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Responsive Amorphous Photonic Structures of Spherical/Polyhedral Colloidal Metal–Organic Frameworks

Ling Bai, Yuheng He, Jiajing Zhou, Yun Lim, Van Cuong Mai, Yonghao Chen, Shuai Hou, Yue Zhao, Jun Zhang and Hongwei Duan**

Dr. L. Bai, Dr. J. J. Zhou, Y. Lim, V. C. Mai, Y. H. Chen, Dr. S. Hou, Prof. H. W. Duan

School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, 637457, Singapore.

Y. H. He, Prof. J. Zhang

School of Chemistry and Chemical Engineering, Inner Mongolia University, 235 West University Street, Hohhot 010021, China

Prof. Y. Zhao

Department of Advanced Functional Materials Research, Takasaki Advanced Radiation Research Institute, National Institutes for Quantum and Radiological Science and Technology (QST), Watanuki-machi 1233, Takasaki, Japan

*E-mail: hduan@ntu.edu.sg. cejzhang@imu.edu.cn

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Abstract

Amorphous photonic structures (APSs) with isotropic structural colors are of great promise for creating reflective full-color displays or responsive colorimetric devices. However, there is a lack of guiding principles in developing stimuli-responsive functional APSs and the building blocks of APSs are still limited to spherical particles despite the increasing emergence of anisotropic functional particles. Moreover, current production of APSs, in particular high-resolution APS patterns, is not fundamentally compatible with industrial manufacturing technologies, forming a major barrier towards their applications. Here we present a proof-of-concept study on scalable fabrication of responsive APSs by colloidal assembly of spherical/polyhedral metal-organic

framework (MOF) particles on flexible liquid-permeable substrates. We have shown that infiltration assisted Mayer rod coating allows for rapid production of customized structural color patterns of MOF APSs by controlling liquid wetting and infiltration on the substrate with printed wax coatings. We have also demonstrated the possibility of developing multicolored APSs with spherical/polyhedral colloidal building blocks of varying sizes. Small-angle X-ray scattering and optical measurements reveal the structural parameters of MOF APSs such as average nearest inter-scattering spacing and particle packing density, theoretically relating the optical properties and responsive color shifts of MOF APSs to factors affecting their scattering profile, which provides the guideline for the development of smart APS photonic devices via a wide spectrum of colloidal particles for diverse applications.

Amorphous photonic structures (APSs)^[1] with a short range order that display isotropic structural colors are widely found in natural creatures (such as bird feathers,^[2] mammalian skins,^[3] odonate,^[4] and the longhorn beetles^[5]). The colors of APSs resulting from constructive interference of scattering lights^[6] are of low angle-dependence, free from photonic/chemical bleaching and environmentally friendly, which are highly desirable characteristics for paints, cosmetics industry and information displays fields. The structural colors of APSs are readily tunable by any mechanism that changes the scattering profile of their structures, providing the opportunities to design photonic structures responsive to external stimuli.^[7] APSs have been successfully prepared by self-assembly of spherical colloidal building blocks under particular conditions that suppress colloidal crystallization, including using bi-dispersed^[8] or soft particles,^[9] salt-containing suspensions^[1a] or rapid dewetting methods.^[10] However, creating responsive APSs of smart materials/particles remains largely unexplored. Also noteworthy is that

APSs with isotropic colors have not been constructed using anisotropic particles of different shapes, compositions, or functionalities, which represent a large family of colloidal particles of potential for developing functional photonic materials.^[11] Besides, roll-to-roll continuous manufacturing of APSs with high resolution patterns is still a challenge, which is key to the large-scale production and practical applications of structural color devices.^[12]

Metal-organic frameworks (MOFs) are hybrid microporous crystalline materials formed through coordination between metal ions/clusters and organic ligands. An interesting array of properties^[13] of MOFs such as large surface areas, defined pore/aperture sizes, structural diversity, and chemical tailorability has offered diverse opportunities in molecular storage/separations,^[14] water harvesting,^[15] catalysis,^[16] and biomedicine.^[17] In particular, their rich host–guest chemistry, excellent sorption kinetics, and framework flexibility is of considerable interest for developing responsive photonic materials or sensors.^[18] MOF structural color devices that afford simple colorimetric responses have been fabricated in the forms of Fabry-Pérot interference films,^[19] 1-D Bragg stacks,^[20] 2-D diffraction grating,^[21] colloidal photonic crystals^[22], inverse opals,^[23] or crystalline photonic constructs,^[24] but employing MOF APSs for responsive photonic devices is still unexplored. Here we demonstrate the fabrication of MOF APSs with isotropic structural colors by colloidal assembly of spherical/polyhedral MOF building blocks. An infiltration-assisted (IFAST) Mayer rod coating method was developed for scalable production of MOF APSs with customized patterns, as illustrated in **Figure 1**. Successful colloidal assembly of APSs relies on rapid infiltration of the dispersing liquid of colloidal particles into the permeable substrates, which provides the driving force to instantly immobilize the particles on the substrates.^[10b] During the Mayer rod coating, aqueous MOF inks only wet the exposed substrates but not the patterns covered by wax. As a result, the IFAST

colloidal assembly can be tailored to occur on the designated part of the substrates to form MOF APS patterns of spherical/polyhedral particles with uniform isotropic structural colors. Small-angle X-ray scattering (SAXS)^[2b, 25] was used to reveal the spatial coherence of scatters in the MOF APSs. The obtained nearest average distance between scatters and refractive index and the reflection peak wavelength of MOF APSs are related by the Bragg's law, making it possible to design multicolored APS displays or responsive colorimetric APSs for monitoring the molecular captures in MOF materials. As homogeneous shapes or uniform sizes are not necessarily needed for the building blocks of APSs, our approach makes it possible to create smart photonic devices with a wide spectrum of anisotropic MOF or other particles, and the rod coating of patterned APSs is of considerable potential for their high-throughput roll-to-roll continuous manufacturing.^[26]

Figure 1. Illustration for the Mayer rod coating of MOF APS patterns by (a) Selective wetting of the hydrophilic area of the substrate during coating by spherical/polyhedral MOF inks; (b)

Formation of APS patterns of spherical or polyhedral MOF particles after the removal of water;
(c) Vapor-responsive color changes of the MOF APS patterns.

Monodispersed zeolite imidazole framework-8 (ZIF-8) colloidal particles with spherical or polyhedral shapes (see Figure S1) were synthesized using a modified method of previous studies,^[27] showing typical X-ray diffraction (XRD) patterns (Figure S2), large surface areas (Figure S3) of crystalline ZIF-8 materials, and a good uniformity (Figure S4) with coefficient of variation (CV) of particles varies between 4% and 6% from batch-to-batch. The Mayer rod coating of aqueous inks of spherical MOF particles on photo paper substrates was first investigated. Successful IFAST colloidal assembly relies on the rapid infiltration of dispersing liquid of colloidal particles, which provides the driving force to rapidly immobilize the particles on the substrates. The photo paper used here is able to absorb a maximum water layer of 22.8 μm in thickness per unit area,^[10b] and the solid wax printing offers a convenient approach to producing patterned hydrophobic barriers on hydrophilic paper substrates. While water undergoes rapid infiltration into the uncovered area, wax coating leads to a water contact angle of 120° (Figure S5) and completely inhibits water penetration, which is of potential for creating APS patterns. The Mayer rods wound with wires of different diameters afford precisely controlled thickness of liquid thin films (Supporting Table S1).^[26b] SEM image in Figure S6 shows that the thickness of wax patterns is around 14 μm , and thereby #3 Mayer rod was selected to produce a thin liquid film of less than 22.8 μm , which is necessitated to prevent saturation of the paper substrate. As a proof of concept, 198 nm MOF particle ink of 5 wt% solid content was coated on a butterfly wax pattern by a #3 rod. During the coating process, aqueous ink only wetted the exposed area in a butterfly shape, and the water layer in wetted regions was

quickly removed by infiltration, leaving behind a butterfly pattern displaying a vivid and uniform blue color (**Figure 2a**). Importantly, when viewing angle changed from 5° to 45° , the color of the butterfly pattern remained unchanged. SEM image of the pattern in Figure 2b and S7 confirms the amorphous arrangement of the ZIF-8 particles with a thickness of around $1.5\ \mu\text{m}$. The two-dimensional Fourier transform (2D-FFT) pattern (Figure S8) of the SEM image shows bright concentric circles, indicating a short-range order of the ZIF-8 particles. Backscattering spectra of the pattern (Figure 2c) were measured by fixing the detection arm while rotating the sample. The spectra show an obvious backscattering peak, which hardly moved when the rotation angle was changed from 0° to 60° , confirming the non-iridescent color of the ZIF-8 APSs.

Figure 2. (a) Optical images of ZIF-8 APS butterfly at different rotation angles. (b) SEM image of the ZIF-8 APS pattern, scale bar: $1\ \mu\text{m}$. (c) Back-scattering spectra of ZIF-8 APS patterns at different rotation angles. (d) The azimuthal average of the experimental SAXS pattern (blue line), experimental reflection data converted to q -space using an effective refractive index of $n_0 = 1.26$ (black line), and theoretical scattering intensity profile (red dashed line), inset: the two-

dimensional SAXS diffraction pattern of MOF APSs, side length: 0.2225 nm⁻¹. (e) Calculated reflection spectra for APSs including only the S-factor or F-factor (the F-factor is timed by 100 between 200-350 nm).

To quantitatively characterize the structure of APSs, we performed SAXS measurements on samples composed of spheres with a mean diameter (D) of ~198 nm (CV = 4.5%). A two-dimensional SAXS pattern with rings of uniform intensity was shown in the inset of Figure 2d, indicating the isotropic nanostructures of APSs with a short-range order. The azimuthal averaged SAXS intensity, $I(q)$, was normalized by the first scattering maximum and plotted as a function of scattering vector q in Figure 2d. The position of the first peak was obtained at $q_0=0.0356$ nm⁻¹. The full width at half maximum (FWHM) of the first peak in the SAXS profile, Δq , corresponds to the range of spatial order, ξ of ~ 615 nm ($\xi=2\pi/\Delta q$), which is about the size of 3 particles.

The optical reflection measurement of APSs was subsequently performed. We directly compared the reflection data to SAXS profile by plotting the reflected intensity as a function of the magnitude of wavevector difference q below:^[2a, 8a]

$$q = \left(\frac{4\pi n_0}{\lambda}\right) \cos (\theta/2) \quad (1)$$

where n_0 is the average refractive index of the APSs, λ is the wavelength of the light, and θ is the angle between illumination and detection. The plot of reflection data at $\theta = 0^\circ$ was also shown in Figure 2d. The peak position of reflection data match q_0 of the SAXS profile well when $n_0 = 1.26$, which allows for calculating the volume fraction of APSs by formula 2 below,

$$n_0 = \sqrt{n_{\text{air}}^2 f_{\text{air}} + n_{\text{ZIF-8}}^2 f_{\text{ZIF-8}}} \quad (2)$$

where n_{air} and $n_{\text{ZIF-8}}$ is the refractive index of air and ZIF-8 particles, f_{air} and $f_{\text{ZIF-8}}$ is the corresponding volume fraction. For ZIF-8 particles with a refractive index of 1.43 (see supporting information section 1), the obtained volume fraction of APSs is 56%. With this value, we calculated the theoretical scattering intensity profile of dense packings of hard-spheres with a particle size of 200 nm and $CV = 4.5\%$ that match our experimental system,^[28] and plotted along with the experimental SAXS data in Figure 2d. The position of the first scattering peak from both simulation and experiment is the same, verifying the correctness of the packing density estimated by formula 2.

To understand the optical properties of APSs, we predicted the reflection curve by calculating the differential scattering cross-section of APSs ($\frac{d\sigma}{d\Omega}$) as a product of the form factor (F) and structure factor (S) as below.^[29]

$$\frac{d\sigma}{d\Omega} = \left(\frac{1}{k^2}\right)FS \quad (3)$$

where $k (=2\pi n_0/\lambda)$ is the magnitude of the wavevector, F is the form factor of a solid sphere,^[30] and S is the solution to the Ornstein-Zernike equation with the Percus-Yevick closure approximation.^[28a,29b,31] The theoretical reflectivity is proportional to the effective scattering intensity, the integration of the differential scattering cross-section over the solid angle of the detector.^[29a,32] In Figure S9, we plotted both experimental and predicted reflection data of APSs as a function of wavelength. Note that the above obtained $n_0 = 1.26$ and the packing density of 0.56 were used in the calculation. The theoretical data reproduced the reflection peak well for particles having diameters of 201 nm ($CV = 5\%$), in good agreement with the size (198 nm, $CV = 4.5\%$) of the particles observed by SEM, confirming the validity of our theoretical analysis. To identify the source of the reflection peak, we also calculated the intensity from S alone or from F alone as shown in Figure 2e. It shows that the reflection peak of the APSs in the wavelength

range of 350-700 nm mainly comes from S but not F. Notably, both S and F show peaks in the wavelength of 240 nm to 270 nm, resulting in a weak reflection peak at short wavelengths in Figure S9.

Figure 3. (a) Photographs of multi-colored letters of ZIF-8 APSs, scale bar: 2 cm. (b) Reflection spectra of four letters. (c) Reflection spectra of four APS films composed of bi-dispersed particles with a ratio of 1:0, 2:1, 1:2 and 0:1. (d) Photographs of PAPSs constructed by polyhedral ZIF-8 particles. (e) Reflection spectra of NTU PAPS films. (f) SEM image of yellow PAPS film, scale bar: 1 μ m. (g) Optical images of the PAPS pattern at different rotation angles. (h) Back-scattering spectra of blue PAPS pattern at different rotation angles.

Multiple structural color letters of MOF APS (**Figure 3a**) in blue, green, yellow, and red were then prepared using four ZIF-8 particles with average diameters of 205, 235, 260 or 282 nm

(measured by the SEM images in Figure S10), respectively. Because the nearest inter-scatter spacing ($2\pi/q_0$) only depends on the particle size if the assemblies have the exact same packing geometries, the positions of main reflection peak (Figure 3b and S11) related to the first peak in the SAXS profiles of APSs can be tuned by the average size of the ZIF-8 particles according to formula 1. Theoretical calculation of the reflectance of APSs reveals the linear relationship between the particle size (<300 nm) and the main reflection peak wavelength in the visible spectral range (Figure S12a). Notably, when the particle size increases to 350 nm, the wavelength of theoretical main reflection peak moves to the near-infrared region, and the colors of APSs are thereby mainly determined by the reflection peak at the lower wavelength in Figure S12b.^[29a] APSs of different colors (Figure 3c) were also prepared by mixing of two ZIF-8 particles of 235 and 275 nm in sizes.^[33] When the ratio of two particles was varied from 1:0, 2:1, 1:2 to 0:1, the colors of APSs gradually changed from green, green-yellow, yellow to red, where CVs of bi-dispersed particles are 9.6% and 9.1% for green-yellow and yellow APSs. The corresponding reflection spectra in Figure 3c show continuous shifts in the wavelength of reflection peaks, APSs composed of bi-dispersed particles display decreased reflectance intensity and increased peak width though.

We further explored the colloidal assembly of polyhedral ZIF-8 particles into APSs. By the IFAST rod coating of rhombic dodecahedral (RD) ZIF-8 particles of different sizes, polyhedral ZIF-8 APSs (PAPSs) with different structural colors were obtained, as shown in Figure 3d. Similar to APSs composed of spherical particles, the colors of PAPSs can be tuned from blue to red by changing the size of polyhedral particles. For example, the reflection peak positions (Figure 3e) of the PAPSs shifted from 544, 593 to 640 nm, when the height H of polyhedral particles changed from 227, 249 to 268 nm (Figure S13-14) and the average L/H ratio of

particles is around 1.3. The microstructures of PAPSs were subsequently visualized by SEM. The top-side view (Figure 3f) and cross-sectional (Figure S15) SEM images show that although some nearby particles (number <10) can form FCC packed clusters, the overall PAPSs lost both positional and orientational order, confirming their disordered glassy structures. Interestingly, although the RD ZIF-8 particles are anisotropic, the PAPSs formed give rise to an isotropic structural color under natural light, as shown in Figure 3g. The peak positions of their back-scattering spectra (Figure 3h) are almost unchanged with increasing rotation angles. It is because the scattering of polyhedra in the small- q region is not shape dependent,^[25d,34] and the RD particles in APSs are randomly packed. We further compare the reflective spectra of APSs composed of spherical/polyhedral particles with a CV of around 5% (see Figure S16), due to the anisotropy of polyhedral particles, the peak width of their assemblies is larger than that of spherical APSs, which lead to paler colors when the thickness of APSs increased. To get a better understanding of the structure of PAPSs, SAXS measurement of PAPSs made of polyhedral ZIF-8 particles with an average height of 218 nm was carried out. The azimuthal averaged SAXS and reflectance spectra of PAPSs are shown in Figure S17, where the reflection peak is observed at 522 nm and by curve fitting of and SAXS peak, the q value is also obtained ($q_0=0.03075 \text{ nm}^{-1}$). By relating the reflection reflectance of PAPSs to their SAXS profile through formula 1, the refractive index of PAPSs $n_0=1.277$ is acquired. For polyhedral ZIF-8 particles with a refractive index of 1.43, the volume fraction of PAPSs is calculated to be 60%. These results suggest that our approach is capable of creating full-spectrum isotropic structural colors by spherical or polyhedral particles, and shows the potential for developing APS smart photonic devices using a wide range of colloidal particles with varying size, uniformity, and anisotropy.

The application of MOF APSs as vapor-responsive structural color devices was then explored. A thermogravimetric analysis (TGA) was carried out to ensure the complete removal of water molecules in ZIF-8 by activation. As shown in Figure S18, no obvious weight loss of spherical ZIF-8 particles was observed until the temperature was over 400 °C. As the weight of the particles hardly changed when the temperature was increased from 95 °C to 150 °C, the activation of APSs was carried out at 95 °C in vacuum in our tests. **Figure 4a** shows that the APSs made of 245 nm spherical ZIF-8 particles displayed an obvious color change from green into yellow upon exposure to ethanol (ETOH) vapor at room temperature. The reflection spectra (Figure 4b) of activated APSs in N₂/ETOH reveal a red-shift of the reflection peak from 550 to 577 nm. Capturing of vapor molecules into the micropores of ZIF-8 would lead to an increase in refractive index of the ZIF-8 particles, thereby causing red-shifts of the reflection peak of the APSs.

Figure 4. (a) Optical images of the activated MOF APSs exposed to N₂ and saturated ETOH vapor. (b) Reflection spectra of the activated APSs upon exposure to N₂ (green line) and saturated ETOH vapors (orange line). Calculated color response of MOF APSs due to the

changes of refractive index of APSs 1.26 (blue dash line) to 1.322 (red dash line). (c) Recycling tests of the activated APSs exposed to N₂ and saturated ETOH vapor alternatively. (d) MOF APS dot array pattern, scale bar: 2 cm. (e) Reflection spectra of the activated APSs upon exposure to saturated water, toluene, isopropanol, methanol, acetone and DMF vapors. (f) Time-dependent reflection peak position shifts of the MOF APSs on exposure to saturated water, toluene, ETOH, isopropanol, methanol, acetone and DMF vapors.

The effective refractive index of the ZIF-8 particles after adsorption of vapor analytes n'_{vapor} is expressed in formula 4:

$$n'_{\text{vapor}} = \sqrt{n_{\text{air}}^2 f_{\text{air}} + n_{\text{ZIF-8}}'^2 f_{\text{ZIF-8}}} = \sqrt{n_{\text{air}}^2 f_{\text{air}} + n_{\text{solid}}^2 f_{\text{solid}} + n_{\text{air}}^2 f_{\text{void}} + n_{\text{guest}}^2 f_{\text{guest}}} \quad (4)$$

where $n'_{\text{ZIF-8}}$ is the refractive index of ZIF-8 particles after adsorption of vapor molecules. Here, f_{solid} , f_{guest} , and f_{void} respectively represent the volume rate of solid ZIF-8 framework, adsorbed guest molecules and unfilled space of ZIF-8 particles, whereas n_{solid} , n_{guest} , and n_{air} are their corresponding refractive index. According to the ETOH adsorption/desorption isotherm (Figure S19), ZIF-8 particles can take up 32% (w/w) of ETOH, from which we can conclude that f_{guest} occupies 60.4% of the volume of micropores, $f_{\text{guest}} = 0.604 (f_{\text{guest}} + f_{\text{void}})$. As a result, for the APSs with f_{air} of 44% and f_{solid} of 24.6%, the f_{guest} (f_{ETOH}) and f_{void} are calculated to be 18.9% and 12.4%, respectively. Thereby, the refractive index of MOF APSs after ethanol adsorption increases from 1.26 to 1.322 (see supporting information section 1). Importantly, by combining formula 1 and 4, we can provide the theoretical model for the color response of MOF APSs. The theoretical reflection spectrum (Figure 4b) of ZIF-8 APSs ($n_0=1.26$, $f_{\text{ZIF-8}}=56\%$) in N₂ with a peak at 550 nm corresponds to a building block size of 248.5 nm (CV = 5%), which is close to the actual size (245 nm) of the ZIF-8 particles used. When the refractive index of APSs increases

from 1.26 to 1.322, the theoretical reflection peak match well with the experimental result, validating our theoretical model. The ZIF-8 APSs (Figure 4c) show reversible reflection peak shifts upon repeated exposure to saturated ETOH vapor and N₂ after activation, demonstrating robust and reproducible response.

A MOF APS dot-array pattern consisting of 14×10 dots were further prepared to detect the response of seven guest molecules, in which each dot can serve as a disposable transducer (Figure 4d). As the diffusion of guest molecules in ZIF-8 depends strongly on the physicochemical properties (size, shape, and affinity to the adsorption sites) of the molecules, the responding time of APSs was also measured. The obtained average results of three tests under a fixed gas flow rate (70 cm³ s⁻¹) are shown in Figure 4e. Due to the framework hydrophobicity of ZIF-8 materials, water molecules were hardly absorbed,^[35] giving rise to the smallest refractive index changes. And an increase over 0.05 of n'_{vapor}/n_0 indicates strong adsorption of corresponding molecules in the APSs. For saturated toluene, methanol, isopropanol, acetone and DMF vapors, the values of n'_{vapor}/n_0 were 1.024, 1.051, 1.053, 1.058 and 1.071 (Figure S20) respectively, which were used to calculate the adsorption of these vapors in micropores (Table S2). Time-dependent reflection peak position shifts of MOF APS on exposure to these vapors are presented in Figure 4f. For vapors with smaller kinetic diameters^[35,36] (methanol-3.6 Å, ETOH-4.5Å, acetone-4.6 Å, and H₂O-2.7 Å), the responding speeds of APSs were all within 15 s. However, for vapor molecules with larger sizes (isopropanol-4.7 Å, DMF-5.2 Å, and toluene-5.3 Å), the responding time was much longer due to their slow diffusions in ZIF-8.^[37] We further carried out studies on responsive properties of PAPSs (H of particles is 230 nm) to saturated ETOH vapor, as shown in Figure S21. Due to a higher packing density of PAPSs, they show larger responsive peak shifts than APSs made of spherical ZIF-8 particles. The reflection peak

position of activated PAPSs red-shifts from 551 to 581 nm. We also calculated the color response of PAPSs by formula 4 (see supporting section S1), where calculated results of peak shifts from 551 to 579.5 nm, which is close to the detected value. Therefore once the packing density of APSs/PAPSs is obtained, the color response of APSs/PAPSs can be predicted by our theoretical calculations.

Conclusions

We have successfully demonstrated scalable fabrication of responsive APS patterns using spherical/anisotropic MOF particles, and explored their uses as full-spectrum displays and responsive structural color devices. The APSs show a good tolerance of size uniformity and anisotropy of the building blocks, which can be generalized for a wide spectrum of colloidal particles. Theoretical calculations were provided to elaborate the optical properties of APSs and their vapor-responsive color changes, which are consistent with the experimental reflectance and SAXS results. Our approach holds great promise in developing photonic materials of functional building blocks of different shapes. Also important is that the ability of preparing patterned APSs via the Mayer rod coating, which is well-established for continuous roll-to-roll manufacturing of liquid thin films, represents a significant progress toward mass-production of structural color devices.

Experimental Section

Synthesis of ZIF-8 colloidal particles. Solution A was made by dissolving 7.5 mM 2-methylimidazole (MIM), 1.25 g PVP and 0-12 mg of NaAC in methanol (250 mL). Methanol solution B (250 mL) of 15 mM $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was subsequently added to solution A and

mixed together, and the reaction mixture was incubated at room temperature for 12 min or overnight to acquire spherical/RD ZIF-8 particles. 500 mL methanol was subsequently added to the reaction solution before the particles were purified by repeated centrifugation and washing with ETOH.

Mayer rod coating of ZIF-8 APSs/PAPSs. ZIF-8 particle inks were prepared by dispersing 10-50 mg spherical or polyhedral ZIF-8 particles into 0.5 ml DI water. Hydrophobic inverse patterns were created on photo papers using a wax printer. Depending on the size of the pattern, 0.05-0.5 ml ZIF-8 colloidal ink was dropped to the edge of the modified pattern. A Mayer rod was pulled over the solution at a speed of 0.5-3 m/s. The liquid only wet the hydrophilic areas, and was rapidly removed by infiltration, leaving behind ZIF-8 APSs of designed patterns. SAXS samples of the APSs with a thickness of over 50 μm were prepared by repeated coating of 10 wt% ZIF-8 colloidal inks.

Characterization: A field emission scanning electron microscope (JSM-6700F, Japan) was used to capture SEM images of APSs/PAPSs. TEM images of ZIF-8 particles were obtained using a Jeol TEM2010 electron microscope. XRD measurements of ZIF-8 particles were performed on a (Bruker D2-Phaser XRD). A digital camera (EOS 700D, Canon) was used to capture images of APSs. An optical fiber UV-vis spectrometer (Ocean Optic HR2000CG) was used to record reflection spectra, where all MOF samples were activated before testing. Transmission spectra of the APSs/ PAPSs were measured by a UV-Vis spectrophotometer (UV-1800). Hydrophobic wax patterns were produced by a wax printer (Xerox Colorcube 8580). Contact angles were measured by an FTA200 contact angle analyzer. N_2 adsorption–desorption isotherm was analyzed on an ASAP 2020 instrument at 77 K. ETOH adsorption–desorption isotherms were tested by A

dynamic vapor sorption analyzer (IGA-100). The SAXS data was collected at 12.4 keV and a camera length of 9.7 m by I22 beamline. TGA was tested by a NETZSCH 409C.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Amorphous photonic structures (APSs) of spherical/polyhedral colloidal metal-organic frameworks (MOFs) are prepared by scalable infiltration assisted rod-coating technology. The optical properties and responsive color shifts of MOF APSs are elaborated by both theoretical calculation and experimental measurements, opening the avenue to developing smart photonic APS devices using a wide spectrum of isotropic/anisotropic colloidal particles.

Keywords: Structural color patterns, amorphous photonic structures, metal-organic frameworks, colloidal assembly, anisotropic particles

L. Bai, Y. H. He, J. J. Zhou, Y. Lim, V. C. Mai, Y. H. Chen, S. Hou, Y. Zhao, J. Zhang^{*}, H. W. Duan^{*}

Responsive Amorphous Photonic Structures of Spherical/Polyhedral Colloidal Metal–Organic Frameworks

ToC figure

Supporting Information

Responsive Amorphous Photonic Structures of Spherical/Polyhedral Colloidal Metal–Organic Frameworks

Ling Bai, Yuheng He, Jiajing Zhou, Yun Lim, Van Cuong Mai, Yonghao Chen, Shuai Hou, Yue Zhao, Jun Zhang and Hongwei Duan**

Dr. L. Bai, Dr. J. J. Zhou, Y. Lim, V. C. Mai, Y. H. Chen, Dr. S. Hou, Prof. H. W. Duan

School of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, 637457, Singapore.

Y. H. He, Prof. J. Zhang

School of Chemistry and Chemical Engineering, Inner Mongolia University, 235 West University Street, Hohhot 010021, China

Prof. Y. Zhao

Department of Advanced Functional Materials Research, Takasaki Advanced Radiation Research Institute, National Institutes for Quantum and Radiological Science and Technology (QST), Watanuki-machi 1233, Takasaki, Japan

*E-mail: hduan@ntu.edu.sg. cejzhang@imu.edu.cn

Figure S1. (a-b) SEM images of ZIF-8 particles generated after 12 min and 24 h, scale bar: 500 nm.

Figure S2. The XRD patterns of ZIF-8 particles generated after different reaction times.

Figure S3. N₂ adsorption/desorption isotherm of the spherical/polyhedral ZIF-8 particles.

Figure S4. (a-b) SEM images of spherical/polyhedral ZIF-8 particles; (c-d) the corresponding particle size distributions of the spherical/polyhedral ZIF-8 particles with Gaussian fit, the CVs of two particles are 4.7% and 4.9% respectively, scale bar: (a) 2 μm ; (b) 1 μm .

Figure S5. Contact angles of a 3 μ l water droplet on (a) photo papers and (b) wax patterns.

Figure S6. Cross-sectional view SEM image of the printed wax pattern, scale bar: 10 μ m.

Figure S7. Cross-sectional view SEM image of the coated APS pattern, scale bar: 1 μm .

Figure S8. 2D-FFT pattern of the SEM image in Figure 2d.

Figure S9. Normalized theoretical (red dashed line) and experimental (blue line) reflection spectra of the APS ($n_0=1.26$, $f_{\text{zif-8}}=0.56$, particle size=201 nm, CV=5%).

Figure S10. SEM images of spherical ZIF-8 particles for construction of APSs with blue/green/yellow/red colors, scale bar: 2 μm .

Figure S11. The relationship between the main reflection peak position of APSs and the average size of spherical ZIF-8 particles.

Figure S12. Theoretical reflection spectra of APSs ($n_0=1.26$, $f_{\text{zif-8}}=0.56$) with particle sizes of (a) blue-201 nm, green-235 nm, orange-260 nm, red-280 nm and (b) 350nm, the CV of all particles is 5%.

Figure S13. SEM images of polyhedral ZIF-8 particles for construction of PAPSs with green/yellow/red colors, scale bar: 1 μm .

Figure S14. The relationship between the main reflection peak position and the height of RD ZIF-8 particles.

Figure S15. Cross-sectional SEM images of PAPSs, scale bar: 1 μm .

Figure S16. Reflection spectra of the APSs composed of spherical/polyhedral particles with a CV of around 5%.

Figure S17. (a) The SAXS spectra and curve fitting of the PAPSs, $q=0.03075 \text{ nm}^{-1}$; (b) Corresponding reflection spectrum of the PAPSs, $H=218 \text{ nm}$.

Figure S18. TGA of spherical ZIF-8 particles.

Figure S19. ETOH adsorption/desorption isotherm of (a) spherical and (b) polyhedral ZIF-8 particles at room temperature.

Figure S20. Reflection peak shifts and responding time of the APSs of spherical ZIF-8 particles for different organic vapors.

Figure 21. Reflection spectra of the activated PAPSs upon exposure to N₂ (green line) and saturated ETOH vapors (orange line), H=230 nm.

Table S1. Wire size selection chart.

Wire size	Diameters of Wire [inches]	Wet film thickness [μm]
3#	0.003	7.6
4#	0.004	10.2
5#	0.005	12.7
6#	0.006	15.2
7#	0.007	17.8
8#	0.008	20.3
9#	0.009	22.9
10#	0.010	25.4
11#	0.011	27.9
12#	0.012	30.5
13#	0.013	33.0
14#	0.014	35.6
15#	0.015	38.1
16#	0.016	40.6
17#	0.017	43.2
18#	0.018	45.7
19#	0.019	48.3
20#	0.020	50.8

Table S2. Calculations for vapor responsive color shifts of APSs of spherical ZIF-8 particles.

Guest molecules					n'_{vapor}/n_0	Peak position in Vapors (nm)
Molecules	Dynamic size (Å)	Refractive index	Calculated Pore filling rate (%)	Calculated Adsorption (mg/g)		
Water	2.64	1.33	4.8	32	1.004	552
Methanol	3.63	1.33	68.7	365	1.051	578
ETOH	4.53	1.36	60.4	320	1.05	577
Isopropanol	4.7	1.38	70.3	321	1.053	579
Acetone	4.6	1.36	70.7	371	1.058	582
DMF	5.2	1.43	71.1	450	1.071	589
Toluene	5.26	1.5	19.4	112.5	1.024	563

Supplementary Section 1: Determination of the Refractive Indexes of ZIF-8

Particles and Color Shifts of the APSs

A. Refractive index of the spherical/polyhedral ZIF-8 particles

Owing to their porous nature, ZIF-8 crystals are composed of micropores and solid framework, each is of a volume rate of 50%. The theoretical pore volume of ZIF-8 is 0.54 cm³/g, whereas the N₂ sorption isotherm of the ZIF-8 spherical/polyhedral samples showed a pore volume of 0.69 and 0.683 cm³/g. Therefore the volume rates of solid framework in both particles are lower, which is calculated to be 44% and 44.2% using equation 1:

$$f_{\text{solid}} = \frac{V_{\text{solid}}}{V_{\text{solid}} + V_{\text{void}}} \quad (1)$$

where the V_{void} , V_{solid} separately represent the volume rate of air and solid ZIF-8 framework in ZIF-8 particles. The lower volume rate of solid framework suggests that the ZIF-8 particles are not of pure crystalline structures, probably have defects or partly amorphous structures inside. The refractive index of the ZIF-8 particles $n_{\text{ZIF-8}}$ was calculated using following formula:

$$n_{\text{ZIF-8}} = \sqrt{n_{\text{void}}^2 f_{\text{void}} + n_{\text{solid}}^2 f_{\text{solid}}} \quad (2)$$

where n_{void} and n_{solid} is the refractive index of void (air) and solid framework, f_{void} and $f_{\text{ZIF-8}}$ is the corresponding volume fraction in ZIF-8 particles. Here n_{solid} is taken to be 1.83 according to previous studies, and the final refractive index of the spherical/polyhedral ZIF-8 particles is calculated to be 1.426 and 1.43, here we take the value 1.43 as refractive index of both particles and 44% as volume rates of solid framework of particles for further calculations.

B. Average refractive index changes and color shifts of APSs of spherical ZIF-8 particles upon exposure to different vapors

For APSs with a starting wavelength of 550 nm in N₂ with $n_0 = 1.26$, their reflection peak positions shifted to 577 nm in saturated EtOH. According to formula 3, the experimental data $n'_{\text{EtOH}} = 1.3223$ are related to the pore filling rate of EtOH in micropores of MOFs, which is calculated to be 60.4%.

$$n'_{\text{vapor}} = \sqrt{n_{\text{air}}^2 f_{\text{air}} + n_{\text{solid}}^2 f_{\text{solid}} + n_{\text{air}}^2 f_{\text{void}} + n_{\text{EtOH}}^2 f_{\text{EtOH}}} \quad (3)$$

And according to the final peak positions of APSs in water (552 nm), methanol (578 nm), isopropanol (579 nm), acetone (582 nm), DMF (589 nm) and toluene (563 nm), the pore filling rates of these vapors in ZIF-8 particles are also calculated, which are summarized in Table S2.

C. Average refractive index changes and color shifts of PAPSs upon exposure to saturated EtOH vapors

For PAPSs with a starting wavelength of 551 nm in N₂ with $n_0 = 1.277$, their reflection peak positions shifted to 581 nm in saturated EtOH according to the experimental results. For polyhedral ZIF-8 particles that take up 32% (w/w) of EtOH, f_{guest} occupies 60.4% of the volume of micropores, $f_{\text{guest}} = 0.604 (f_{\text{guest}} + f_{\text{void}})$. As a result, for the PAPSs with f_{air} of 40% and f_{solid} of 26.4%, the f_{guest} (f_{EtOH}) and f_{void} are calculated to be 20.3% and 13.3%, respectively. Thereby, the refractive index of MOF PAPSs after ethanol adsorption increases from 1.277 to 1.343, indicating the theoretical reflection peak position of PAPSs should shift from 551 nm to 579.5 nm, which is close to our measured results.

$$n'_{\text{vapor}} = \sqrt{n_{\text{air}}^2 f_{\text{air}} + n_{\text{ZIF-8}}'^2 f_{\text{ZIF-8}}} = \sqrt{n_{\text{air}}^2 f_{\text{air}} + n_{\text{solid}}^2 f_{\text{solid}} + n_{\text{air}}^2 f_{\text{void}} + n_{\text{guest}}^2 f_{\text{guest}}} \quad (4)$$