Visual Indication of Enviromental Humidity by Using Poly(ionic liquid) Photonic Crystals

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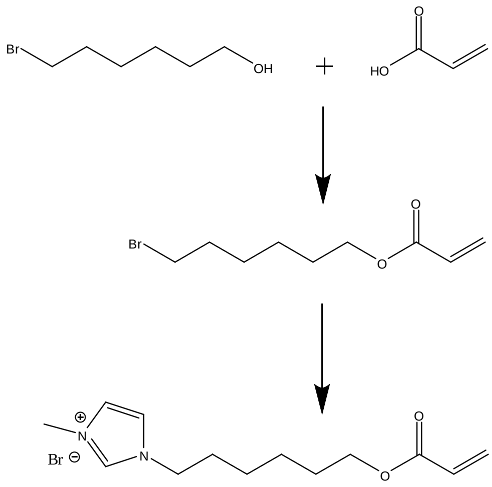
Materials：

Lithium bis(trifluoromethanesulfonimide) ($LiTf_2N$), trimethylolpropane triacrylate (TMPTA), 2, 2’-azobisisobutyronitrile (AIBN), and methyl methacrylate (MMA) were obtained from Acros 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 specially explained. 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–$CH_2(CH_2)_6O$–), 1.68–1.65 (2H, m, –$OCOCH_2CH_2$), 1.41–1.21 (4H, m, –$3CH_2CH_2$–).



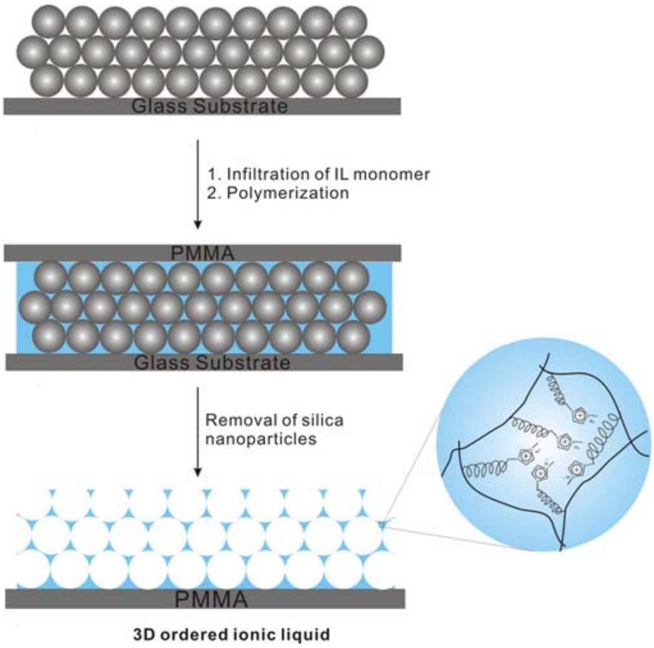
Scheme S1 Synthesis of ionic liquid monomer

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 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 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:

Colloidal crystal templating method was employed for preparation of poly(ionic liquid)s with ordered macroporous structure (Scheme S1). 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. Silicon oxide was completely removed after HF etching for 2 hours. FT-IR spectrometer was employed to confirm the removal of SiO_2. It is found that, after the treatment using HF, the strong and characteristic absorption band at about 1085 cm^{-1} of SiO_2 completely disappeared from the prepared inverse opal film in comparison with the initial sample. We also found that the optical property of the prepared inverse opal did not change with further increased treatment time using HF. For the preparation of free-standing PIL films, the glass slides were used as cover instead of PMMA slides.



Scheme S1 Schematic illustration of the preparation of photonic poly (ionic liquid) films

Characterization:

^1H 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 Data physics contact angle system. TEM images were obtained by using JEM 2010 high-resolution transmission electronic microscope.

Proposed mechanism of swell/deswell of PIL inverse opal:

Our PIL inverse opal swells with increasing humidity. The mechanism behind this phenomenon may be as follows. Just like surfactant, upon exposure to water vapor, the ionic liquid units (ionic pairs) in PIL film solvate into polycation-based network with free anions as counterions. As a consequence, the polycation network swells due to the electrostatic interaction, and the osmotic pressure can be generated by the anions existed in the film, which make more water go into the polymer network. With increasing humidity, the PIL film switches from one equilibrium to a new one. Counter anion plays a crucial role in determining the solvability of the ionic liquid units, and thus, the extent of swell/deswell of PIL. The PIL inverse opal with hydrophilic counteranion (Br^- or PO_4^{3-}) exhibits large swelling. In contrast, for the PIL film with hydrophobic anion (SDS^-), water molecule is difficulty to diffuse into the polymer network and thus, the PIL film shows less swelling capability.

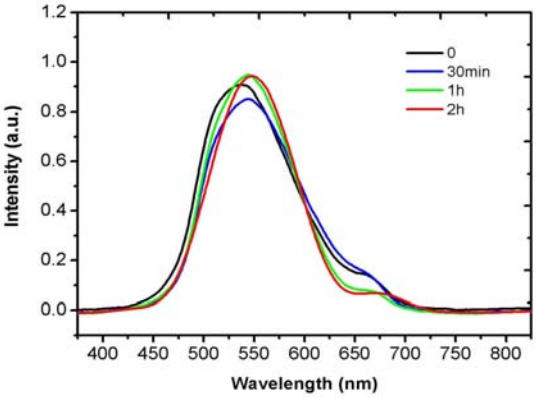


Figure S1 Peak position change of the prepared photonic PIL film with the increased exposure time to RH 60%

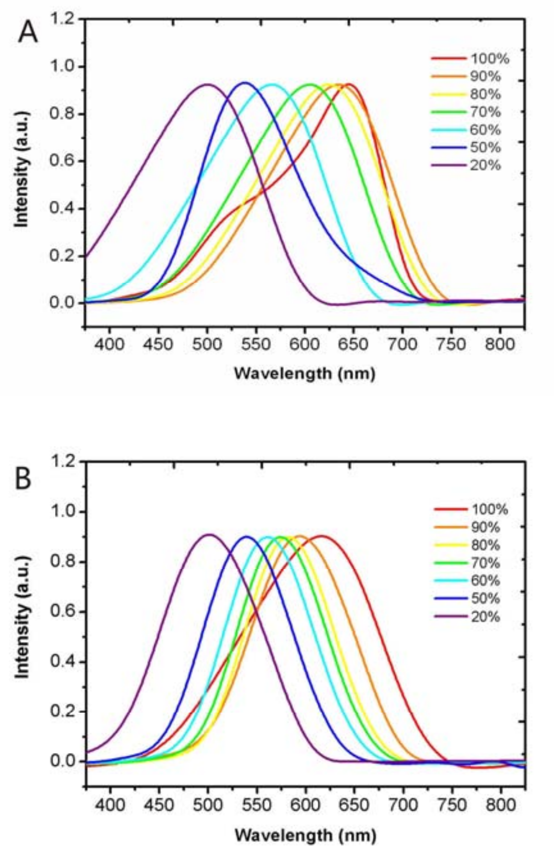


Figure S2 Optical responses of the photonic PIL films prepared under different ratios of cross-linker to monomer: A) 1:1; B) 2:1

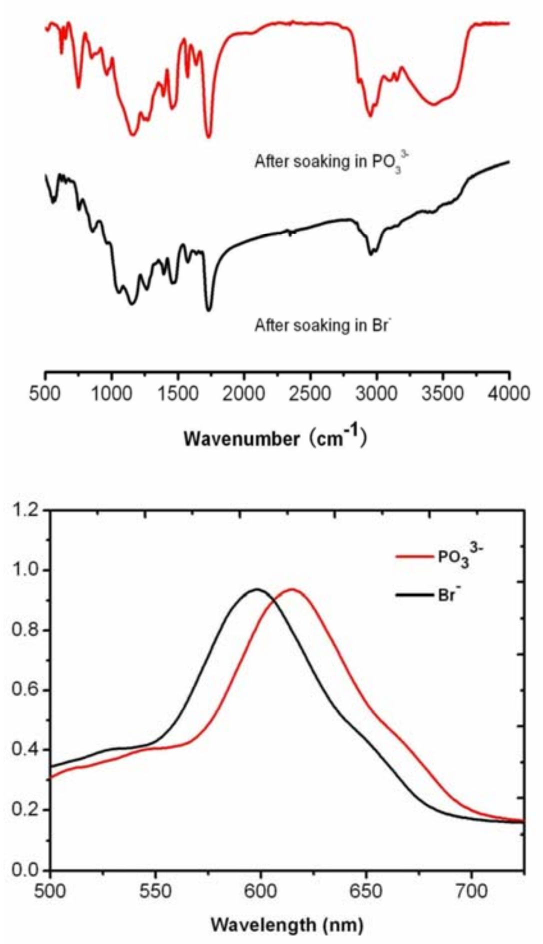


Figure S3 FTIR spectra (top) and optical response (below) of the PIL film with Br^- as counteranion as well as after anion exchange with PO_3^{3-}

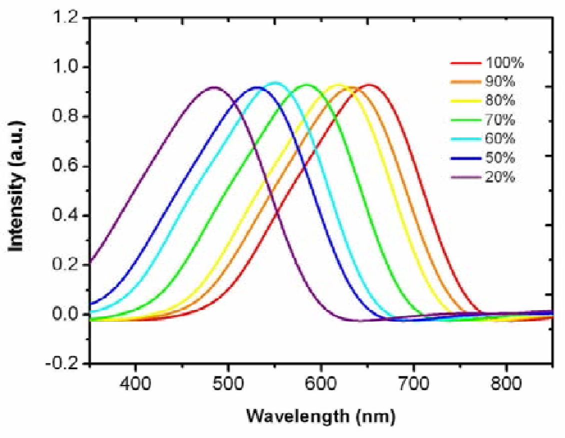


Figure S4 Optical response of the photonic PIL film with PO_3^{3-} as counteranion with the exposure to different humidity

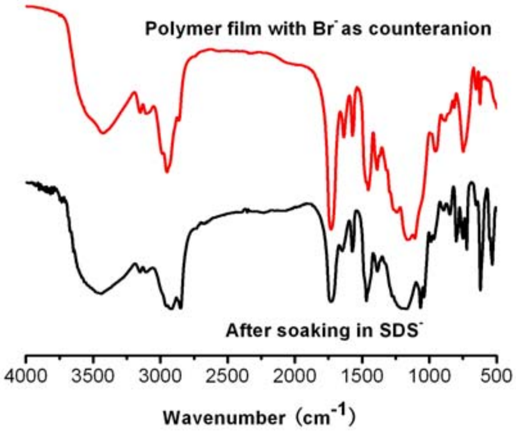


Figure S5 FTIR spectra of the PIL film with Br⁻ as counteranion as well as after anion exchange with SDS

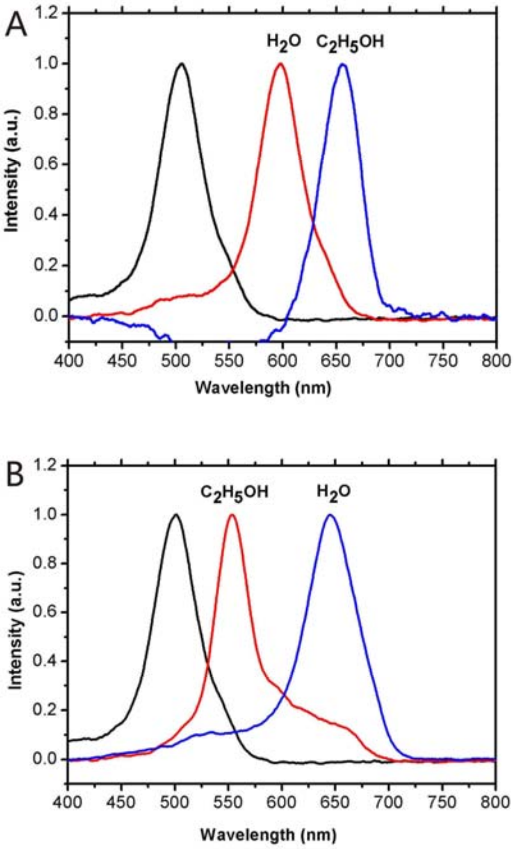


Figure S6 Optical response of the PIL films with different counteranions toward humidity (RH 100%) and saturated ethanol vapor: A) PIL film with Br- as counteranion; B) PIL film with SDS- as counteranion

Acknowledgements

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