

## Supporting Information

# Poly(ionic liquid) Complex with Spontaneous Micro-/Mesoporosity: Template-Free Synthesis and Application as Catalyst Support

Qiang Zhao, Pengfei Zhang, Markus Antonietti, Jiayin Yuan\*

Max-Planck-Institute of Colloids and Interfaces, Department of Colloid Chemistry, D-14476

Potsdam, Germany

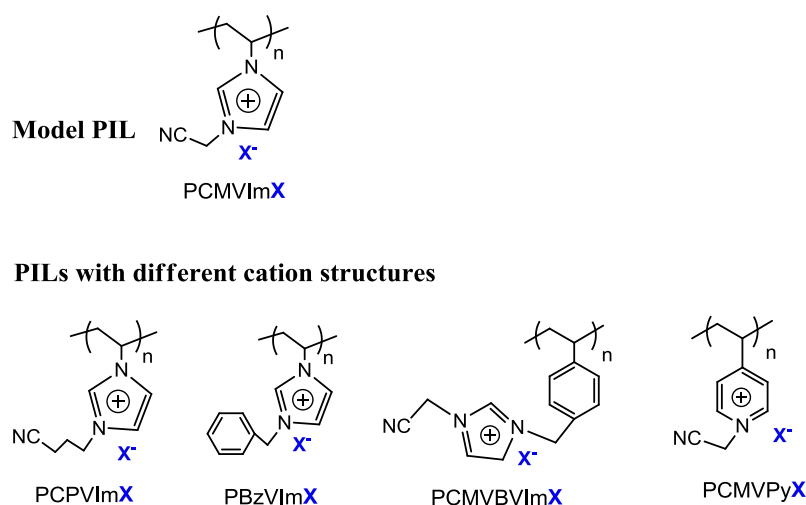
### 1. Materials and characterization methods

Lithium bis(trifluoromethanesulfonyl)imide ( $\text{LiTf}_2\text{N}$ , 99.95%), sodium tetraborate ( $\text{NaBF}_4$ , 98%), 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%), poly(4-vinylpyridine) (P4VP,  $M_w \sim 60,000$  g/mol), 4-bromobutyronitrile (99%), benzyl bromide (98%), imidazole (99%), 4-vinylbenzyl chloride (90%), bromoacetonitrile (97%) and potassium hexafluorophosphate ( $\text{KPF}_6$ , 97%) were obtained from Sigma-Aldrich and used without further purification. Poly(acrylic acid) (MW: 2000 g/mol, solid powder; MW: 100 000 g/mol, 35 wt% in water) were obtained from Sigma Aldrich. Poly(acrylic acid) (MW: 5000 g/mol, 50 wt% in water; MW: 240 000 g/mol, 25 wt% in water) were obtained from Acros. Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile (MeCN), ethylene glycol (EG), ethanol, acetone, tetrahydrofuran (THF), isopropanol, and butanol were of analytic grade.

Scanning electron microscopy (SEM) was performed on a GEMINI LEO 1550 microscope at 3 kV, and samples were coated with gold before examination. Nitrogen ( $\text{N}_2$ ) sorption experiments were performed with a Quantachrome Autosorb-1 or Quadrasorb at liquid nitrogen temperature, and data analysis was performed by Quantachrome software. The specific surface area and pore volume were calculated using the Brunauer–Emmett–Teller (BET) equation, and the Barrett-Joyner-Halenda (BJH) method, respectively. Pore size

distribution was calculated by density functional theory (DFT) method. Samples for BET were degassed at 80 °C for 20 hours before measurements. Elemental analysis was performed for carbon, hydrogen and nitrogen using a Vario EL Elemental. X-ray diffraction experiments were done with a Bruker D8 diffractometer using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) and a scintillation counter. All gas chromatography (GC) experiments were carried out and recorded using a GC-MS (Agilent Technologies, GC6890N, MS5970). Inductively coupled plasma (ICP) was conducted with an ICP OES Optima 2100 DV from Perkin-Elmer after acidic microwave digestion.  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$ -NMR) measurements were carried out at room temperature using a Bruker DPX-400 spectrometer operating at 400.1 MHz. DMSO- $d_6$  and D $_2$ O were used as solvents.

## 2. Synthesis of Poly(ionic liquid)s



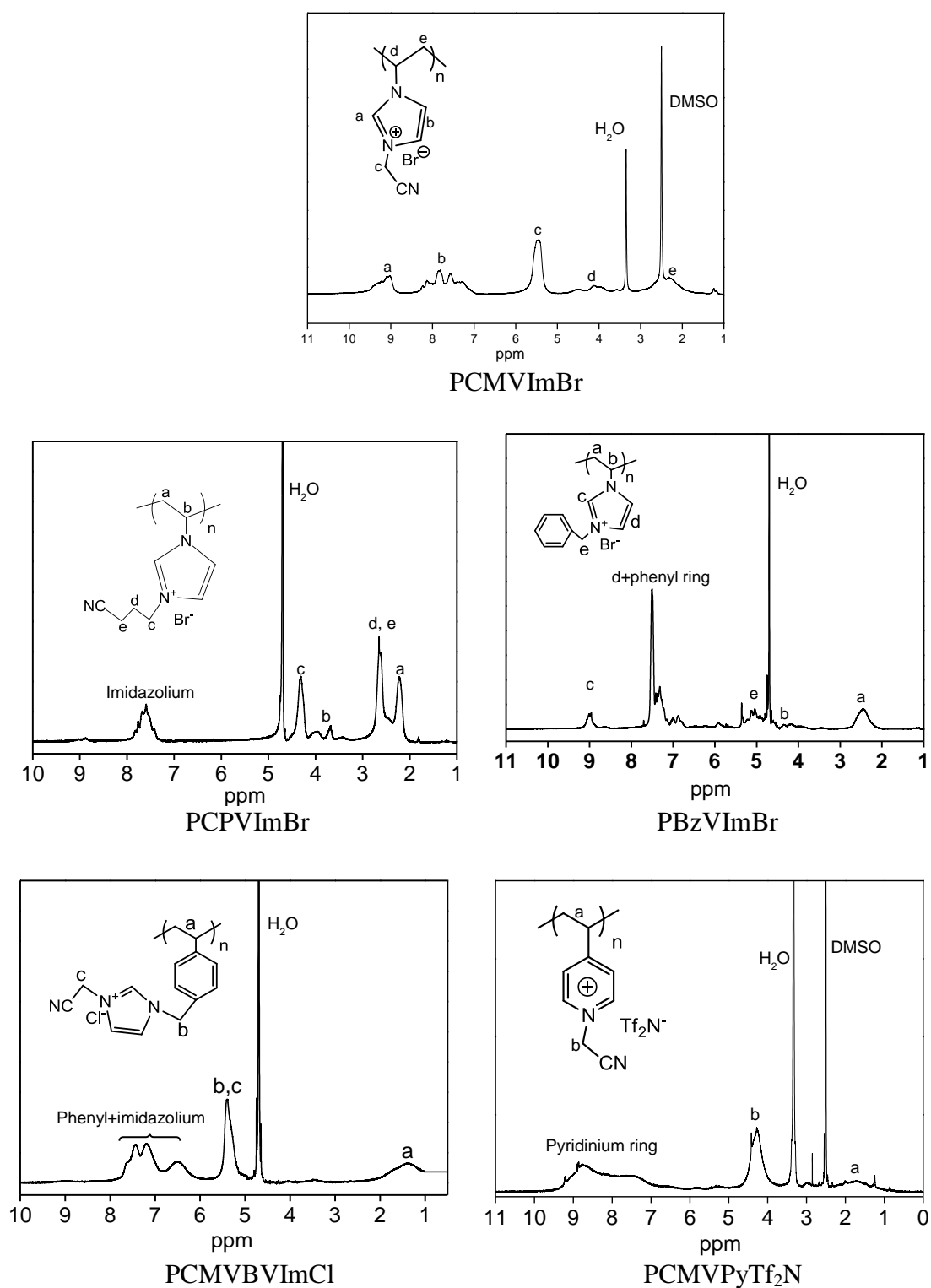
**Scheme S1** Chemical structures of PILs employed in this work. X denotes the anions (Br/Cl, Tf $_2$ N, PF $_6$ , and BF $_4$ ).

The PILs of PCMVImBr, PCPVIImBr, PBzVIImBr and PCMVBIImCl were prepared via polymerization of the corresponding ionic liquid monomers similar to our previous method (*Chem. Mater.* 2010, 22, 5003–5012). In a typical polymerization procedure (taking

PCMVImBr as an example), 5 g of CMVImBr ionic liquid monomer, 100 mg of AIBN and 50 ml of DMSO were mixed and deoxygenated by three cycles of freeze-pump-thaw process. After backfilled with argon, the reactor was placed in an oil bath thermostated at 90°C for 20 h. When cooling down to room temperature, the reaction mixture was dropwise added to an excess of THF. The precipitate was re-dissolved in methanol and precipitated in THF. The products were then dried at 90 °C by high vacuum ( $10^{-3}$  mbar) overnight. The chemical structures were confirmed by  $^1\text{H}$ -NMR spectra in Figure S1.

In a typical anion exchange process (taking  $\text{Tf}_2\text{N}^-$  as an example), PILs with Br or Cl anion were dissolved in an aqueous solution by gentle heating at a concentration of 10 g/L. An aqueous solution of  $\text{LiTf}_2\text{N}$  (50 g/L) was added dropwise into the aqueous PIL solution to reach a molar ratio of  $[\text{Tf}_2\text{N}]/[\text{Br}]=1.15$ . After addition, the stirring continued for 30 min. The precipitate was collected by filtration, washed several times with deionized water and dried at 90 °C by high vacuum overnight.

The PIL with pyridinium cation (PCMVPy $\text{Tf}_2\text{N}$ ) was prepared via a post-polymerization modification procedure similar to our previous method (Polym. Chem., 2011, 2, 1654-1657). In brief, 3.2 g of P4VP was dissolved under argon atmosphere in a mixture of 100 ml of DMSO and 20 ml of ethylene glycol at 90 °C. After dropwise addition of 11 g of bromoacetonitrile, the reaction temperature was raised to 100°C and the stirring was kept for 24 h. When cooling down to a room temperature, the reaction mixture was dropwise added to an excess of THF. The dark precipitate was re-dissolved in 300 ml of water, and an aqueous solution of  $\text{LiTf}_2\text{N}$  (50 g/L) was added to reach a molar ratio of  $[\text{Tf}_2\text{N}]/[\text{Br}]=1.15$ . The precipitate was collected by filtration, washed several times with deionized water and dried at 90 °C by high vacuum ( $10^{-3}$  mbar) overnight. The chemical structure was confirmed by  $^1\text{H}$ -NMR spectrum in Figure S1.



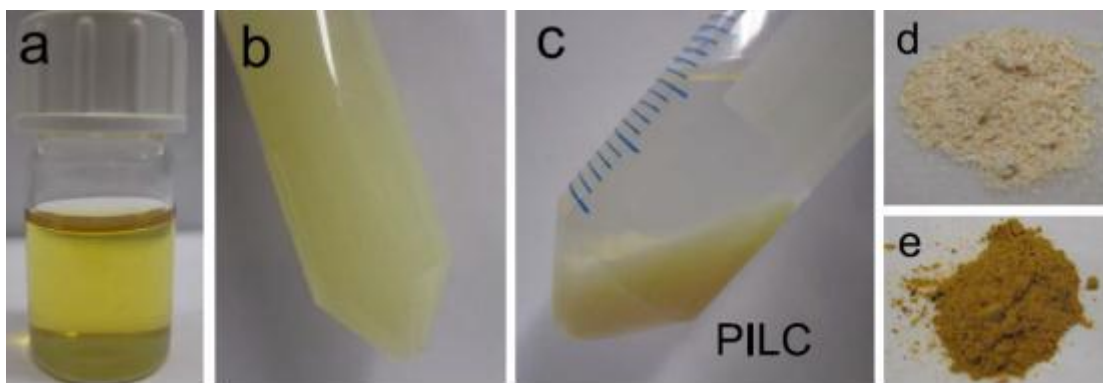
**Figure S1**  $^1\text{H}$ -NMR spectra of PCMVImBr, PCPVIImBr, PBzVIImBr, PCMVBVIImCl and PCMVPyTf<sub>2</sub>N. The integration ratios matched each sample. In the sample PCMVPyTf<sub>2</sub>N, a quaternization degree of 95% can be calculated.

## Preparation and characterization of PILC

### 3.1 PCMVImTf<sub>2</sub>N-PAA PILC and Cu@PILC

PCMVImTf<sub>2</sub>N and PAA were dissolved in DMF at a designed concentration and mole ratio to form a clear transparent mixture solution (**Figure S2a**). 30 mL of ethanol (denoted as complexation solvent) containing 0.5 wt% of NH<sub>3</sub> (prepared from 6 wt% aqueous NH<sub>3</sub> solution) was added into a plastic tube, and was placed in an ultrasonication (Sonifier W-450 D) bath thermostated at 25 °C. 3 mL of PCMVImTf<sub>2</sub>N-PAA mixture solution was added dropwise (2 ml/min) in to the plastic tube under stirring (900 rpm) and sonication (40 % sonication amplitude). Turbidity happened immediately upon the adding of the PCMVImTf<sub>2</sub>N-PAA mixture solution (**Figure S2b**), and the ultrasonication was kept for additional 5 min after the addition. PCMVImTf<sub>2</sub>N-PAA PILC were collected by centrifugation (**Figure S2c**), washed with ethanol 4 times, and dried at 50 °C under vacuum till constant weight (**Figure S2d**). PILC based on PCMVImPF<sub>6</sub>, PCMVImBF<sub>4</sub>, PCMVImBr were prepared in a similar way.

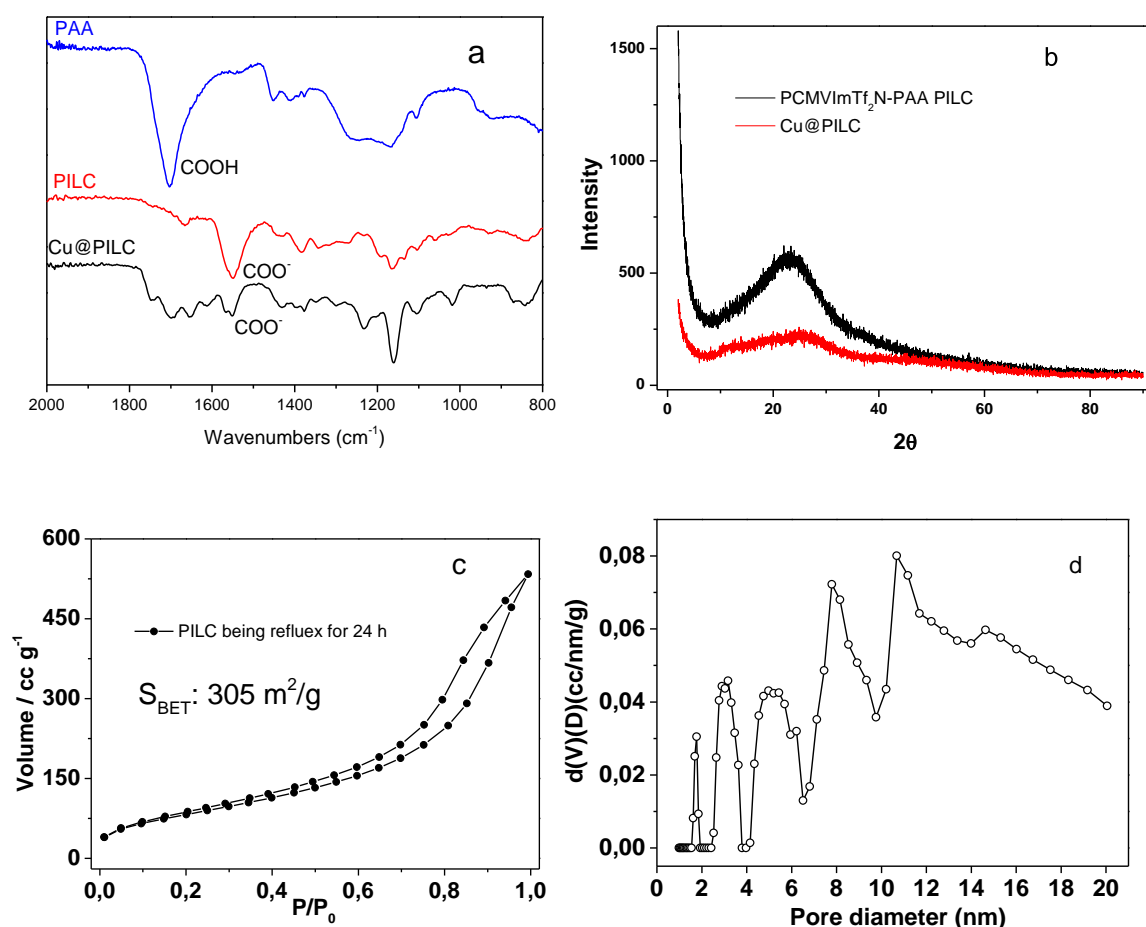
For synthesizing PCMVImTf<sub>2</sub>N-PAA PILC loaded with copper (II) salt (Cu@PILC), 1.5 g of freshly prepared PILC was dispersed in 20 mL of ethanol and its pH value was adjusted to 5 using 0.1M HCl. Then, 100 mL of CuCl<sub>2</sub> solution in ethanol (2 wt%) was added into the PILC dispersion. The mixture was refluxed at 80 °C for 24 h. Afterward, Cu@PPILC was obtained by centrifugation, washed with ethanol four times, and dried at 50 °C under vacuum till constant weight (**Figure S2e**).



**Figure S2** Optical micrographs of (a) PCMVImTf<sub>2</sub>N-PAA mixture solution in DMF (10 wt%), (b) adding PCMVImTf<sub>2</sub>N-PAA mixture into ethanol containing NH<sub>3</sub>H<sub>2</sub>O, (c) PCMVImTf<sub>2</sub>N-PAA PILC obtained by centrifugation, (d,e) PILC and Cu@PILC catalysis dried at 50 °C.

As shown in **Figure S3a**, the absorption band at 1700 cm<sup>-1</sup> is attributed to C=O bond in COOH group in PAA. This absorption shifts to 1550 cm<sup>-1</sup> in the PCMVImTf<sub>2</sub>N-PAA PILC due to the deprotonation of COOH groups into COO<sup>-</sup> groups. Such an absorption shift was usually utilized to characterize the ionic complexation structure based on COO<sup>-</sup> groups.<sup>1-3</sup> The weak absorption at 1660 cm<sup>-1</sup> in PCMVImTf<sub>2</sub>N-PAA PILC is attributed to the stretching of imidazolium rings.<sup>4</sup> Compared with pristine PILC, absorption bands in the range of 1600 cm<sup>-1</sup> to 1750 cm<sup>-1</sup> for Cu@PILC catalyst is due to the ion pair adsorption of CuCl<sub>2</sub> onto the PILC matrix driven by the affinitive interaction between imidazolium rings and CuCl<sub>2</sub>. Orto et.al has synthesized a copolymer containing both imidazolium and methacrylic acid groups, and found that imidazolium rings were the main group for copper uptake while the carboxylic acid groups play an assisting role.<sup>4</sup> This agrees with our observation, and explains the large copper uptake (12.4 wt%) of PCMVImTf<sub>2</sub>N-PAA PILC. The XRD curves of PILC and Cu@PILC (**Figure S3b**) show that both are noncrystalline. Elemental analysis (**Table S1**) of PCMVImTf<sub>2</sub>N-PAA PILC shows that it has a stoichiometric composition, which is in

accordance with its feed ratio. The pore size distribution curve in Figure S3d proves the existence of both micropores (<2 nm) and mesopores (2~50 nm).



**Figure S3** (a) FT-IR spectra of PAA, PCMVImTf<sub>2</sub>N-PAA PILC and Cu@PILC, (b) XRD of PCMVImTf<sub>2</sub>N-PAA PILC and Cu@PILC, (c) Nitrogen sorption isothermals of PCMVImTf<sub>2</sub>N-PAA PILC after reflux in ethanol for 24 h, (d) Pore size distribution curve of the PCMVImTf<sub>2</sub>N-PAA PILC No. 2 in Table 1, main text.

**Table S1** Elemental analysis of PCMVImTf<sub>2</sub>N-PAA PILC (No. 2, Table 1 in the main text).

N (wt%)	C (wt%)	H (wt%)	PCMVImTf <sub>2</sub> N /PAA ratio <sup>a</sup>
16.81	49.14	5.51	1.07

a: The monomer mole ratio of PCMVImTf<sub>2</sub>N to PAA is calculated based on the equation: PCMVImTf<sub>2</sub>N:PAA = (6×N)/(7×(C-2×N)), where N and C are nitrogen and carbon content.

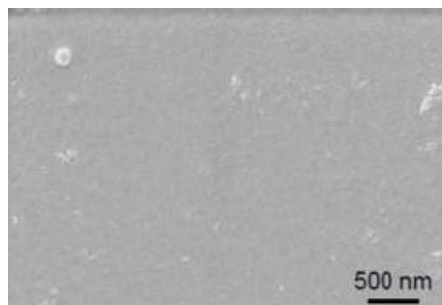
### 3.2 Preparation of PCPVI<sub>m</sub>Tf<sub>2</sub>N-PAA, PBzVI<sub>m</sub>Tf<sub>2</sub>N-PAA, PCMVBVI<sub>m</sub>Cl-PAA, PCMVBVI<sub>m</sub>Tf<sub>2</sub>N-PAA and PCMVPyTf<sub>2</sub>N-PAA PILC

The adding rate, ultrasonication, stirring condition, and temperature for preparing all PILCs were fixed as 2 mL/min, 40 % sonication amplitude, 900 rpm, and 25 °C, respectively. All PILCs were collected by centrifugation, purified by washing them with their respective complexation solvents 4 times, and were dried at 50 °C under vacuum till constant weight. Because **PCMVBVI<sub>m</sub>Cl** is insoluble in DMF, all PILs and PAA were dissolved in DMSO to form the mixture solution. The solvent replacement did not disturb the obtained porous structure. For instance, under the same preparation conditions, when PCMVI<sub>m</sub>Tf<sub>2</sub>N and PAA were pre-dissolved in DMF and DMSO, the specific surface area of **PCMVI<sub>m</sub>Tf<sub>2</sub>N-PAA PILCs** is 310 m<sup>2</sup>/g and 321 m<sup>2</sup>/g, respectively.

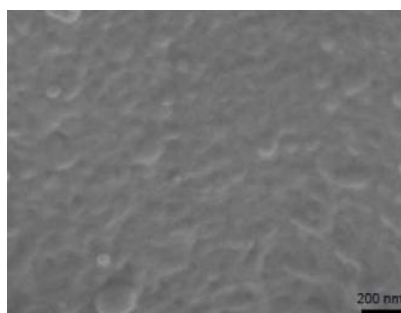
In a typical procedure to prepare PILCs (taking **PCPVI<sub>m</sub>Tf<sub>2</sub>N-PAA PILC** as an example), PCPVI<sub>m</sub>Tf<sub>2</sub>N (0.16 g) and PAA (0.027 g) were dissolved in DMSO (3 mL) and added into complexation solvents (30 mL) containing 0.5 wt% NH<sub>3</sub> (prepared from 33 wt% aqueous NH<sub>3</sub> solution) under sonication and stirring. Then, PILC precipitates were collected, washed, and dried as described above.



### 3. Morphology of PCMVImTf<sub>2</sub>N-PAA physical blend and PCMVImTf<sub>2</sub>N-PAA PILC prepared from water.



**Figure S4** SEM morphology of PCMVImTf<sub>2</sub>N-PAA physical blend, which was prepared by drying PCMVImTf<sub>2</sub>N-PAA solution in DMF (PCMVImTf<sub>2</sub>N concentration: 10 wt%; Monomer mole ratio of PCMVImTf<sub>2</sub>N to PAA: 1:1) at 80 °C for 24 h.



**Figure S5** SEM micrograph of PCMVImTf<sub>2</sub>N-PAA PILC prepared from water (No. 15, Table 1, main text).

#### 4. Effect of preparation conditions on PCMVImTf<sub>2</sub>N-PAA PILC's porous structures.

**Table S2.** Specific surface area and pore volume of PCMVImTf<sub>2</sub>N-PAA PILCs prepared under various conditions. X denotes anions.

PILC <sup>a</sup>	X <sup>-</sup>	PAA MW (g/mol)	Adding rate (mL/min)	Ammonia content (wt %) <sup>b</sup>	S <sub>BET</sub> (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
No. 16	PF <sub>6</sub>	2000	2	0.5	260	0.84
No. 17	BF <sub>4</sub>	2000	2	0.5	210	0.52
No. 18	Br	2000	2	0.5	200	1.42
No. 19	Tf <sub>2</sub> N	5000	2	0.5	326	0.86
No. 20	Tf <sub>2</sub> N	100 000	2	0.5	285	1.16
No. 21	Tf <sub>2</sub> N	240 000	2	0.5	297	1.09
No. 22	Tf <sub>2</sub> N	2000	1	0.5	297	1.17
No. 23	Tf <sub>2</sub> N	2000	9	0.5	294	0.94
No. 24	Tf <sub>2</sub> N	2000	35	0.5	302	1.17
No. 25 <sup>c</sup>	Tf <sub>2</sub> N	2000	2	0	n/a	n/a
No. 26	Tf <sub>2</sub> N	2000	2	0.07	135	0.25
No. 27	Tf <sub>2</sub> N	2000	2	0.13	238	0.54
No. 28	Tf <sub>2</sub> N	2000	2	0.25	273	0.84
No. 29	Tf <sub>2</sub> N	2000	2	0.75	315	1.05

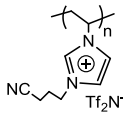
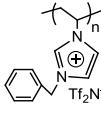
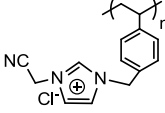
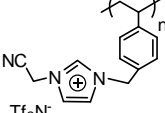
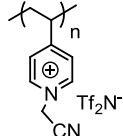
<sup>a</sup> all other preparation conditions are the same as PILC No. 2 in Table 1, main text.

<sup>b</sup> The ammonia content in complexation solvents.

<sup>c</sup> No PILC materials were obtained under this condition.

## 5. Characterization of PILCs made from PAA and another four PILs

**Table S3.** Specific surface area of PILCs prepared from PAA (MW: 2000 g/mol) and PILs with four different cation structures.

PILs <sup>a</sup>	Ethanol	Isopropanol	Butanol
	Solubilized <sup>b</sup> 36 m <sup>2</sup> /g	Not soluble 115 m <sup>2</sup> /g	Not Soluble 102 m <sup>2</sup> /g
	Solubilized 52 m <sup>2</sup> /g	Not soluble 109 m <sup>2</sup> /g	Solubilized 45 m <sup>2</sup> /g
	Solubilized 25 m <sup>2</sup> /g	Not soluble 151 m <sup>2</sup> /g	Not soluble 114 m <sup>2</sup> /g
	Solubilized 15 m <sup>2</sup> /g	Solubilized 42 m <sup>2</sup> /g	Solubilized 13 m <sup>2</sup> /g
	Solubilized 35 m <sup>2</sup> /g	Not soluble 205 m <sup>2</sup> /g	Not soluble 201 m <sup>2</sup> /g

<sup>a</sup> All PILCs prepared by using water and methanol as complexation solvents are nonporous (< 20 m<sup>2</sup>/g) because PAA is soluble in both solvents.

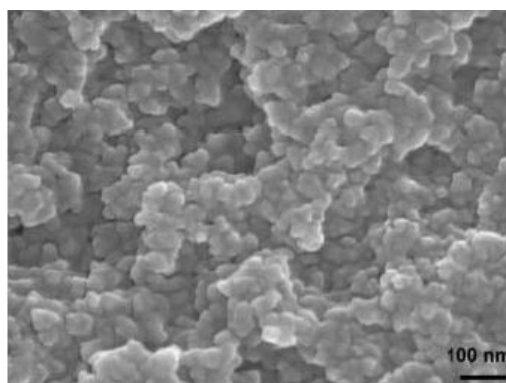
<sup>b</sup> Solubility of PIL in organic solvents was measured at 25 °C. The word “solubilized” means that PIL powders become swollen although not completely dissolved.

## 6. Aerobic oxidation and catalyst recycling

In a typical oxidation test, 5 mmol of substrate, catalysts used as described in the manuscript and 8 mL of CH<sub>3</sub>CN were added into a 25 mL round bottom glass-reactor, which was fitted with a magnetic stirrer and an air inlet tube. The reaction was performed at 50 °C in an oil bath under magnetic stirring. A stream of air was conducted into the reaction mixture and controlled by a gas flowmeter at a constant flow rate (10 mL min<sup>-1</sup>). After completion of

the reaction, biphenyl was added to the mixture as the internal standard. Then, Cu@PILC catalyst was filtered, and the reaction mixture was injected into the GC-MS for analysis.

When the first oxidation finished, Cu@PILC catalyst was obtained by centrifugation (10 mins, 4500 rpm), and washed with ethanol for 4 times. The recovered Cu@PILC catalyst was dried in a vacuum oven at 50 °C for 24 h and used in the subsequent reactions. Figure S6 shows the morphology of Cu@PILC after 4 times recycling.



**Figure S6** SEM morphology of Cu@PILC catalyst (Entry 1 and Entries 5~8 in Table 2, main text).

#### Reference for SI

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