ADVANCED MATERIALS

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Photonic Ionic Liquids Polymer for Naked-Eye Detection of Anions**

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It is well known that anions play numerous fundamental roles in chemical, biological, physiologic and environmental processes, mainly because of their ubiquity.[1] Many literatures have been reported to synthesize special receptors for certain anion recognition,[2] more appealing approaches of which involve the design of luminescent and colorimetric molecules for optical anion recognition and sensing.[3] Such optical sensors generally recur to the synergic strategies by combining specific anionic recognition receptor and signaling chromophore unit, in which the receptor is designed to selectively bind a certain anion and the signaling unit transforms an anion binding into readable signals. However, for many anionic receptors time-consuming and tedious synthetic work is required, and the available optical anionic sensing systems undergoing color changes, even ''naked-eye'' sensing, at present remain quite limited.[4] On the other hand, the inherent limitation of anionic receptors is that many anion-binding sites suffer competition from the strong hydrogen-bonding ability of water molecule, especially for the selective recognition of analogous anions.[5] Hence, it is still a challenge and highly desirable to develop a handy and sensitive signaling protocol for both qualitative and quantitative analysis of anions without complex organic synthesis and precious instrumental involvement.

Ionic liquids (ILs), mainly involving imidazolium cation, have attracted increasing interest due to their unique physicochemical properties and ever-expanding applications.[6] Recently, a number of literatures have described the use of imidazolium-based ILs for the regeneration of biopolymers, anion sensing, protein detection and sensitive nanomaterials.[6,7] An interesting property of ILs is that their hydrophilicity and hydrophobicity can be easily tuned by simply exchanging counteranions, and consequently the solubility of ILs in organic solvents as well as in water can be adjusted.[6] Utilization of this tunable property of ILs opens a new way to control the properties of the surface and materials.[8] For example, Texter and coworkers have synthesized an imidazolium-based IL copolymer, which can be reversibly tuned between a hydrogel and a porous structure by exchanging counteranions,[9] due to the substantial volume change of ILs induced by its hydrophilicity or hydrophobicity change. It is conceivable that, if two unique properties of ILs and photonic crystal are combined, a novel anionic signaling strategy for ''naked-eye'' anions detection could be developed based on the counteranion exchanging to turn the stop band of photonic crystals.[10] The signaling unit is a photonic IL, which has a 3D ordered inverse opal structure. The intentional photonic IL has not only the 3D highly ordered macroporous structure, but also is sensitive to the type of counteranions and can transform anion exchanging events into readable optical signals (color change), due to the shift of its stop bands derived from its volume change (Scheme 1). In this communication, we demonstrate that based on the combination of the unique properties of both ILs and photonic crystals this new concept can be efficiently employed for handy, rapid, and sensitive naked-eye detection of anions.

Three-dimensional ordered photonic IL was made from a polymerization of imidazolium-based IL monomer in a two-step procedure. Silica colloidal crystal arrays were used as templates to obtain the inverse opal structure. The polymerization system of IL monomer (1 mM), methyl methacrylate (1 mM) and initiator (AIBN) were mixed with cross-linker ethylene glycol dimethacrylate (2 mM) in a mixed solvent of methanol and chloroform (1:1 v/v), and infiltrated into the silica colloidal crystal voids until they were transparent, then exposure to an UV light for photopolymerization. After the removal of silica particles by HF etching and thoroughly washing with an amount of deionized water, the 3D ordered photonic IL films with inverse opal structure were obtained on PMMA substrate and used for anion detection. Figure 1 shows the SEM images of the used SiO_2 colloidal crystal and the resulting photonic IL film. This film has a thickness of about 2 μm and possesses a 3D highly ordered and interconnected macroporous structure. When the same colloidal templates are used, the preparation of photonic IL material is highly reproducible.

The initial structure of the fabricated photonic IL film is shown as Figure 2A. The interconnected, highly ordered porous structure cannot only directly generate optical signals due to Bragg diffraction, but also be favorable for the rapid counteranion exchanging within IL films. Since different anion of imidazolium moiety greatly affects the hydrophilicity or hydrophobicity of IL units,[6,7] when a photonic IL film is

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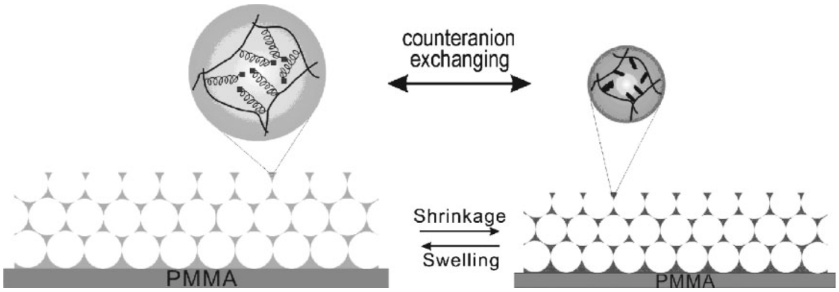


Scheme 1. Schematic illustration of the concept for anion detection based on the combination of the unique properties of both ILs and photonic crystals.

soaked in an anion aqueous solution, counteranion exchanging will induce its volume change[9] and as a consequence, cause well-defined shift of the stop band of the photonic IL film depending on the type of counteranion. As shown in Figure 2C, the prepared photonic IL film selectively exhibits different stop band shifts upon soaking in diversified aqueous anion solutions. More interestingly, these stop band shifts can be directly observed by the naked eye because of the substantial color changes (Fig. 2D). For example, the original photonic IL film is pink in deionized water, but changes to blue upon exposure to an aqueous solution of lithium bis(trifluoromethylsulfonyl) imide ($LiTf_2N$). Moreover, with the increase of the hydrophobicity of IL units upon counteranion exchange, the photonic IL film changes gradually from the transparent into semitransparent, even opaque, probably due to the increased light scattering of the interface between water phase and hydrophobic gel. Correspondingly, the opened pores become closed, due to the strong shrinkage of IL film (Fig. 2B). Indeed, FTIR confirmed the occurrence of the anion exchange and the existence of the detected anions. Figure 3 shows the FTIR spectra of the photonic IL films after the exposure to different anion aqueous solutions (0.02 M). It is clearly seen that the characteristic absorption bands of the detected anions 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}.[11]

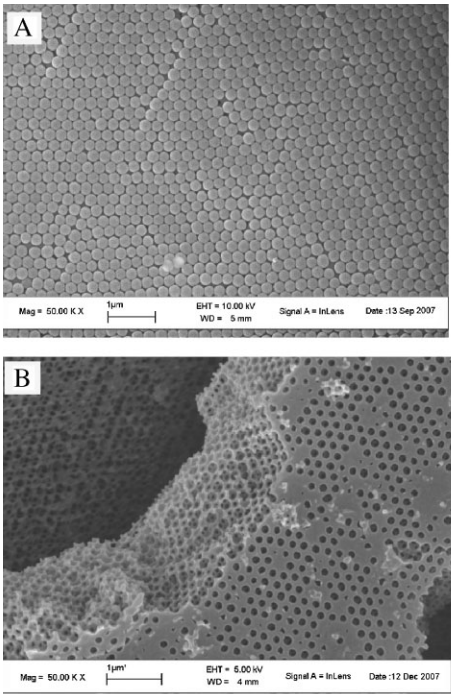


Figure 1. SEM images of the used silica colloidal crystal template with about 260 nm particle size (A) and the prepared photonic IL film (B).

In the present work, counteranion exchanging was carried out from the hydrophilic to the hydrophobic anions. The conversed way was also tested, but the photonic IL films presented partial reversibility in aqueous solution. The possible reason is that the IL gel binding more hydrophobic anions forms a hydrophobic interface between the gel and water phase, which baffles the diffusion and exchange of the more hydrophilic anions onto binding sites of ILs in aqueous solution. However, if the IL gel is soaked in 0.2 M NaOH for 12 h, it is found that the IL gel could be regenerated. Three different sodium phosphates (Na_3PO_4, Na_2HPO_4 and NaH_2PO_4) were also selected as an example to examine the impact of valence of anions on the photonic IL films. The obtained result shows that the photonic IL films seem insensitive to the valence of anions in our case (Fig. 4A). Additionally, it was found that the prepared photonic IL films are also insensitive to pH diversification (Fig. 4B), which is beneficial for the anionic sensors based on photonic ILs to avoid the strong hydrogen-bonding influence from water.

For quantitative determination of anions in aqueous solutions, both NO_3^- (more hydrophilic) and Tf_2N^- (more hydrophobic) were taken as examples of anions to determine their concentrations by two photonic IL films. Figure 5 shows that the stop bands of both films shift to the short wavelength range. With the increase of anionic concentrations for both cases, more anions bind onto IL films by anion exchange, and as the consequence, the increase of hydrophobicity of ILs gradually induces volume change and shift of the stop bands of photonic IL films towards shorter wavelength range. To compare both anions, the latter causes a maximum blue-shift of 76 nm (Fig. 5A), which is much larger than that of the first one (18.4 nm, Fig. 5B). Obviously, the reason is that NO_3^- is more hydrophilic than Tf_2N^-.

In the photonic IL films, the alkyl chains with terminal IL groups show varied interactions with different polar solvents, and thus can shrink or extend like a spring upon exposure to different solvents (Scheme 1). Therefore, besides the detection of anions, we found that the photonic IL films can in principle be used to detect solvents of different polarity. Figure 6 demonstrates that the pink photonic IL film is achromatic and transparent in strongly polar dimethyl sulfoxide, but becomes blue and semitransparent in nearly nonpolar hexane. The reason is that these photonic IL films with many ionized side

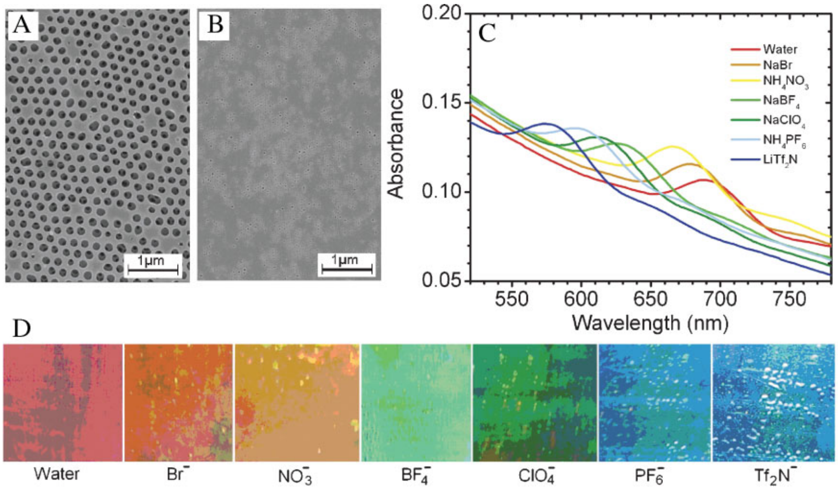


Figure 2. SEM images of the fabricated photonic ionic liquid film with opened pore structure (A) and closed pore structure (B). C) Stop band shifts of the photonic ionic liquid film upon soaking in diversified 0.02 M anions aqueous solutions. D) The induced color changes of the photonic ionic liquid film upon soaking in diversified 0.02 M anions aqueous solutions.

chains are solvophilic to strong polar solvents, but solvophobic to non polar solvents. As a consequence, these photonic IL films present different volume changes and stop band shifts in different solvents due to the different solvation effects, suggesting that the polarity of solvents can also shift the stop bands of the photonic IL films. Like in diversified anion solutions, the photonic IL films show reversible color changes in different solvents.

The area of anion detection and the development of chemoresponsive receptors and reporting systems that work on anions has been a challenge. Electrochemical, optical, colorimetric, and chromatographic techniques to detect anions already exist. But despite being accurate, most of the techniques are labor-intensive, expensive, and require a high level of expertise.[12] Compared to these methods, however, the new concept described here does not have such problems and exhibits several desirable advantages.

In conclusion, based on the combination of the unique properties of both ILs and photonic crystals, this work demonstrates a new concept for anion detection in a handy, rapid and sensitive way. Through simple counteranion exchanging of the pendant imidazolium IL units the 3D highly ordered IL porous structure can directly sense different anions and easily convert the anion detection events into readable optical signals with color changes. On the other hand, the constructed photonic IL also shows promise for the detection of solvents with different polarities. Besides imidazolium IL units, this reported concept or protocol might be general and easily amenable to adaptation for other ionic liquids. Since there are thought to be at least one million possible ionic liquids,[13] we believe that the combination of the unique properties of both ILs and photonic crystals could open immense opportunities for constructing novel advanced materials. The resulting 3D

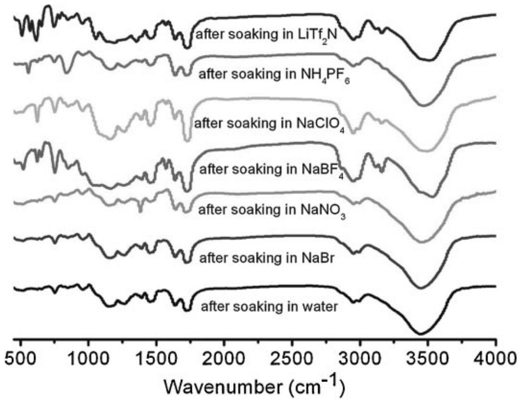


Figure 3. FTIR spectra of dried photonic IL films after soaking in diversified anions aqueous solutions for 2 h.

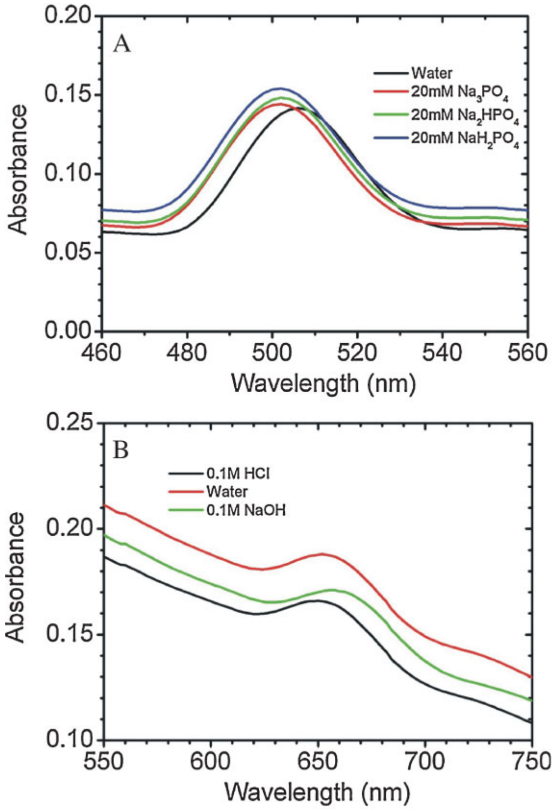


Figure 4. A) Stop band shifts of a photonic IL film soaked in three sodium phosphates with 0.02 M; B) stop band shifts of a photonic IL film soaked in 0.01 M HCl, deionized water and 0.01 M NaOH.

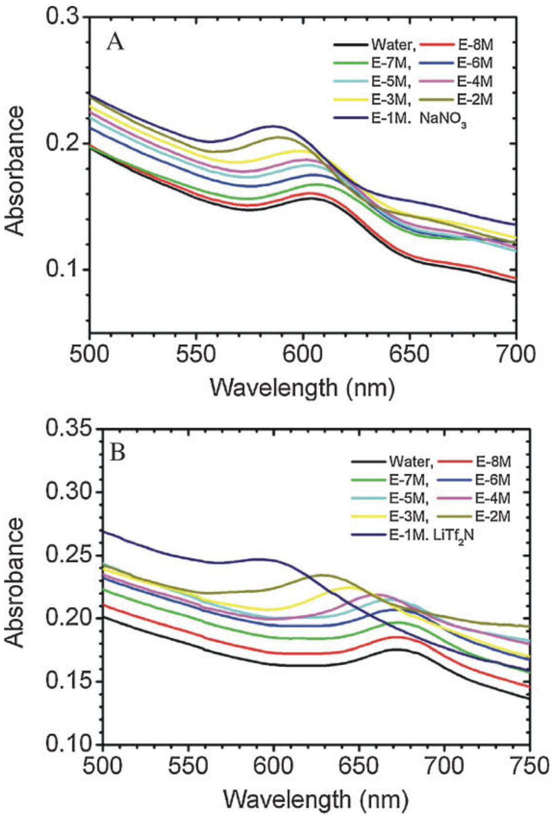


Figure 5. A) Stop band shifts of a photonic ionic liquid film upon soaking in diversified concentrations of $NaNO_3$. B) Stop band shifts of a photonic ionic liquid film upon soaking in diversified concentrations of $LiTf_2N$.

ordered IL should not only be a useful and versatile platform for the design and development of anion sensory systems and multifunctional materials, such as separation, ionic conductive or catalytic membranes by simple ionic exchange process, but also holds considerable potential in tuning optical properties of photonic crystals.[14]

At present, the reported photonic IL film has anion selectivity only when all anions have the same concentration. To overcome this drawback, we will resort to the cross-reactive sensor array approach.[15] The related work is ongoing in our lab.

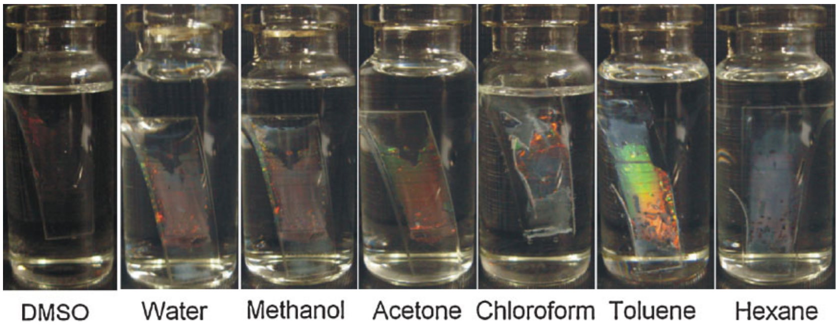
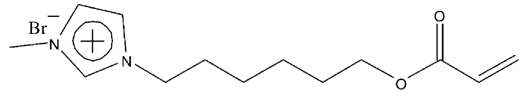


Figure 6. Colors of the photonic ionic liquid films upon soaking in diversified solvents.

Experimental

Chemicals: All solvents and chemicals are of reagent quality and were used without further purification unless special explanation. 2,2′-Azobisisobutyronitrile (AIBN), ethylene glycol dimethylacrylate (EGDMA) and lithium bis(trifluoromethylsulfonyl)imide ($LiTf_2N$) were obtained from Arcos. All solvents and chemicals were supplied by local suppliers. Common glass slides were cut to be 50 × 20 mm and immerged in H_2SO_4/H_2O_2 mixture for 12 h, following rinsing with deionized water in ultrasonic bath for three times and then dried for use. All 10 ml vials for colloidal crystals growth and a reactive flask must be very cleaned by rinsing with H_2SO_4/H_2O_2 mixture and deionized water. PMMA slides with 50 mm × 20 mm × 1.5 mm for photonic IL film supports were cleaned with anhydrous ethanol.

Synthesis of Polymerizable Ionic Liquid [1-(2-acryloyloxyhexyl)-3-methylimidazolium bromide, IL-Br]: A mixture of crylic acid (1 g, 1 mol), 6-bromo-1-hexanol (3.018 g, 1.2 mol), *N,N′*-dicyclohexyl carbodiimide (DCC 3.15 g, 1.1 mol), and 4-dimethylaminopyridine (DMAP 1.7 g, 1 mol) in anhydrous CH_2Cl_2 (150 mL) was stirred at room temperature for 24 h. After the reaction mixture 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 7-bromohexylacrylate as a pale yellow liquid for the next step.



Polymerizable ionic liquid monomer (IL-Br)

A mixture of 7-bromohexylacrylate (1.50 g, 4.25 mmol) and 1-methylimidazole (0.42 g, 5.10 mmol) and a small amount of 2,6-di-*tert*-butyl-4-methylphenol (inhibitor) was stirred at 45 °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 yellow viscous liquid 1-(2-acryloyloxyhexyl)-3-methylimidazolium bromide (IL-Br). The viscous liquid was dried under vacuum at room temperature as the pale yellow liquid. ^1H NMR (300 MHz, $CDCl_3$, δ): 10.48 (m, 1H, N–CH–N), 7.28–7.27 (s, 2H, N–CH=CH–N), 6.37–6.36 (m, 1H, CH_2=CH), 6.16–6.12 (m, 1H, CH_2=CH), 5.85–5.84 (m, 1H, CH_2=CH), 4.38–4.35 (t, 2H, N–$CH_2(CH_2)_6$O–), 4.13 (s, 3H, N–CH_3), 2.05–1.98 (t, 2H, N–$CH_2(CH_2)_6$O–), 1.68–1.65 (m, 2H, –$OCOCH_2CH_2$), 1.41–1.21 (m, 4H, –$3CH_2CH_2$–).

Instrumentation: ^1H NMR spectra were obtained by a JEOLJNM-ECS 300NMR spectrometer. UV-vis spectra were carried out by a PerkinElmer Lambda35 spectrometer. The photopolymerization was carried out under UV light (FUSI Electric ST3) at 16 W. A centrifuge (Anke TDL-60B, Shanghai, China) was used for centrifugation of colloidal particles from reactants. Photographic images of the color change of IPP films were obtained by using a common digital camera under daylight lamp.

Synthesis of Monodisperse SiO_2 Particles: First, 12 g tetraethoxylsilane (TEOS) and 180 ml anhydrous ethanol were mixed in a 250 ml flask, stirred intensively with a magnetic beater, and then pouring in slowly 25 mL ammonia. After 24 h, the colloidal particles were obtained by centrifugation and rinsed using anhydrous ethanol for 3 times to expunge residues. The size of SiO_2 particles is about 260 nm.

Preparation of Silica Colloidal Crystals and 3D Ordered Photonic IL Films: The obtained monodisperse SiO_2 particles were dispersed in anhydrous ethanol to form a SiO_2 colloidal solution with weight concentration of about 1%, and then allotted into 10 mL cleaning vials. A cleaning glass slide (50 mm × 20 mm) was put vertically into each vial. After complete volatilization of ethanol, SiO_2 colloidal crystal was formed on both sides of the glass slide. During that time, it is very important to avoid vials from shake and airflow disturbance. Normally, there are few to tens layers of SiO_2 arrays on glass slides depending on concentration of colloidal solution, the thickness of colloidal arrays are thus few to tens micrometers. Figure 1 is the SEM image of SiO_2 colloidal crystals, which shows that the crystal array is a close-packed face-centered cubic (fcc) structure.

Prior to fabrication of a photonic IL film, 1 mM IL-Br, 1 mM MAA, and 2 mM EGDMA were mixed in a mixing solvent of 1 g methanol and 1 g chloroform under ultrasonic for 5 min. After adding 0.05 mM AIBN and degassing by nitrogen for 10 min, the homogeneous monomer mixture was dropped onto silica arrays. Once the colloidal crystals became transparent, indicating successful infiltration, excess precursors were removed by covering a clean PMMA slide (50 mm × 20 mm × 1.5 mm), and the remaining mixture was photopolymerized in an ice bath under an UV light at 365 nm for 2 h. The sandwich was immerged into 1% hydrofluoric acid for 2 h to separate double slides and fully etch the silica colloids. After washed by an amount of deionized water, the photonic IL film on PMMA substrate is ready for anions signaling test. For free films preparation, the covering PMMA slides were changed to be glass slides.

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