: liquid/liquid phase separation, S: solid/liquid phase separation, –[a]: not detected, –[b]: not measured, [c]: at 60 °C.

ATR-FTIR spectra of ILs

ATR-FTIR spectra were measured with FT/IR-4200 from JASCO to analyse the dissociated state of carboxylate anion in prepared ILs. In the case of the introduction of sulfonic acid group, it was clear that the carboxylate anion of [P_{4444}][Bz-*o*-SO_3] became undissociated.

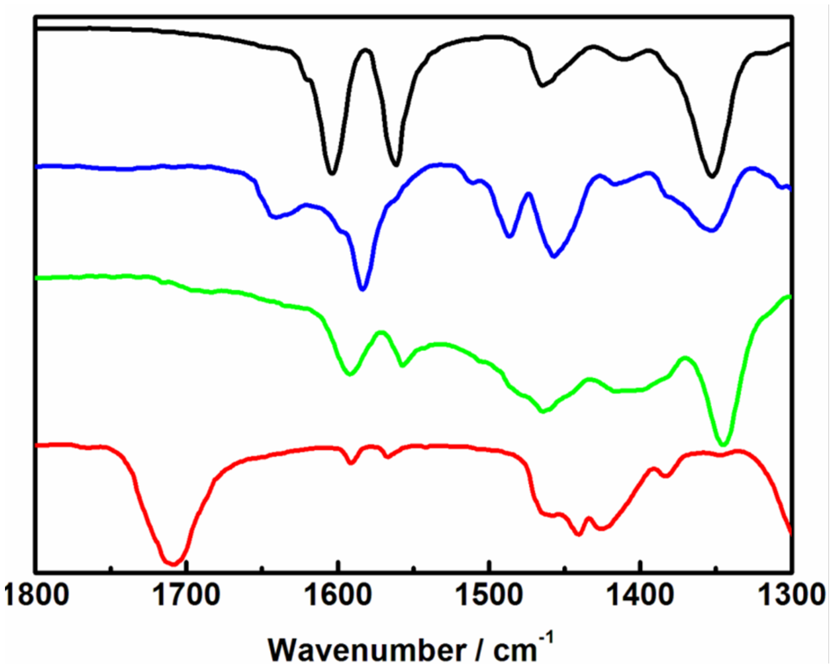

Fig. S6 ATR-FTIR spectra of [P_{4444}][Bz] (black line), [P_{4444}][Bz-*o*-OH] (blue line), [P_{4444}][Bz-*o*-COOH] (green line), and [P_{4444}][Bz-*o*-SO_3] (red line).

References

1 Y. Kohno, H. Arai, S. Saita, and H. Ohno, *Aust. J. Chem.*, 2011, **64**, 1560.

2 CCDC deposition number: 950650.

3 P. Munshi and T. N. Guru Row, *Acta Crystallogr., Sect. B: Struct. Sci.,* 2006, **62**, 612