Electronic Supplementary Information

Poly(ionic liquid)s with superior swelling and enrichment properties in solvents

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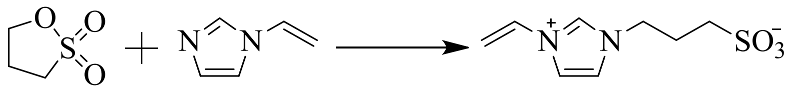
1. Synthesis of ionic liquid monomer 1-vinyl-3-(3-sulfopropyl)imidazolium (VSpIm)



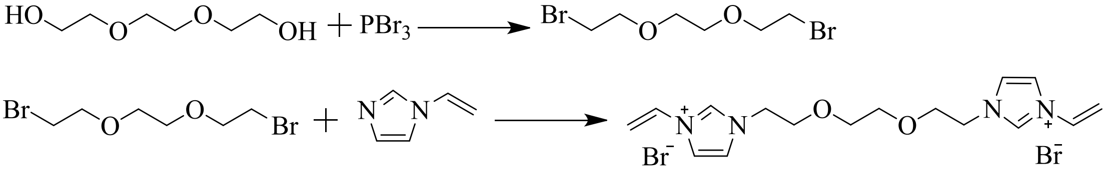
Scheme S1 Synthetic route of VSpIm.[1]

1,3-Propane sultone (12.21 g, 0.1 mol) was dissolved in 20 mL THF in a 100 mL round-bottom flask. Then, a solution of 1-vinylimidazole (9.41 g, 0.1 mol) in 5 mL THF was slowly added to the flask. The mixture was stirred at room temperature for 24 h. The obtained white solid was washed with diethyl ether and dried under vacuum at 60 ºC for 12 h. The desired product, VSpIm, was obtained at the yield of approximately 80 %, and was structurally characterized by NMR spectroscopy.

^{1}H NMR (400 MHz, DMSO-d$_6$, TMS) δ (ppm): 9.48 (s, 1H), 8.19 (s, 1H), 7.94 (s, 1H), 7.29 (dd, J = 15.6, 8.8 Hz, 1H), 5.95 (dd, J = 15.6, 2.4 Hz, 1H), 5.40 (dd, J = 8.8, 2.4 Hz, 1H), 4.34 (t, J = 7.0 Hz, 2H), 2.45 (t, J = 7.0 Hz, 2H), 2.17–2.09 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$, TMS) δ (ppm): 135.68, 128.96, 123.33, 119.08, 108.46, 48.23, 47.38, 25.92.

2. Synthesis of cross-linkers

2.1. Synthesis of 1,8-triethylene glycoldiyl-3,3'-divinylimidazolium bromide ([EG$_3$(VIm)$_2$]Br$_2$)



Scheme S2 Synthetic route of [EG$_3$(VIm)$_2$]Br$_2$.[2]

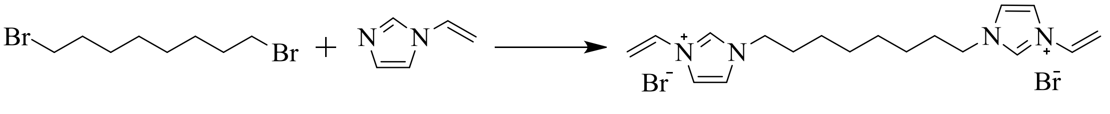
First, triethylene glycol (15.02 g, 0.1 mmol) and CH$_2$Cl$_2$ (50 mL) were added into a 250 mL two-necked round-bottom flask equipped with a magnetic stirrer and stirred under ice-water bath. Then PBr$_3$ (27.07 g, 0.1 mmol) was dropwise added to the above solution. After adding, the mixture was stirred at room temperature for 24 h. After the reaction finished, CH$_2$Cl$_2$ phase was washed with H$_2$O (30 mL × 5) to remove the excessive reactants and by-products. The CH_2Cl_2 phase was concentrated and dried under vacuum. The desired product, 1,2-bis(2-bromoethoxy)ethane (Br-$(EG)_3$-Br), was obtained at the yield of approximately 34 %, and was structurally characterized by NMR spectroscopy.

^1H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 3.83 (t, J = 6.0 Hz, 4H), 3.69 (s, 4H), 3.49 (t, J = 6.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 71.27, 70.53, 30.35.

Second, the first step synthesized Br-$(EG)_3$-Br (5.52 g, 20 mmol) and 1-vinylimidazole (3.95 g, 42 mmol) were dissolved in $CHCl_3$ (10 mL) in a 100 mL round-bottom flask. Then the mixture was stirred under reflux conditions for 24 h. After the reaction finished, the upper phase was removed, and the lower phase was washed with diethyl ether until 1-vinylimidazole was not detected in washing liquid by thin layer chromatography (TLC). The desired product, $[EG_3(VIm)_2]Br_2$, was obtained after the solvents were removed under reduced pressure distillation, and structurally characterized by NMR spectroscopy. White solid was obtained at the yield of approximately 93 %.

^1H NMR (400 MHz, DMSO-d_6, TMS) δ (ppm): 9.67 (s, 2H), 8.29 (s, 2H), 7.93 (s, 2H), 7.40 (dd, J = 15.6, 8.8 Hz, 2H), 6.02 (dd, J = 15.6, 1.6 Hz, 2H), 5.43 (dd, J = 8.8, 1.6 Hz, 2H), 4.41 (t, J = 4.8 Hz, 4H), 3.80 (t, J = 4.8 Hz, 4H), 3.56 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ (ppm): 135.59, 128.76, 123.59, 118.87, 108.78, 69.34, 67.81, 49.09.

2.2. Synthesis of 1,8-dioctyl-3,3'-divinylimidazolium bromide ($[O(VIm)_2]Br_2$)

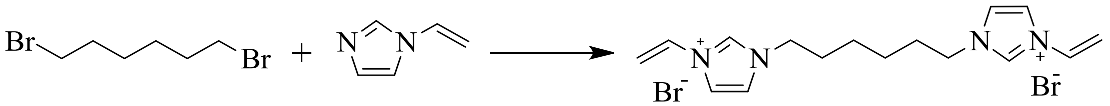


Scheme S3 Synthetic route of $[O(VIm)_2]Br_2$.[3]

Similarly, the cross-linker $[O(VIm)_2]Br_2$ was synthesized via the reaction of 1-vinylimidazole with 1,8-dibromooctane, and was structurally characterized by NMR spectroscopy.

^1H NMR (400 MHz, DMSO-d_6, TMS) δ (ppm): 9.66 (s, 2H), 8.24 (s, 2H), 7.98 (s, 2H), 7.32 (dd, J = 15.6, 8.8 Hz, 2H), 5.99 (dd, J = 15.6, 2.0 Hz, 2H), 5.42 (dd, J = 8.8, 2.4 Hz, 2H), 4.21 (t, J = 7.4 Hz, 4H), 1.86–1.76 (m, 4H), 1.31–1.22 (m, 8H); ^{13}C NMR (100 MHz, DMSO-d$_6$, TMS) δ (ppm): 135.28, 128.84, 123.24, 119.16, 108.61, 49.10, 29.01, 28.09, 25.34.

2.3. Synthesis of 1,6-dihexyl-3,3'-divinylimidazolium bromide ([H(VIm)$_2$]Br$_2$)

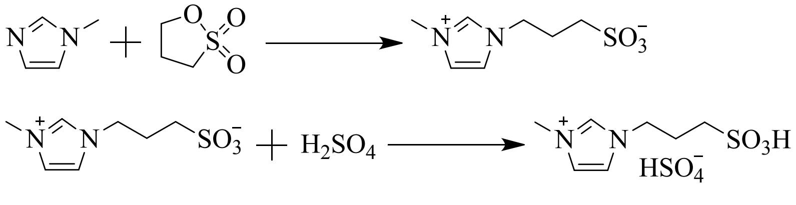


Scheme S4 Synthetic route of [H(VIm)$_2$]Br$_2$.[3]

Similarly, the cross-linker [H(VIm)$_2$]Br$_2$ was synthesized via the reaction of 1-vinylimidazole with 1,6-dibromohexane, and was structurally characterized by NMR spectroscopy.

^{1}H NMR (400 MHz, D$_2$O) δ (ppm): 9.06 (s, 2H), 7.78 (s, 2H), 7.59 (s, 2H), 7.14 (dd, J = 15.6, 8.4 Hz, 2H), 5.81 (d, J = 15.6 Hz, 2H), 5.43 (d, J = 8.4 Hz, 2H), 4.25 (t, J = 6.4 Hz, 4H), 1.98–1.83 (m, 4H), 1.44–1.32 (m, 4H); ^{13}C NMR (100 MHz, D$_2$O) δ (ppm): 134.31, 128.21, 122.80, 119.46, 109.28, 49.76, 28.87, 24.83.

3. Synthesis of ionic liquid 1-(3-sulfopropyl)-3-methylimidazolium hydrogen sulfate ([SpMIm]HSO$_4$)



Scheme S5 Synthetic route of [SpMIm]HSO$_4$.[4]

Similarly, the zwitterionic 1-(3-sulfopropyl)-3-methylimidazolium (SpMIm) was synthesized via the reaction of 1-methylimidazole and 1,3-propane sultone. Then, SpMIm (2.04 g, 10 mmol) was dissolved in 1 mL deionized water in a 50 mL round bottom flask and equimolar amount of sulfuric acid was slowly dropped into the flask at 0 ºC. After dropping was finished, the mixture was heated up to 60 ºC gradually and then stirred for 12 h. After the reaction, the resulting liquid was washed with diethyl ether and dried under vacuum at 60 ºC for 12 h. The desired product [SpMIm]HSO_4 was obtained in a yield of about 100 % (3.02 g) and structurally characterized by NMR spectroscopy.

^{1}H NMR (400 MHz, D_2O) δ (ppm): 8.60 (s, 1H), 7.39 (s, 1H), 7.31 (s, 1H), 4.21 (t, J = 7.2 Hz, 2H), 3.76 (s, 3H), 2.78 (t, J = 7.2 Hz, 2H), 2.22–2.11 (m, 2H). ^{13}C NMR (100 MHz, D_2O) δ (ppm): 136.17, 123.68, 122.13, 47.68, 47.13, 35.68, 25.09.

4. Synthesis of the PILs

Table S1 The yields of each step and the overall yields of the PILs.

PIL	Yield of Step 1 (%)	Yield of Step 2 (%)	Total yield (%)
P-[VSpIm-HSS]$_1$-CL1-2.5%	93	89	83
P-[VSpIm-HSS]$_1$-CL1-5%	95	90	86
P-[VSpIm-HSS]$_1$-CL1-10%	94	90	85
P-[VSpIm-HSS]$_1$-CL1-20%	95	88	84
P-[VSpIm-HSS]$_3$-CL1-2.5%	97	91	88
P-[VSpIm-HSS]$_2$-CL1-2.5%	95	93	88
P-[VSpIm-HSS]$_{0.5}$-CL1-2.5%	92	91	84
P-[VSpIm-HSS]$_{0.33}$-CL1-2.5%	93	89	83
P-[VSpIm]-CL1-2.5%	93	87	81
P-[HSS]-CL1-2.5%	91	86	78
P-[VSpIm-HSS]$_1$-CL2-2.5%	95	91	86
P-[VSpIm-HSS]$_1$-CL3-2.5%	95	90	86
P-[VSpIm-HSS]$_1$-CL4-2.5%	97	86	83

5. Characterization of the PILs

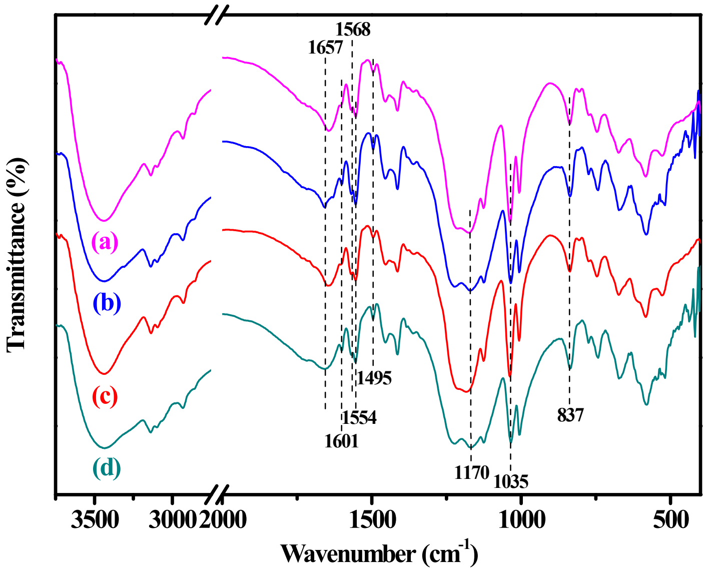


Fig. S1 FT-IR spectra of (a) P-[VSpIm-HSS]$_1$-CL1-2.5%, (b) P-[VSpIm-HSS]$_1$-CL2-2.5%, (c) P-[VSpIm-HSS]$_1$-CL3-2.5%, and (d) P-[VSpIm-HSS]$_1$-CL4-2.5%. (Wavenumber from 2750 to 2000 cm^{-1} was broken.)

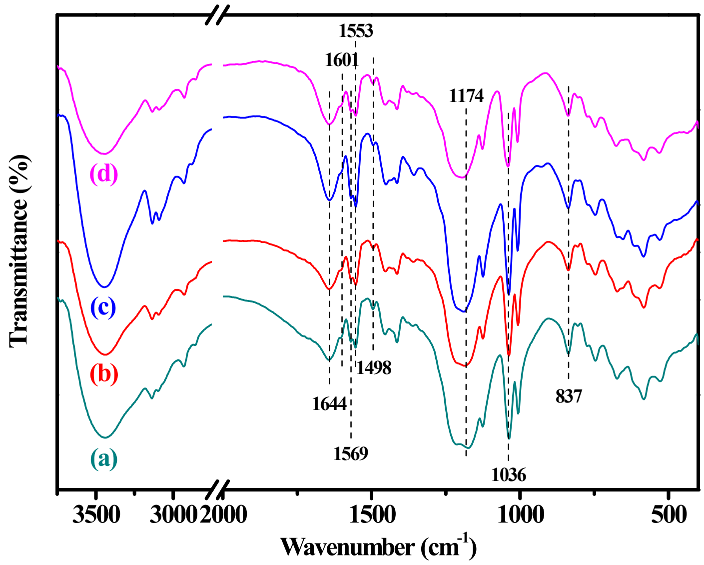


Fig. S2 FT-IR spectra of (a) P-[VSpIm-HSS]$_1$-CL1-2.5%, (b) P-[VSpIm-HSS]$_1$-CL1-5%, (c) P-[VSpIm-HSS]$_1$-CL1-10%, and (d) P-[VSpIm-HSS]$_1$-CL1-20%. (Wavenumber from 2750 to 2000 cm^{-1} was broken.)

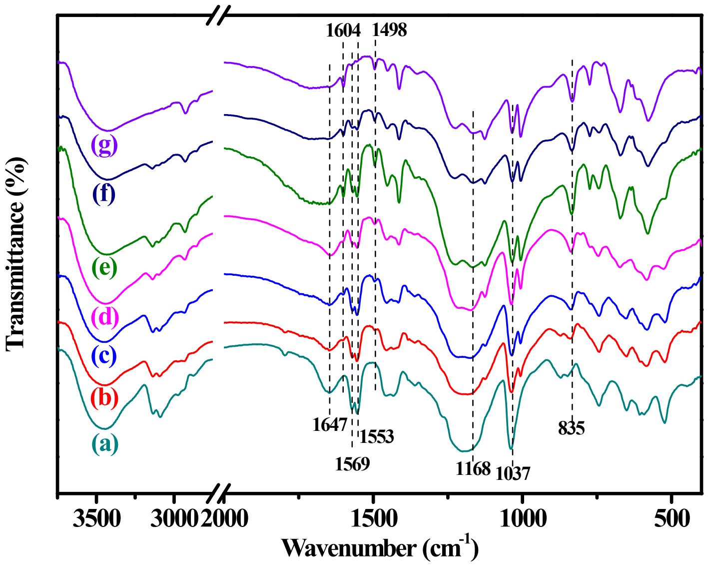


Fig. S3 FT-IR spectra of (a) P-[VSpIm]-CL1-2.5%, (b) P-[VSpIm-HSS]$_3$-CL1-2.5%, (c) P-[VSpIm-HSS]$_2$-CL1-2.5%, (d) P-[VSpIm-HSS]$_1$-CL1-2.5%, (e) P-[VSpIm-HSS]$_{0.5}$-CL1-2.5%, (f) P-[VSpIm-HSS]$_{0.33}$-CL1-2.5%, and (g) P-[HSS]-CL1-2.5%. (Wavenumber from 2750 to 2000 cm^{-1} was broken.)

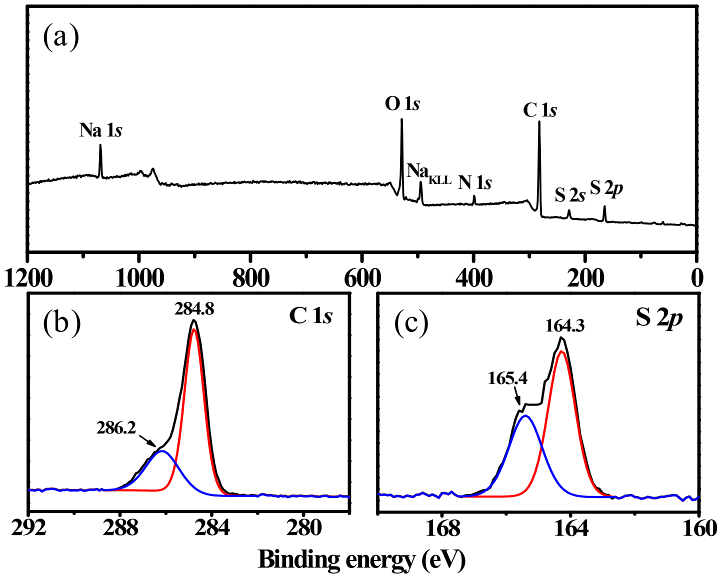


Fig. S4 XPS measurements of (a) survey, (b) C 1*s*, and (c) S 2*p* spectra over the P-[VSpIm-NaSS]$_{0.33}$-CL1-2.5%.

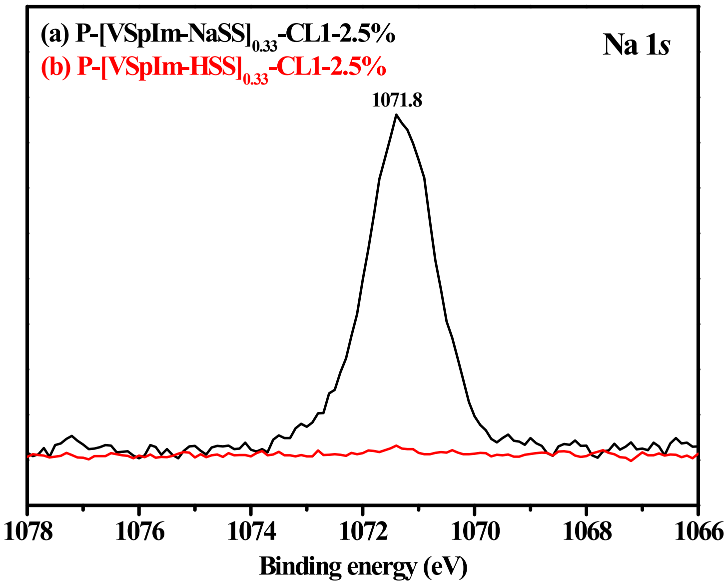


Fig. S5 XPS measurements of Na 1*s* spectra over (a) P-[VSpIm-NaSS]$_{0.33}$-CL1-2.5% and (b) P-[VSpIm-HSS]$_{0.33}$-CL1-2.5%.

6. Swelling and enrichment properties of the PILs

Table S2 The parameters of solvents.[5–9]

Solvent	Hansen solubility parameter				Dielectric constant	Dipole moment	Relative polarity
	δ_T (MPa$^{1/2}$)	δ_D (MPa$^{1/2}$)	δ_P (MPa$^{1/2}$)	δ_H (MPa$^{1/2}$)	ε	μ (D)	E_T^N
Water	47.8	15.5	16.0	42.3	78.3	1.94	1.000
Formamide	36.7	17.2	26.2	19.0	111.0	3.37	0.775
Ethylene glycol	33.0	17.0	11.0	26.0	38.7	2.20	0.790
2-Aminoethanol	31.3	17.0	15.5	21.2	37.7	2.27	0.651
Methanol	29.6	15.1	12.3	22.3	32.7	1.66	0.762
Dimethyl sulfoxide	26.7	18.4	16.4	10.2	46.5	4.00	0.444
Ethanol	26.5	15.8	8.8	19.4	24.6	1.68	0.654
Dimethyl formamide	24.9	17.4	13.7	11.3	36.7	3.86	0.386
Acetonitrile	24.4	15.3	18.0	6.1	35.9	3.44	0.460
Acetic acid	21.4	14.5	8.0	13.5	6.2	1.68	0.648
Dichlormethane	20.2	18.2	6.3	6.1	8.9	1.14	0.309
Acetone	19.9	15.5	10.4	7.0	20.6	2.69	0.355
Tetrahydrofuran	19.5	16.8	5.7	8.0	7.6	1.75	0.207
Chloroform	18.9	17.8	3.1	5.7	4.8	1.15	0.259
Toluene	18.2	18.0	1.4	2.0	2.4	0.37	0.099
Ethyl acetate	18.2	15.8	5.3	7.2	6.0	1.88	0.228
Tetrachloromethane	17.8	17.8	0	0.6	2.2	0	0.052
n-Hexane	14.9	14.9	0	0	1.9	0.08	0.009

Data from references 5–9.

Table S3 Molar swelling ratios (Q_M) of PILs with different cross-linkers in solvents.[a]

Solvent	P-[VSpIm-HSS]$_1$-CL1-2.5%	P-[VSpIm-HSS]$_1$-CL2-2.5%	P-[VSpIm-HSS]$_1$-CL3-2.5%	P-[VSpIm-HSS]$_1$-CL4-2.5%
Water	1209.2	936.2	808.5	847.9
Formamide	611.0	439.8	407.4	431.4
Ethylene glycol	299.3	246.2	185.4	223.0
2-Aminoethanol	46.2	45.8	36.2	102.8
Methanol	22.2	15.9	13.1	25.6
Dimethyl sulfoxide	14.6	12.7	12.2	61.6
Ethanol	8.7	6.1	5.6	3.9
Dimethyl formamide	8.6	4.8	4.8	9.2
Acetonitrile	4.9	0	2.2	0.7
Acetic acid	6.2	4.0	2.8	8.6
Dichlormethane	1.5	0.9	0.4	0
Acetone	1.5	0.5	1.4	0.5
Tetrahydrofuran	1.2	0.7	0	0.3
Chloroform	1.1	0.3	0	0.5
Toluene	1.3	0	2.1	0.9
Ethyl acetate	1.2	0.7	0	0.8
Tetrachloromethane	1.1	0.4	0.4	0.6
n-Hexane	0	1.2	0	0

[a] 50 mg dried PIL sample swelled in 10 mL solvent for 24 h. Unit for Q_M is mmol/g.

Table S4 Molar swelling ratios (Q_M) of PILs with different cross-linker contents in solvents.[a]

Solvent	P-[VSpIm-HSS]$_1$-CL1-2.5%	P-[VSpIm-HSS]$_1$-CL1-5%	P-[VSpIm-HSS]$_1$-CL1-10%	P-[VSpIm-HSS]$_1$-CL1-20%
Water	1209.2	741.4	343.0	89.9
Formamide	611.0	382.8	165.4	50.2
Ethylene glycol	299.3	187.2	40.6	22.1
2-Aminoethanol	46.2	31.1	15.6	8.7
Methanol	22.2	15.6	10.6	3.1
Dimethyl sulfoxide	14.6	10.5	8.3	2.8
Ethanol	8.7	6.3	2.0	0.9
Dimethyl formamide	8.6	5.1	4.0	1.9
Acetonitrile	4.9	5.1	0.7	0
Acetic acid	6.2	7.8	5.0	6.5
Dichlormethane	1.5	0	0	0
Acetone	1.5	1.4	0	0
Tetrahydrofuran	1.2	0	0	0
Chloroform	1.1	0	0.9	0
Toluene	1.3	1.7	0.5	0.9
Ethyl acetate	1.2	1.9	0	0
Tetrachloromethane	1.1	1.4	0.9	1.0
n-Hexane	0	1.0	0	0

[a] 50 mg dried PIL sample swelled in 10 mL solvent for 24 h. Unit for Q_M is mmol/g.

Table S5 Molar swelling ratios (Q_M) of PILs with different VSpIm-to-NaSS molar ratios in solvents.[a]

Solvent	P-[VSpIm]-CL1-2.5%	P-[VSpIm-HSS]$_3$-CL1-2.5%	P-[VSpIm-HSS]$_2$-CL1-2.5%	P-[VSpIm-HSS]$_1$-CL1-2.5%	P-[VSpIm-HSS]$_{0.5}$-CL1-2.5%	P-[VSpIm-HSS]$_{0.33}$-CL1-2.5%	P-[HSS]-CL1-2.5%
Water	261.9	851.3	915.6	1209.2	1442.8	1681.2	3245.3
Formamide	165.6	400.1	504.0	611.0	674.7	756.6	1476.9
Ethylene glycol	4.7	17.6	149.3	299.3	393.4	428.0	826.8
2-Aminoethanol	3.3	4.7	22.3	46.2	152.6	228.8	459.6
Methanol	0	2.2	3.1	22.2	98.6	173.5	759.0
Dimethyl sulfoxide	4.1	3.6	4.7	14.6	195.8	244.6	591.2
Ethanol	0	0	1.5	8.7	20.0	37.6	393.7
Dimethyl formamide	3.8	5.1	7.9	8.6	14.9	33.0	389.4
Acetonitrile	0	0	0	4.9	3.2	2.8	6.3
Acetic acid	5.3	5.0	6.3	6.2	5.3	5.0	12.0
Dichlormethane	0	0.7	0.9	1.5	0.7	1.2	2.5
Acetone	0	0.3	1.9	1.5	2.9	1.4	4.1
Tetrahydrofuran	0	0	1.1	1.2	1.9	0.6	4.0
Chloroform	0	0.4	0.3	1.1	0.3	0.5	2.0
Toluene	0	1.1	0.6	1.3	2.2	1.3	2.5
Ethyl acetate	0	0	0	1.2	0.3	1.0	3.6
Tetrachloromethane	0	0	0.5	1.1	0.7	0.2	1.4
n-Hexane	0	0.9	1.3	0	1.6	1.0	0.9

[a] 50 mg dried PIL sample swelled in 10 mL solvent for 24 h. Unit for Q_M is mmol/g.

Table S6 Molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and P-[VSpIm-NaSS]$_{0.33}$-CL1-2.5% in solvents.[a]

Solvent	P-[VSpIm-HSS]$_{0.33}$-CL1-2.5%	P-[VSpIm-NaSS]$_{0.33}$-CL1-2.5%
Water	1681.2	1515.0
Formamide	756.6	708.5
Ethylene glycol	428.0	384.7
2-Aminoethanol	228.8	29.3
Methanol	173.5	7.5
Dimethyl sulfoxide	244.6	7.4
Ethanol	37.6	4.1
Dimethyl formamide	33.0	4.4
Acetonitrile	2.8	2.2
Acetic acid	5.0	4.2
Dichlormethane	1.2	0
Acetone	1.4	0.5
Tetrahydrofuran	0.6	0.6
Chloroform	0.5	0.9
Toluene	1.3	1.4
Ethyl acetate	1.0	1.1
Tetrachloromethane	0.2	0.6
n-Hexane	1.0	1.2

[a] 50 mg dried PIL sample swelled in 10 mL solvent for 24 h. Unit for Q_M is mmol/g.

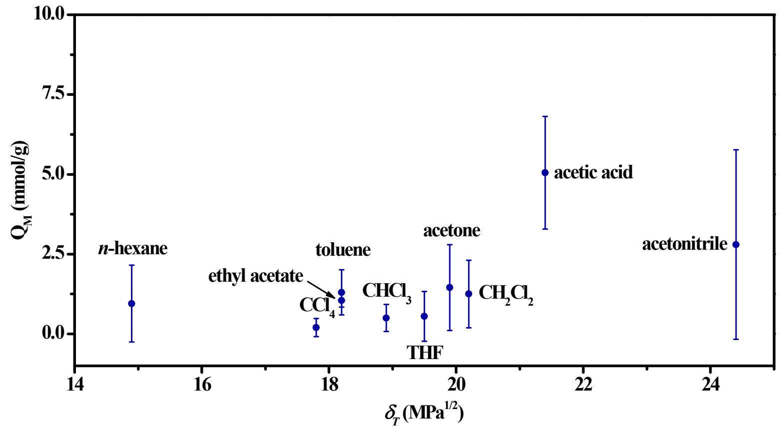


Fig. S6 Relationships between the molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and the Hansen solubility parameter (δ_T) of solvents.

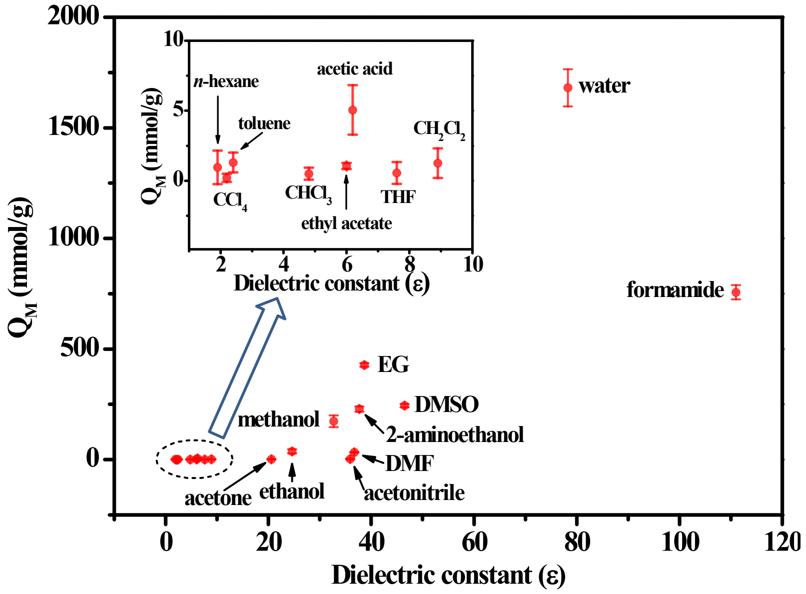


Fig. S7 Relationships between the molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and the dielectric constant (ε) of solvents.

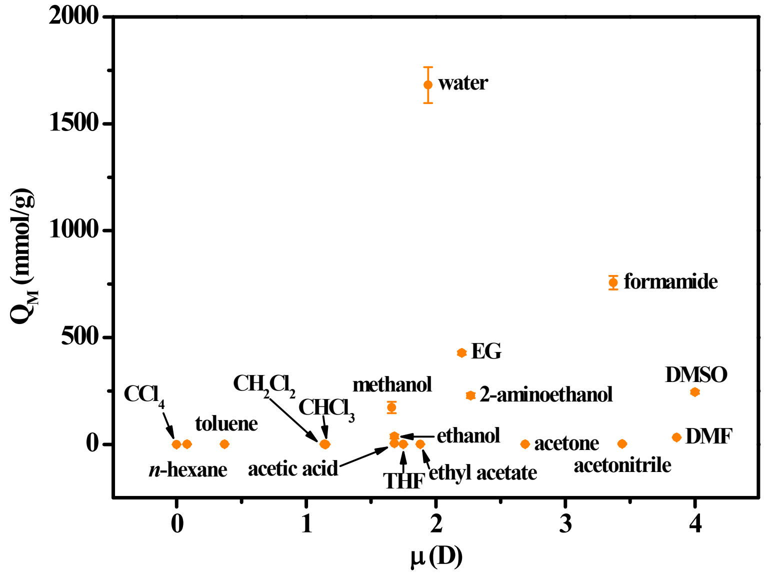


Fig. S8 Relationships between the molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and the dipole moment (μ) of solvents.

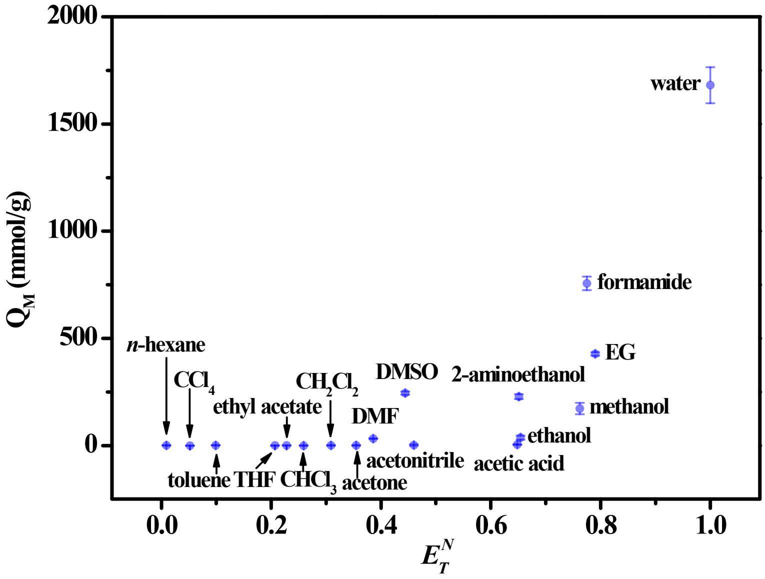


Fig. S9 Relationships between the molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and the relative polarity (E_T^N) of solvents.

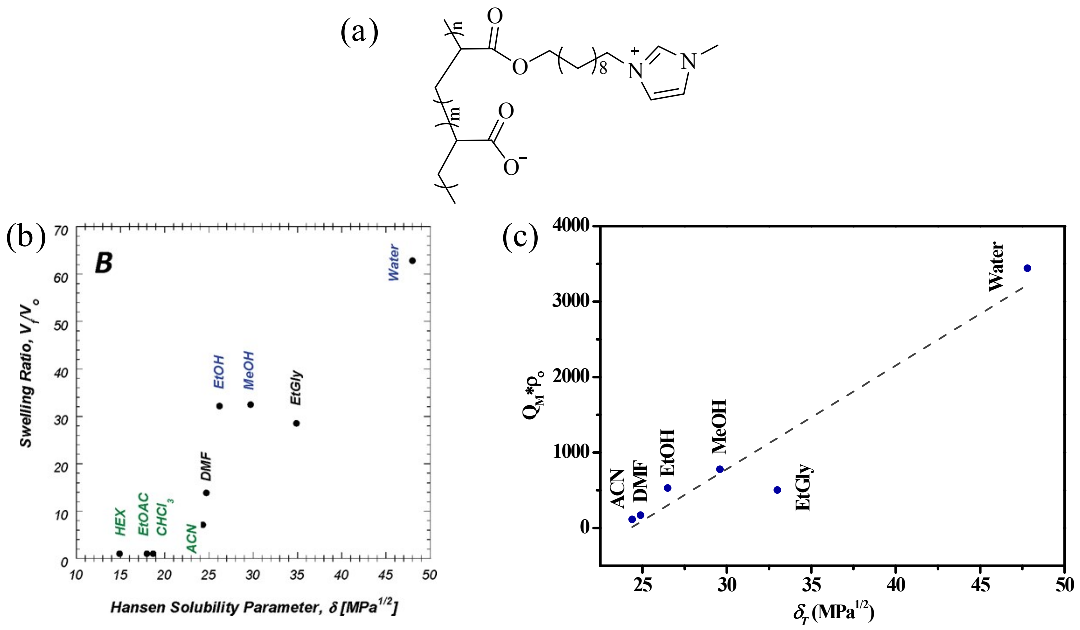


Fig. S10 (a) The chemical structure of poly-[AcrC$_{10}$mim^{+}]-inter-poly[Acr^{-}]. (b) The relationship between the swelling ratio (V$_f$/V$_o$) of poly-[AcrC$_{10}$mim^{+}]-inter-poly[Acr^{-}] and the Hansen solubility parameter (δ_T) of solvent (Reproduced from *Macromolecules*, 2011, **44**, 1421–1428.[10]). (c) The relationship between the $\mathbf{Q_M} \times \boldsymbol{\rho}_\mathbf{o}$ of poly-[AcrC$_{10}$mim^{+}]-inter-poly[Acr^{-}] and the Hansen solubility parameter (δ_T) of solvent.

$\mathbf{Q_M} \times \boldsymbol{\rho}_\mathbf{o}$ was calculated according to the following equation:

$$Q_M \times \rho_o = \left(\frac{V}{V_o} - 1\right) \times \frac{\rho_S}{M_S}$$

where $\mathbf{Q_M}$ represents the molar swelling ratio, V/V$_o$ represents the equilibrium volume changes, $\boldsymbol{\rho}_\mathbf{o}$ represents the density of the polymer, ρ_S represents the density of the absorbed solvent, M$_S$ represents the molar mass of the absorbed solvent.

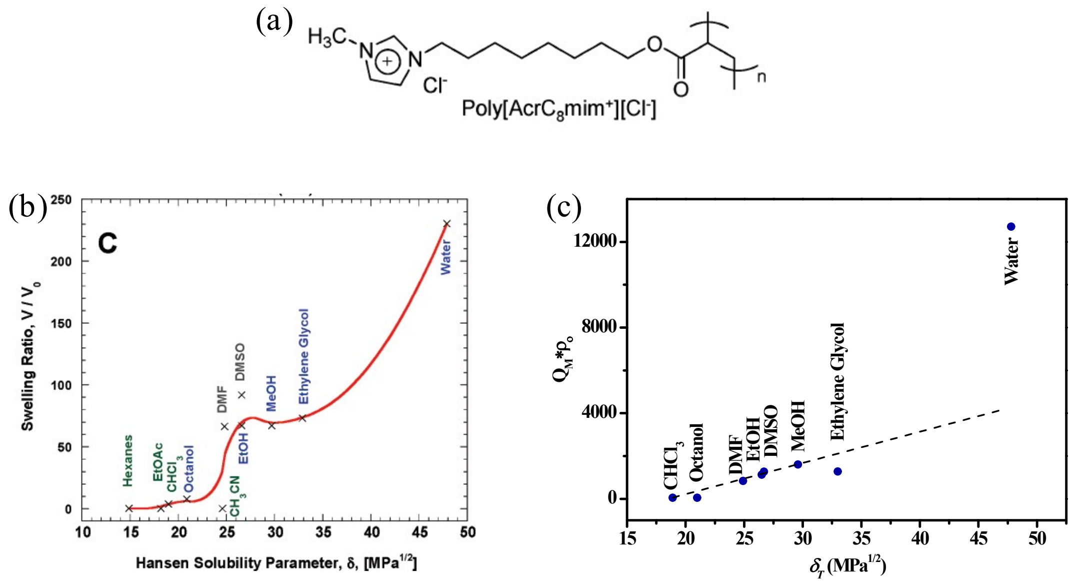


Fig. S11 (a) The chemical structure of poly[AcrC$_8$mim$^+$][Cl$^-$]. (b) The relationship between the swelling ratio (V/V$_o$) of poly[AcrC$_8$mim$^+$][Cl$^-$] and the Hansen solubility parameter (δ_T) of solvent (Reproduced from *Chem. Mater.*, 2007, **19**, 4423–4431.[11]). (c) The relationship between the $\mathbf{Q_M} \times \boldsymbol{\rho}_\mathbf{o}$ of poly[AcrC$_8$mim$^+$][Cl$^-$] and the Hansen solubility parameter (δ_T) of solvent ($\mathbf{Q_M} \times \boldsymbol{\rho}_\mathbf{o}$ was calculated according to the above mentioned equation.).

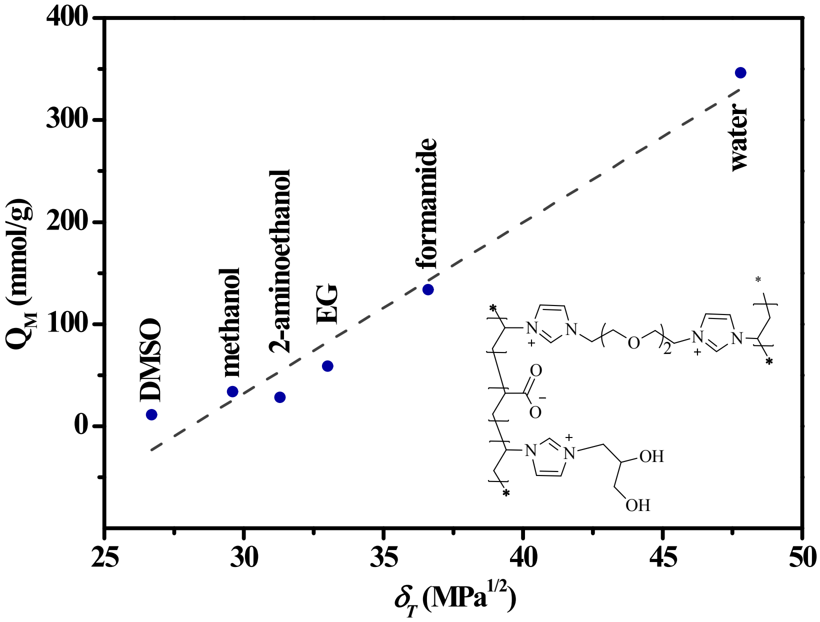


Fig. S12 The relationship between the molar swelling ratio (Q_M) of poly[DHP-VIm-AA-DVIm][12] and the Hansen solubility parameter (δ_T) of solvent.

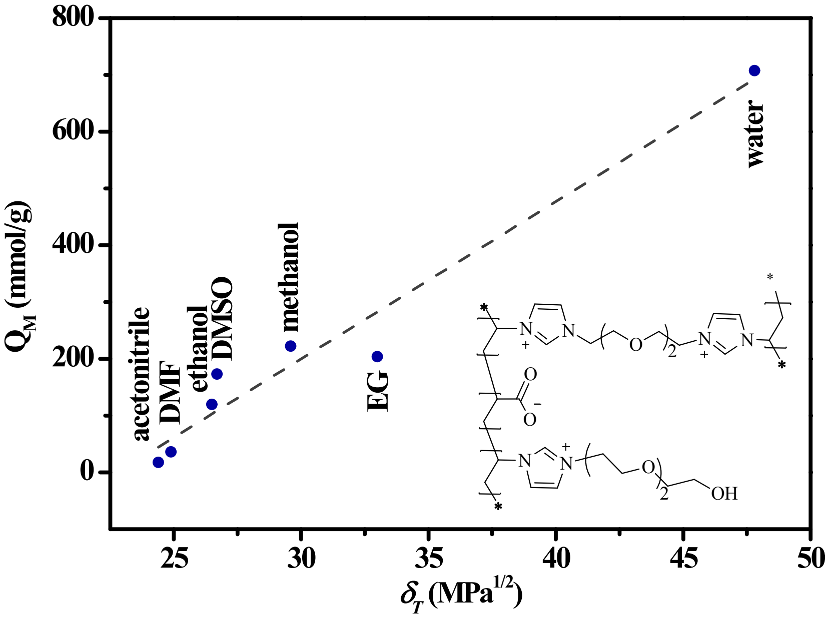


Fig. S13 The relationship between the molar swelling ratio (Q_M) of poly[(EG)$_3$-VIm-AA-DVIm][12] and the Hansen solubility parameter (δ_T) of solvent.

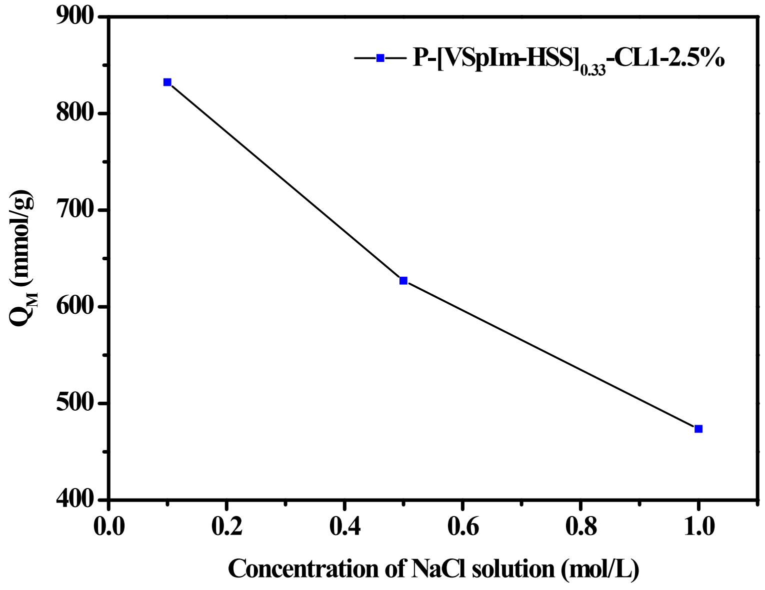


Fig. S14 The relationship between the molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and the concentration of NaCl solution.

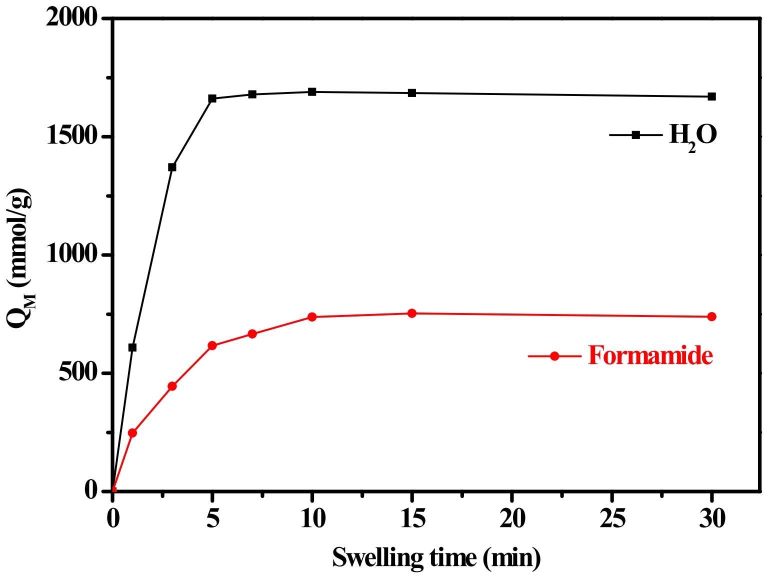


Fig. S15 Molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% in water and formamide at different swelling times.

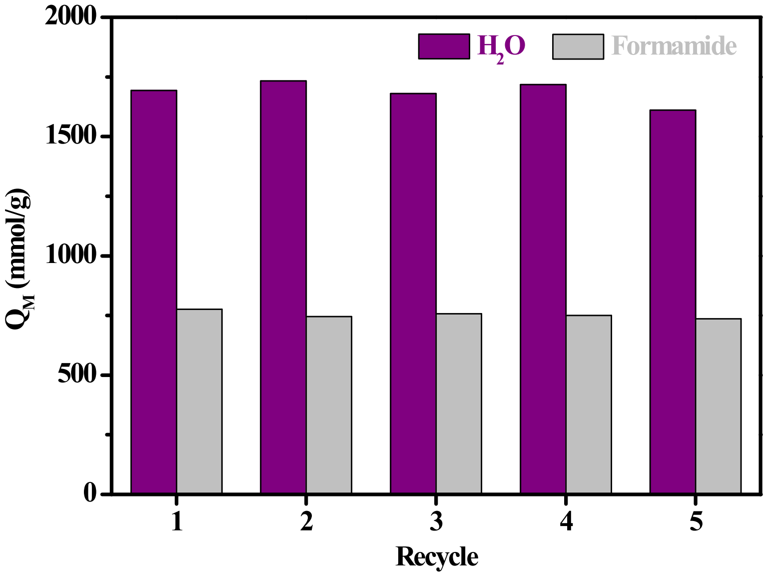


Fig. S16 Molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% in water and formamide during recycling.

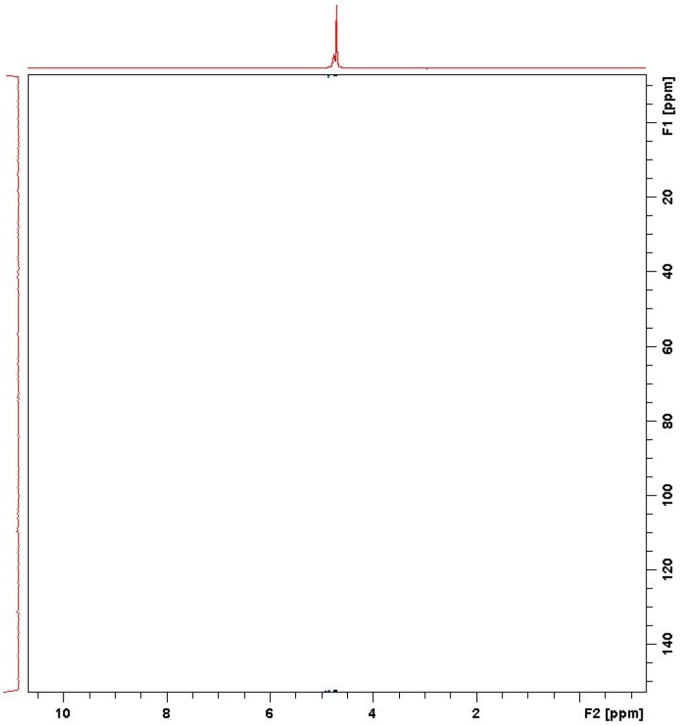


Fig. S17 2D ^1H–^{13}C HSQC NMR spectrum of 10 mg P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and 200 mg water in CD_3CN.

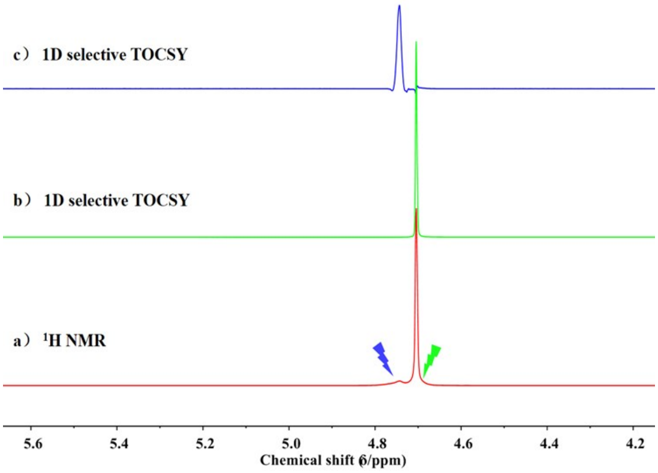


Fig. S18 SelTOCSY spectra of 10 mg P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and 200 mg water in CD_3CN. The signals pointed with the lightning were excited in the SelTOCSY experiments.

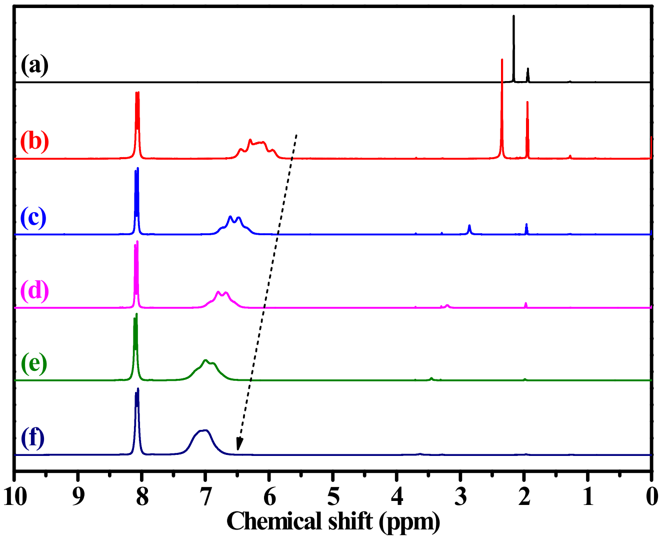


Fig. S19 ^{1}H NMR spectra of the –NH_2 resonance of formamide in CD_3CN (360 mg). (a) 10 mg P-[VSpIm-HSS]$_{0.33}$-CL1-2.5%, (b) formamide : P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% = 1 : 1, (c) 5 : 1, (d) 10 : 1, (e) 20 : 1, and (f) 30 : 1 (mass ratio).

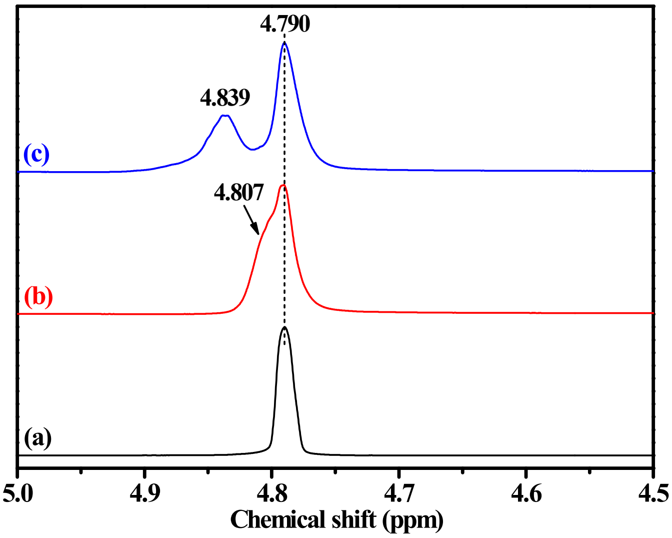


Fig. S20 ^{1}H NMR spectra of (a) 630 mg D_2O,
(b) 11 mg P-[VSpIm-NaSS]$_{0.33}$-CL1-2.5% with 640 mg D_2O, and (c) 10 mg P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% with 640 mg D_2O.

Table S7 The molar swelling ratios of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% in deuterated solvents and non-deuterated solvents.[a]

Entry	Solvent	Q_M (mmol/g)
1	deuterated water (D_2O)	1735.4
	water	1681.2
2	deuterated methanol (CD_3OD)	210.1
	methanol	173.5
3	deuterated dimethyl sulfoxide (DMSO-d_6)	246.4
	dimethyl sulfoxide	244.6
4	deuterated acetonitrile (CD_3CN)	3.4
	acetonitrile	2.8

[a] 50 mg dried PIL sample swelled in 10 mL solvent for 24 h.

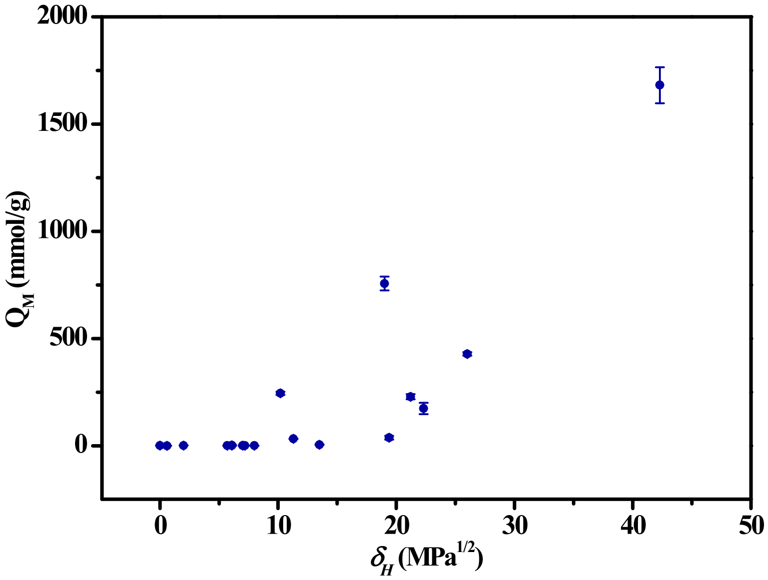


Fig. S21 Relationships between molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and Hansen hydrogen-bonding solubility parameter (δ_H) of solvents.

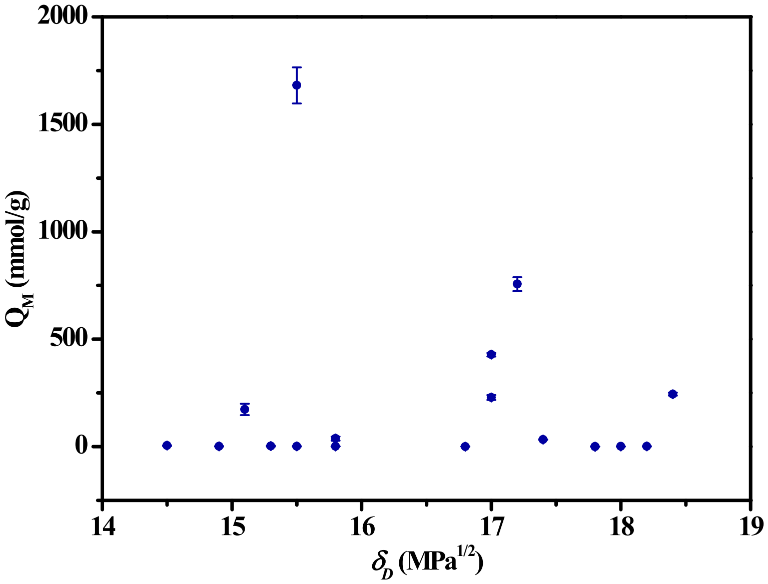


Fig. S22 Relationships between molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and Hansen dispersion solubility parameter (δ_D) of solvents.

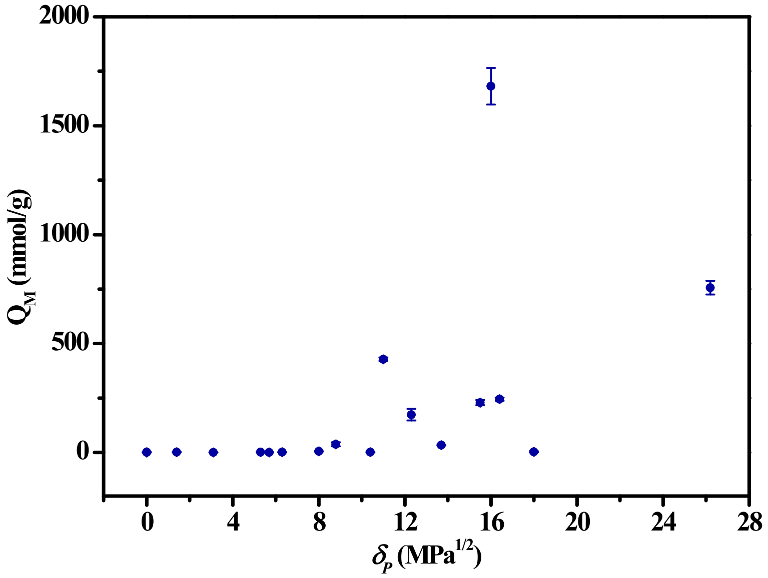


Fig. S23 Relationships between molar swelling ratios (Q_M) of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% and Hansen polar solubility parameter (δ_P) of solvents.

Table S8 The enrichment factors (EF) of P-[VSpIm-HSS]$_3$-CL1-2.5% to water in water/solvent monophasic mixed solvents.[a]

Mixed solvent	EF (water)
Water/methanol	2.42
Water/ethanol	6.56
Water/acetonitrile	15.13
Water/acetone	29.03
Water/THF	39.82

[a] 50 mg P-[VSpIm-HSS]$_3$-CL1-2.5%, 200 mmol water, 200 mmol solvent, stirring for 6 h and standing for 3 h.

Table S9 The enrichment factors (EF) of P-[VSpIm-HSS]$_3$-CL1-2.5% to formamide in formamide/solvent monophasic mixed solvents.[a]

Mixed solvent	EF (formamide)
Formamide/methanol	1.36
Formamide/ethanol	1.93
Formamide/acetonitrile	8.53
Formamide/acetone	14.24
Formamide/THF	17.69

[a] 50 mg P-[VSpIm-HSS]$_3$-CL1-2.5%, 200 mmol formamide, 200 mmol solvent, stirring for 6 h and standing for 3 h.

Table S10 The enrichment factors (EF) of the PILs to water in water/methanol mixed solvent.[a]

Mixed solvent	EF (water)
P-[VSpIm-HSS]$_{0.33}$-CL1-2.5%	1.60
P-[VSpIm-HSS]$_{0.5}$-CL1-2.5%	1.64
P-[VSpIm-HSS]$_1$-CL1-2.5%	1.86
P-[VSpIm-HSS]$_2$-CL1-2.5%	2.13
P-[VSpIm-HSS]$_3$-CL1-2.5%	2.42

[a] 50 mg PIL sample, 200 mmol water, 200 mmol methanol, stirring for 6 h and standing for 3 h.

Enrichment properties of the PILs in water/solvent biphasic mixed solvents

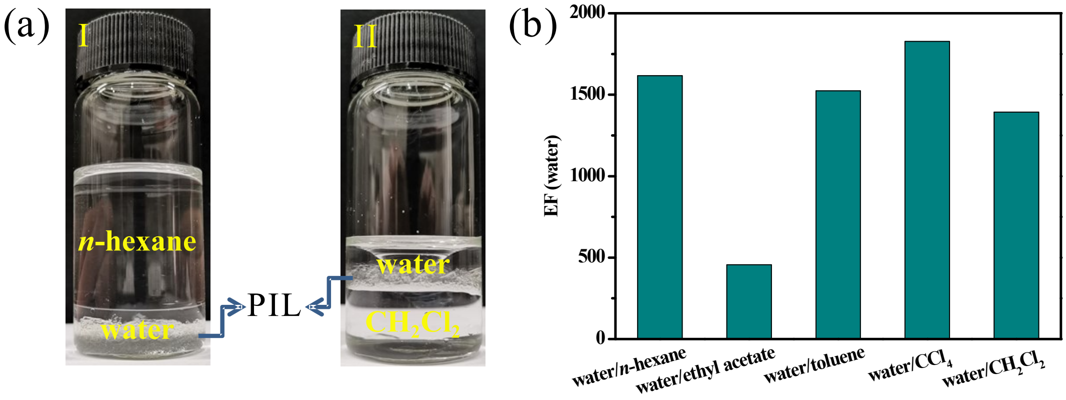


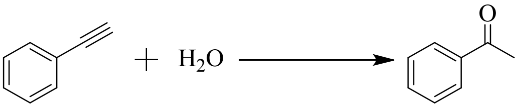
Fig. S24 (a) Digital photographs of P-[VSpIm-HSS]$_3$-CL1-2.5% in water/solvent biphasic mixed solvents. 50 mg P-[VSpIm-HSS]$_3$-CL1-2.5%, and I) 200 mmol water and 100 mmol *n*-hexane; II) 200 mmol water and 100 mmol CH_2Cl_2. (b) The enrichment factor (EF) of P-[VSpIm-HSS]$_3$-CL1-2.5% to water in water/solvent biphasic mixed solvents. Initial mixed solvents: 200 mmol water and 100 mmol solvent. Stirring for 6 h and standing for 3 h.

The enrichment properties of P-[VSpIm-HSS]$_3$-CL1-2.5% in a series of water/solvent biphasic mixed solvents were studied, including water/*n*-hexane, water/ethyl acetate, water/toluene, water/CCl_4 and water/CH_2Cl_2. The P-[VSpIm-HSS]$_3$-CL1-2.5% was always in the water phase after equilibrium swelling in these biphasic mixed solvents (Fig. S24a). Further, the enrichment factors (EF) of P-[VSpIm-HSS]$_3$-CL1-2.5% to water in these mixed solvents were also measured. As shown in Fig. S24b, the enrichment factor reached an astonishing 1617 (water/*n*-hexane), 456 (water/ethyl acetate), 1524 (water/toluene), 1827 (water/CCl_4) and 1393 (water/CH_2Cl_2), that was the content of water in the absorbed mixed solvent was over 99.89 mol% (EF > 456). The PILs had high swelling abilities in water, but almost no swelling abilities in these organic solvents. When the PILs swelled in these water/solvent biphasic mixed solvents, large amounts of water were absorbed into the PILs, and water layers were formed on their surfaces under the effect of water solvation, thereby preventing the contact of organic solvents with the organic PILs.[2]

Mainly for the above reasons, the PILs exhibited excellent enrichment properties for water when they swelled in water/solvent biphasic mixed solvents.

7. PIL catalyzed the hydration of alkyne

Table S11 Influence of solvent and the amount of solvent on the hydration of phenylacetylene.[a]



Entry	Solvent	Amount of solvent (mL)	Conversion[b] (%)	Yield[c] (%)
1	–	1	30.1	29.7
2	Methanol	1	27.5	27.3
3	DMSO	1	2.0	1.9
4	Ethanol	1	19.4	18.2
5	DMF	1	1.0	0.7
6	Acetonitrile	1	7.8	7.1
7	Trifluoroethanol	1	75.3	74.6
8	Trifluoroethanol	0.5	41.8	41.0
9	Trifluoroethanol	2	91.2	90.3
10	Trifluoroethanol	3	98.0	97.3
11	Trifluoroethanol	4	97.9	97.7

[a] Reaction conditions: phenylacetylene (0.511 g, 5 mmol), deionized water (0.360 g, 20 mmol), P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% (0.156 g, 0.5 mmol H^+), 100 °C, 12 h, carried out in a 15 mL thick-walled pressure bottle. [b] Conversion of phenylacetylene. [c] Yield of acetophenone.

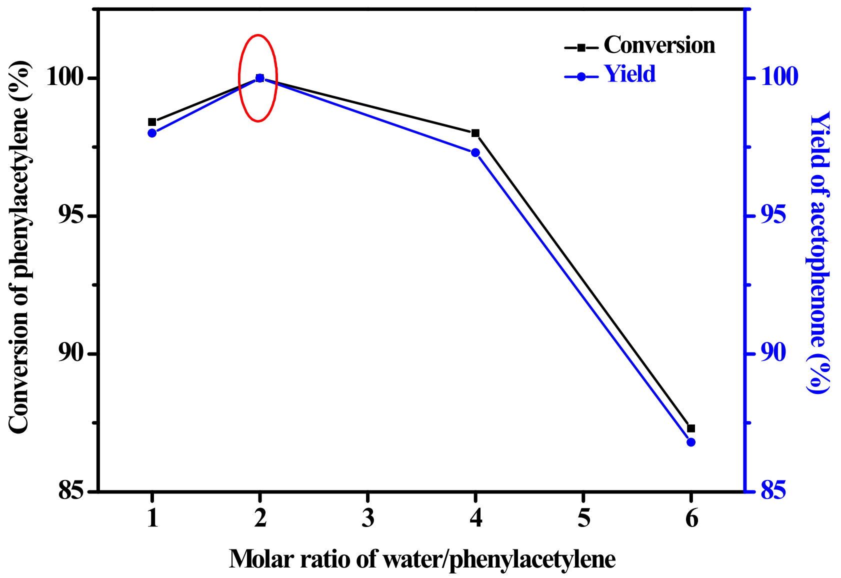


Fig. S25 Influence of water/phenylacetylene molar ratio on the hydration of phenylacetylene. (Reaction conditions: 5 mmol phenylacetylene, 10 mol% P-[VSpIm-HSS]$_{0.33}$-CL1-2.5%, 3 mL trifluoroethanol, 100 ºC, 12 h.)

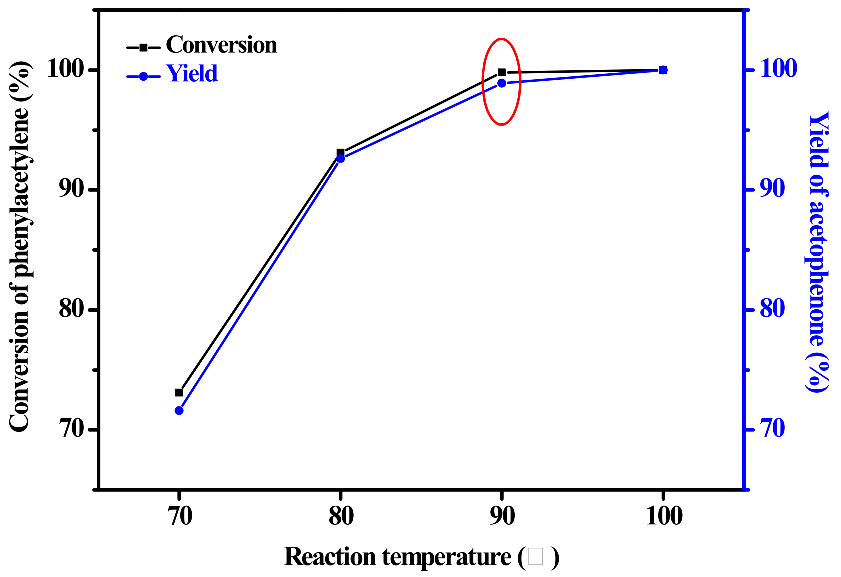


Fig. S26 Influence of reaction temperature on the hydration of phenylacetylene. (Reaction conditions: 5 mmol phenylacetylene, 10 mmol deionized water, 10 mol% P-[VSpIm-HSS]$_{0.33}$-CL1-2.5%, 3 mL trifluoroethanol, 12 h.)

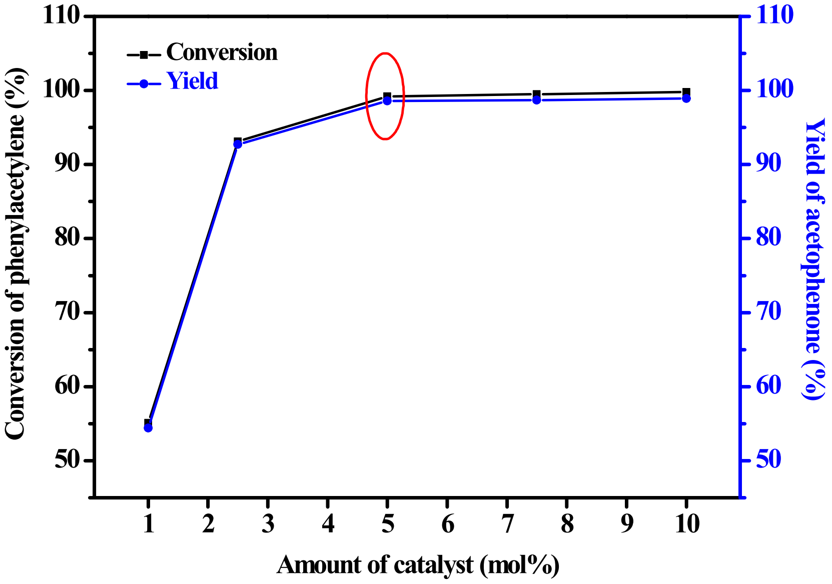


Fig. S27 Influence of catalyst amount on the hydration of phenylacetylene. (Reaction conditions: 5 mmol phenylacetylene, 10 mmol deionized water, 3 mL trifluoroethanol, 90 ºC, 12 h.)

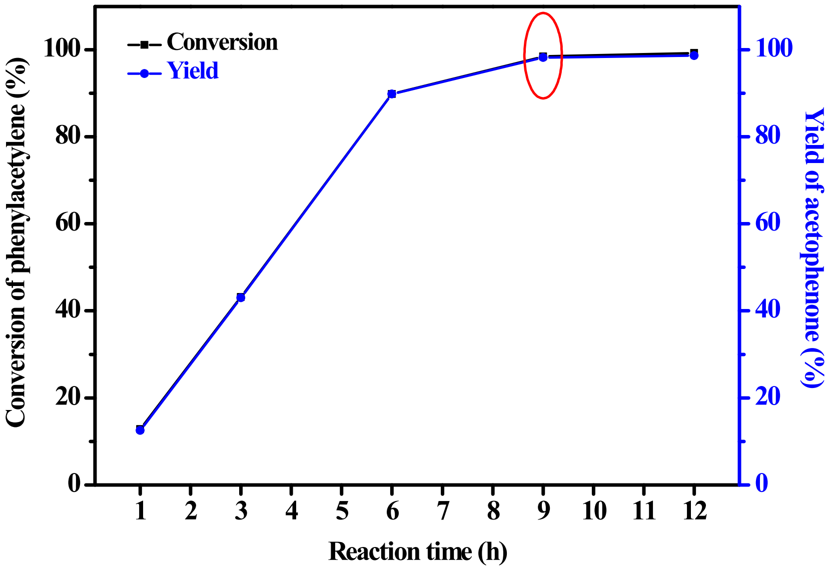


Fig. S28 Influence of reaction time on the hydration of phenylacetylene. (Reaction conditions: 5 mmol phenylacetylene, 10 mmol deionized water, 5 mol% P-[VSpIm-HSS]$_{0.33}$-CL1-2.5%, 3 mL trifluoroethanol, 90 ºC.)

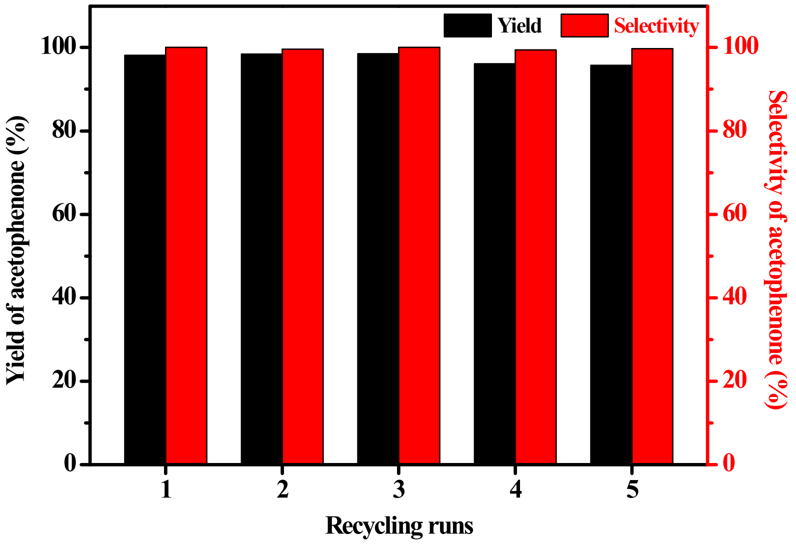


Fig. S29 Catalytic reusability of P-[VSpIm-HSS]$_{0.33}$-CL1-2.5% for the hydration of phenylacetylene to acetophenone. (Reaction conditions: 5 mmol phenylacetylene, 10 mmol deionized water, 5 mol% PIL catalyst, 3 mL trifluoroethanol, 90 ºC, 9 h.)

8. References

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