Supporting Information

Organic Acids Can Crosslink Poly(ionic liquid)s into Mesoporous Polyelectrolyte Complex

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1. Chemicals

Lithium bis(trifluoro methanesulfonyl)imide (LiTf$_2$N, 99.95%), benzoic acid, terephthalic acid, benzene-1,3,5-tricarboxylic acid, 1,2,4,5-benzenetetracarboxylic acid, benzenehexacarboxylic acid, citric acid, oxalic acid, trans-aconitic acid, and methyl orange were purchased from Sigma-Aldrich and used without further purification. Poly(3-cyanomethyl-1-vinylimidazolium bromide) (PCMVImBr) was synthesized according to our previous method (Chem. Mater. 2010, 22, 5003–5012), and its $^1$H-NMR spectrum was shown in Figure S1. Poly(3-cyanomethyl-1-vinylimidazolium bis(trifluoro methanesulfonyl)imide) (PCMVImTf$_2$N) was prepared by anion exchange of PCMVImBr with LiTf$_2$N. All the solvents in this study were of analytic grade. The apparent molecular weight of the model PCMVImBr was measured by GPC (eluent: water with 0.2 M Na$_2$SO$_4$ + 1% acetic acid at room temperature) to be $5.93 \times 10^4$ g/mol (PDI: 2.95), thus the apparent molecular weight of the PCMVImTf$_2$N is calculated to be $1.15 \times 10^5$ g/mol.
**Figure S1** $^1$H-NMR spectrum of PCMVImBr in DMSO-$d_6$.

2. **Characterization methods**

Nitrogen ($N_2$) sorption experiments were performed with a Quantachrome Autosorb-1 or Quadrasorb at liquid nitrogen temperature, and data analysis was performed by Quantachrome software. The surface area and pore volume were calculated using the Brunauer–Emmett–Teller (BET) equation, and the Barrett–Joyner–Halenda (BJH) method, respectively. Samples for BET measurements were degassed at 80 °C for 20 h before measurements.

FT-IR spectra were performed on a BioRad 6000 FT-IR spectrometer; samples were measured in solid state using a Single Reflection Diamond ATR. Scanning electron microscopy (SEM) was performed on a GEMINI LEO 1550 microscope at 3 kV, and samples were coated with gold before examination.

3. **Preparation of PCMVImTf$_2$N-based PILC networks**

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The chemical structures of all multi-valent anion molecules utilized to prepare mesoporous PILC networks with PCMVImTf$_2$N were shown in Scheme S1. PCMVImTf$_2$N and small acid molecules were dissolved in DMSO solvent at room temperature to form mixture solution, in which the PCMVImTf$_2$N concentration was kept at 5 wt%, and the mole ratio of carboxylic acid groups to the monomer units on PCMVImTf$_2$N was fixed at 1. 30 mL of diethyl ether containing 0.3 wt% of NH$_3$ (prepared by using 2M NH$_3$ in isopropanol as ammonia source) was placed in a glass beaker, into which 3 mL of polymer mixture solution was dropped (speed: 3 mL/min) under stirring (900 rpm) and sonication (40 % sonication amplitude). The sonication was kept for 1 min after the addition was finished. The PIL complex materials precipitated out from the solution, washed by diethyl ether three times, and dried under vacuum at 50 °C for 12 h.

Scheme S1. Chemical structures of small acid molecules utilized in this study. R refers to carboxylic acid groups.
4. Supplementary data

Figure S2 Pore size distribution curve of PILC network prepared from PCMVImTf$_2$N and 1,2,4,5-BCA. It was calculated from the DFT method.

Figure S3 Nitrogen sorption isothermals of PILC networks (from PCMVImTf$_2$N and 1,2,4,5-BCA) being refluxed in acetone for 24 h.
Scheme S2. Definition of degree of ionic complexation (DIC): \( DIC = \frac{x}{x+y} \), wherein \( x \) and \( y \) were the imidazolium anions that have and do not have ionic complexation with BCA, respectively. DIC were calculated on basis of element analysis (sulfur and nitrogen element) because the sulfur element in the PILC only exist in rest \( \text{Tf}_2\text{N} \) counter ions.

Figure S4 UV absorption (\( \lambda \approx 435 \text{ nm} \)) of methyl orange solution (0.02 M in ethanol) after being treated with PILC (10 mg) and an anion exchange resin (Ambersep 900(OH), Alfa Aesar, 10 mg), respectively.