**Electronic supplementary information**

# Controllable Construction of Metal-Organic Polyhedra in Confined Cavities via In Situ Sites-Induced Assembly

Ying-Hu Kang, Ni Yan, Zhen-Yu Gao, Peng Tan, Yao Jiang, Xiao-Qin Liu, and Lin-Bing Sun[*]

*State Key Laboratory of Materials-Oriented Chemical Engineering, Jiangsu National Synergetic*

*Innovation Center for Advanced Materials (SICAM), College of Chemistry and Chemical*

*Engineering, Nanjing Tech University, Nanjing 210009, Nanjing*

*[*]Email: lbsun@njtech.edu.cn*

## Experimental Section

### Chemicals

Copper nitrate trihydrate [$Cu(NO_3)_2 \cdot 3H_2O$; Aladdin, 99.999%], butanol (Sigma, ≥99%), hydrochloric acid (HCl; Sigma-Aldrich, 37%), *N,N*-dimethylacetamide (DMA; Sigma-Aldrich, ≥99.9%), 1-methyl-2-pyrrolidinone (NMP; Sigma-Aldrich, ≥99%), (3-aminopropyl)triethoxysilane (APTES; Aladdin, 99%), tetramethylammonium hydroxide (TMAOH; Aladdin, AR, 25% aqueous solution), ethanol (Sigma-Aldrich, ≥99.8%), styrene oxide (Aldrich, ≥97%), and methanol (Aladdin, ≥99.9%) were commercially available chemicals. The ligands 5-sulfoisophthalic acid sodium salt (H$_2$L1), 5-hydroxy-1,3-benzenedicarboxylic acid (H$_2$L2), and 5-*tert*-butyl-1,3-benzenedicarboxylic acid (H$_2$L3) were purchased from Aladdin Chemicals. The triblock copolymer F127 ($EO_{106}PO_{70}EO_{106}$) and tetraethylorthosilicate (TEOS) were obtained from Sigma-Aldrich. All of the starting materials were used without further purification. Deionized water was generated by a Milli-Q integral pure and ultrapure water purification system and used in all experiments.

### Materials Synthesis

*Synthesis of MOP1*. MOP**1** was synthesized following a similar procedure to previous reports.[1,2] A methanol solution (10 mL) of H$_2$L1 (538 mg) was mixed with a methanol solution (40 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (484 mg) in a glass vial (55 mL). After the addition of two drops of 2,6-lutidine, the vial was allowed to stand at room temperature. After one night, homogeneous dark-blue block crystals of MOP**1** with a molecular formula of [$Cu_{24}(L1)_{24}S_{24}$]·$x$S were harvested, where S represents a solvent molecule.

*Synthesis of MOP2*. MOP**2** was synthesized following a similar procedure to previous reports.[1,2] A methanol solution (10 mL) of H$_2$L2 (364 mg) was mixed with a methanol solution (40 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (484 mg) in a glass vial and 10 mL DMA was added in the mixed solution. After the addition of two drops of 2,6-lutidine, the vial was allowed to stand at room temperature. After one night, homogeneous dark-blue block crystals of the MOP**2** with a molecular formula of [$Cu_{24}(L2)_{24}S_{24}$]·$x$S were harvested, where S represents a solvent molecule.

*Synthesis of MOP3*. MOP**3** was synthesized following a similar procedure to previous reports.[1,2] A DMA solution (10 mL) of H$_2$L3 (446 mg) was mixed with a DMA solution (10 mL) of

Cu(NO$_3$)$_2$·3H$_2$O (484 mg) in a glass vial (55 mL) and 4.4 mL methanol was added in the mixed solution. After the addition of two drops of 2,6-lutidine, the vial was allowed to stand at room temperature. After one night, homogeneous dark-blue block crystals of the MOP**3** with a molecular formula of [Cu$_{24}$(L3)$_{24}$S$_{24}$]·$x$S were harvested, where S represents a solvent molecule.

*Synthesis of Mesoporous Silica SBA-16.* Mesoporous silica SBA-16 was prepared as follows.[3] In a typical synthesis, 3 g of copolymer F127 was dissolved in a solution of 144 g of distilled water and 5.94 g of concentrated HCl. After about 30 min, 9 g of the co-surfactant butanol was added in order to achieve a 1:3 F127/butanol mass ratio in the ternary system. After stirring for 1 h, 14.2 g TEOS was added to the solution. At a constant temperature of 318 K, the mixture was further stirred for 24 h. The mixture was then placed under static conditions at 318 K for 48 h. After the hydrothermal treatment, the precipitated solid was isolated by filtration and dried at 373 K for 24 h. The template was removed by calcination at 823 K under air for 6 h.

*Synthesis of Amine-functionalized Mesoporous Silica NH$_2$-SBA-16 (NS).* NS was prepared through a modified co-condensation approach.[4] 3 g of copolymer F127 was dissolved in a solution of 144 g of distilled water and 5.94 g of concentrated HCl. After about 30 min, 9 g of the co-surfactant butanol was added in order to achieve a 1:3 F127/butanol mass ratio in the ternary system at 318 K. After 1 h of stirring, 14.2 g TEOS was added to the solution. After 6 h of stirring, 3.2 g APTES was added to the solution. At a constant temperature of 318 K, the mixture was further stirred for 18 h. The mixture was then placed under static conditions at 373 K for 48 h. After the hydrothermal treatment, the precipitated solid was isolated by filtration and dried at 318 K for 24 h. The template was removed through ethanol extraction at 353 K for 24 h. Then 1 g of the modified sample was suspended in 50 mL of 0.2 M methanol solution of TMAOH at room temperature for 30 min. The solid was recovered by filtration, washed with methanol, and finally dried at 318 K for 24 h.

*Synthesis of the MOP**1**@NH$_2$-SBA-16 Composites M**1**N.* A precursor solution was first prepared by mixing a methanol solution (2 mL) of Cu(NO$_3$)$_2$·3H$_2$O (0.012, 0.023, 0.046, and 0.070 g) and a methanol solution (5 mL) of H$_2$L1 (0.013, 0.026, 0.052, and 0.077 g, respectively). Then 0.2 g NS was added to the precursor solution. After 0.5 h of stirring at room temperature, the solids was isolated by centrifugation and wash twice with methanol. After the removal of methanol, blue solids were obtained and denoted as M**1**N-1, M**1**N-2, M**1**N-3, and M**1**N-4, respectively.

*Synthesis of the MOP**2**@NH$_2$-SBA-16 Composite M**2**N.* A precursor solution was first prepared

by mixing a methanol solution (2 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.046 g) and a methanol solution (5 mL) of H2L2 (0.035 g). Then 0.2 g NS was added to the precursor solution. After 0.5 h of stirring at room temperature, the solids was isolated by centrifugation and wash twice with methanol. After the removal of methanol, a blue solid was obtained and denoted as M**2**N-3.

*Synthesis of the MOP3@NH$_2$-SBA-16 Composite M3N.* A precursor solution was first prepared by mixing a methanol solution (2 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.046 g) and a methanol solution (5 mL) of H2L3 (0.043 g). Then 0.2 g NS was added to the precursor solution. After 0.5 h of stirring at room temperature, the solids was isolated by centrifugation and wash twice with NMP. After the removal of the solvent, a blue solid was obtained and denoted as M**3**N-3.

## Characterization

X-ray diffraction (XRD) patterns of the materials were recorded with a Bruker D8 Avance diffractometer with Cu Kα radiation at 40 kV and 40 mA. Transmission electron microscopy (TEM) was performed on a JEM-2010 UHR electron microscope operated at 200 kV. Fourier transform infrared (IR) spectra of the samples diluted with KBr were carried out on a Nicolet Nexus 470 spectrometer with KBr wafer. UV-vis spectra were collected on the SHIMADZU UV-2600 in the region of 220-850 nm. Thermogravimetric (TG) curves and their derivatives (DTG) were obtained by use of a thermobalance (STA-499C, NETZSCH). The sample was heated from room temperature to 973 K with the heating rate 10 K·min$^{-1}$ under a flow of nitrogen (10 mL·min$^{-1}$). The amounts of copper in the composites were measured by inductively coupled plasma-atomic emission spectrometer (ICP-AES). A PerkinElmer sequential ICP spectrometer (Optima 2000 DV) was used for measurement. Samples were dissolved in hydrofluoric acid before measurement. The $N_2$ adsorption-desorption isotherms were examined at 77 K. The samples were degassed at 423 K for 4 h prior to analysis. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.04 to 0.20. The total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore diameter was calculated from the adsorption branch by using the nonlocal density functional theory (NLDFT) methods.

## Catalytic Reactions

The ring-opening reactions of styrene oxide with methanol were performed in sealed glassware.

The solid catalysts were vacuumed at 120 ºC for 2.5 h. The whole reaction process was conducted under a nitrogen atmosphere. For a typical reaction, the reactant styrene oxide (5 mmol) and a solid catalyst (0.1 g M1N-3 or NS, 0.016 g MOP1 calculated from the content of MOP1 in the composite) were stirred in methanol (7.5 mL) at 333 K. The reaction mixtures were periodically withdrawn at the intervals of 5, 20, 30, 60, 90, and 120 min throughout the reaction. The obtained upper liquid was analyzed by using an Agilent Technologies 7890A gas chromatograph (GC) equipped with a flame ionization detector (FID) and an HP-5 capillary column. The used catalyst was isolated from reaction mixture by centrifugation. After being washed with methanol for three times, isolated by centrifugation and dried in vacuum, the recovered catalyst was used in the next cycle of reaction. To examine the stability of materials, MOPs and MOPs@SBA-16 composites were exposed to humid atmosphere (relative humidity, RH = 50%) at 298 K for a given period of time. The resultant materials were measured by UV-vis and used to catalyze the same reactions.

## References

[1] J. R. Li, H. C. Zhou, *Nat. Chem.* **2010**, *2*, 893-898.

[2] Kang, Y.-H.; Liu, X.-D.; Yan, N.; Jiang, Y.; Liu, X.-Q.; Sun, L.-B.; Li, J.-R. *J. Am. Chem. Soc.* **2016**, *138*, 6099-6102.

[3] F. Kleitz, T.-W. Kim, R. Ryoo, *Langmuir* **2006**, *22*, 440-445.

[4] Chong, A. S. M.; Zhao, X. S. *J. Phys. Chem. B* **2003**, *107*, 12650-12657

**Table S1.** Textual parameters of different samples

| Classification | Sample | $S_{BET}$ (m²·g⁻¹) $^a$ | $V_p$ (cm³·g⁻¹) $^b$ | $D_1$ (nm) $^c$ | $D_2$ (nm) $^c$ |
|---|---|---|---|---|---|
| Mesoporous matrix | NS | 510 | 0.52 | 2.0 | 6.4 |
| Composite | M1N-1 | 484 | 0.51 | 2.0 | 6.1 |
| | M1N-2 | 380 | 0.41 | 2.0 | 6.0 |
| | M1N-3 | 360 | 0.36 | 2.0 | 5.6 |
| | M1N-4 | 352 | 0.35 | 2.0 | 5.6 |
| | M2N-3 | 332 | 0.41 | 2.0 | 5.8 |
| | M3N-3 | 323 | 0.42 | 2.0 | 5.7 |
| MOP | MOP1 | 1.3 | 0.004 | | |
| | MOP2 | 0.7 | 0.003 | | |
| | MOP3 | 12.0 | 0.007 | | |

$^a$ $S_{BET}$ = BET surface area. $^b$ $V_p$ = pore volume. $^c$ $D_1$ = size of pore entrance, $D_2$ = size of cavity. $D_1$ and $D_2$ were calculated from the adsorption branch by using the nonlocal density functional theory (NLDFT).
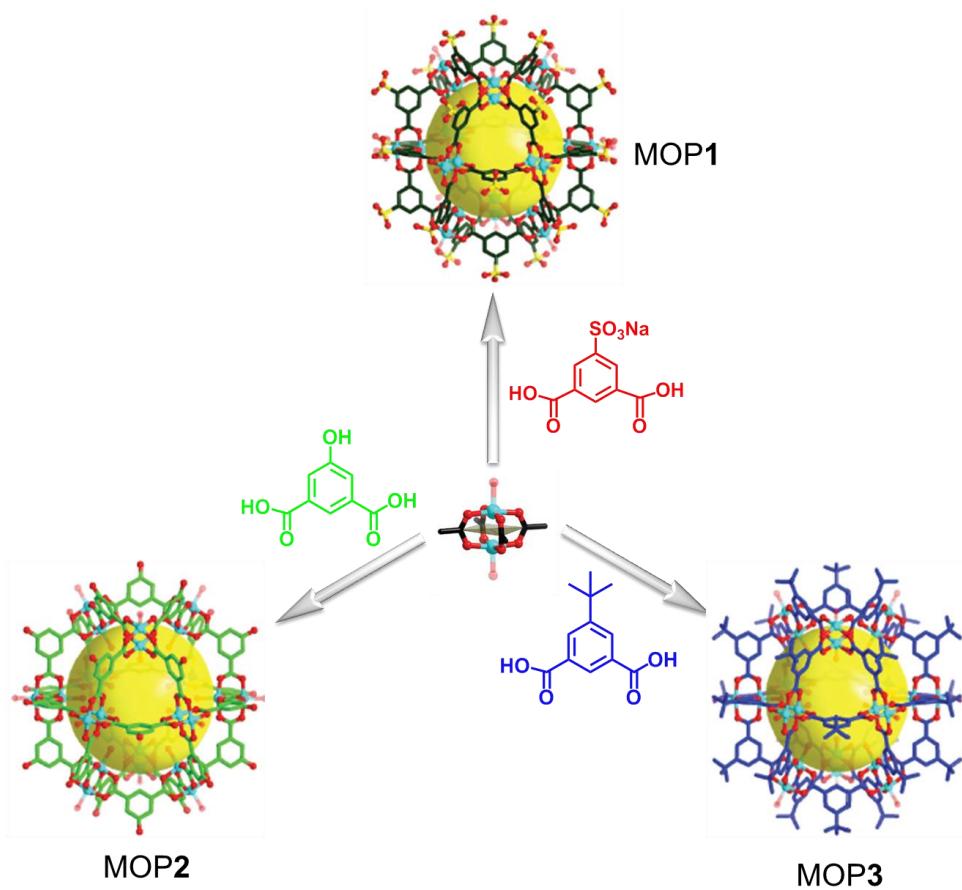
**Scheme S1.** Diagrams for the synthesis and crystal structure of MOP**1**, MOP**2**, and MOP**3**. Color scheme for Cu atoms, cyan; for O atoms, red; for S atoms in MOP**1**, yellow; and for C atoms, all atoms in each ligand have the same color, but different ligands have distinct colors. The yellow sphere represents the free space inside each molecular cage.
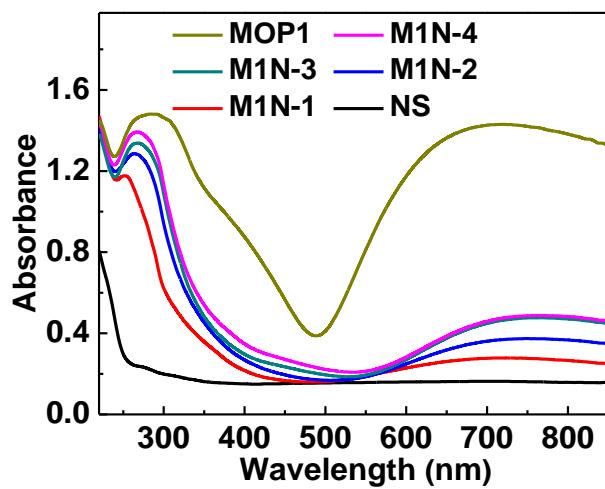
**Figure S1.** UV-vis absorption spectra of the samples MOP**1**, NS, and their composites with different MOP contents.
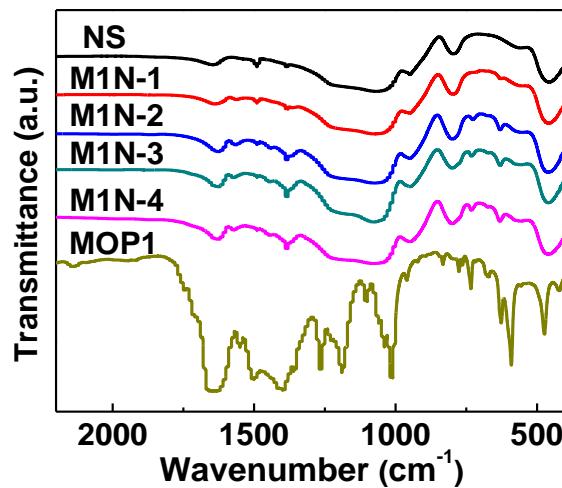


**Figure S2.** IR spectra of the samples MOP**1**, NS, and their composites with different MOP contents.
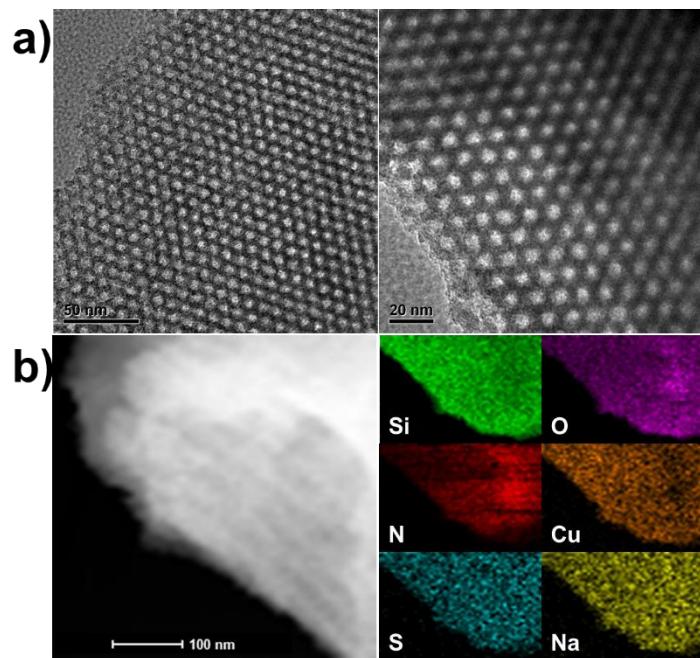
**Figure S3.** (a) TEM images as well as (b) STEM and elemental mapping of the sample M**1**N-1.
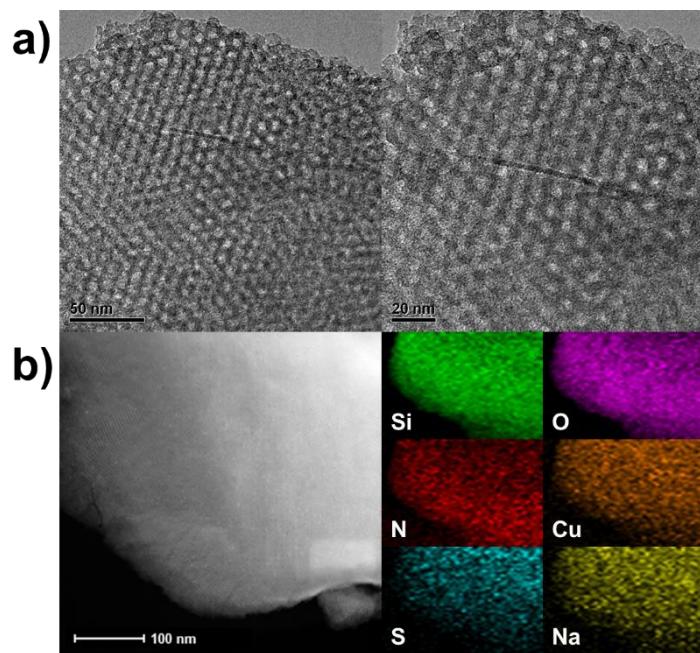


**Figure S4.** (a) TEM images as well as (b) STEM and elemental mapping of the sample M**1**N-2.
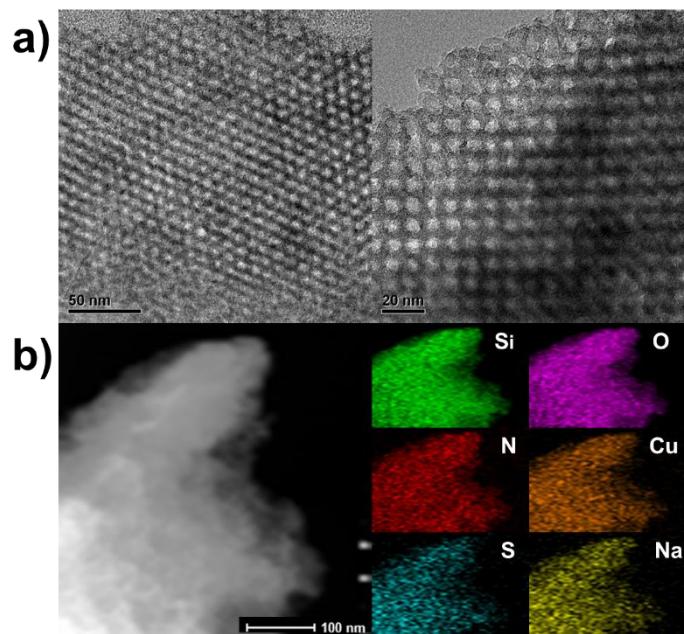
**Figure S5.** (a) TEM images as well as (b) STEM and elemental mapping of the sample M**1**N-4.
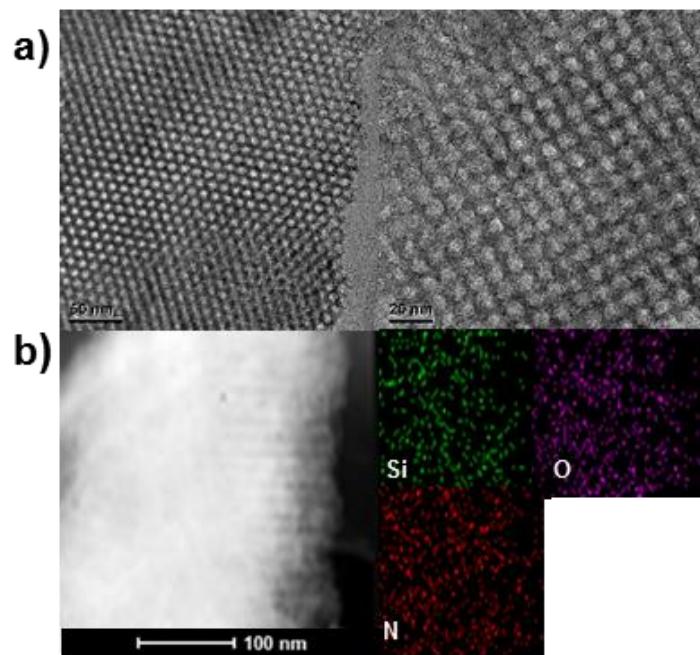


**Figure S6.** (a) TEM images as well as (b) STEM and elemental mapping of the sample NS.
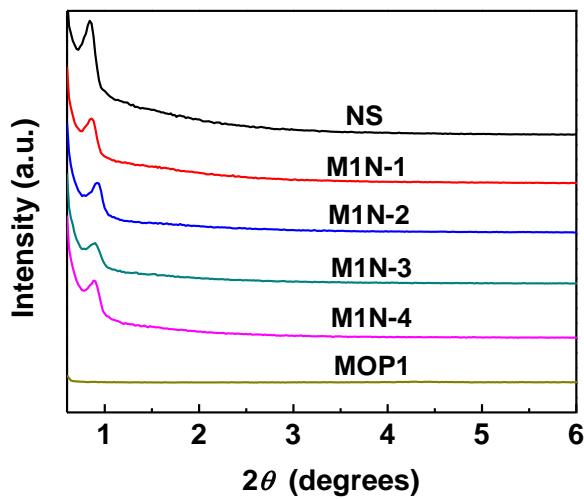
**Figure S7.** Low-angle PXRD patterns of NS, M**1**N-1, M**1**N-2, M**1**N-3, M**1**N-4, and MOP**1**.
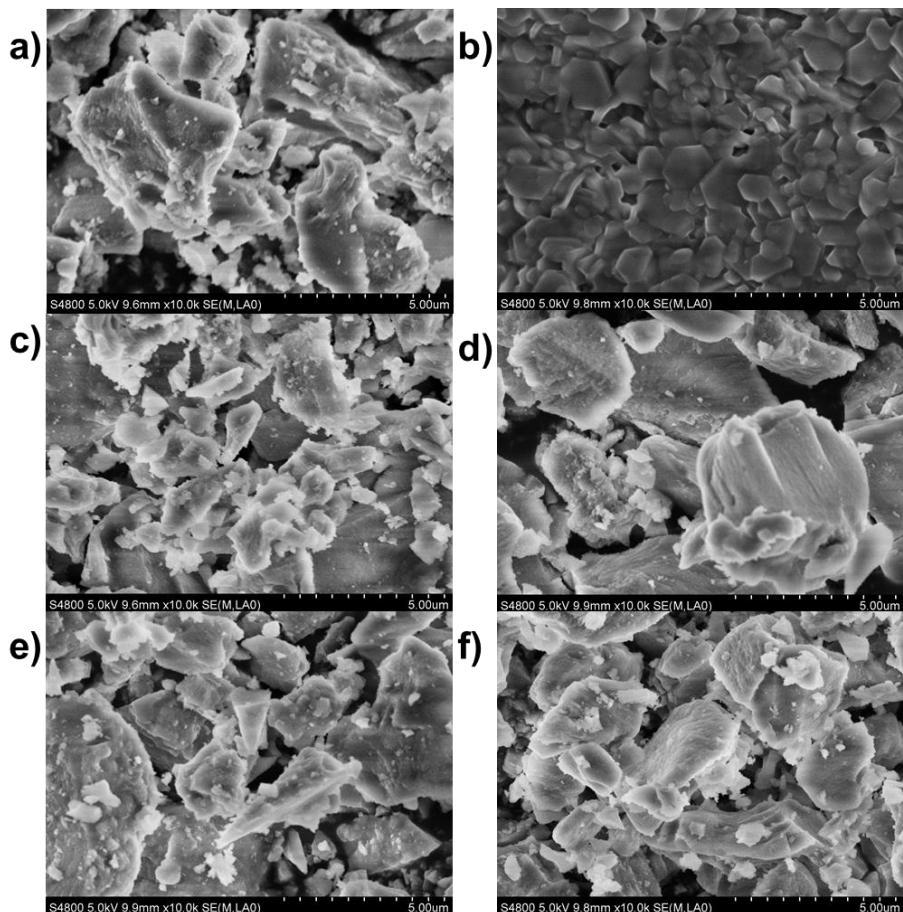


**Figure S8.** SEM images of the samples (a) NS, (b) MOP**1**, (c) M**1**N-1, (d) M**1**N-2, (e) M**1**N-3, and (f) M**1**N-4.
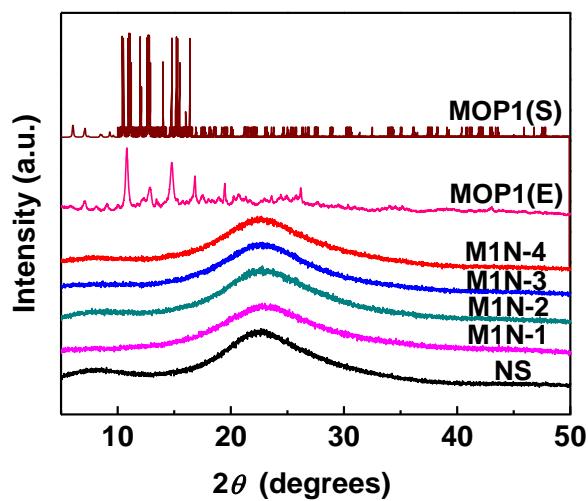
**Figure S9.** Wide-angle PXRD patterns of NS, M**1**N-1, M**1**N-2, M**1**N-3, M**1**N-4, simulated pattern from single-crystal structure MOP**1**(S), and experimental pattern MOP**1**(E).
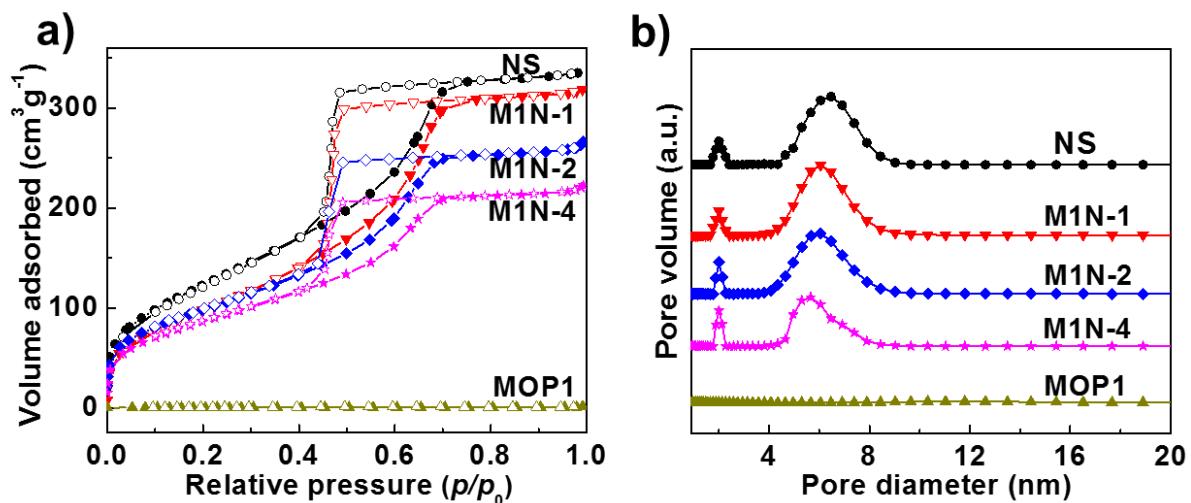


**Figure S10.** N$_2$ sorption isotherms and (b) pore size distributions of MOP**1**, NS, and their composites with different MOP contents.
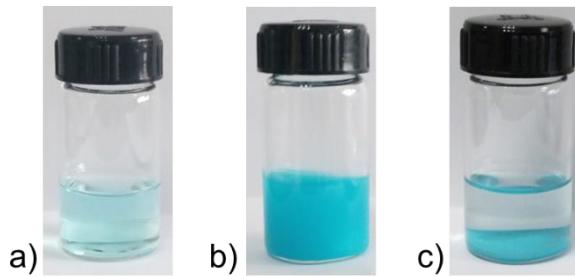
**Figure S11.** Photographs for the synthesis of M**2**N-3 through (a) dissolving copper nitrate and H$_2$L2 in methanol, (b) adding NS to the solution, and (c) washing the obtained solid twice with methanol.
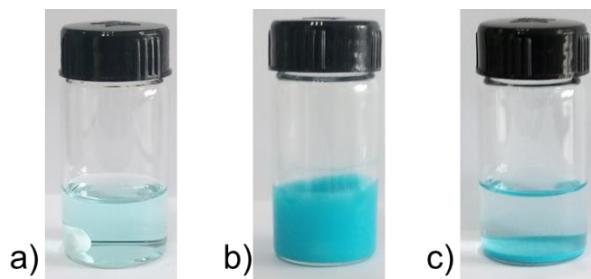


**Figure S12.** Photographs for the synthesis of M**3**N-3 through (a) dissolving copper nitrate and H$_2$L3 in methanol, (b) adding NS to the solution, and (c) washing the obtained solid twice with NMP.
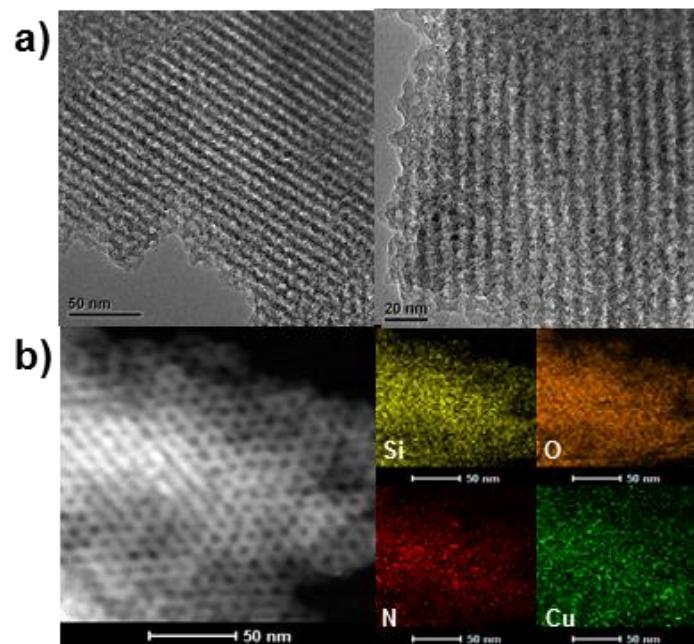
**Figure S13.** (a) TEM images as well as (b) STEM and elemental mapping of the sample M**2**N-3.
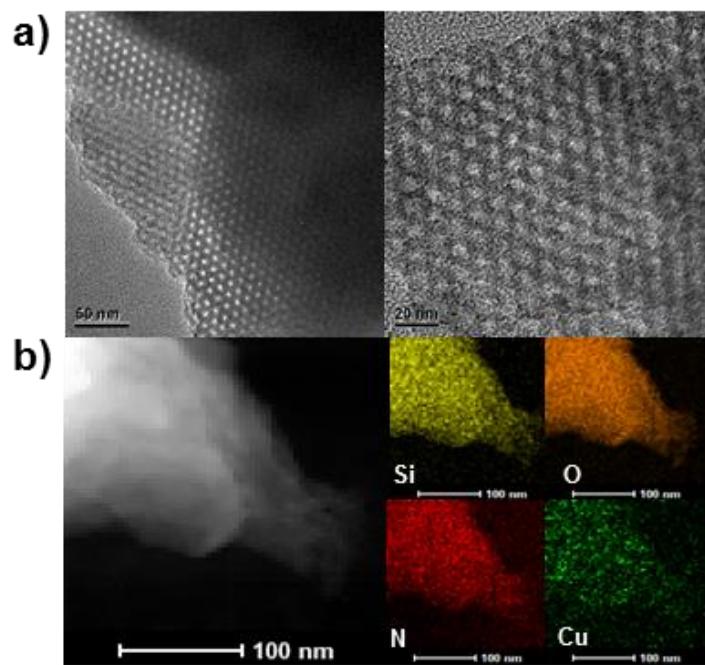


**Figure S14.** (a) TEM images as well as (b) STEM and elemental mapping of the sample M**3**N-3.
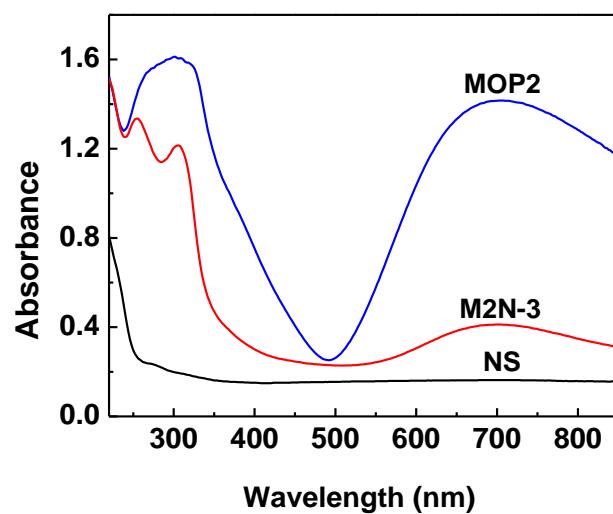
**Figure S15.** UV-vis absorption spectra of the samples NS, M**2**N-3, and MOP**2.**
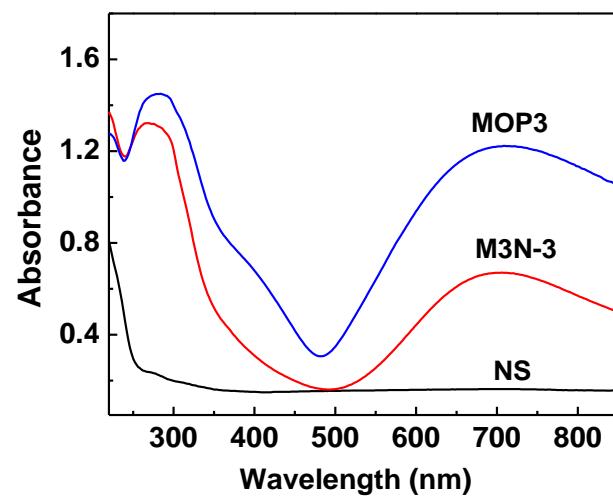


**Figure S16.** UV-vis absorption spectra of the samples NS, M**3**N-3, and MOP**3**.
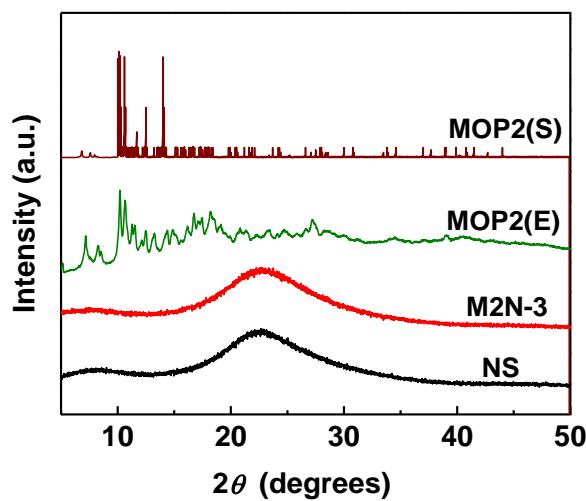
**Figure S17.** Wide-angle PXRD patterns of NS, M**2**N-3, simulated pattern from single-crystal structure MOP**2**(S), and experimental pattern MOP**2**(E).
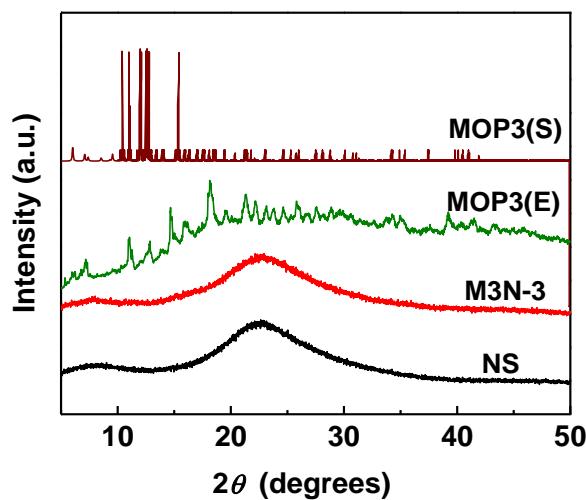


**Figure S18.** Wide-angle PXRD patterns of NS, M**3**N-3, simulated pattern from single-crystal structure MOP**3**(S), and experimental pattern MOP**3**(E).
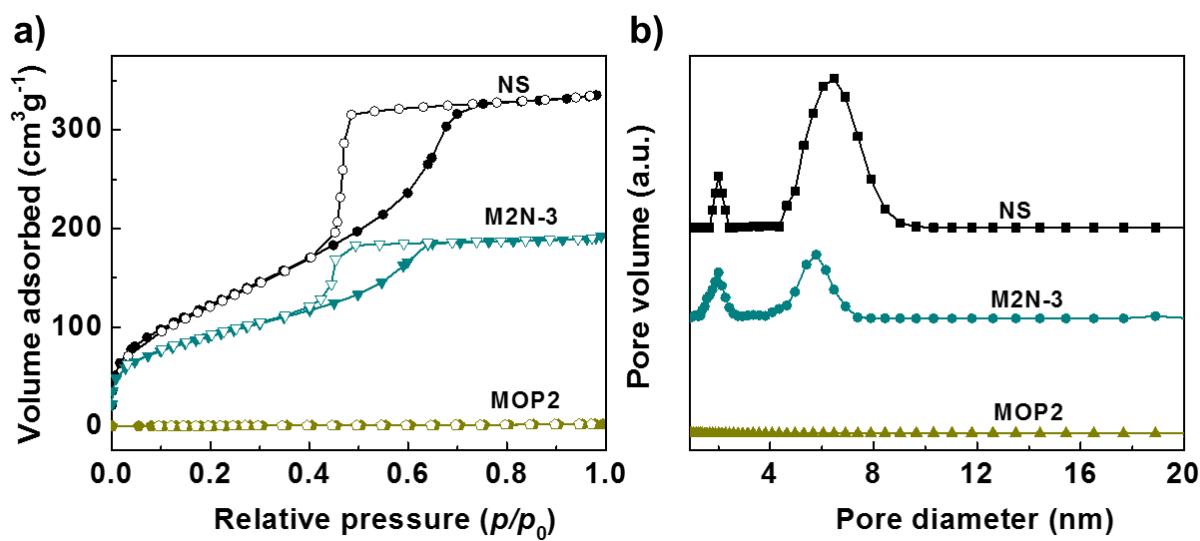
**Figure S19.** (a) $N_2$ adsorption-desorption isotherms and (b) pore size distributions of the samples NS, M**2**N-3, and MOP**2**.
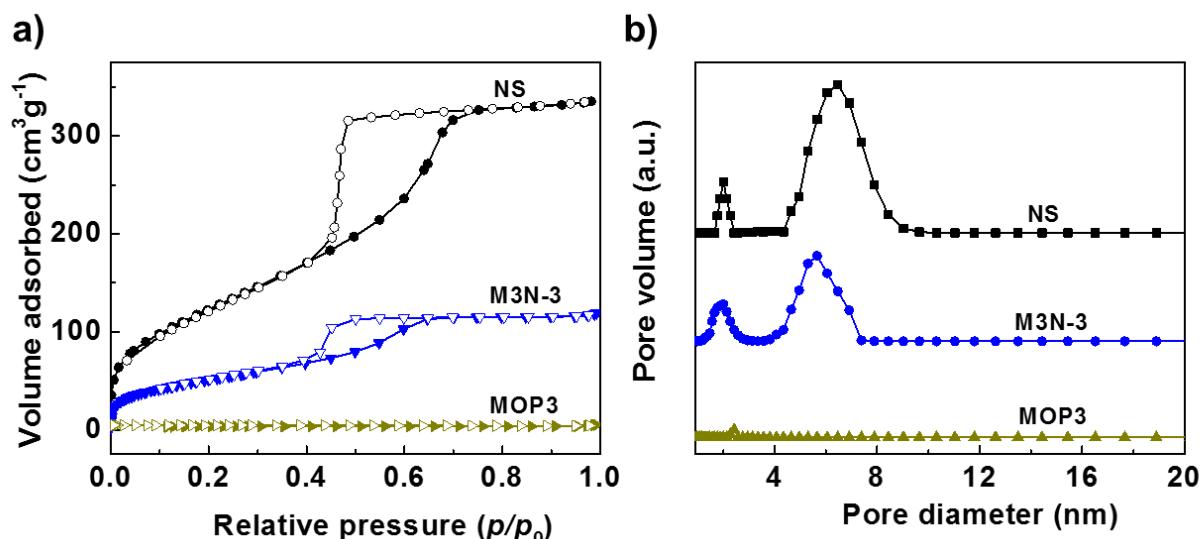


**Figure S20.** (a) $N_2$ adsorption-desorption isotherms and (b) pore size distributions of the samples NS, M**3**N-3, and MOP**3**.