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 ($LiTf_2N$, 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) ($PCMVImTf_2N$) was prepared by anion exchange of PCMVImBr with $LiTf_2N$. 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_2SO_4 + 1% acetic acid at room temperature) to be 5.93×10^4 g/mol (PDI: 2.95), thus the apparent molecular weight of the $PCMVImTf_2N$ is calculated to be 1.15×10^5 g/mol.

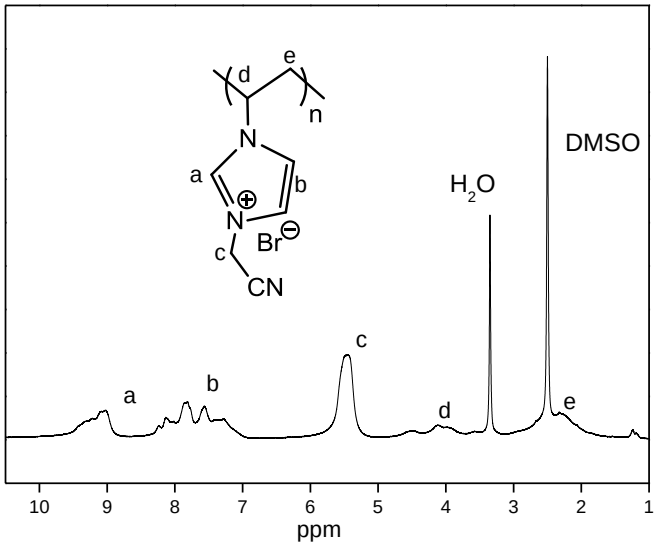


Figure S1 ^{1}H-NMR spectrum of PCMVImBr in DMSO-d_6.

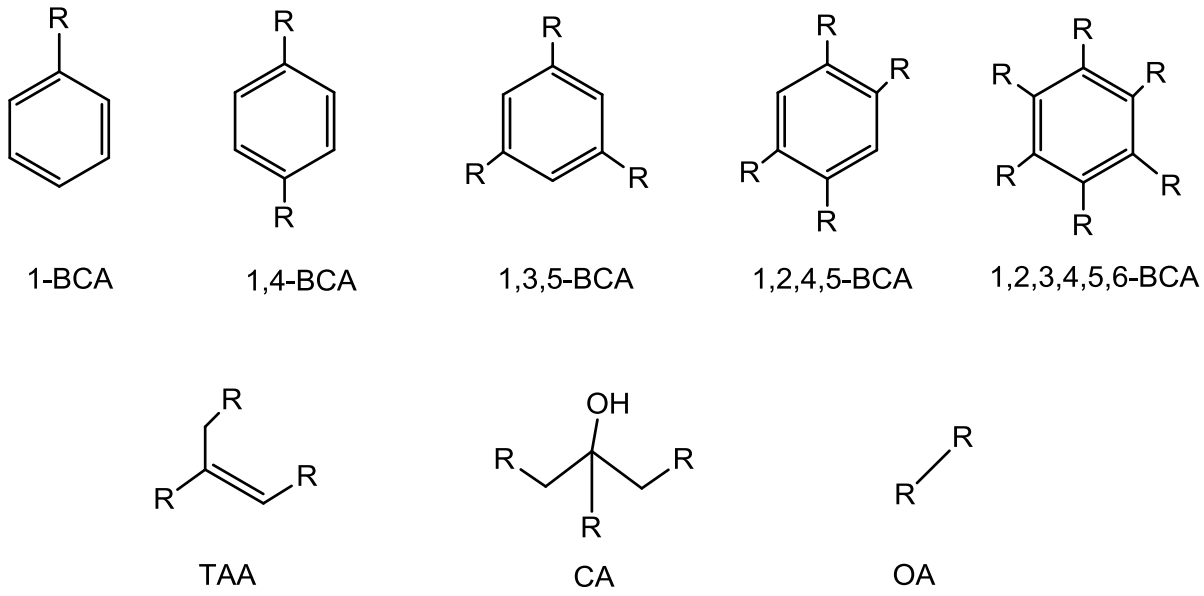
2. Characterization methods

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 Brunaer–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_2N-based PILC networks

The chemical structures of all multi-valent anion molecules utilized to prepare mesoporous PILC networks with PCMVImTf_2N were shown in Scheme S1. PCMVImTf_2N and small acid molecules were dissolved in DMSO solvent at room temperature to form mixture solution, in which the PCMVImTf_2N concentration was kept at 5 wt%, and the mole ratio of carboxylic acid groups to the monomer units on PCMVImTf_2N 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 ^{o}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

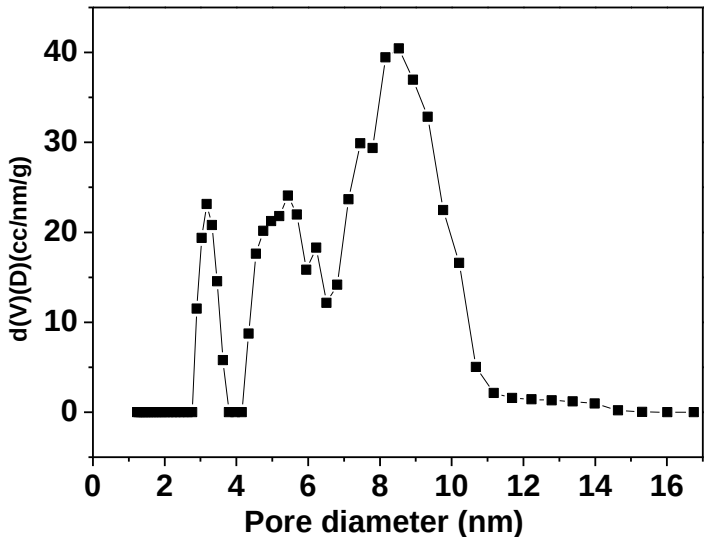


Figure S2 Pore size distribution curve of PILC network prepared from PCMVImTf$_2$N and 1,2,4,5-BCA. It was calculated from the DFT method.

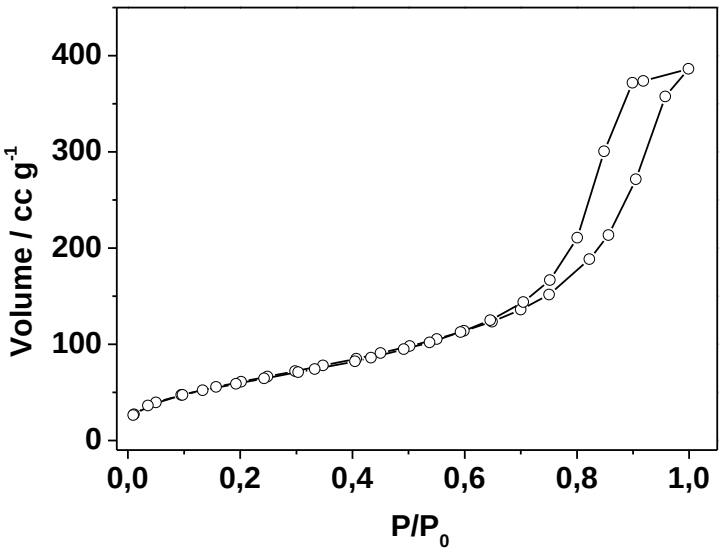
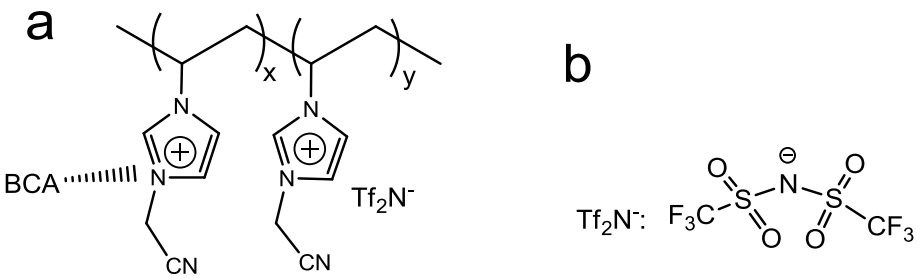


Figure S3 Nitrogen sorption isothermals of PILC networks (from PCMVImTf$_2$N and 1,2,4,5-BCA) being refluxed in acetone for 24 h.



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 Tf_2N counter ions.

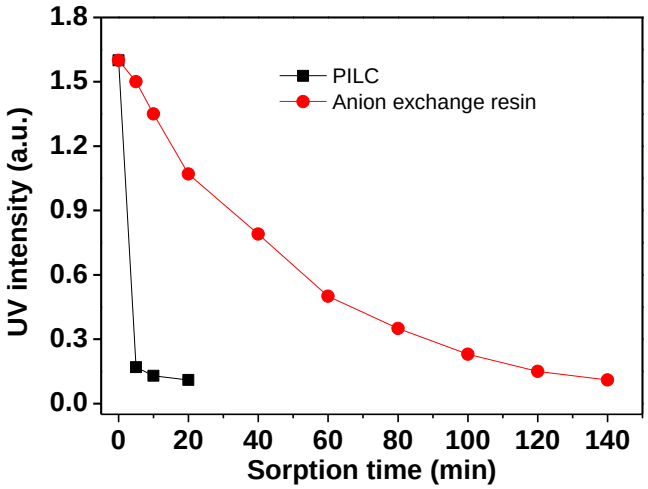


Figure S4 UV absorption (λ ~ 435 nm) of methyl orange solution (0.02 M in ethanol) after being treated with PILC (10 mg) and an anion exchange resin (Ambersep 900(OH), Alfa Aesar, 10 mg), respectively.