

Electronic Supplementary Information (ESI) for

Hierarchical bicontinuous porosity in metal-organic frameworks templated from functional block co-oligomer micelles

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Section S1. Materials

All the chemicals were of reagent grade and used as purchased from their respective suppliers without any further purification. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%) and 1,3,5-benzenetricarboxylic acid (Trimesic acid, 95%) were obtained from Sigma-Aldrich. 2-methylimidazole (2-MeIm, 99%) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99%) were supplied by Acros Organics. 4,13-Diaza-18-crown-6-Ether (>98%) was obtained from Tokyo Chemical Industry UK. The solvents used, namely deionised water, ethanol, tetrahydrofuran (THF) and *N,N*-dimethylformamide (DMF) (all lab reagent grade), were obtained from Fisher Scientific.

Section S2. Characterization methods

¹H-Nuclear magnetic Resonance (¹H NMR)

¹H-Nuclear Magnetic Resonance (¹H NMR) spectra were recorded in deuterium oxide (D_2O) and in dimethyl sulfoxide- d_6 (DMSO-d_6) on a Bruker Avance 200 or 300 working respectively at 200MHz and 300MHz.

Size Exclusion Chromatography (SEC)

SEC was performed on a Shimadzu SEC system with a guard column and four Waters HR1-HR2-HR3-HR4 Styragel columns set in an oven maintained at 40 °C. The columns were attached to a Shimadzu differential refractive index (DRI) detector (RID-10A) linked with a Shimadzu UV detector (APD-10AVP). THF with 5% w/w acetic acid as eluent with a flow rate of 1 mL min⁻¹ and toluene (0.5%) was used as a flow rate marker. Polystyrene standards from 162 to 6*10⁶ g·mol⁻¹ were used for calibration. Molecular weights are reported as polystyrene equivalents based on the refractive index detector.

Dynamic light scattering (DLS)

Particle size measurements were carried out by dynamic light scattering (DLS) using a Malvern Instrument Zetasizer 3000 instrument with a detection angle of 173°, where the intensity weighted mean hydrodynamic size (*Z*-average) and the width of the particle size distribution were obtained from analysis of the autocorrelation function. Samples were filtered through a 0.45 μm membrane to ensure the minimization of dust and other particulates. At least five measurements at 25 °C were made for each sample with an equilibrium time of 5 minutes before starting measurement.

Powder X-ray diffraction (PXRD)

Room temperature PXRD data (2θ range 5-50°) were collected with a Bruker-AXS D8 diffractometer using Cu K α 1 ($\lambda = 1.540598 \text{ \AA}$) radiation and a LynxEye position sensitive detector in Bragg-Brentano parafocusing geometry. Analysis of the data was carried out using the X'pert HighScore Plus program.

Small angle X-ray diffraction (SAXS)

The SAXS experiment was carried out on Bruker Nanostar with Cu K α point source radiation using a CCD area detector. The sample to detector distance is ~ 1060 mm, giving a 2θ range of 0.1 to 2.9° . The collected 2D data was integrated over χ to produce 1D data.

Transmission electron microscope (TEM)

Bright-field TEM was carried out using a FEI Tecnai F20-G² FEG-TEM operating at 200 keV in the energy filtered TEM (EFTEM) mode with an energy selective slit width of 20 eV, while maintaining the electron dose as low as possible, consistent with obtaining acceptably sharp images.

Energy-filtering transmission electron microscopy (EF-TEM)

The EF-TEM was taken on Tecnai F20-G² FEG-TEM using the Gatan imaging filter and the M edge of Zn was selected.

Selected area electron diffraction (SAED)

The SAED pattern was obtained on a JEOL 2000FX operating at 200 keV using a low dose mode and a quick imaging technique to minimize the electron beam damage of the sample. The camera length used was 2 m.

Field-emission Scanning electron microscope (FE-SEM)

SEM images were taken on un-coated samples using a Hitachi S-5500 operating at 2 keV and 10 μ A under TV mode on a STEM sample holder.

Helium Pycnometry

Skeletal density values were collected using a Micromeritics AccuPyc 1340 helium pycnometer, equipped with a 1 cm³ insert. Typically, sample masses of between 100 and 150 mg were used and the values quoted are the mean and standard deviation from a cycle of 15 measurements. Before density measurements, all samples were degassed thoroughly under vacuum (< 1 mbar) at 120 °C for 5 hours.

N₂ physisorption analysis

Textural characteristics were measured by N₂ physisorption isotherm at 77 K on a Micromeritics ASAP 2020 instrument. Samples were outgassed in vacuum ($\sim 5\mu$ bar) for 8 hours at 393 K before starting the physisorption measurements. The surface areas were estimated using the Brunauer–Emmett–Teller (BET) equation for the relative pressure range (P/P_0) of 0.002 to 0.3. The saturation pressure, P_0 , corresponds to ca. 103.4 kPa. The t_{HJ} -plot micropore volume is the calculated pore volume with dimensions < 20 Å, using the Harkins and Jura method. Density functional theory (DFT) calculation was used to generate the pore size distribution data, based on the carbon slit pores geometry assumption.

Thermal gravimetric analysis (TGA)

TGA was performed on TA Instrument Q600 (simultaneous TGA-DSC). Typically, around 10 mg of sample was placed in an alumina pan under pure N₂ flow (100 mL·min⁻¹) and heated at a rate of 10 °C·min⁻¹ to 1000 °C.

Fourier-transform infrared spectroscopy (FTIR)

FT-IR analysis was carried out using a Bruker Tensor 27 Infrared Spectrometer, which is fitted with an attenuated total reflectance (ATR) cell to allow fast data collection. The data were collected in the wavenumber range of 500 – 4000 cm^{-1} at a resolution of 4 cm^{-1} .

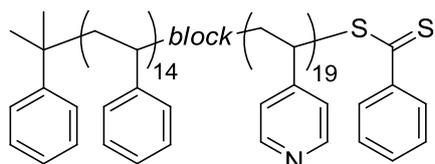
Elemental microanalysis

Elemental analysis was carried out at the Department of Chemistry, the University of Cambridge (UK) as a technical service.

Section S3. Full synthetic procedures

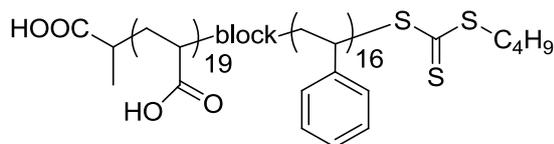
The two block co-oligomers, PSty₁₄-*b*-P4VP₁₉ and PSty₁₆-*b*-PAA₁₉, were synthesized according to reported methods.¹ The single crystals of ZIF-8 and HKUST-1 were synthesized according to previously published methods.²

Self-assembly of PSty₁₄-*b*-P4VP₁₉ into spherical micelles ($M_{n, NMR} \approx 3690 \text{ g}\cdot\text{mol}^{-1}$)



The self-assembly of this block co-oligomer was carried out via a direct dissolution method: PSty₁₄-*b*-P4VP₁₉ (30 mg, 8.13×10^{-6} mol) was dissolved in 10 mL deionized H₂O followed by adding 2 M HCl solution to pH ~ 1 under vigorous stirring. Then the solution was sonicated for 40 min, leading to a clear solution. The solution was filtered through a 0.45 μm membrane filter. The diameter of the micelles was measured as 18.9 nm by DLS.

Self-assembly of PSty₁₆-*b*-PAA₁₉ into spherical micelles ($M_{n, NMR} \approx 3270 \text{ g}\cdot\text{mol}^{-1}$)



The self-assembly of this block co-oligomer was carried out via a direct dissolution method: PSty₁₆-*b*-PAA₁₉ (45 mg, 1.38×10^{-5} mol) was dissolved in a 12 mL sodium hydroxide (11.03 mg, 2.75×10^{-4} mol, 1 equiv. per COOH group) aqueous solution (deionized water) under vigorous stirring. Then the solution was sonicated for 40 min, leading to a clear solution. The solution was filtered through a 0.45 μm membrane filters. The diameter of the micelles was measured as 36.5 nm by DLS.

Synthesis of hierarchical ZIF-8-VP templated from PSty₁₄-*b*-P4VP₁₉

Typically, 30 mg of PSty₁₄-*b*-P4VP₁₉ was pre-assembled into spherical micelle templates. The pH of this template micelle aqueous solution was adjusted to ~4.5 by adding 2M NaOH aqueous solution under vigorous stirring. 11 mL of the template aqueous solution was added to a vial containing 0.362 mmol of Zn(NO₃)₂·6H₂O and 0.380 mmol of 4,13-diaza-18-crown 6-ether previously dissolved in 20 mL EtOH 2 hours beforehand, and thoroughly mixed by vigorous stirring. The vial was then transferred to a 45 °C oven for 12 hours. The precipitates were collected by centrifugation and washed with EtOH for three cycles. The washed materials were then transferred to a vial containing 1.449 mmol of 2-MeIm dissolved in 20 mL EtOH, and thoroughly mixed by vigorous stirring. The vial was transferred into a 45 °C oven for 12 hours. The precipitates were collected by centrifugation and washed with EtOH for two cycles, followed by two cycles of washing with THF/DMF (v/v ratio 1/1) to remove the templates. Then, the products were collected and dried under vacuum at 120 °C for 8 hours. Yield: 47.2 mg. Elemental microanalysis (formula: [Zn(2-MeIm)₂]. Calcd. C, 42.22; H, 4.40; N, 24.63. Found. C, 41.40; H, 4.34; N, 23.82).

The synthesis of hierarchical HKUST-1-VP followed the same precursor molar ratios and procedures to ZIF-8-VP, except that the pH of template micelle aqueous solution was adjusted to ~3.5 before

synthesis. Yield: 96.5 mg. Elemental microanalysis (formula: $[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]$). Calcd. C, 32.79; H, 1.82; N, 0.00. Found. C, 46.31; H, 3.97; N, 3.28).

Synthesis of hierarchical ZIF-8-AA templated from PSty₁₆-*b*-PAA₁₉

Typically, 45 mg of PSty₁₆-*b*-PAA₁₉ was pre-assembled into spherical micelle templates. The pH of this template micelle aqueous solution was adjusted to ~7 by adding 2M HCl aqueous solution. 11 mL of the template aqueous solution was added to a vial containing 0.4116 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.432 mmol of 4,13-diaza-18-crown 6-ether previously dissolved in 20 mL EtOH 2 hours beforehand, and thoroughly mixed by vigorous stirring. The vial was then transferred to a 45 °C oven for 12 hours. The precipitates were centrifuged and washed with EtOH for three cycles. The washed materials were then transferred to a vial containing 1.646 mmol of 2-MeIm dissolved in 20 mL EtOH, and thoroughly mixed by vigorous stirring. The vial was transferred into a 45 °C oven for 12 hours. The precipitates were collected by centrifugation and washed with EtOH for two cycles, followed by two cycles of washing with THF/DMF (v/v ratio 1/1) to remove the templates. Then, the products were collected and dried under vacuum at 120 °C for 8 hours. Yield: 76.5 mg. Elemental microanalysis (formula: $[\text{Zn}(2\text{-MeIm})_2]$). Calcd. C, 42.22; H, 4.40; N, 24.63. Found. C, 52.18; H, 5.10; N, 6.50).

The synthesis of hierarchical HKUST-1-AA followed the same precursor molar ratios and procedures to ZIF-8-AA. Yield: 98.2 mg. Elemental microanalysis (formula: $[\text{Cu}_3(\text{btc})_2(\text{H}_2\text{O})_3]$). Calcd. C, 32.79; H, 1.82; N, 0.00. Found. C, 51.95; H, 4.50; N, 1.07).

Section S4. Materials characterizations and results

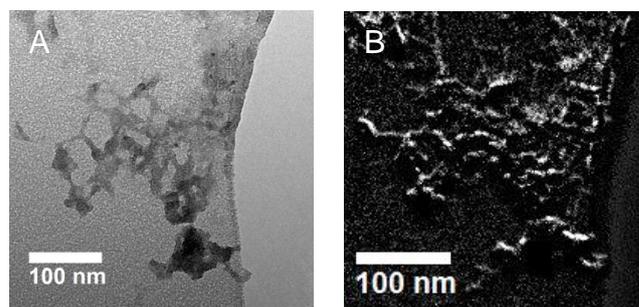


Figure S1. A) Bright field TEM and B) corresponding Zn energy-filtering transmission electron microscopy (EF-TEM) chemical mapping of PSty₁₄-*b*-P4VP₁₉ template micelles with captured Zn²⁺ ions (bright regions correspond to Zn²⁺ locations). They showed homogeneous distribution of captured Zn²⁺ ions around the micelle networks.

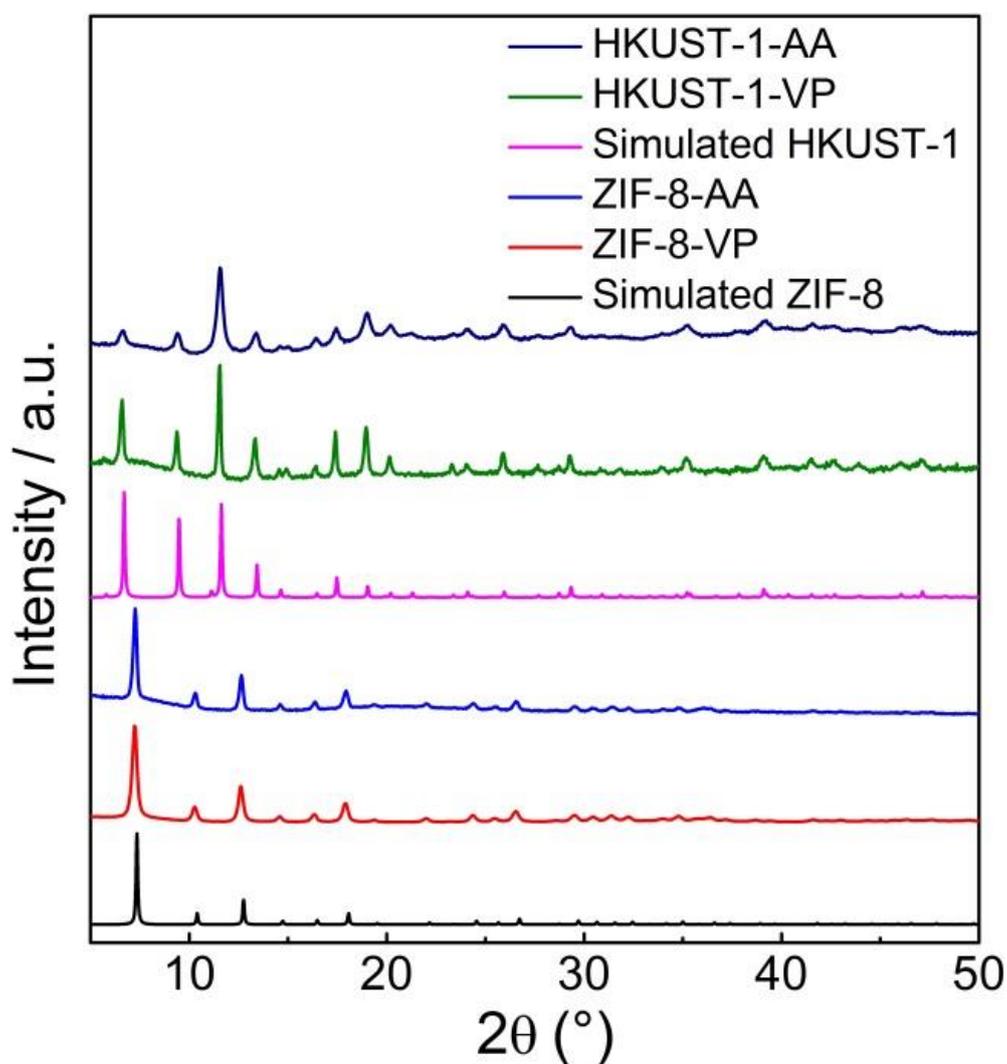


Figure S2. PXRD patterns of all four hierarchical MOFs as compared to the simulated data.

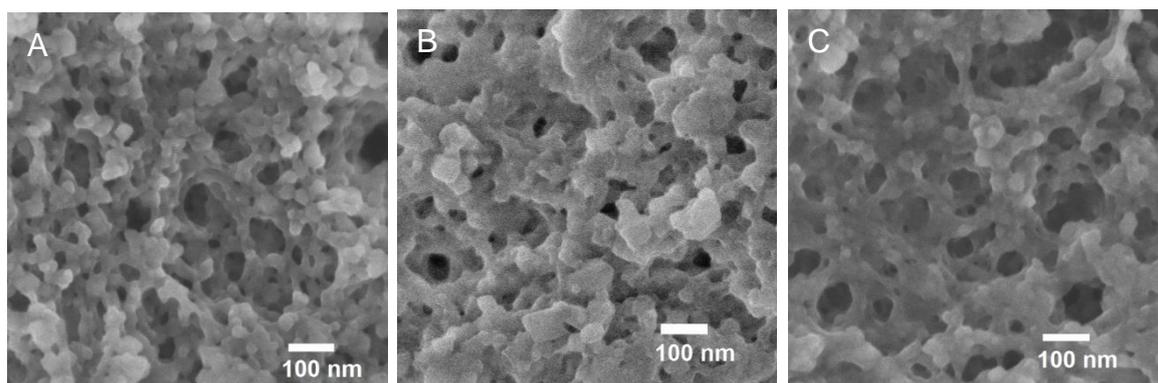


Figure S3. FEG-SEM images of A) ZIF-8-AA, B) HKUST-1-VP and C) HKUST-1-AA, showing their bicontinuous hierarchical porous structure.

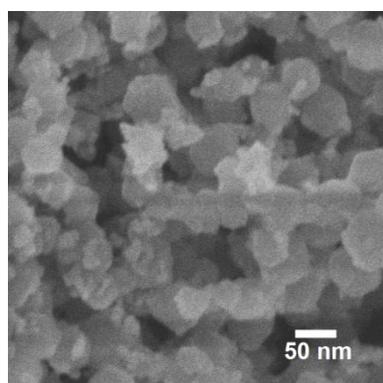


Figure S4. FEG-SEM image of ZIF-8-VP after thermal treatment at 300 °C for 6 hours under N₂ atmosphere.

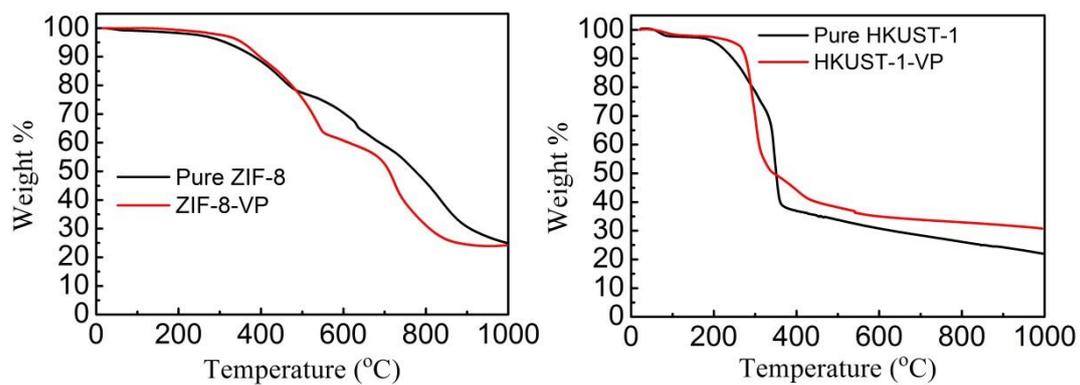


Figure S5. TGA curves of ZIF-8-VP and HKUST-1-VP compared to their pure single crystal forms, showing their good thermal stability.

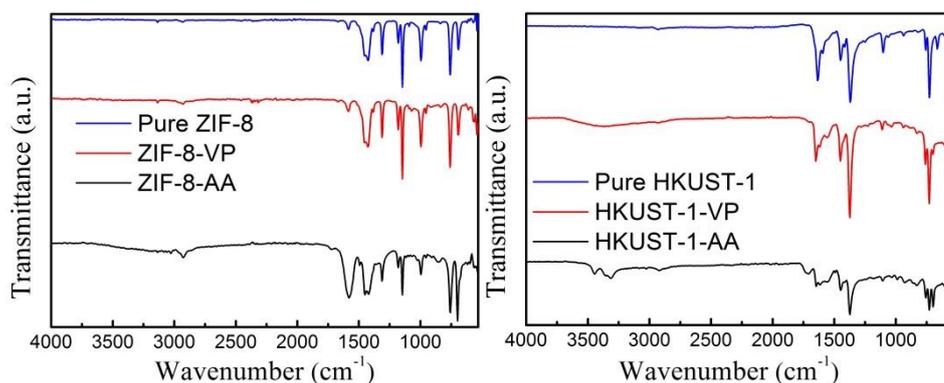


Figure S6. FT-IR spectra of hierarchical ZIF-8-VP, ZIF-8-AA, HKUST-1-VP, and HKUST-1-AA, compared to their pure single crystal counterparts.

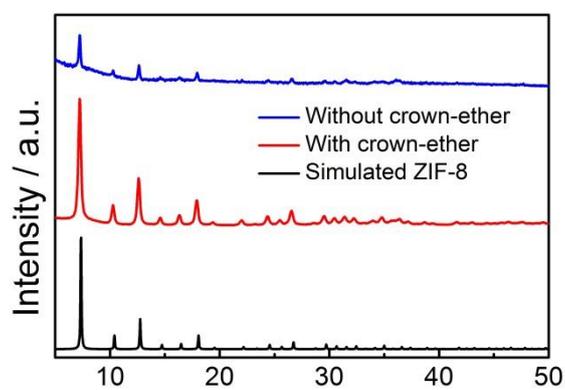


Figure S7. PXRD patterns of ZIF-8-VP synthesized with and without crown-ether, illustrating the improved materials' crystallinity by adding crown-ether.

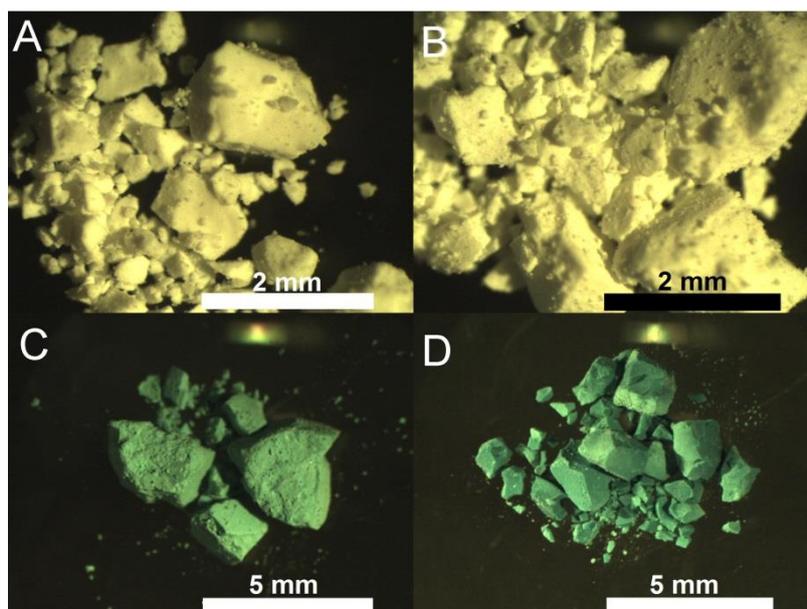


Figure S8. Optical microscopy images of all four hierarchical MOFs systems. A) ZIF-8-VP, B) ZIF-8-AA, C) HKUST-1-VP and D) HKUST-1-AA.

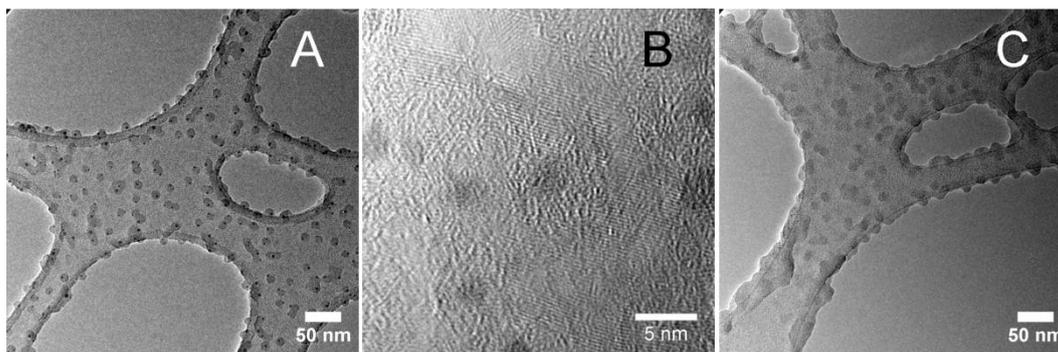


Figure S9. Bright-field TEM images of PSty₁₄-*b*-P4VP₁₉ template micelles. A & B) when they were self-assembled at pH ~ 1, and C) after the solution pH was tuned to ~ 4.5 prior to adding metal ion precursors. The darker regions in B correspond to the cores of the template micelles.

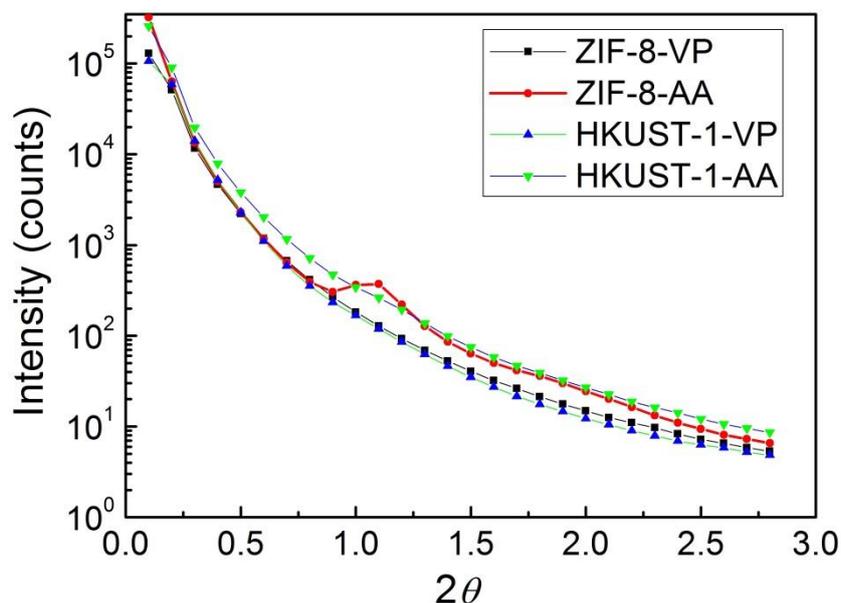


Figure S10. Small angle X-ray scattering data of all four hierarchical MOFs systems. Among them, ZIF-8-AA shows a weak diffraction peak at $2\theta = 1.1^\circ$, corresponding to a repeating distance of ~ 40.16 Å. It suggests that there is some ordered mesoporosity in this system.

Table S1. Particle size measurements of the two template micelle particles by DLS using Malvern Zetasizer 3000.

Template molecules	Number-averaged diameter (nm) [#]	
PSty ₁₄ - <i>b</i> -P4VP ₁₉	18.9 (at pH ~ 1)	18.5 (at pH ~ 4.5)
PSty ₁₆ - <i>b</i> -PAA ₁₉	36.5 (at pH ~ 12)	30.8 (at pH ~ 7)

[#] The first column of diameters corresponds to micelles when they were self-assembled. And the second column of diameters corresponds to micelles after their pH were tuned respectively. There are no significant changes in their dimensions before and after pH adjustments.

References:

- (a) M. Siau, B. S. Hawkett and S. Perrier, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 187-198; (b) M. Zamfir, C. S. Patrickios, F. Montagne, C. Abetz, V. Abetz, L. Oss-Ronen and Y. Talmon, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 1636-1644.
- (a) Q. Shi, Z. Chen, Z. Song, J. Li and J. Dong, *Angew. Chem. Int. Ed.*, 2011, **50**, 672-675; (b) S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148-1150.