Supporting Information

Experimental Section

Chemicals:

All solvents and chemicals were purchased from Alfa and used as received. All solvents and chemicals are of reagent quality and were used without further purification unless special explanation. Polydimethylsiloxane (KF-96 10cSt) was gained from Shin-Etsu Chemical, Japan. Silicon oil was brought from Yunuo Chemicals Ltd., China.

Fabrication of silica spherical colloidal crystals:

Monodisperse silica particles of various sizes (200 nm, 250 nm, 300 nm) were synthesized through sol–gel chemistry by the Stöber–Fink–Bohn method and seeded growth. The prepared particles were washed with ethanol three times, then selectively evaporated the ethanol at 70°C,and dispersed the particles in water with concentration of about 15%(w/v).To produce monodisperse silica colloidal crystal beads, we used the co-flow microfluidic device which was homemade by glass capillary tubes and a T-junction. The aqueous suspension containing monodisperse silica nanoparticles and silicon oil phases were pumped into the inner and outer capillaries at volumetric flow rates of about 0.5mL/h and 50mL/h, respectively. Then, the water in emulsion droplets were evaporated at 60°C and the silica nanoparticles self-assembled into ordered lattices. After solidification, the silica colloidal crystal beads were washed with hexane to remove the silicon oil and calcined at 800°C for 3 h to improve their mechanical strength.

Fabrication of the HKUST-1 composite microspheres:

Clear HKUST-1 precursor solutions were prepared according to the literature. In a typical preparation, 1.22 g $Cu(NO_3)_2 \cdot 3H_2O$ and 0.58 g 1,3,5-benzenetricarboxylate (H_3BTC) were dissolved in 5.0 g DMSO. The clear precursor solution was heated to 90°C and then was infiltrated into silica spherical colloidal crystals template. After evaporation at 90°C for 24 h, the resulting HKUST-1-Based Photonic colloidal molecules were obtained.

Fabrication of the MOF-5 composite microspheres:

$Zn(NO_3)_2 \bullet 6H_2O$ (0.357g) and terephthalic acid (0.067 g) were dissolved in 10 ml pure diethylformamide (DEF) at 75 °C and the mixture was kept at this temperature for 72 hrs. Then a short heating to 105 °C initiates crystallization of MOF-5 which can be detected with the unaided eye as a faint turbidity of the solution. After rapid cooling to 25 °C and filtration, the clear supersaturated MOF-5 mother solution were obtained, and after infiltration of the template with clear supersaturated MOF-5 mother solution, the evaporation of DEF at 90°C resulted in the formation of well-defined MOF-5 crystals in the confined spaces of the silica spherical colloidal crystals template.

Fabrication of the ZIF-8 composite microspheres:

The silica colloidal crystal spheres were immersed in a 2 mM of $Zn(NO_3)_2 \cdot H_2O$ methanol solution and 5 mM of 2-Methylimidazole methanol solution for 1 hour at 40 ℃. Between each step the spheres were rinsed with methanol and dried in air at 60℃. After 10-cycle growth, the resultant spheres were rinsed with methanol, dried and kept at room temperature.

Fabrication of the MIL-100 composite microspheres:

The silica colloidal crystal spheres were immersed subsequently in a 2 mM of $FeCl_3 \cdot 9H_2O$ ethanol solution for 1 hour and in a 2 mM of 1,3,5-benzenetricarboxylate (H_3BTC) ethanol solution for 1 hour at 40 ℃. Between each step the spheres were rinsed with ethanol and dried in air at 60℃. After 10-cycle growth, the resultant spheres were rinsed with ethanol, dried and kept at room temperature.

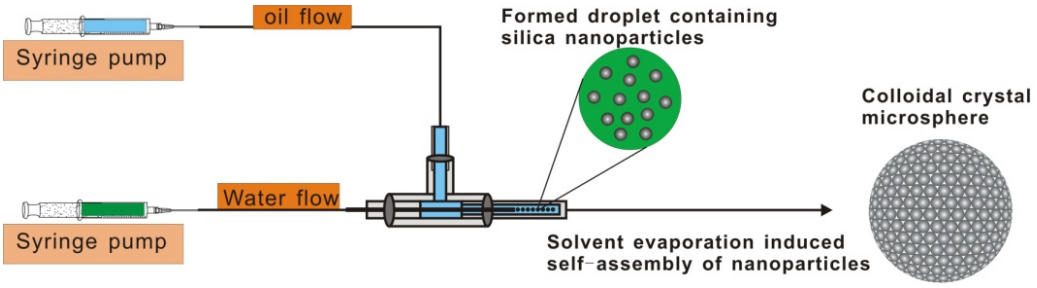
Fabrication of the isotropic and anisotropic MOF composite spheres:

The isotropic composite spheres were fabricated by entrapping guest molecules within the MOF cavities through host-guest chemistry. The MOF-5 composite microspheres were immersed into the dye molecules solution (10^{-8}mM, DEF solution of fluorescent dye molecules). Then the resultant microspheres were filtered off and rinsed with extensive DEF several times to remove the physically trapped dye molecules. The anisotropic MOF composite spheres were fabricated with a versatile strategy by using a “sandwich” contact printing (μCP) method

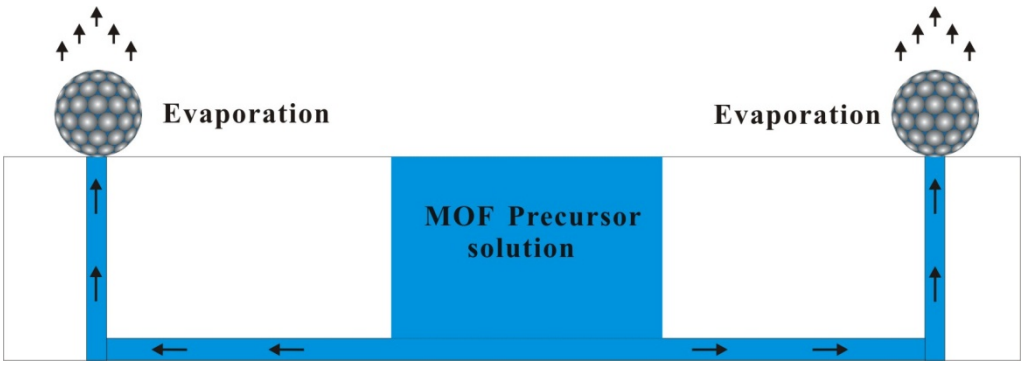
as our previous work. The PDMS stamps were loaded with a few drops of the respective chemical ink solution (10^{-8}mM, DEF solution of fluorescent dye molecules) and the excess ink solution was removed under a stream of argon. Then the composite MOF spheres were loaded onto the stamp and a second stamp, loaded with the second ink (like the first one) was put on top using a press. The samples were left at the room temperature. It took several minutes to transfer the "ink" into composite MOF spheres via host-guest chemistry only in the area of contact.

Characterization:

The co-flow microfluidic device used for the silica colloidal crystal beads generation was homemade by glass capillary tubes with inner diameter of 75 μm and outer diameter of 200 μm and a T-junction. UV-vis spectra were carried out by a PerkinElmer Lambda35 spectrometer. XRD measurements were performed on Bruker D8 Advance X-Ray powder diffractmeter. The optical spectra of the Spherical colloidal crystals were acquired with an Ocean Optics USB2000 fiber optic spectrophotometer coupled to an optical microscope. The microstructures of Spherical colloidal crystals were characterized by a scanning electron microscopy (SEM, HITACHI, S-300N). Photographs of the Spherical colloidal crystals were taken with an optical microscope (OLYMPUS BXFM) equipped with a CCD camera. The FT-IR spectra measurements were carried out on a Spectrum One FTIR spectrometer (Perkin-Elmer) by the KBr pellet method.



Scheme S1: Schematic illustration of the preparation of silica colloidal crystal microspheres.



Scheme S2. Schematic illustration of the preparation of composite MOF photonic spheres with complete volume filling using a simple microfluidic device.

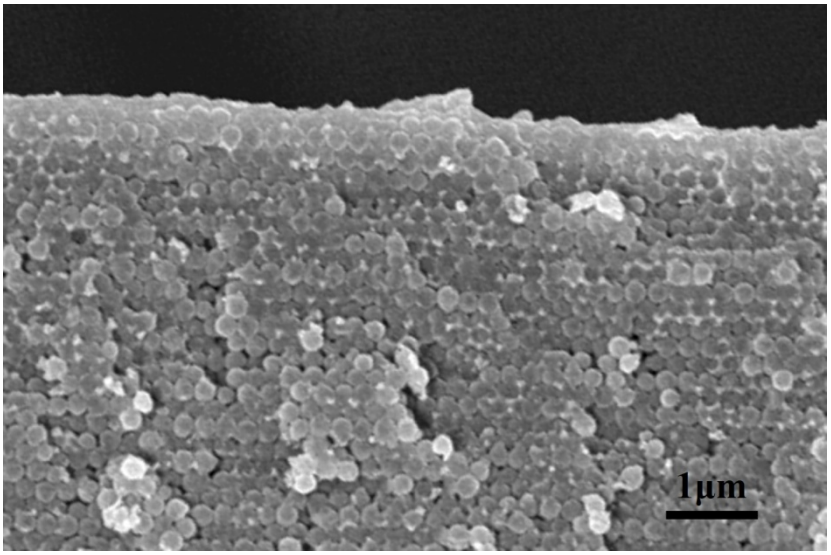


Figure S1: SEM cross-section image of the MOF composite microspheres.

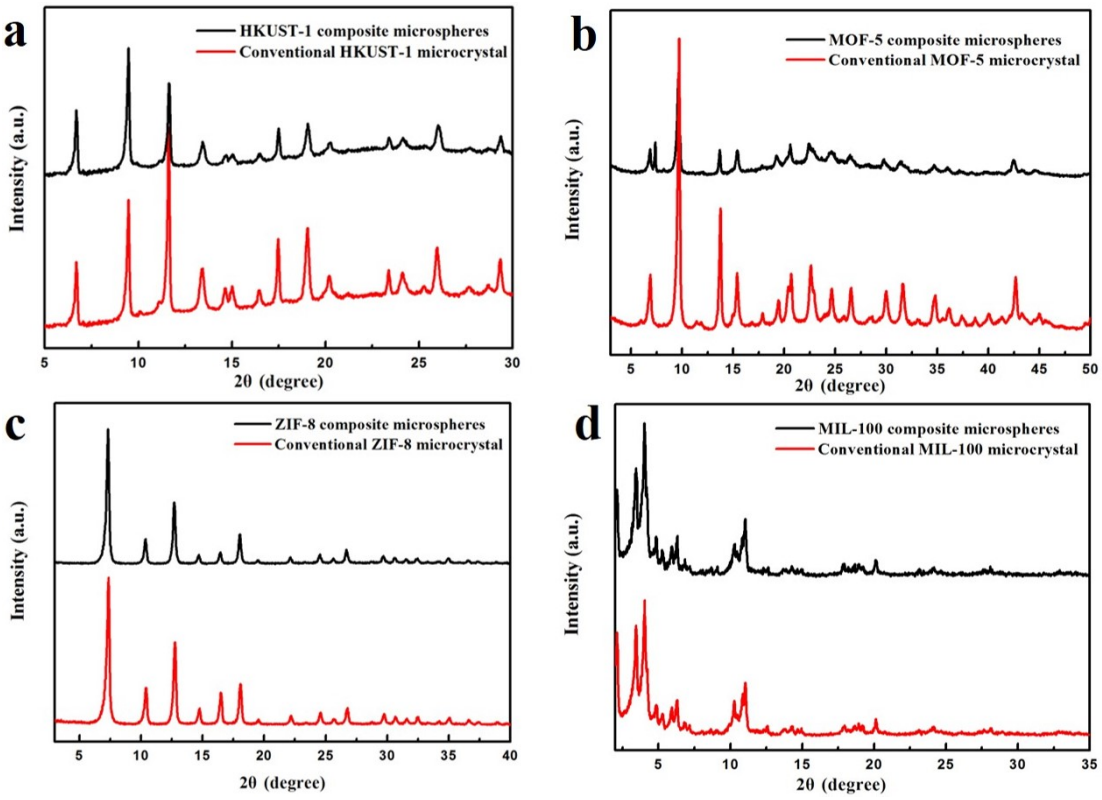


Figure S2: XRD pattern of HKUST-1 (a); MOF-5 (b); ZIF-8 (c); and MIL-100 (d).

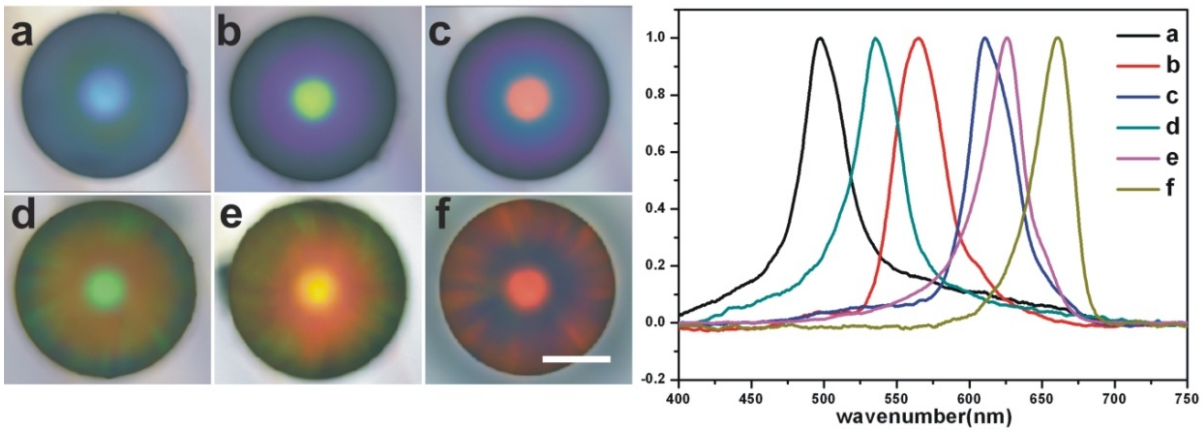


Figure S3: Optical images (a-c) and reflection spectra (a-c) of three silica spherical colloidal crystals with different diffraction-peak positions; and optical images (d-f) and reflection spectra (d-f) of the resulting three MOF-5 composite spheres. The scale is 100μm.

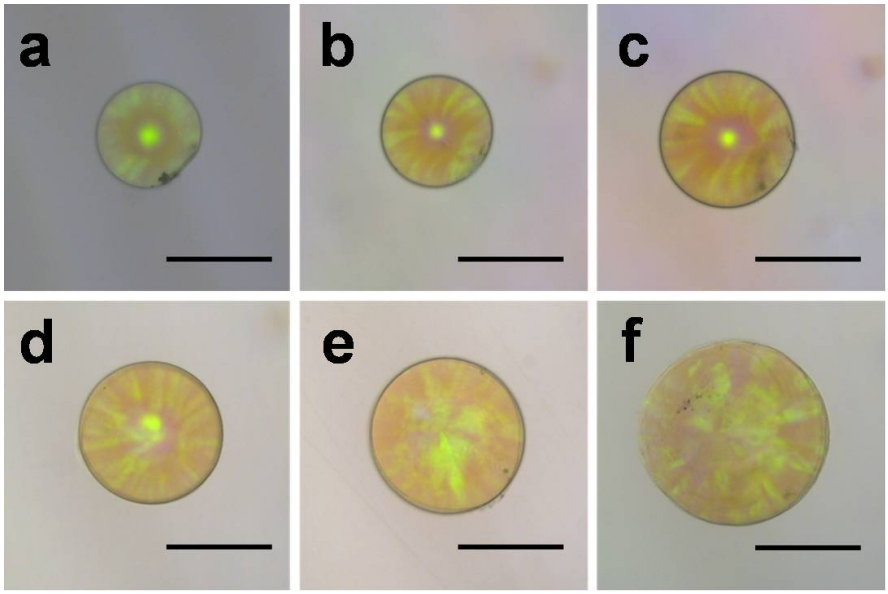


Figure S4: Optical images of the monodisperse MOF composite spheres with different diameter. The scale bar is 150μm.

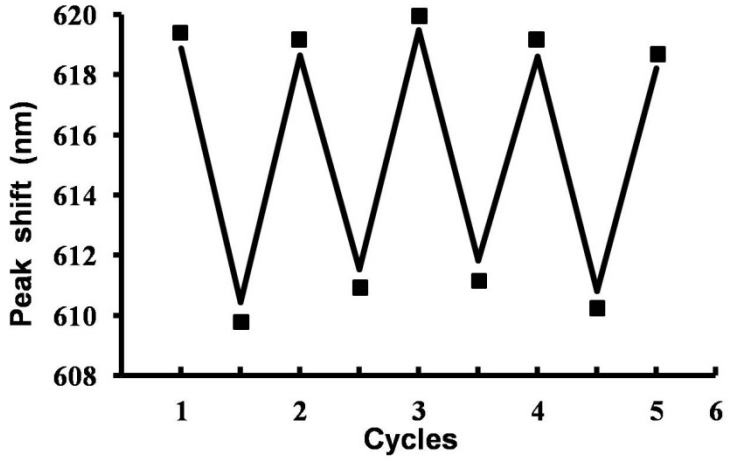


Figure S5: Recoverability of the MOF-5composite spheres exposed to n-hexane (4 cycles)

$$\lambda = 2\mathrm{d}n_{eff} = \left(\frac{\pi}{3\sqrt{2\phi}}\right)^{1/3}\left(\frac{8}{3}\right)^{1/2} D\left(n_p^2\phi + n_m^2(1-\phi)\right)^{1/2}$$

Figure S6: Bragg diffraction equation. Under a normal incident beam the wavelength of maximum peak is determined by lattice parameter (d) and effective reflective index (n_{eff}), where D is the nanoparticle diameter; N_p and n_m are the refractive indices of the nanoparticles and medium, respectively; Θ is the volume fraction of the nanoparticles.

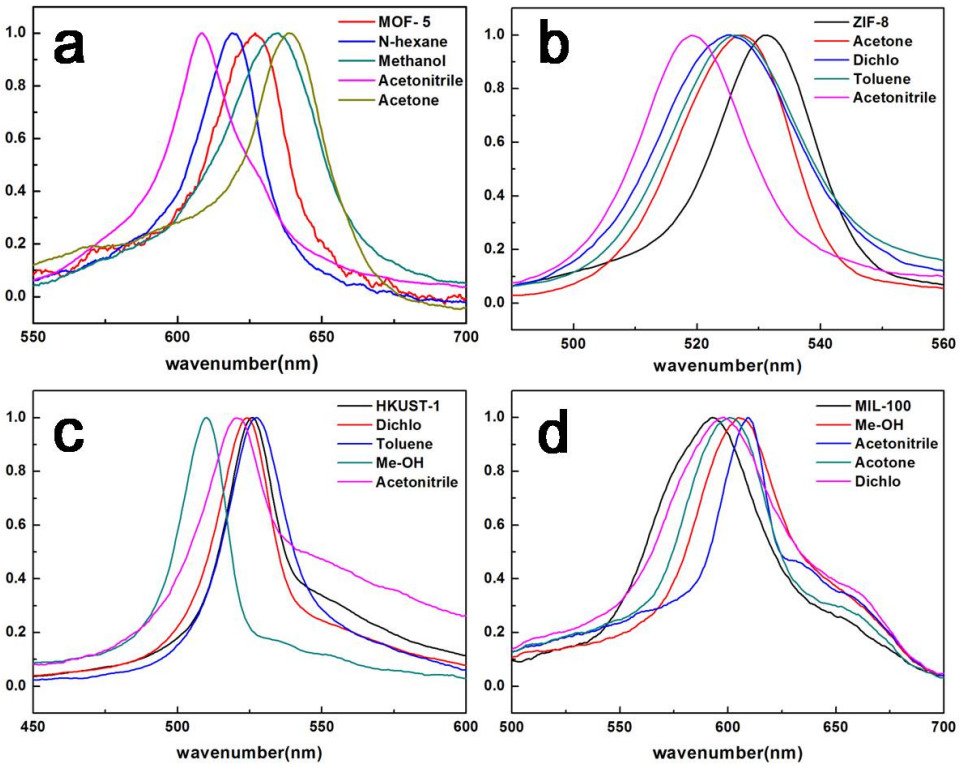


Figure S7: Optical responses of the MOF (HKUST-1, MOF-5, ZIF-8 and MIL-100) composite spheres upon exposure to different organic solvents.