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Electronic Supporting Information

Single crystalline hollow metal-organic frameworks: a metal-organic polyhedron single crystal as a sacrificial template

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Experimental Section

General Procedures

All reagents were purchased from commercial sources and used without further purification. Elemental analyses were conducted using a Flash 2000 elemental analyzer at the Ulsan National Institute of Science and Technology, Korea. Fourier transform–infrared (FT–IR) spectra were recorded as KBr pellets using a NICOLET iS 10 FT–IR spectrophotometer (4000–400 cm^{-1}). ^{1}H nuclear magnetic resonance (NMR) spectra were recorded using a VNMRS 600 MHz FT-NMR spectrophotometer. Scanning electron microscope (SEM) images were obtained using an S-4800 field-emission SEM (Hitachi). Sonication of samples was achieved using a Powersonic 410 (Hwashin Technology). Powder X-ray diffraction (PXRD) data were recorded using a Bruker D2 Phaser automated diffractometer at room temperature with a step size of 0.02° in 2θ angle. Simulated PXRD patterns were calculated with Material Studio software[S1] using single-crystal data.

Preparation of metal-organic polyhedra (MOPs)

Synthesis of $[Cu_{24}(hip)_{24}(DMF)_8(H_2O)_{16}]\cdot 39DMF\cdot 29H_2O$, MOP-micro. A 0.2906 g (1.250 mmol) amount of $Cu(NO_3)_2\cdot 2.5H_2O$ was dissolved in 25 mL *N,N'*-dimethylformamide (DMF) and 0.2278 g 5-hydroxyisophthalic acid (H_2hip) (1.251 mmol) was added to the solution. The solution was stirred in a 50 mL vial for 12 h at ambient temperature. The cyan crystalline powder product thus obtained was washed with DMF, filtered, and dried under dynamic vacuum for 36 h at ambient temperature. Yield = approx. 31 mg, about 5.9% based on the Cu(II) ion concentration. Elemental analysis (EA) was performed using the sample exposed to air for a couple of minutes before analysis. EA for $[Cu_{24}(hip)_{24}(DMF)_8(H_2O)_{16}]\cdot 39DMF\cdot 29H_2O = C_{333}H_{515}N_{47}O_{212}Cu_{24}$ (fw = 10094.04 g/mol): Calc. (%): C, 39.62; H, 5.14; N, 6.52; Found (%): C, 39.61; H, 5.14; N, 6.58. FT-IR (KBr, 4000–400 cm^{-1}): 3423 (br, w), 2962 (w), 2927 (w), 1655 (m), 1633 (m), 1591(s), 1493 (w), 1421(sh), 1386 (vs), 1304(w), 1281 (w), 1221(w), 1130(w), 1107(w), 1004 (w), 979 (w), 897 (w), 778(m), 735 (m), 666 (w), 496 (w).

Synthesis of $[Cu_{24}(hip)_{24}(DMF)_8(H_2O)_{16}]\cdot 100DMF\cdot 32H_2O$, MOP-macro. The reaction solution for **MOP-macro** crystals was prepared using the same procedure as used for **MOP-micro** crystals. The solution was divided into five portions. Each aliquot was heated to 60 °C in a flame-sealed glass tube for 8 d. Greenish-cyan square-pyramidal and truncated octahedral crystals harvested were washed with DMF, soaked in fresh DMF for 1 d to remove any residuals in the solvent pore of the crystals, filtered, and dried under inert conditions for 15 min. Yield = 0.2070 g, 27.2% based on the Cu(II) ion. EA was performed using the sample exposed to air for a couple of minutes before analysis. EA for $[Cu_{24}(hip)_{24}(DMF)_8(H_2O)_{16}]\cdot 100DMF\cdot 32H_2O$ = $C_{516}H_{948}N_{108}O_{276}Cu_{24}$ (fw = 14606.87 g/mol): Calc. (%): C, 42.43; H, 6.54; N, 10.36; Found (%): C, 42.09; H, 6.13; N, 10.75. FT-IR (KBr, 4000–400 cm^{-1}): 3408 (br, w), 2965 (w), 2930 (w), 2656 (w), 1651 (vs), 1634 (sh), 1589(vs), 1548(sh), 1493 (m), 1414(sh), 1385 (vs), 1300(sh), 1282 (m), 1126(sh), 1107(w), 1060 (w), 1003 (w), 979 (w), 896 (w), 845 (w), 778(m), 735 (m), 668 (w), 490 (w).

Preparations of metal-organic frameworks (MOFs) via stepwise reactions using a MOP as a molecular precursor

Synthesis of $[Cu_{24}(hip)_{24}(dabco)_6(H_2O)_{12}]$, 1-micro. An approximately 50 mg amount of dried **MOP-macro** crystals was dissolved in 1 mL MeOH. When 14 mL of a 0.428 mM MeOH solution of 1,4-diazabicyclo[2.2.2]octane (dabco) was slowly added into the MeOH solution of **MOP-macro**, the solution immediately turned turbid. After leaving the solution undisturbed for 1 h in ambient conditions, a precipitate of approx. 50-nm-sized crystals was collected and washed twice using fresh MeOH.

Synthesis of $[Cu_{24}(hip)_{24}(pz)_6(H_2O)_{12}]$, 2-micro. 2-micro crystals were synthesized via a procedure similar to that used for the preparation of **1-micro** using 3 mL of a 20 mM MeOH solution of pyrazine (pz) instead of 14 mL of a 0.428 mM MeOH solution of dabco. After leaving the solution undisturbed for 4 h in ambient conditions, a precipitate of approx. 2-μm-sized crystals was collected and washed twice with fresh MeOH.

Synthesis of $[Cu_{24}(hip)_{24}(bipy)_6(H_2O)_{12}]$, 3-micro. 3-micro crystals were synthesized via the same procedure as used for the preparation of the **1-micro** crystals. When 14 mL of a 0.428 mM MeOH solution of 4,4′-bipyridine (bipy) was slowly added into the MeOH solution of dried **MOP-macro** crystals, the solution immediately turned turbid. After letting the solution stand for 12 h undisturbed in ambient conditions, a precipitate of approx. 100-nm-sized crystals was collected and washed twice using fresh MeOH.

Preparations of hollow MOFs via stepwise reactions using a MOP crystal as a crystalline template

Synthesis of [$Cu_{24}(hip)_{24}(dabco)_6(H_2O)_{12}$], 1-macro-h. Hollowed **1-macro-h** was synthesized via a procedure similar to that used for the preparation of **1-micro** except using dried **MOP-macro** single crystals as crystalline templates instead of MOPs as a molecular precursor in a MeOH solution of **MOP-macro**. Approximately 20 mg of dried **MOP-macro** crystals was transferred into a vial containing 6 mL of a 0.3 M MeOH solution of dabco. The solution was tightly sealed in a vial stood at ambient temperature for 1 h. The resulting crystals were harvested and washed twice with fresh MeOH.

Synthesis of [$Cu_{24}(hip)_{24}(pz)_6(H_2O)_{12}$], 2-macro-h. Hollowed **2-macro-h** was synthesized via the same procedure as used for the preparation of hollowed **1-macro-h** using 6 mL of a 0.35 M MeOH solution of pz instead of 6 mL of a 0.3 M MeOH solution of dabco.

Synthesis of [$Cu_{24}(hip)_{24}(bipy)_6(H_2O)_{12}$], 3-macro-h. Hollowed **3-macro-h** was synthesized via the same procedure as used for the preparation of hollowed **1-macro-h** using 6 mL of a 0.12 M MeOH solution of bipy instead of 6 mL of a 0.3 M MeOH solution of dabco.

Synthesis of [$Cu_{24}(hip)_{24}(dabco)_6(H_2O)_{12}$], 1-micro-h. Hollowed **1-micro-h** was synthesized via a similar procedure as used for the preparation of hollowed **1-macro-h** single crystals using **MOP-micro** single crystals as crystalline templates instead of **MOP-macro** single crystals. 10 mL of a 0.3 M MeOH solution of dabco was quickly added to approximately 30 mg of wet crystals of **MOP-micro** harvested from DMF. The mixture was stored in a tightly sealed vial at ambient temperature for 1 h. The **1-micro-h** crystals were harvested and washed twice with fresh MeOH.

Synthesis of [Cu_{24}(hip)$_{24}$(pz)$_6$(H_2O)$_{12}$], 2-micro-h. Hollowed **2-micro-h** was synthesized via the same procedure as used for the preparation of hollowed **1-micro-h** using 10 mL of a 0.35 M MeOH solution of pz instead of 10 mL of a 0.3 M MeOH solution of dabco.

Synthesis of [Cu_{24}(hip)$_{24}$(bipy)$_6$(H_2O)$_{12}$], 3-micro-h. Hollowed **3-micro-h** was synthesized via the same procedure as used for the preparation of hollowed **1-micro-h** using 10 mL of a 0.06 M MeOH solution of bipy instead of 10 mL of a 0.3 M MeOH solution of dabco.

Crystallographic data collection and refinement of the structures

A single crystal of **MOP-macro** was coated with paratone-*N* oil and the diffraction data measured at 100 K with synchrotron radiation using a ADSC Quantum-210 detector at 2D SMC with a silicon (111) double crystal monochromator (DCM) at the Pohang Accelerator Laboratory, Korea. ADSC Q210 ADX software[S2] was used for data collection (detector distance is 63 mm, omega scan; Δω = 1°, exposure time was 1 s per frame) and HKL3000sm (ver. 703r)[S3] was used for cell refinement, reduction, and absorption correction.

MOP-macro. $[Cu_{24}(hip)_{24}(DMF)_8(H_2O)_{16}]$ ($C_{216}H_{184}N_8O_{144}Cu_{24}$), fw = 6720.66 g·mol^{-1}, tetragonal, space group $I4/m$, $a = b = 28.096(4)$ Å, $c = 40.947(8)$ Å, $V = 32{,}323(9)$ Å^3, $Z = 2$, μ ($\lambda = 1.00000$ Å) = 2.005 mm^{-1}, 60,455 reflections were collected, of which 8507 were unique ($R_{\mathrm{int}} = 0.0420$). The crystal structure was solved with a direct method using the SHELXS and refined by full-matrix least-squares calculations using the SHELXL.[S4] Four copper sites including two at crystallographic *m* symmetry sites (Wyckoff *h* site), three 5-hydroxyisophthalate ligands, one DMF molecule and three water molecule sites including two at crystallographic *m* symmetry sites (Wyckoff *h* site) were observed as an asymmetric unit. All nonhydrogen atoms were refined anisotropically; the hydrogen atoms except on hydroxyl groups and on coordinated water molecules were assigned isotropic displacement coefficients U(H) = 1.2U (C) and 1.5U (C_{methyl}), and their coordinates were allowed to ride on their respective atoms. The hydrogen atoms of the hydroxyl groups and the coordinated water molecules are not included in the least-squares refinement. The refinement of the structural model was performed under geometry restraints, such as DFIX, DANG, and FLAT, and displacement parameter restraints, such as ISOR, DEMU, and SIMU. The final refinement was performed with a modification of the structural factors for the electron densities of the disordered solvents (70.1% of the total unit cell volume; 2517 solvent electrons correspond to about 63 DMF molecules per unit cell) using the SQUEEZE option of the PLATON software package.[S5] Refinement converged at a final $R1 = 0.1132$ and $wR2 = 0.3621$ for 4439 reflections with $I > 2\sigma(I)$; $R1 = 0.1456$ and $wR2 = 0.4021$ for all 8507 reflections. The largest difference peak and hole were 0.407 and –0.377 e·Å^{-3}, respectively.

A summary of the crystal and some crystallography data is given in Table S1. CCDC 985419 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

Table S1 Crystal data and structure refinement for **MOP-macro**.

Empirical formula	$C_{216}H_{184}N_8O_{144}Cu_{24}$	
Formula weight	6720.66	
Temperature	100(2) K	
Wavelength	1.00000 Å	
Crystal system	Tetragonal	
Space group	*I*4/*m*	
Unit cell dimensions	a = 28.096(4) Å	α = 90°
	b = 28.096(4) Å	β = 90°
	c = 40.947(8) Å	γ = 90°
Volume	32323(11) $Å^3$	
Z	2	
Density (calculated)	0.691 Mg/m^3	
Absorption coefficient	2.042 mm^{-1}	
F(000)	6768	
Crystal size	0.180 x 0.180 x 0.180 mm^3	
Theta range for data collection	2.885 to 29.997°	
Index ranges	-28<=h<=28, -28<=k<=28, -39<=l<=39	
Reflections collected	60455	
Independent reflections	8507 [R(int) = 0.0420]	
Completeness to theta = 29.997°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.710 and 0.710	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8507 / 190 / 406	
Goodness-of-fit on F^2	1.446	
Final R indices [I>2sigma(I)]	R1 = 0.1132, wR2 = 0.3621	
R indices (all data)	R1 = 0.1456, wR2 = 0.4021	
Largest diff. peak and hole	0.407 and −0.377 $e \cdot Å^{-3}$	

PXRD patterns of MOP-micro and MOP-macro

Attempts to prepare an isoreticular Cu-MOF of the reported $[Zn_{24}(mip)_{24}(dabco)_6(H_2O)_{12}]$[S6] via a similar one-pot solvothermal reaction using H_2hip as a ligand and dabco as a potential linker between the MOP building units in DMF only produced MOP crystals, $[Cu_{24}(hip)_{24}(DMF)_8(H_2O)_{16}]$. Similar reactions under slightly different reaction conditions in the absence of the dabco linker also produced MOP crystals, and **MOP-micro** and **MOP-macro** crystals. The PXRD patterns of the **MOP-micro** and **MOP-macro** crystals were identical although the crystals were prepared using slightly different reaction conditions (Fig. S1).

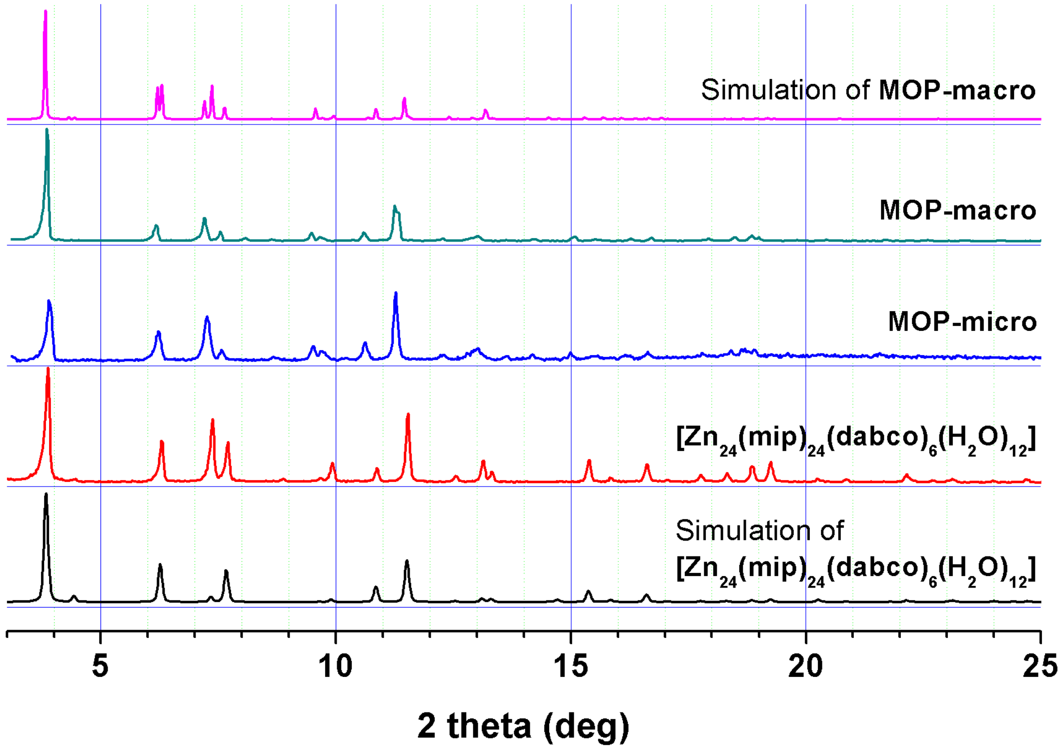

Fig. S1 PXRD patterns of **MOP-micro** and **MOP-macro**.

The single crystal structure of MOP-macro

A single crystal structure analysis of **MOP-macro** showed that the cuboctahedral MOPs were in the same cubic close-packing arrangement as the MOP building units in the reported MOF, $[Zn_{24}(mip)_{24}(dabco)_6(H_2O)_{12}]$, of **ubt** topology (Figs. S2 and S3).

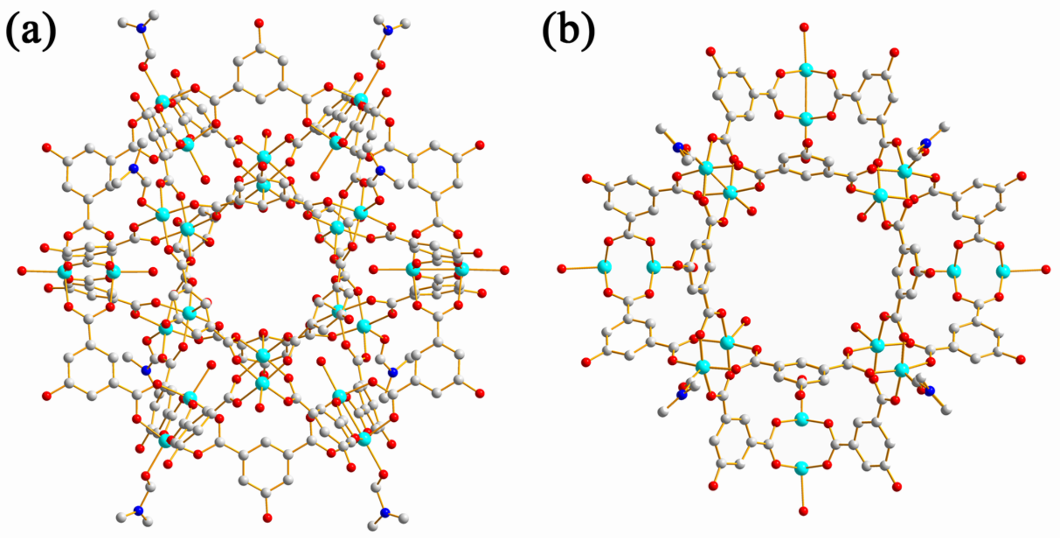

Fig. S2 Crystal structure of **MOP-macro**. Ball-and-stick diagrams of the cuboctahedral MOP in views showing (a) a triangular window and (b) a square window, respectively.

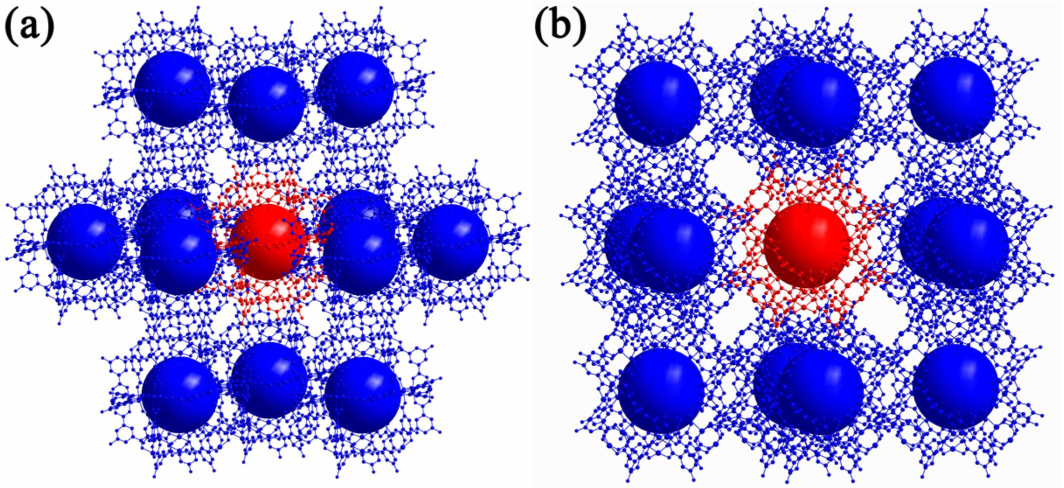

Fig. S3 Packing diagrams of the **MOP-macro** structure in the cubic close-packing arrangement of the cuboctahedral MOPs, where the large red and blue dummy balls are drawn in the cavities of the individual MOPs. Packing views emphasizing (a) cubic close packing and (b) face-centered cubic lattice arrangement of the MOPs, respectively.

The ^{1}H NMR spectra of MOP-macro

The ^{1}H NMR spectra of **MOP-macro** crystals in CD_3OD showed only a broad and weak peak in the diamagnetic region for the protons of the hip ligand together with the peaks corresponding to DMF and water molecules from the crystals and to methanol molecules from the NMR solvent (Fig. S4). The broad and weak peak indicates that the hip is ligated to the paramagnetic Cu(II) ion in the solution. The presence of the hip ligand in **MOP-macro** crystals was confirmed using the ^{1}H NMR spectrum of the crystals digested in CD_3OD/DCl. The two new peaks corresponding to the aromatic protons of the hip ligand appeared at about 7.5 and 8.0 ppm. The acidic DCl solution led to the dissociation of the MOP and the release of the free hip ligand. The ^{1}H NMR spectra indicate that the MOPs in **MOP-macro** crystals were intact in the MeOH solution.

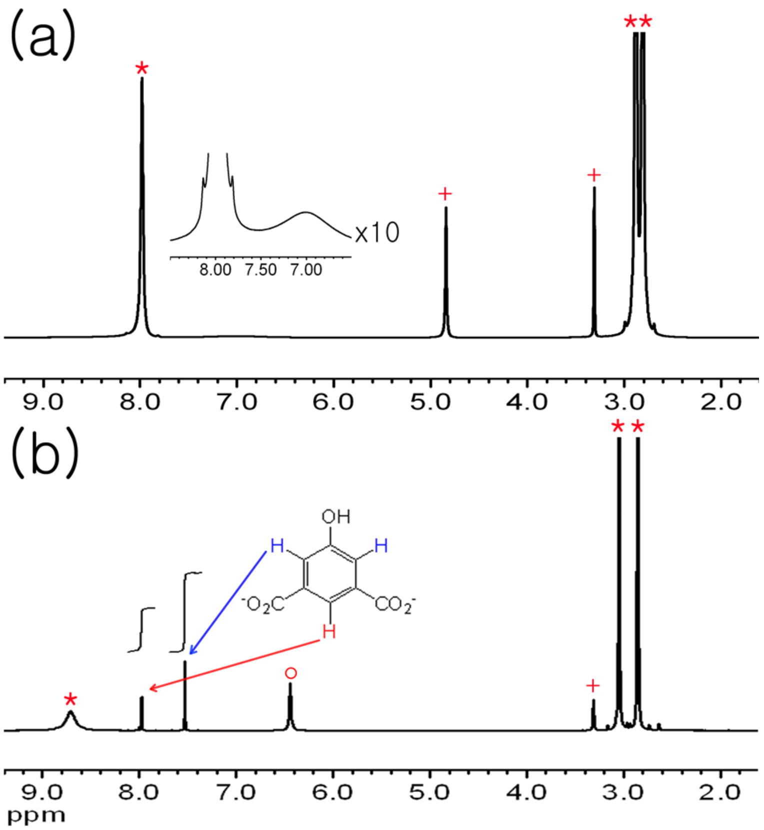

Fig. S4 The ^{1}H NMR spectra of **MOP-macro** (a) in CD_3OD and (b) in CD_3OD/DCl. The asterisks (*) indicate DMF proton peaks, the crosses (+) indicate MeOH proton peaks, and the open circles (○) indicate H_2O proton peaks.

Stability of MOP-macro

The crystalline **MOP-macro** sample was very unstable in ambient conditions. The PXRD patterns of the crystalline **MOP-macro** sample in ambient conditions show that it loses its crystallinity within 14 min (Fig. S5). Addition of a small amount of DMF to the amorphous **MOP-macro** sample restores the crystallinity of the sample.

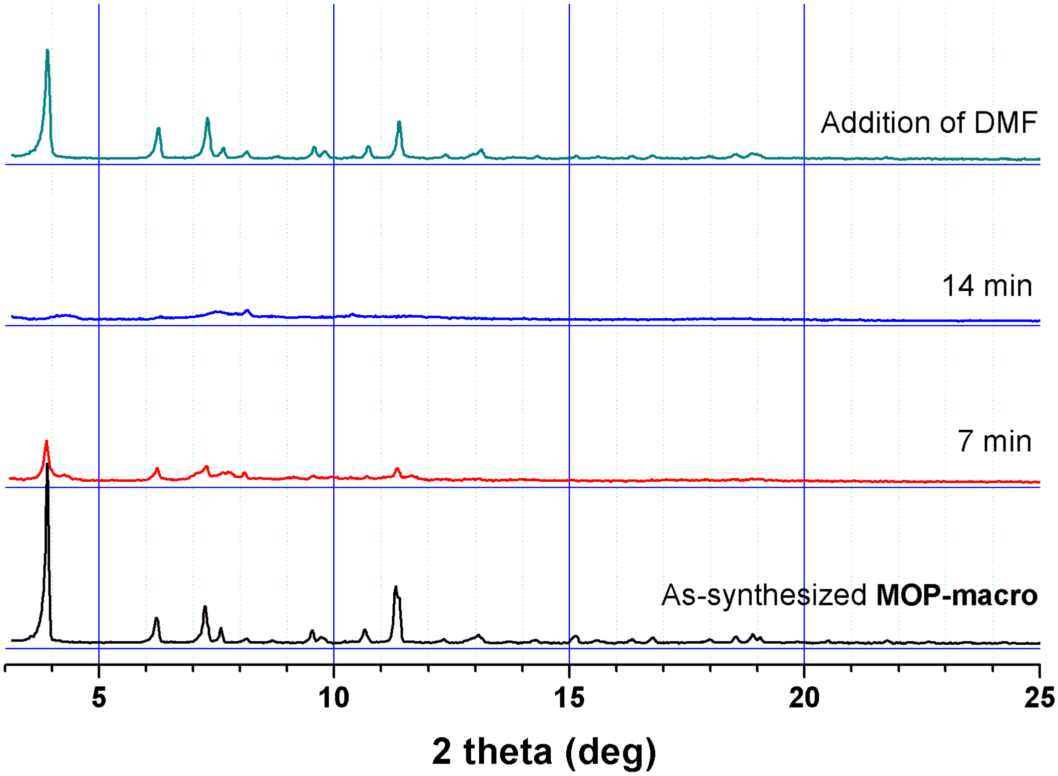

Fig. S5 The PXRD patterns of the as-synthesized **MOP-macro** crystalline sample in ambient condition and the restoration of its crystallinity by solvent addition.

Comparison of the PXRD patterns of 1-macro-h, 2-macro-h and 3-macro-h crystals with those of the corresponding isoreticular Cu- and Zn-MOFs

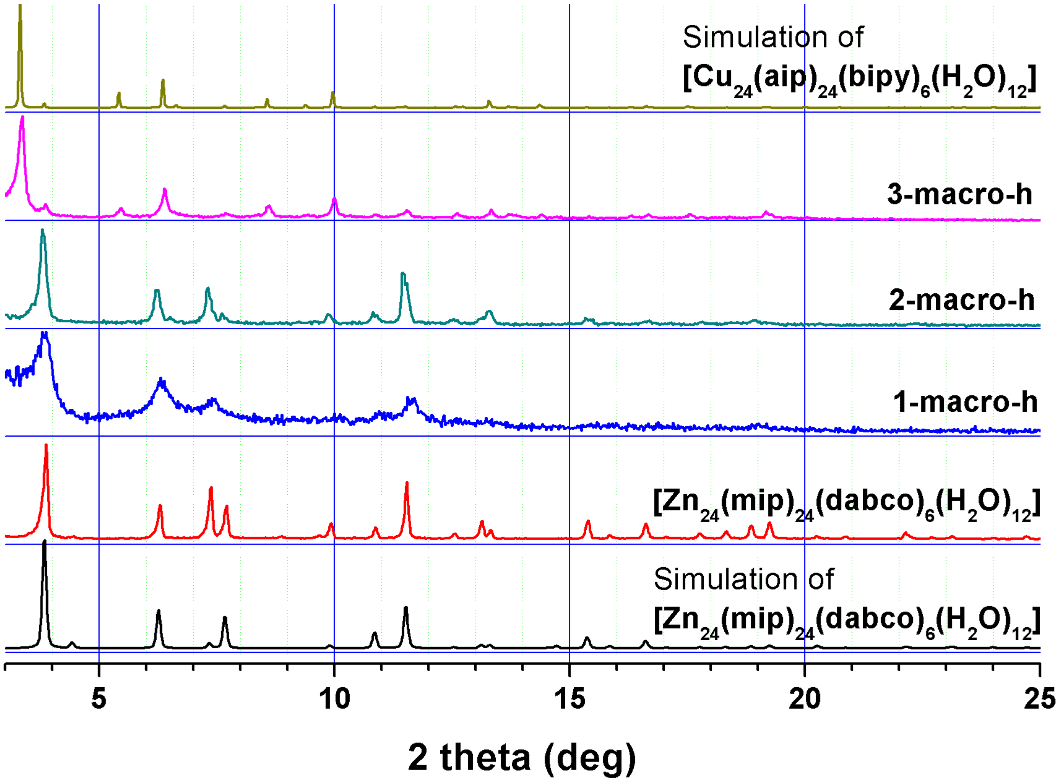

Fig. S6 Comparison of the PXRD patterns of **1-macro-h**, **2-macro-h** and **3-macro-h** with those of $[Zn_{24}(mip)_{24}(dabco)_6(H_2O)_{12}]$[S6] and $[Cu_{24}(aip)_{24}(bipy)_6(H_2O)_{12}]$.[S7]

A diffraction pattern of 2-macro-h

A diffraction pattern of a **2-macro-h** single crystal was measured using an imaging plate in a Rigaku RAPID II X-ray diffraction camera system equipped with a graphite crystal incident beam monochromator. The discrete diffraction peaks indicate the single crystallinity of hollow **2-macro-h** sample (Fig. S7). The hollow pattern in the diffraction image might be due to the microcrystals in the hollow cavity.

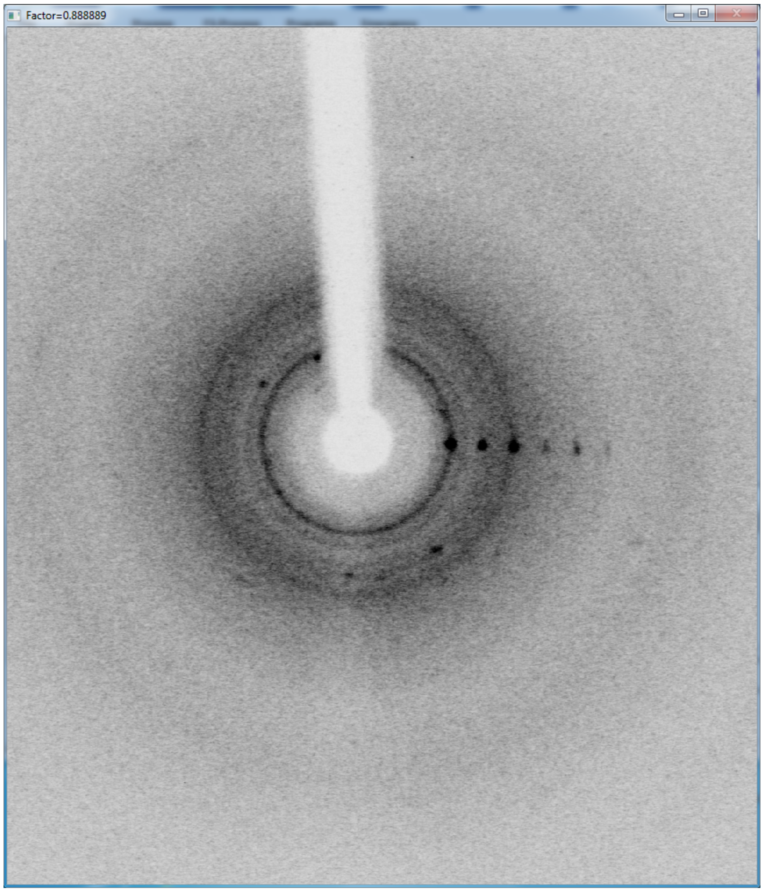

Fig. S7 A diffraction pattern of a **2-macro-h** single crystal.

SEM images of 1-micro, 2-micro, and 3-micro

The scanning electron microscope (SEM) images of **1-micro** and **3-micro** samples showed that the dimensions of the crystalline particles were approximately 50 nm and 100 nm, respectively (Fig. S8). However, the morphologies of the microcrystalline particles were not well developed. In particular, the crystalline particles in the **1-micro** sample are aggregates of smaller particles. A SEM image of a **2-micro** sample indicated that the particles had well-developed octahedral faces with approximately 2 μm dimensions.

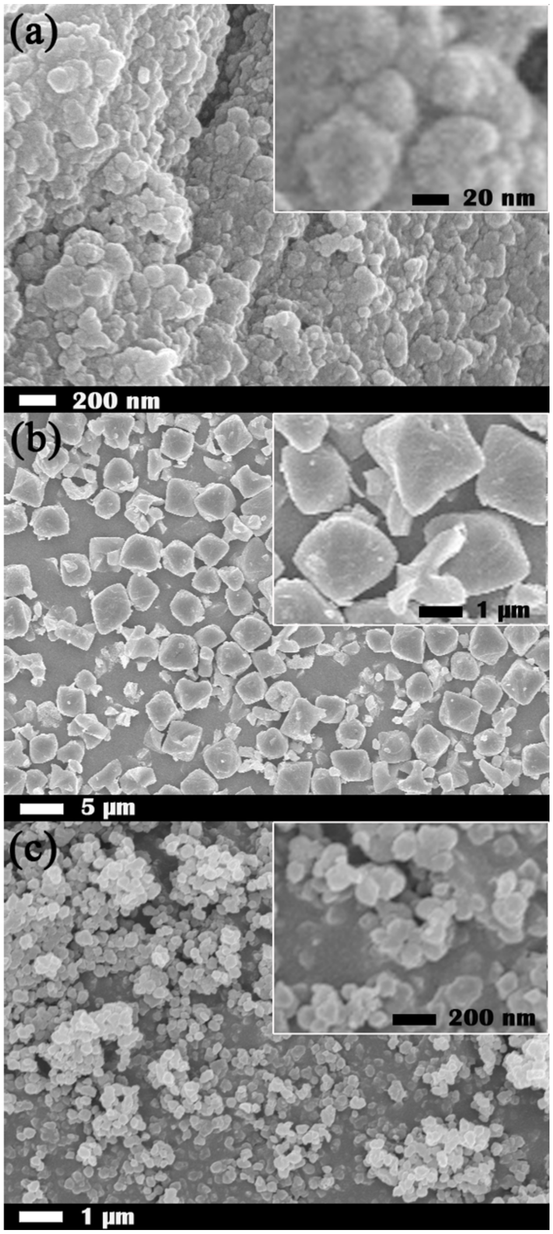

Fig. S8 SEM images of **1-micro**, **2-micro**, and **3-micro**.

PXRD patterns of 1-micro-h, 2-micro-h, and 3-micro-h

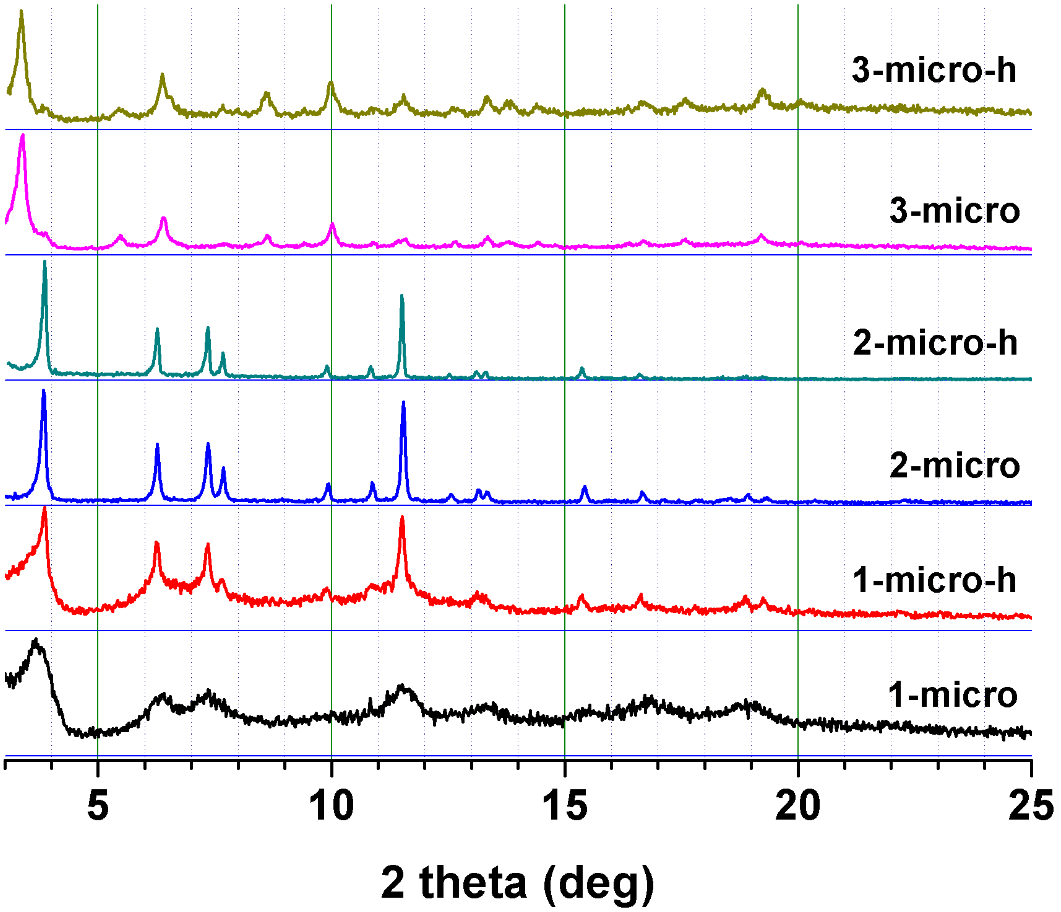

Fig. S9 Comparison of the PXRD patterns of nonhollow crystals, **1-micro**, **2-micro** and **3-micro**, with those of the corresponding hollow crystals, **1-micro-h**, **2-micro-h**, and **3-micro-h**.

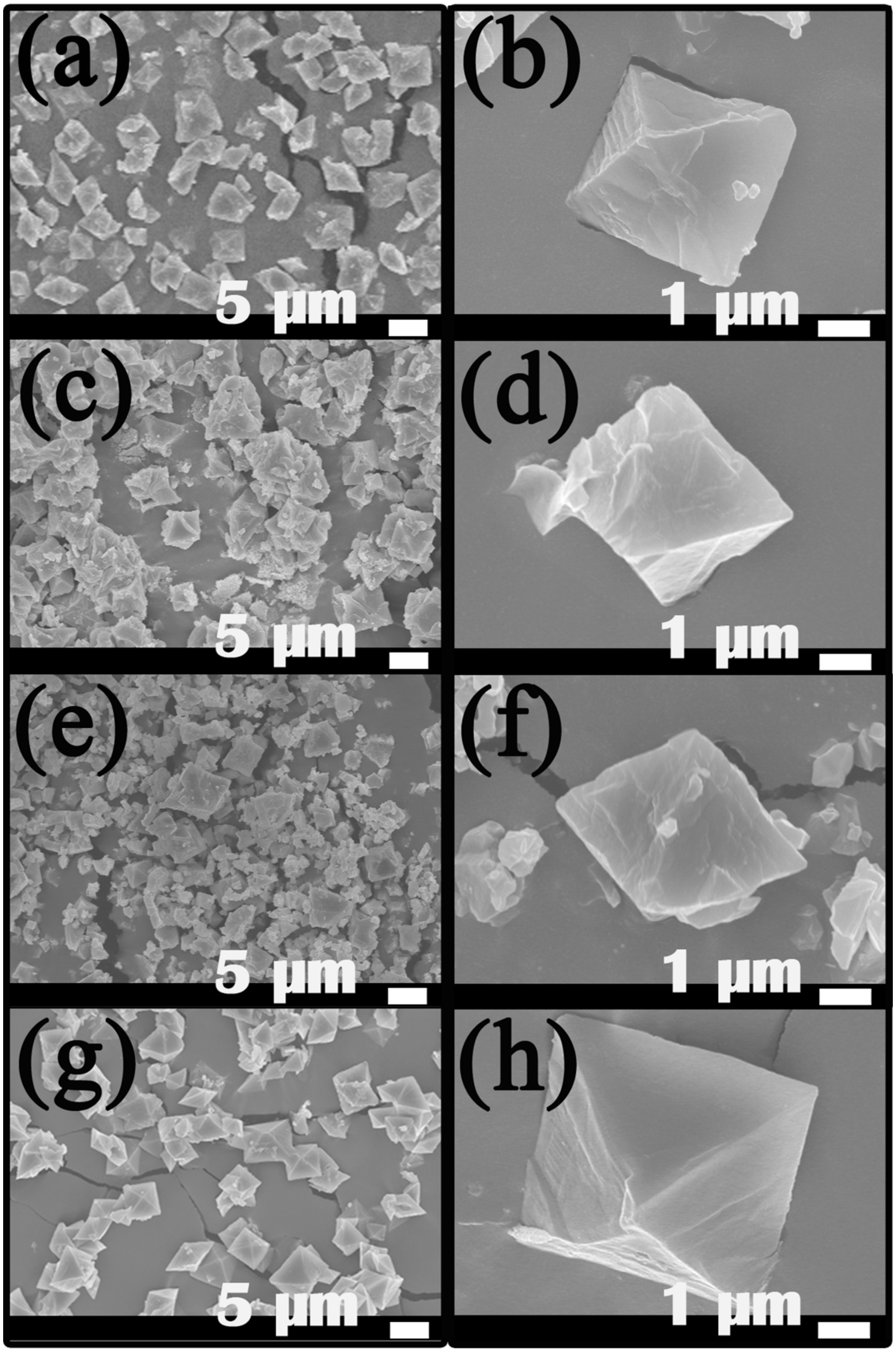

Fig. S10 SEM images of MOP and MOFs. (a) and (b) Nonhollow **MOP-micro** crystals, (c) and (d) hollow **1-micro-h** crystals, (e) and (f) hollow **2-micro-h** crystals, and (g) and (h) hollow **3-micro-h** crystals.

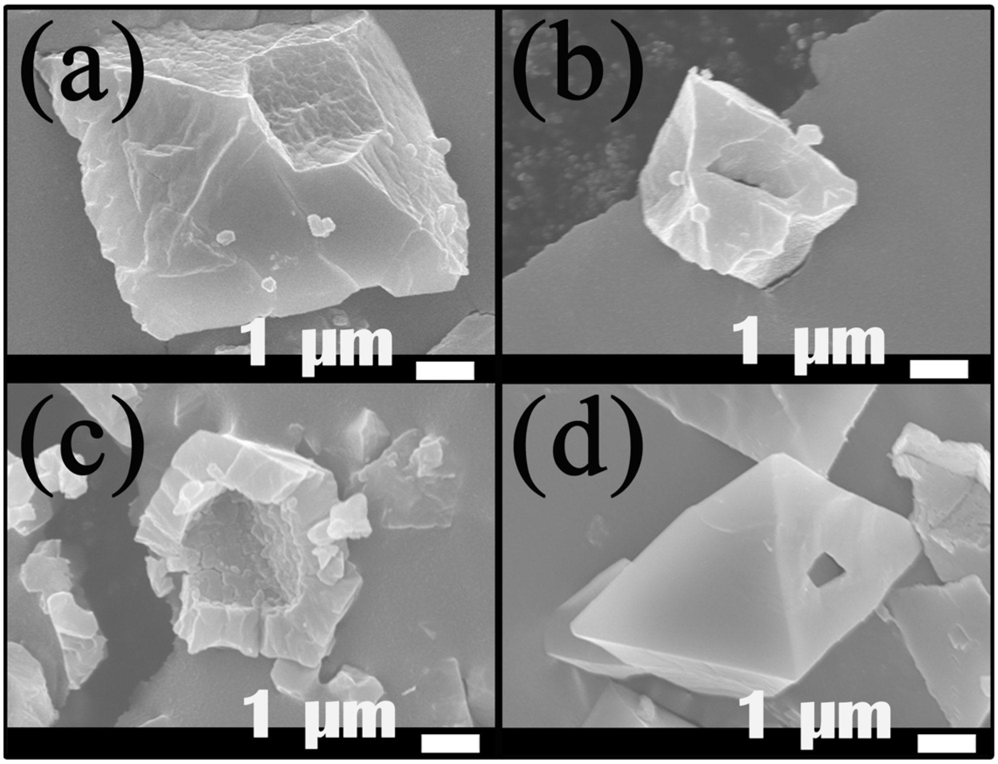

Fig. S11 SEM images of MOP and MOFs. (a) A nonhollow **MOP-micro** crystal, (b) a hollow **1-micro-h** crystal with an aperture in the shell, (c) a fragment of a hollow **2-micro-h** crystal with an exposed inner cavity, and (d) a hollow **3-micro-h** crystal with a small aperture in the shell.

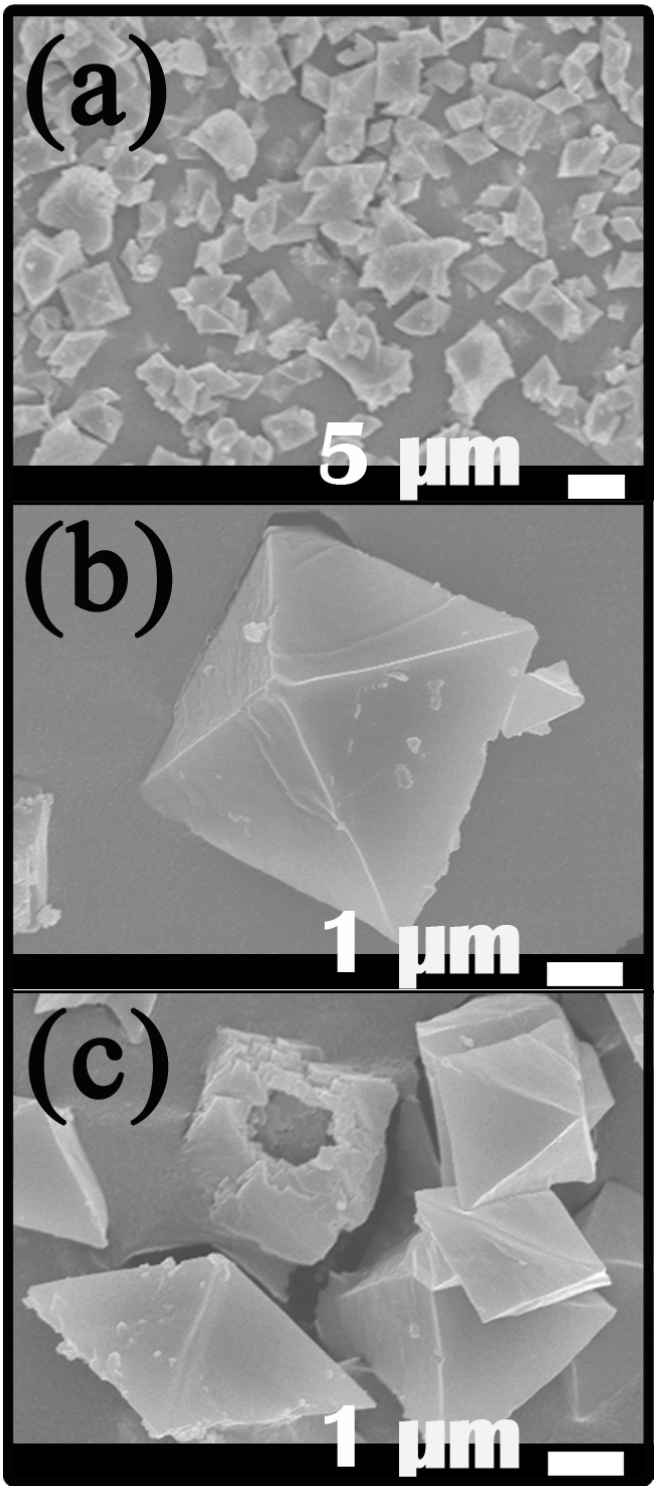

Fig. S12 SEM images of hollow **3-micro-h** crystals sonicated at 40 kHz for 5 min. (a) Bulk **3-micro-h** crystals, (b) a selected **3-micro-h** crystal with clean crystal faces, and (c) a fragmented hollow **3-micro-h** crystal with an exposed inner cavity.

FIB-SEM procedure

The samples washed using acetone and methanol were dried under vacuum for 12 hrs at ambient temperature and glued onto a holder using either silver paste or carbon tape. The images were collected with a FEI Helios 450 HP system. The mounted samples were adjusted to eucentric height so that the sliced surface could be imaged directly in SEM mode without repositioning (Fig. S13). The sample surface was perpendicular to the ion gun and at an angle of 52◦ with respect to the electron gun. The FIB milling was performed with Ga ion-beam current of 430 pA at 30 kV and the SEM image was taken with electron beam current 100 pA at 5 kV.

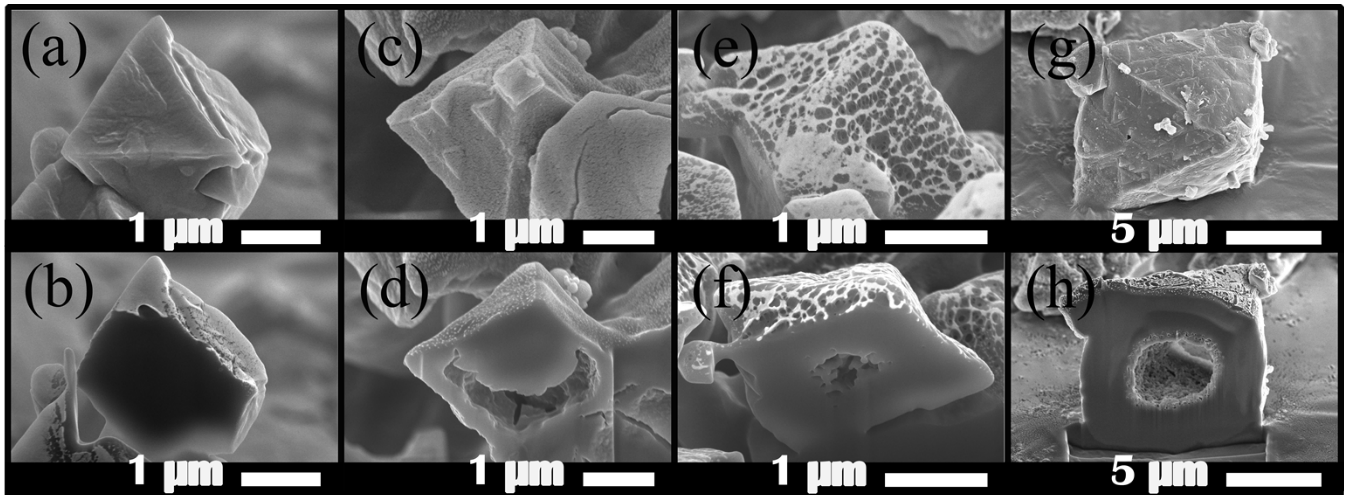

Fig. S13 SEM and FIB-SEM images of MOP and MOFs. (a) and (b) A nonhollow **MOP-micro** crystal and the corresponding MOP crystal sliced using FIB, (c) and (d) a hollow **1-micro-h** crystal and the sliced **1-micro-h** crystal, (e) and (f) a hollow **2-micro-h** crystal and the sliced **2-micro-h** crystal sliced, and (g) and (h) a hollow **3-micro-h** crystal and the sliced **3-micro** crystal.

To reduce an artifact known as "waterfalling" or "curtaining" effect, seen on the cross section in Fig. S12,[S8] the FIB-SEM image of a **3-micro-h** crystal sliced by FIB milling was obtained with carbon deposition process before ion milling (Fig. 4d).

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