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Photonic Metal-Organic Framework Composite Spheres: A New kind of Optical Materials with Self-Reporting Molecular Recognition

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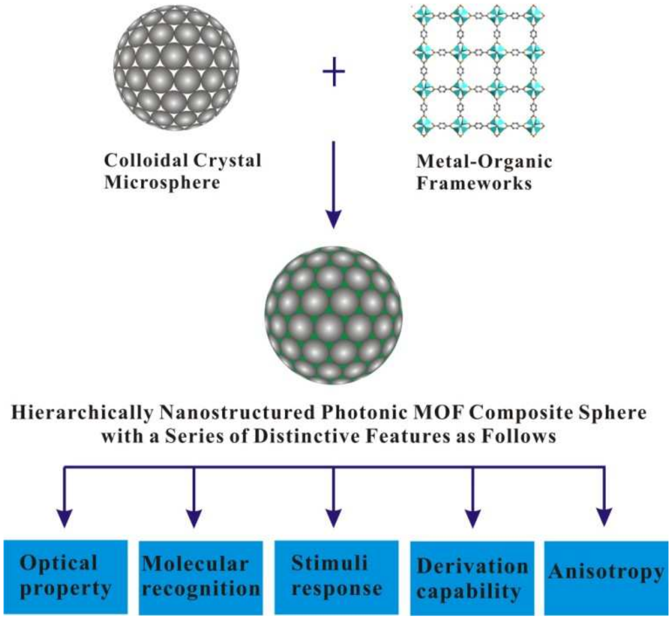
Exploiting metal-organic framework (MOF) materials as novel building blocks to construct superstructures with extended and enhanced functions represents a big challenge. In biological systems, the ordering of many components is not achieved by interaction of the components with each other, but by interaction of each component with the host protein which provides a matrix to support the entire assembly. Inspired by biological systems, in this work, a general strategy for efficiently spatial arrangement of MOF materials was developed by using spherical colloidal crystals as host matrices, affording a new class of highly tunable MOF composite spheres with a series of distinctive properties. It was found that the synergetic combination of the unique features of both MOF and photonic colloidal crystal imparted these hierarchically structured spheres intrinsic optical property, specific molecular recognition with self-reporting signalling, derivatization capability, and anisotropy. More importantly, the unique photonic band-gap structure integrated in these composite spheres provides a more convenient means to manipulate the photophysical and photochemical behaviour of the trapped guest molecules in MOF nanocavities.

Introduction

Metal-organic frameworks (MOFs) are a fascinating class of hybrid porous crystalline materials and are characterized by high porosity, large internal surface areas, tremendous porous structure diversity and tailorable chemistry.[1] These distinctive features make them very attractive for numerous applications, and especially when the sizes of MOFs are reduced into the micrometer or nanometer scale, their potential applications can be significantly extended due to the superior adsorption kinetics of guest species and dispersible nature distinct from bulk crystals.[2] In this respect, the synthesis of monodisperse MOF nanoparticles as building blocks to construct superstructures is expected to open up a new avenue for the development of sophisticated applications, in particular the fabrication of advanced materials with additional optical or photonic property. Recently, some progress has been made in this endeavor.[3] However, as the synthesis of monodisperse crystals with uniform sizes and shapes as well as the exploration of appropriate assembly techniques are prerequisite for the assembly of MOF nanocrystals, the construction of MOF superstructures represents a big challenge in this emerging area.[3] In this work, we report on a colloidal crystal spheres assisted strategy to facilely produce MOF superstructures with unprecedented flexibility, and demonstrate that the formed MOF photonic objects can be used as a novel class of optical materials for various advanced applications (Scheme 1).

Spherical colloidal crystals are three-dimensional (3D) periodic arrays of colloidal nanoparticles with a spherical geometry.[4] In comparison with conventional 2D or 3D film-type colloidal crystals,[5] the spherical colloidal assemblies can behave like “supracolloids”. They show the solution behaviour typical of conventional colloidal suspensions and have higher diffusion flux due to the radial diffusion. More importantly, these spheres exhibit isotropic photonic properties and display the same reflection colour for a fixed incident light source independently of the rotation of spheres.[6] These distinctive structural and optical features make supracolloids more flexible and attractive for the exploration of new sophisticated applications. In our case, the 3D-ordered internal void space of supracolloids is employed to realize the spatially arrangement of MOF materials. We found that this host matrix-assisted strategy is efficient to access MOF superstructures with tunable sizes, compositions and optical properties. Importantly, the synergistic combination of both unique properties of MOF and superstructure endows the used MOF with additional optical properties, and enable the formed MOF composite spheres to exhibit molecular recognition with self-reporting signalling.



Scheme 1 Schematic illustration of the strategy for efficient fabrication of MOF superstructures using colloidal crystal spheres as host matrices and their applications as a new kind of multifunctional materials.

Interestingly, when these photonic MOF spheres are arranged to form cross-reactive sensor array, label-free detection and discrimination of organic molecules can be easily achieved. Additionally, the rich host-guest chemistry of MOF offers convenient way to realize the spatio-temporal engineering of the surface of the photonic MOF spheres in a modular fashion, leading to isotropic and anisotropic spheres decorated with various functions. Moreover, these photonic spheres can be used as a new kind of building blocks to create hierarchically nanostructured materials with advanced optical properties.

Results and discussion

A droplet-based microfluidic approach was employed to fabricate the desired host matrices or scaffolds: colloidal crystal spheres (Scheme S1). Silicon oil was used as continuous phase and aqueous suspension containing uniform silica nanoparticles is dispersed phase. In our case, silica nanoparticles with a diameter of 200 nm, 250 nm or 300 nm were used. As droplet-based microfluidic synthesis is a well-established technique,[7] large numbers of droplets with different sizes and narrow dispersity can be easily generated by controlling the flow rates of the continuous and dispersed phases. After slow evaporation of the solvent in formed droplets, monodisperse spherical colloidal crystals formed and were used as scaffolds to mould the formation of superstructures of MOF materials.

Figure 1a displays the optical image of the resulting 300 μm microspheres composed of hexagonal arrays of 200 nm silica nanoparticles (Figure 1b), showing brilliant colour due to the ordered structure. As a proof of our concept, a clear precursor solution of HKUST-1 (a prototype MOF)[8] was firstly infiltrated into the interstitial sites of the prepared colloidal crystal scaffold followed by solvent evaporation for crystallization of MOF. To fabricate the MOF composite spheres with complete volume filling a simple microfluidic device was designed in our work (Scheme S2). Concretely, colloidal crystal spheres (hosts) were placed at the ends of microchannels, and due to capillary force MOF precursor solution were automatically infiltrated into the interstices. With the slow evaporation of the solvent from air-exposed side of the host, MOF precursor solution were continually infiltrated into the interstices and finally the MOF composite spheres with complete volume filling were achieved. Figure 1c shows the resultant composite products with uniform spherical morphology and blue colour. The SEM observation reveals that the composite products consist of the ordered silica nanoparticles with intergrown MOF crystals (Figure 1d). The SEM cross-section image also indicates that the MOF material grew homogeneously throughout the silica colloidal crystal sphere (Figure S1). X-ray diffraction (XRD) data (Figure S2) confirm the crystalline nature and identity of the MOF material grown inside the SiO_2 colloidal crystal spheres. Importantly, compared with commonly bulk MOF material, the colloidal crystal sphere as scaffold or host matrix offers a way to impose order on the MOF formed in the well-defined internal cavities, so that the resultant MOF composite spheres exhibit additional optical property characterized by occurrence of the reflection peak (so-called photonic stop-band) in UV/vis spectrum (Please see following sections).

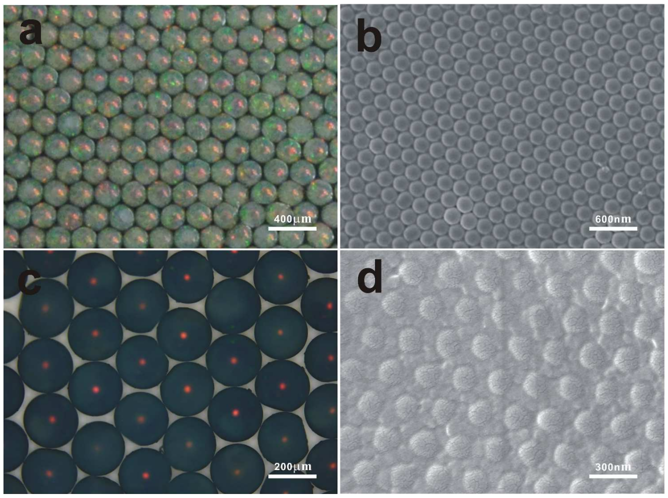


Figure 1. Optical (a) and SEM (b) images of the fabricated silica spherical colloidal crystals; optical (c) and SEM (d) images of the formed HKUST-1 composite superstructure.

The scaffold assisted strategy described above could be generally applicable to access composite MOF superstructures with a great flexibility. Besides HKUST-1, other prototypic MOFs such as ZIF-8,[9a] MOF-5,[9b] and MIL-100[9c] could also be efficiently converted to the corresponding MOF superstructures (composite spheres). As in the case of HKUST-1 similar results were obtained, as shown in Figure 2a-h. Since metal-organic complex is usually color material, the integration of different MOF with iridescent colloidal crystal led to microspheres with different colors (Figure 2a-h). It should be noted that both the infiltration of MOF precursor followed by crystallization and

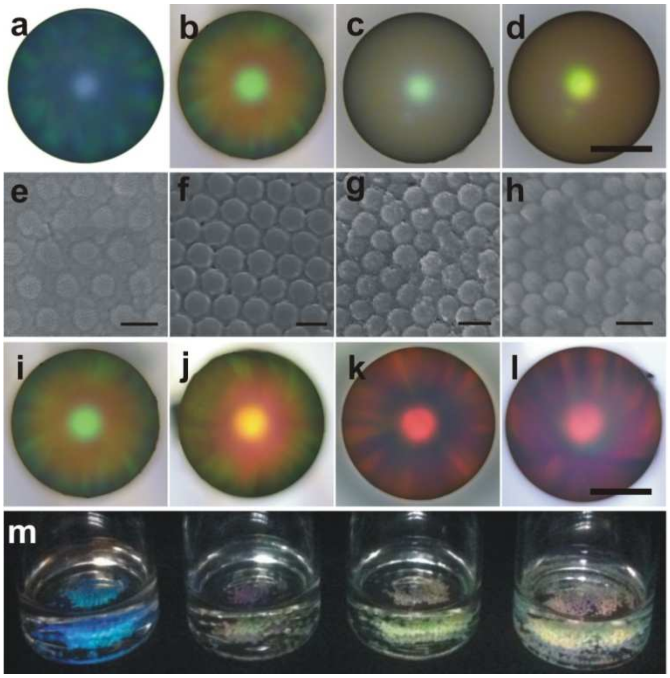


Figure 2. Optical images of four different prototypic MOF composite spheres (a: HKUST-1, b: MOF-5, c: ZIF-8, d: MIL-100), and their corresponding SEM images (e, f, g, h); optical images of MOF-5 composite spheres with different diffraction peak positions (I, j, k, l); optical images of the fabricated MOF composite spheres dispersed in organic solvents (methanol, $CHCl_3$ or Hexane)(m). The scale is 100 µm (a-d and i-l) and 300 nm (e-h), respectively.

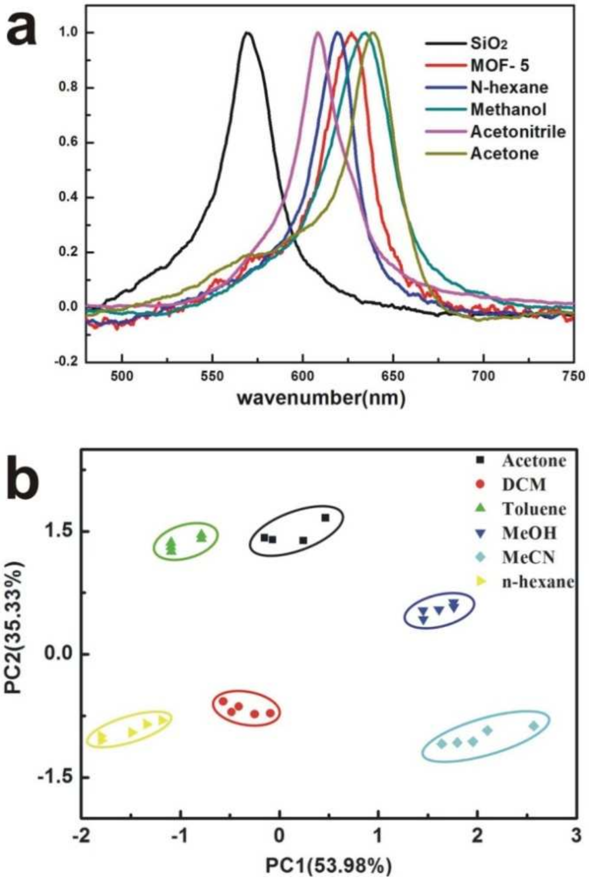


Figure 3. a) Optical response of the MOF-5 composite spheres upon the exposure to different organic solvents; b) PCA plot of the optical changes resulting from the exposure of the MOF composite spheres array to different organic solvents.

layer-by-layer approach can be employed for the construction of MOF composite superstructures. Remarkably, depending on the sizes of the used silica nanoparticles, the optical property of the resultant MOF superstructures could be widely tunable (Figure 2i-l and Figure S3). Moreover, by adjusting the microfluidic preparation parameters the diameters of the used spherical colloidal scaffolds (hosts) and thus the created MOF superstuctures could be easily tuned from 150 µm to 600 µm (Figure S4). Importantly, compared to normal 2D and 3D film-type colloidal crystals deposited on a solid substrate, the well-defined discrete MOF composite microspheres can be dispersed in various solvents (Figure 2m), providing unique opportunities for advanced applications demonstrated in following section.

It is well-known that the permanent porosity of MOFs permits the accommodation of guest molecules within their frameworks and exhibits a rich host-guest chemistry.[1] In previous works, the observation of guest inclusion in MOF host requires the use of special instruments (e.g. X-ray diffraction, N_2 adsorption) or the use of luminescent MOF or guest molecule. For the case of the composite MOF spheres described above, however, the recognition event of the common MOFs toward normal guest molecules can be directly converted into readable optical signal through their periodically ordered photonic structure without any use of label, namely self-reporting signalling, and is even observable by the naked eye. Figure 3a exemplifies the optical response of the prepared MOF spheres upon dispersion in different organic solvents. Clearly, the stop-band position of the MOF-5 based composite sphere shifted to different wavelengths from 626 nm to 619 nm, 634 nm, 639 nm, and 608 nm respectively after exposure of hexane, methanol, acetone, and acetonitrile. The observed recognition process is completely reversible, and after the removal of the included guest molecules by simply heating or under vacuum the shifted stop-band of MOF spheres returns to their initial position (Figure S5). It should be noted that there is a big red shift after the silica photonic crystal beads infiltrated by MOF-5 (Figure 3a). The reason for this observation is that the infiltration of MOF-5 into the interstices of silica beads caused a dramatic change of the effective refractive index of the silica beads, leading to a big red shift of photonic stop-band of the beads according Bragg equation. As the optical property (stop-band) of the 3D-ordered superstructure can be described by Bragg equation (Figure S6) and determined by the lattice constant d and the refractive index n_{eff} under normal incidence geometry.[10] In our case, the change of lattice parameter of composite microspheres is negligible. Thus, the change of the effective reflective index should mainly be responsible for the observed shift of stop-band. These results imply that the prepared MOF composite superstructure could be used as a novel probe "dye molecule" to sense its environments with a series of advantages.

As mentioned, the permanent porosity of MOFs enables to accommodate guest species therein, but usually does not possess specific recognition capability. Inspired by the concept of cross-reactive sensory array,[11] we found that the prepared composite MOF spheres could be used conveniently as self-reporting sensing elements to collect the fingerprints of the dispersed media. Based on the formed fingerprint pattern, specific sensing and discrimination of the exposed media can be efficiently realized by statistical analysis such as principal component analysis (PCA) and linear discrimination analysis (LDA). Figure S7 shows the optical responses (fingerprints) of each of the prepared MOF spheres to target organic solvents. For all the samples five repetitions were performed. In this work, PCA, an important chemometric method,[12] was used to decompose complex optical fingerprint patterns obtained from multiple signalling MOF spheres and repeating experiments into simplified components: principal component 1 (PC1) and principal component 2 (PC2) that can be plotted to allow the description of the discriminatory power of the composite MOF sensor array. Figure 3b displays the obtained two-dimensional PCA plot for acetone, dichloromethane, toluene, methanol, acetonitrile and hexane to the array composed of MOF-5, HKUST-1, ZIF-8 and MIL-100-based MOF spheres. The PCA plot shows an excellent discrimination of the 5 tested solvents and the first principle component possesses 53.98% of variance. In this PCA plot (Figure 3b), all analytes are grouped in well-separated clusters, demonstrating the reproducibility of the response for each solvent. To better exhibit 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 solvents in our case.

The obtained results clearly indicate that like small molecules, the fabricated "dye molecule" MOF composite spheres indeed can be arranged to form an array for realizing specific molecular recognition. Moreover, compared to the reported sensor arrays,[11] the array built from composite MOF spheres exhibits a series of distinct advantages. First, since the optical property of MOF spheres origins from their periodic superstructure, the quenching and bleaching problem of common dye molecules is circumvented (label-free detection), Importantly, the molecular recognition can be conveniently and directly converted into readable optical signal (self-reporting feature), and the shortcomings of indicator displacement, a strategy often used in the common sensor arrays,[11] can be avoided. Second, the composite MOF superstructures are robust microspheres which are easily dispersed in various media. These unique features make such composite MOF spheres excellent handling in array construction and permit the user to avoid tedious handling of multiple liquid solutions in well plates.

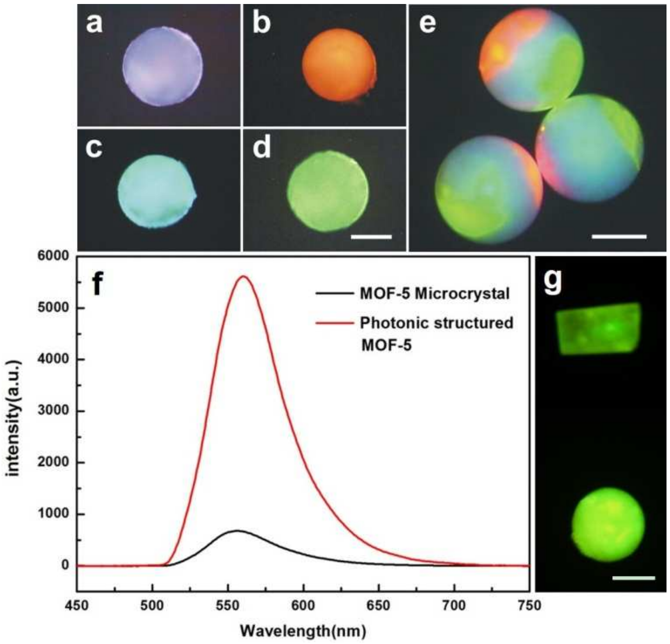


Figure 4. Fluorescent images of the isotropic (a-d) and anisotropic (e) MOF-5 composite spheres modified with methyl orange (a), methylene blue (b), methyl red (c), brilliant green (d) and methylene blue and brilliant green (e), respectively; comparison of rhodamine 6G captured at the out layers of the normal MOF-5 microcrystal and its photonic MOF-5 composite spheres (f) and their fluorescent images (g); The scale is 100 μm.

Benefiting from both distinctive properties of colloidal crystal scaffolds and MOFs, the fabricated MOF composite spheres can further serve as a unique platform to conveniently produce various multifunctional optical objects by entrapping guest molecules within the MOF nanocavities. Numerous active species including nanoparticles and molecules (e.g., Au and QD nanoparticles, polyoxometalates, organic dyes and drugs) have been reported to be intercalated into the pore spaces by using appropriate MOFs.[13] In this work, for easily visual inspection four different dye molecules (methylene blue, methyl red, brilliant green and methyl orange) were chosen to demonstrate the incorporation of additional functionality through host-guest chemistry. As shown in Figure 4a-d, the derived products display the clear corresponding colours under a fluorescent confocal microscope, indicating that the pore spaces of MOFs act as the anchor sites to stabilize and confine functional species.[14] Interestingly, the MOF composite spheres exhibit a great flexibility in surface engineering and allow for producing various anisotropic structures and can be functionalized correspondingly. By using a "sandwich" contact printing (μCP) method developed by us,[15] the patchy MOF spheres with A-B-C structure were fabricated as a demonstration (Figure 4e). Similarly, for better visualization two fluorescent molecules were used as chemical "ink" and the PDMS elastomer was utilized as a stamp. We found that the μCP process in our case proceeded fast. It took only several minutes to transfer the "ink" to MOF spheres via host-guest chemistry exclusively in the area of contact. Additionally, the contact time and pressure could be utilized to turn the size of the formed patchy. Although only fluorescent patchy MOF composite spheres were fabricated, in principle an unlimited variety of functional patchy particles could be easily accessible through simple host-guest chemistry in a modular fashion, when appropriate MOF materials are used. Compared with numerous anisotropic microparticles,[16] to our knowledge, this is the first example of

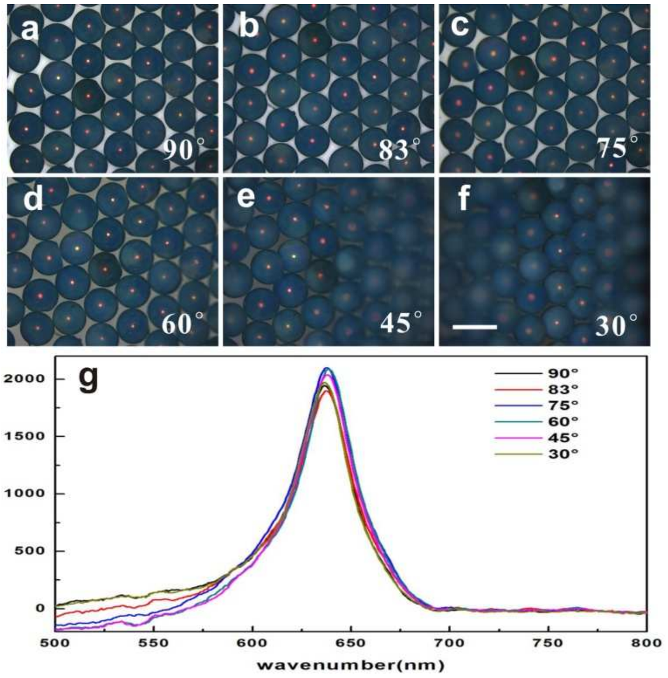


Figure 5. Optical images (a-f) and reflection spectra (g) of the 2D-photonic films constructed by using the MOF-5 composite spheres as elements at various viewing angles. The scale is 300 μm.

photonic patchy particles fabricated by using host-guest chemistry, showing versatile tunabilty.

Recently, numerous luminescent MOFs have been designed to tune the photophysics of the encapsulated chromophore molecules, leading to the emergence of new emission bands, shift of emission wavelength, luminescence quenching or antenna effect.[17] In fact, the integration of MOF with colloidal crystal structure endows the MOF composite sphere with additional optical property (photonic stop-band). Actually, the stop-band structure[18] provides a more convenient means to manipulate the photophysical and photochemical behaviour of trapped guest molecules without the need of designing luminescent MOF materials. As demonstration, dye molecules (Rhodamine 6G) were captured at the out layers of the normal MOF-5 microcrystal and its photonic structured MOF-5 composite spheres by diffusion approach. As expected, when the photonic stop-band of the photonic system is engineered to partially overlaps with the luminescence emission band of the entrapped dyes the spontaneous emission of the dyes was significantly enhanced,[19] compared to the reference system (normal MOF microcrystals) (Figure 4f-g). Evidently, by exploiting the interplay between the trapped guest molecules (even MOF host materials) and photonic band-gap structure, numerous advanced applications such as light harvesting systems, enhanced photocatalysis, miniature lasers, solar cells and light emitting diodes could be envisaged on the base of the developed MOF composite spheres.[17,20]

Besides the interesting properties described above, the uniform MOF composite spheres can be used as a new class of building blocks to form hierarchical nanomaterials with advanced optical properties. Figure 5 shows the constructed 2D-photonic films from the MOF composite spheres as elements. These films have structural colours similar to those of nanoparticles. Attractively, they exhibit excellent full angle independence, displaying constant colours and reflection peaks at different viewing angles (Figure 5a-g). Usually, due to the effect of Bragg diffraction, most photonic materials show different structural colours when observed from different angles.[21] This angle dependence is disadvantageous for the construction of some optical materials and devices such as sensors and display devices.[22] Thus, in conjunction with molecular recognition feature, the created hierarchical MOF photonic films should hold great promises for the development of advanced devices.

In 2011 we and J. Hupp group simultaneously reported the fabrication of the MOF-filled colloidal crystal films on a solid substrate and their organic vapour sensing.[23] Compared to these previous works, the well-defined discrete MOF composite microspheres display the same reflection colour for a fixed incident light source independently of the rotation of spheres and can be dispersed in various solvents. These unique features opened up new opportunities for advanced applications of MOF materials, such as efficient creation of cross-reactive sensory array for specific molecular recognition, formation of new type of patchy particles, and as a new kind of optical building block for construction of hierarchical functional nanomaterials as demonstrated above. These preliminary results are encouraging. By simple use of uniform colloidal crystal spheres as host materials spatially ordered arrangement of MOF materials can be efficiently realized, leading to a new kind of optical MOF materials with additional new functions. Although this new strategy was tested with HKUST-1, ZIF-8, MOF-5 and MIL-100, in principle, it could be unlimitedly extended to other MOFs and used as a general and effective preparation scheme for creating MOF-based photonic materials. In fact, in nature the similar assembly strategy is widely applied in many cases.[24] The ordering of many components is not achieved by interaction of the components with each other, but by interaction of each component with the host protein which provides a matrix to support the entire assembly.

Conclusions

In summary, by using spherical colloidal crystals as 3D-ordered host matrices, a general strategy for efficiently spatially arrangement of MOF materials has been developed, affording a new class of highly tunable optical superstuctures or composite spheres with a series of distinctive properties. It was found that the synergetic combination of the unique features of both MOF and photonic colloidal crystals endowed these hierarchically structured composite spheres with intrinsic optical property, specific molecular recognition with self-reporting signalling, derivatization capability, and anisotropy. Beyond multifunctional materials these MOF composite spheres could also serve as a new class of building blocks for the high level construction of hierarchically structured functional systems.

More importantly, the unique photonic band-gap structure integrated in these composite microspheres provides a more convenient means to manipulate the photophysical and photochemical behaviour of MOF materials and the trapped guest molecules. It can be anticipated that exploiting the interplay between photonic band-gap structure and the trapped guest molecules could create tremendous opportunities for the development of more advanced applications in numerous fields.

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