3D-Ordered Macroporous Poly(ionic liquid) Films as Multifunctional Materials

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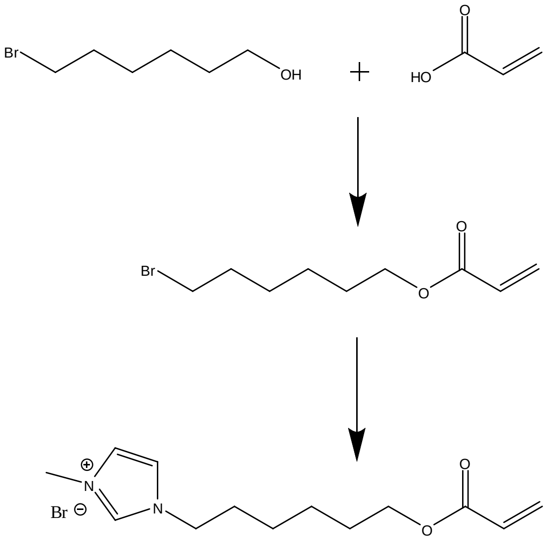
Materials:

Lithium bis(trifluoromethanesulfonimide) ($LiTf_2N$), trimethylolpropane triacrylate (TMPTA), 2, 2'-azobisisobutyronitrile (AIBN), and methyl methacrylate (MMA) were obtained from Arcos Organics. All solvents and other chemicals were supplied by local suppliers. All solvents and chemicals are of reagent quality and were used without further purification unless special explanation. Common glass slides were cut to be 50×20 mm and immerged in H_2SO_4/H_2O_2 mixture for 12 hours, following rinsing with deionized water in ultrasonic bath for three times and then dried for use. All 7 ml vials for colloidal crystals growth and a reactive flask must be cleaned by rinsing with H_2SO_4/H_2O_2 mixture and deionized water. PMMA slides (50 mm×20 mm×1.5 mm) as substrates for the preparation of poly(ionic liquid) films supports were cleaned with anhydrous ethanol.

Synthesis of polymerizable ionic liquid 1-(2-acryloyloxyhexyl)-3-methylimidazolium bromide:

The ionic liquid monomer was synthesized as shown in Scheme S1. A mixture of acrylic acid (0.72 g, 10 mmol), 6-bromo-1-hexanol (2.2 g, 12mmol), N, N'-Dicyclohexyl carbodiimide (DCC 2.5 g, 12mmol) and 4-Dimethylaminopyridine (DMAP 1.2g, 10mmol) in anhydrous CH_2Cl_2 (150 mL) was stirred at room temperature for 24 h. After the reaction mixture was filtrated, the organic layer was washed with 4% hydrochloric acid, saturated aqueous sodium bicarbonate and brine, respectively. And then the product was dried by anhydrous magnesium sulfate, filtered and evaporated in vacuum. The last residue was purified by flash chromatography on silica gel (eluent: dichloromethane/ petroleum ether = 1/5) to afford a pale yellow liquid for the next step synthesis. A mixture of 7-bromohexylacrylate (1.5 g, 4.3 mmol) and 1-methylimidazole (0.42g, 5.1 mmol) and a small amount of 2,6-ditertbutyl-4-methylphenol (inhibitor) was stirred at 45 ^{o}C for 20 h under N_2 atmosphere, and yielded a viscous liquid. The viscous liquid was purified by the precipitation method with diethyl ether to obtain the desired monomer (viscous yellow liquid) 1-(2-acryloyloxyhexyl)-3-methylimidazolium bromide. The viscous liquid was dried under vacuum at room temperature as the pale yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): 10.48 (1H, m, N–CH–N), 7.28–7.27 (2H, s, N–CH=CH–N), 6.37–6.36 (1H, m, CH_2=CH), 6.16–6.12 (1H, m, CH_2=CH), 5.85–5.84 (1H, m, CH_2=CH), 4.38–4.35 (2H, t, N–$CH_2(CH_2)_6$O–), 4.13 (3H, s, N–CH_3), 2.05–1.98 (2H, t, N–$CH_2(CH_2)_6$O–), 1.68–1.65 (2H, m, –$OCOCH_2CH_2$), 1.41–1.21 (4H, m, –3CH_2CH_2–).



Scheme S1 Synthesis of ionic liquid monomer

Formation of silica colloidal crystal templates:

The highly uniform silica colloidal microspheres were synthesized based on a Stöber method. In a typical preparation, 8.74 g TEOS and 180 ml anhydrous ethanol were mixed in a 250 ml flask under intensively stirring with a magnetic beater. Then, 15.4 ml ammonia and 4.46 g deionized water were slowly added and the resulting reaction mixture was kept for overnight. After alternative centrifugation and dispersion using anhydrous ethanol for 4 or 5 times to expunge residues, the monodispersed silica particles (260 nm) were obtained and fully dispersed in anhydrous ethanol with weight concentration of about 1-4%, which were allotted into 7 ml clean vials for the formation of colloidal crystal templates. A clean glass slide was put into each vial in vertically for colloidal crystal growth. After complete volatilization of ethanol, silica colloidal crystal templates were formed on both sides of each glass slide.

Preparation of the 3D-ordered macroporous PIL films:

Uniform SiO_2 nanoparticles with diameters ranging from 200 to 400 nm were used in this work, and for improving the film formability of PILs methyl methacrylate (MMA) was utilized as co-monomer in the polymerization process. In a typical preparation of 3D-ordered macroporous PIL film, 0.8 g (2.5 mmol) ionic liquid monomer (IL-Br), 0.25 g (2.5 mmol) methyl methacrylate (MMA), and 0.74 g (2.5 mmol) cross-linker (TMPTA) were dissolved in 5 ml mixed solvent of methanol and chloroform (v/v=1:1) under ultrasonication. Then, 0.2 g (1.2 mmol) AIBN was given, and the resulting mixture was degassed by nitrogen for 10 minutes. Glass silde with colloidal crystal template was coated with a PMMA slide (50×20×1.5 mm) and hold together to imbibe the above-mentioned precursor mixture. Once the colloidal crystal of the formed sandwich structure became transparent, a successful infiltration process was completed. After the removal of excess precursors, photopolymerization was performed in an ice bath under an UV light (365 nm) for 2h. The sandwiches were immersed into 1% hydrofluoric acid for 2 h to separate double slides and fully etch the used silica particles. The formed polymer films remained on the PMMA substrate. For the preparation of free-standing PIL films, the glass slides were used as cover instead of PMMA slides.

Characterization:

^{1}H NMR spectra were recorded at 300MHz on a JOEL JNMECA300 spectrometer. The photopolymerization was implemented in an UV light (FUSI Electric ST3) with 16 watts. A centrifugation (Anke TDL-60B, Shanghai, China) was used for centrifugation of colloidal particles from reactants. Photographic images of the colour change of PIL films were obtained by using a common digital camera under daylight lamp. Optical spectra were acquired with an Ocean Optics USB2000 fibre optic spectrophotometer coupled to an optical microscope. Morphology and microstructure of silica colloidal crystals and PIL films was observed by a Hitachi S-6700 field emission scanning electron microscope. The electrochemical studies were performed using a conventional electrochemical cell consisting of a Pt counter electrode, a calomel reference electrode, and a glass carbon working electrode modified with PIL film. Water ccontact angles were measured with a Dataphysics contact angle system. TEM images were obtained by using JEM 2010 high-resolution transmission electronic microscope.

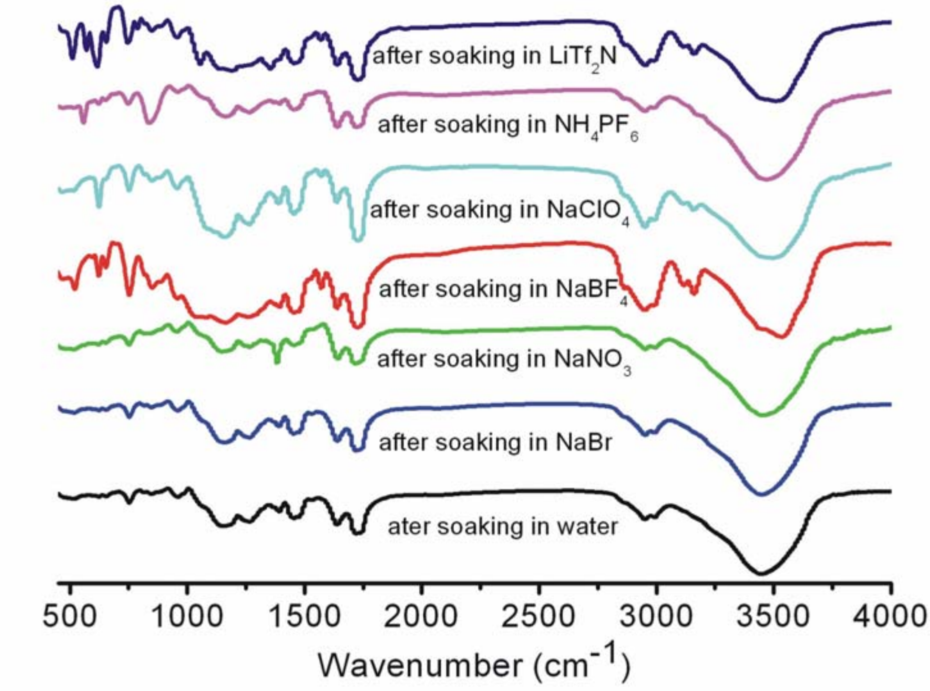


Figure S1. FTIR spectra of dried photonic IL films after soaking in diversified anions aqueous solutions for 2 hours. FTIR confirmed the occurrence of the anion exchange and the existence of the exchanged anions. It is clearly seen that the characteristic absorption bands of the counteranions were observed: NO_3^- at 1641 cm^{-1}, BF_4^- at 1083 cm^{-1}, ClO_4^- at 958 cm^{-1}, PF_6^- at 838 cm^{-1}, Tf_2N^- at 1356 cm^{-1}.

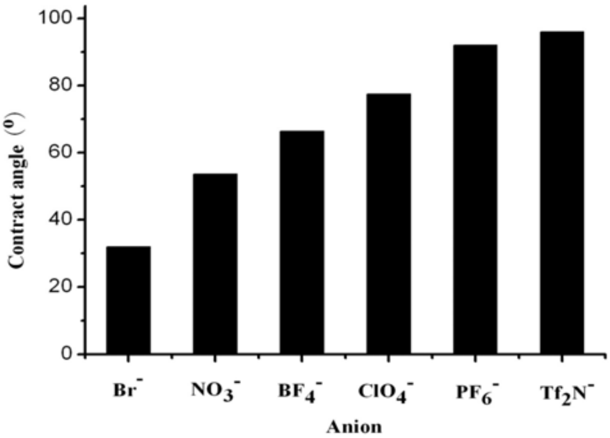


Figure S2. Effects of counteranions on water contact angles of the 3D macroporous PIL films.

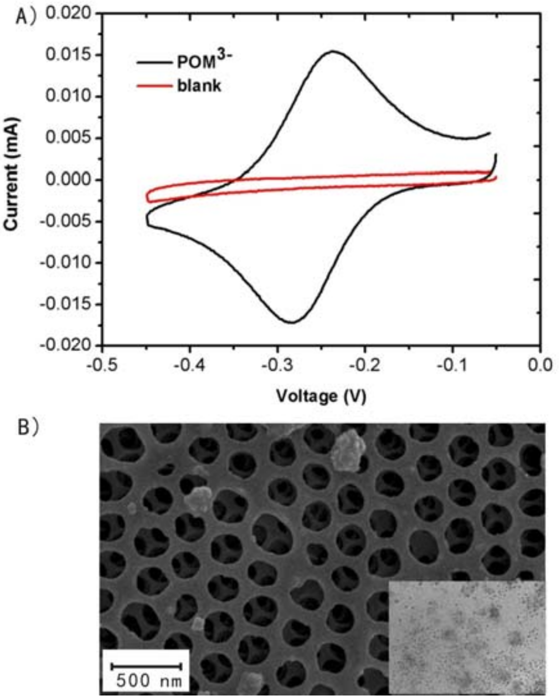


Figure S3. A) Cyclic voltammograms of the PIL film modified glass carbon electrodes (red line: with BF4- as counteranion; black line: with $W_6O_{192}^-$ as counteranion); B) SEM image of the macroporous PIL film containing Ag^+ ions followed by reduction. Inset in panel B is the TEM image of the corresponding PIL film.

Acknowledgements

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