Functional Microspheres

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Inverse Opal Spheres Based on Polyionic Liquids as Functional Microspheres with Tunable Optical Properties and Molecular Recognition Capabilities**

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***Abstract:** Based on the combination of the unique features of both polyionic liquids and spherical colloidal crystals, a new class of inverse opaline spheres with a series of distinct properties was fabricated. It was found that such photonic spheres could not only be used as stimuli-responsive photonic microgels, but also serve as multifunctional microspheres that mimic the main characteristics of conventional molecules, including intrinsic optical properties, specific molecular recognition, reactivity and derivatization, and anisotropy.*

Self-assembled periodic arrays of colloids (colloidal crystals) and their inverted structures (inverse opals) have drawn considerable attention in recent years, which is due to their unique band-gap optical (photonic) properties and high porosity.[1] Based on these useful structures, various functional materials and chemical systems have been developed and exploited in numerous applications such as in sensing and diagnostic systems, photonic-plasmonic devices, high-efficiency energy conversion and storage, hierarchically structured catalysts, and drug delivery.[1,2]

In this respect, spherical colloidal crystals (photonic spheres), three-dimensional periodic arrays of colloidal particles with a spherical geometry, are of particular interest.[3] Unlike conventional 2D or 3D film-type colloidal crystals, the spherical colloidal assemblies or their inverted structures can behave like “supracolloids”. They have the mobility of conventional colloidal suspensions and higher diffusion flux owing to the radial diffusion. Moreover, these spheres exhibit an isotropic band-gap property that is not observed for conventional colloidal crystals in film form; that is, these spheres exhibit the same reflection color for a fixed incident light source independent of the rotation of balls.[3] These distinctive structural and optical features make supracolloids more flexible and attractive for the exploration of new sophisticated applications. Herein, a new kind of monodisperse inverse opaline sphere, namely polyionic liquid-based spherical inverse opal, is reported. We found that such photonic microspheres can mimic the main characteristics (for example, intrinsic optical properties, molecular recognition, derivation, and anisotropy) of simple conventional molecules and serve as multifunctional microspheres.

Ionic liquids (ILs), a class of compounds consisting of organic cations and anions, show a series of unique properties, including negligible vapor pressure, nonflammability, good chemical and thermal stability, a wide electrochemical window, and high ionic conductivity.[4] Moreover, such distinct properties can be easily and individually manipulated by modulating the combination of cation and anion, providing unprecedented tunability.[5] Thereby, these favorable properties and features make them ideal candidates not only as green solvents for synthesis, catalysis and separation, but also as designable building blocks for the development of advanced materials with controllable physical and chemical properties or even specific functions.[6] It is conceivable that if the unique properties of ILs and spherical colloidal crystals are combined, a chemical system with novel properties beyond those of their constituent components could be developed. Indeed, we found that the prepared polyionic liquid (PIL) inverse opaline microspheres (PIL-IOMS) could not only be used as stimuli-responsive photonic microgels, but also serve as functional microspheres that mimic the main characteristics of conventional molecules. The PIL-IOMS exhibit intrinsic photonic property arising from their 3D-ordered macroporous structure, which is very sensitive to their environment. The presence of imidazolium moieties endows PIL-IOMS with unique reactivity, and in principle unlimited products could be derived from the original PIL-IOMS through simple counterion exchange reaction. Interestingly, like small molecules, the PIL-IOMS homologues could be arranged to form a cross-reactive sensor array for label-free discrimination of anions and organic solvents. Furthermore, anisotropy could be easily introduced into PIL-IOMS by simple contact printing using an aqueous solution of desired anion as chemical “ink”, offering the capability of the interaction of PIL-IOMS in specific directions.

The PIL-IOMS were fabricated by using a two-step procedure (Supporting Information, Scheme S1). First, uni-

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form silica nanoparticles were assembled into monodisperse spherical colloidal crystals by droplet-based microfluidic synthesis.[7] Silica nanoparticles with a diameter of 200 nm, 250 nm or 300 nm were used, and the resulting 300 μm microspheres were composed of hexagonal arrays of silica nanoparticles (Supporting Information, Figure S1). Second, the imidazolium-based IL monomers were infiltrated into the voids of the photonic microspheres by capillary force. After polymerization under UV radiation followed by removal of silica nanoparticles using HF, the inverted structure, namely PIL-IOMS, were obtained. In our case, three different IL monomers (Supporting Information, Scheme S1) were used, and the corresponding PIL-IOMS homologues were fabricated. Figure 1 a shows a typical optical image of the prepared PIL-IOMS. All spheres within a given batch display excellent uniformity in size and show brilliant color, indicative of the presence of periodically ordered structure. Under SEM observation, an ordered interconnected porous structure was detected (Figure 1 b) and the ordering structure on the surface extended through the entire spheres to its center (Figure 1 c). Dependent on the diameter of the silica nanoparticles used, the optical property (stop-band) could be widely tuned from 400 nm to 700 nm. Figure 1 d shows UV/Vis reflection spectrum of the PIL-IOMS prepared using 200 nm silica particles, which exhibit an isotropic stop-band at 420 nm.

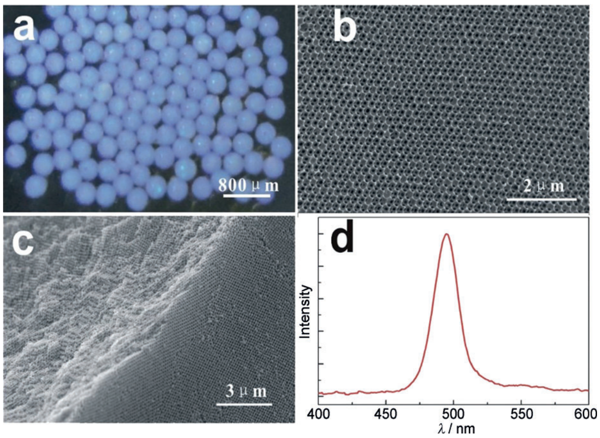


Figure 1. a) Optical image of the prepared PIL-IOMS; b) SEM image of the PIL-IOMS; c) SEM image of the cross-section of the PIL-IOMS; d) UV/Vis reflection spectrum of the PIL-IOMS.

Compared to conventional organic molecules, the imidazolium-based ILs possess multiple intra- and intermolecular interactions including electrostatic forces, π–π, hydrogen bonding, and van der Waals forces,[6a] which make them very sensitive to external environments. Indeed, we found that the prepared PIL-IOMS showed remarkable multiple stimuli-responses. Upon exposure of PIL-IOMS to different solvents, the stop-band shifted to different extent and a dramatic change of optical property was observed (Supporting Information, Figure S2). Interestingly, when PIL-IOMS are immersed in an aqueous solution of a given anion, counterion exchanging will induce a volume change, and as a result, cause the shift of stop-band of the photonic microspheres. Figure 2 shows the optical response of the PIL-IOMS upon dispersed in different counterion aqueous solutions. Clearly, the stop-band of the PIL-IOMS shifted to short wavelength from 604 nm to 569 nm, 530 nm, 511 nm, 502 nm, 490 nm, respectively, after the replacement of Br^- with ClO_4^-, NO_3^-, BF_4^-, PF_6^-, and Tf_2N^- as counterions. Remarkably, these anion exchange processes took place rapidly and were accompanied with clear color change of polymer spheres that is directly observable by the naked eye (Figure 2). FTIR spectroscopy confirmed the rapid occurrence of the counterion exchange process. After one minute exposure of PIL-IOMS to aqueous solution of a given anion, the absorption bands of Br^- disappeared and the characteristic bands of the used anions were clearly detectable: NO_3^- at 1641 cm^{-1}, ClO_4^- at 958 cm^{-1}, BF_4^-at 1083 cm^{-1}, PF_6^-at 838 cm^{-1}, and Tf_2N^-at 1356 cm^{-1}.

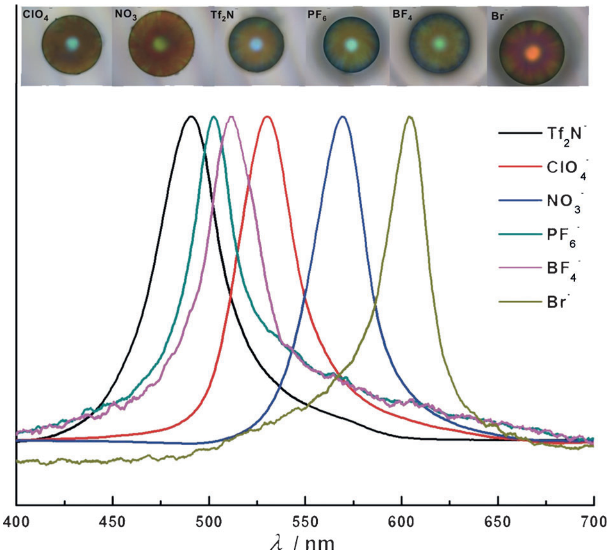


Figure 2. Optical response of the prepared PIL-IOMS upon exposure to aqueous solution of six different counterions. Inset: Optical images of the PIL-IOMS after the exposure of different counterions.

Under normal incidence geometry, the Bragg reflection (stop-band) wavelength λ is determined by the lattice constant d and the refractive index of inverse opal structure n_{eff} [Equation (1)].[8]

$$\lambda = 2\,d\,n_{\mathrm{eff}} \qquad (1)$$

In our case, the refractive index of the prepared PIL-IOMS remains nearly unchanged after the anion exchange. Thus, the change of the lattice constant d should be responsible for the observed significant shift of the stop-bands. In fact, we also found that with the increased hydrophobicity of the introduced counterion the size and pore structure of the PIL-IOMS shrank continuously, leading to the reducing of parameter d. For the case of Tf_2N^- as counterion, for example, the size of resulting spheres became only half of that of the original PIL-IOMS (NO_3^- as anion) and the initial interconnected open pores closed up (Supporting Information, Figure S3). In previous studies,[6,9] had already been shown that the physicochemical properties of PILs are very sensitive to the counterions and precisely tunable by variation of the counterions. For our system (PIL-IOMS), however, this sensitivity of PIL can be rapidly, being directly converted into readable optical signal through its periodically ordered pore structure. This result implies that, in contrast with conventional photonic films, the prepared PIL-IOMS, which are easily dispersible in various media, could be used as a probe "dye molecule" to sense its environments.

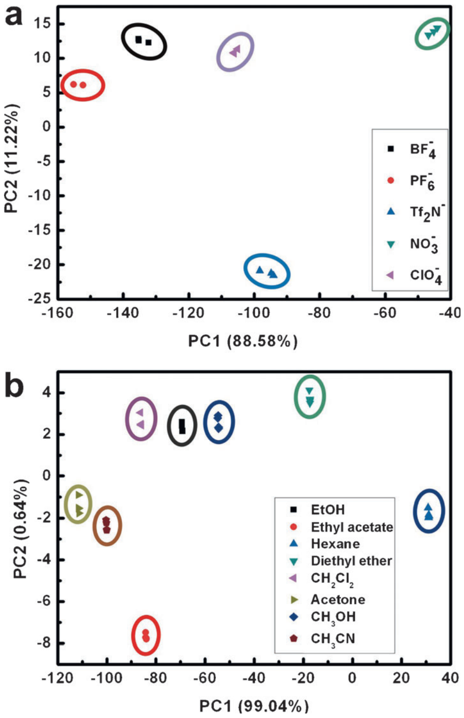


Figure 3. PCA plot of the color changes resulting from the exposure of the PIL-IOMS array to different counterion solutions (a) and different solvents (b).

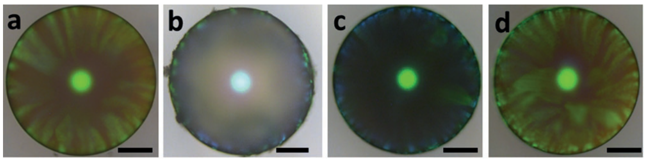
Inspired by the concept of a cross-reactive sensor array,[10] the PIL-IOMS homologues (PIL-IOMS-A, PIL-IOMS-B and PIL-IOMS-C) were fabricated to collect the fingerprint of the dispersed media. Whereas classical chemosensing techniques inspired by the "lock-and key" approach depend on the synthesis of a selective receptor for a target analyte, fingerprint-based sensing depends on the development of an array of cross-reactive receptors, which produce a collection of responses (fingerprints) upon interaction of the array with a target analyte.[10] Based on the fingerprint pattern, a specific sensing and discrimination of the exposed environments is expected. The optical responses (fingerprints) of each of the PIL-IOMS to target anions is shown in the Supporting Information, Figure S4. In our case, five anions (ClO_4^-, NO_3^-, BF_4^-, PF_6^- and Tf_2N^-) were selected for investigation. In the created anion-sensing array, the initial optical signal (P_0) of each PIL-IOMS sensing element was first determined. Then, each sensing element was exposed to the five different anion containing media for a given time and the shifted optical signal (P) was obtained. The sensing measurement was repeated five times for each anion. A plot of the change ($P-P_0$) in optical signal (stop-band) as a difference of the original (P_0) gives a 3D fingerprint of each detected anion (Supporting Information, Figures S4, S5), showing the differential optical responses. The principal component analysis (PCA), an important chemometric method, was used to decompose complex optical fingerprint patterns obtained from multiple signaling PIL-IOMS and repeating experiments into simplified components. PCA is a non-supervised mathematical method that can transform a number of correlated variables into uncorrelated variables called principal components (PCs).[11] Commonly, the first principal component (PC1) contains the highest degree of variance, and the other PCs follow in the order of decreasing variance. Thus, by using PCA, the most significant characteristics of the whole data can be into a lower dimensional data set without losing much information. In other words, we can use only principal component 1 (PC1) and principal component 2 (PC2) to be plotted graphically to allow the description of the discriminatory power of the PIL-IOMS photonic sensor array. Figure 3a shows the obtained two-dimensional PCA plot for ClO_4^-, NO_3^-, BF_4^-, PF_6^-, and Tf_2N^- to the array composed of PIL-IOMS-A, PIL-IOMS-B, and PIL-IOMS-C. The PCA plot shows an excellent discrimination of the five tested anions and the first principle component possesses 99.80% of variance. In this PCA plot (Figure 3a), each anion could be clustered into tight distinct groups, demonstrating the reproducibility of the response for each anion. To highlight the discrimination power, a "jack-knife matrix" validation procedure was used to test the predictability of the formed array. All performed analysis allows 100% classification of anions in our case.

For the applicability of the fabricated sensor, the sensing in complex fluids such as a mixture of anions is important and necessary. Thus, we performed the related tests as demonstration. It was found that the PIL-IOMS cross-reactive sensor array shows an excellent discrimination not only for different anions (five tested anions) but also for their binary or tertiary mixtures (Supporting Information, Figure S6). Additionally, in the presence of trace one ion in another ion solution the PIL-IOMS sensor array still shows the corresponding optical responses and exhibits the differential sensing (Supporting Information, Figure S7). In our case, the NO_3^- aqueous solutions containing 20 mol%, 10 mol%, or 5 mol% BF_4^- anion were used in our experiments.

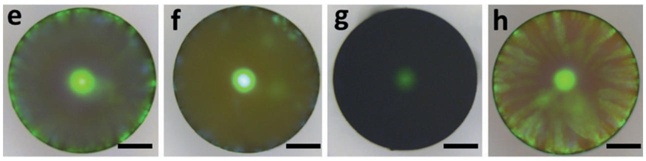
Additionally, we also found that the PIL-IOMS photonic sensor array could be used to discriminate organic solvents with different polarity. As in the case of anion detection, the individual PIL-IOMS sensor element shows varied interactions with different solvents, and thus response fingerprints can be easily collected from the shifts of the stop-bands of PIL-IOMS array. As shown in the generated PCA plot (Figure 3b), all analytes are grouped in well-separated and tight clusters even for chemically similar organic solvents (for example methanol and ethanol) and strong discriminary power is achieved by using our sensor array. All these results indicate that, like small molecules, the constructed "dye molecule" PIL-IOMS indeed can be arranged to form an array for realizing specific molecular (ionic) recognition. Moreover, compared to the reported sensor arrays, the array built from PIL-IOMS exhibits a series of distinct advantages.

First, as the optical property of PIL-IOMS originates from their periodic pore structure, the quenching and bleaching problem of dye molecules could be avoided (label-free detection). Importantly, the molecular recognition can be directly converted into readable optical signal and the shortcomings of indicator displacement, the strategy often used in arrays,[10] can be avoided. Second, the PIL-IOMS are microscale spheres and easily dispersible in various media. These features make PIL-IOMS excellent handling in array construction and permit the user to avoid tedious handling of multiple aqueous solutions in well plates. Finally, based on the simple counterion exchange of ionic liquid, cross-reactive sensor array with dynamic tunable feature can be rapidly and efficiently constructed.

Apart from the novel molecular recognition function, the PIL-IOMS show attractive "reactivity", like conventional molecules, and new products can be derived in a wide extent in a non-covalent and modular manner. Based on the concept of "task-specific" ionic liquids,[12] a variety of functional groups as anions can be readily introduced into the PIL-IOMS by simply anion exchange reaction, leading to new photonic spheres with desired functions. As a demonstration, a series of functional products was derived from the original PIL-IOMS, including photonic spheres with magnetic, catalytic, electrochemical active, redox-active, oxidative, or plasmonic function (Figure 4). Various spectroscopy methods, microscopy techniques, and electrochemical means were used to confirm the successful introduction of the corresponding functions into the PIL-IOMS (Supporting Information, Figure S8). For clarity, anionic dyes were taken as an example, and confocal fluorescence microscopy was employed to investigate whether the dyes penetrated into the microspheres. The result confirmed that the dye did not remain at the surface, but penetrated into the interior of the microspheres. In fact, as one of the distinct properties, counterion exchange capability of ionic liquids, offers virtually unlimited tunability. Thus, through rational modulation of the combination of cations and anions, it is envisaged that tremendous new functional photonic systems could be derived from the PIL-IOMS (Figure 5).



Hydrophilic PIL-IOMS (Br^- as anion) | Hydrophobic PIL-IOMS (Tf_2N^- as anion) | Redox active PIL-IOMS ($FeCN_6^{3-}$ as anion) | Magnetic PIL-IOMS ($FeCl_4^-$ as anion)



Catalytic PIL-IOMS (POM as anion) | Oxidative PIL-IOMS ($AuCl_4^-$ as anion) | Plasmonic PIL-IOMS (Au particles as dopant) | Bioactive PIL-IOMS (Dextran as anion)

Figure 4. Optical images of diverse functional products derived from original PIL-IOMS through a simple counterion exchange reaction. The scale bar is 100 μm.

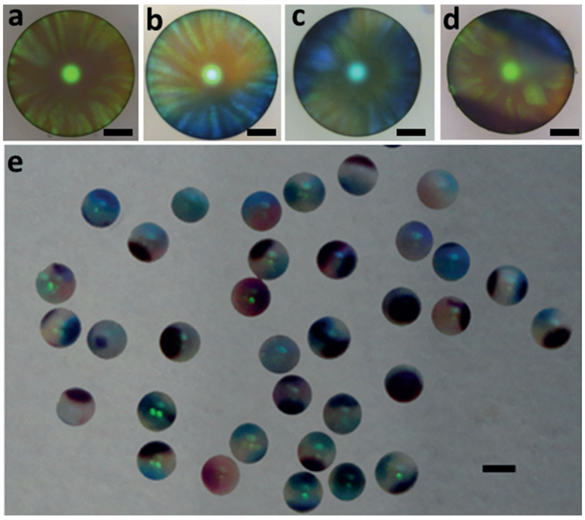


Figure 5. Optical images of the PIL-IOMS with different patchy structures: a) original isotropic PIL-IOMS; b) A-B type; c) A-B-A type; d–e) A-B-C type. Scale bars: 100 μm and 500 μm.

To mimic atoms and molecules in their directional interactions, various strategies have been developed to impart colloidal particles with chemical and morphological anisotropy.[13] In this respect, owing to the counterion exchange property of ionic liquids, the PIL-IOMS exhibit great flexibility in surface engineering and allow various anisotropic structures to be produced, and they can be functionalized correspondingly. By using a "sandwich" contact printing (μCP) method developed by us,[14] the patchy PIL-IOMS with A-B, A-B-A, or A-B-C structure were fabricated as a demonstration (Figure 5). In this work, for visualization two fluorescent counterions (Indigo carmine and SPADNS) were used as chemical "ink" and the PDMS elastomer was utilized as a stamp. We found that the μCP in our case proceeded very fast at room temperature. It took only several minutes to transfer the "ink" to PIL-IOMS by anion exchange exclusively in the area of contact. Furthermore, the contact time and pressure could be used to turn the size of the patches. Although only fluorescent patched PIL-IOMS were fabricated, in principle unlimited functionalized PIL-IOMS patchy particles are easily accessible through a simple anion-exchange reaction, including biomolecule-binding patchy particles and magnetic patchy particles. Compared to numerous anisotropic particles,[13] to the best of our knowledge, this is the first example of photonic patchy particles with such versatile tunabilty. The self-assembly of this new kind of patchy particles should afford novel hierarchically nanostructured optical materials or functional systems, which could hold promising applications in numerous areas.

In summary, based on the combination of the unique features of both PIL and spherical colloidal crystals, a new class of optical spheres with a series of distinct properties was fabricated. These spheres can serve as functional microspheres that mimic the main characteristics of real molecules, including intrinsic optical property, specific molecular recognition, reactivity and derivatization, and anisotropic features.

As multifunctional materials or a new class of building blocks, we believe these optical spheres could provide tremendous opportunities for the development of advanced applications or construction of new hierarchically nanostructured functional systems.

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