

Poly(isophthalic acid)(ethylene oxide) as a Macromolecular Modulator for Metal–Organic Polyhedra

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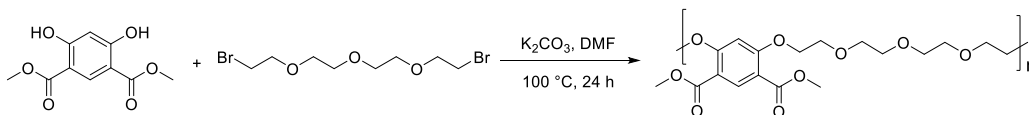
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Supporting Information

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Experimental

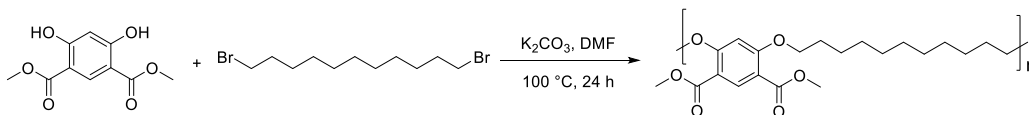
General. Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, and others). Chromatography was performed using a CombiFlash Rf 200 automated system from TeledyneISCO (Lincoln, USA). ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were collected on Varian Mercury spectrometers running at 400 and 500 MHz, respectively. Chemical shifts are quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. Electrospray ionization mass spectrometry (ESI-MS) and matrix-assisted laser desorption ionization coupled with time of flight (MALDI-TOF) mass spectroscopy were performed at the Molecular Mass Spectrometry Facility (MMSF) in the Department of Chemistry & Biochemistry at the University of California, San Diego. ~5–10 mg of dried material was used for thermogravimetric analysis (TGA) measurements. Samples were analyzed under a stream of dinitrogen (80 mL/min) using a Mettler Toledo TGA/DSC 1 STAR^e System running from 30 to 500 °C with a ramping rate of 5 °C/min.



Synthesis of Polymer 1'

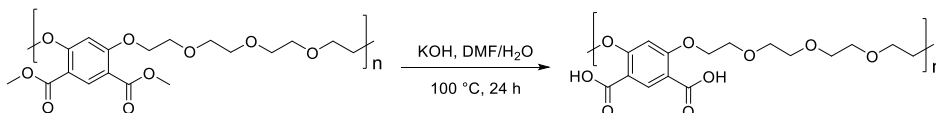
Dimethyl 4,6-dihydroxyisophthalate¹ (500 mg, 2.2 mmol), 1-bromo-2-[2-[2-(2-bromoethoxy)ethoxy]ethoxy]ethane² (700 mg, 2.2 mmol), and K_2CO_3 (1.2 g, 8.8 mmol) were added into 10 mL of DMF. The suspension was stirred for overnight and then heated at 100 °C for 24 h. After cooling down, 20 mL of DMF was added to the mixture and the solid was separated from solution by centrifugation. The collected solution was dried in vacuo by rotary evaporation to give oily product. The oil was washed by acetone (3×5 mL) and dried in a 60 °C oven. Yield: 608 mg (72%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.15 (s, 1H, ArH), 6.73 (s, 1H, ArH), 4.23 (t, 4H, CH_2 , $J = 4.8$ Hz), 3.75 (t, 4H, CH_2 , $J = 4.8$ Hz), 3.72 (s, 6H, CH_3), 3.62 (t, 4H, CH_2 , $J = 4.8$ Hz), 3.52 (t, 4H, CH_2 , $J = 4.8$ Hz). FT-IR: $\tilde{\nu} = 2948$ (m), 2872 (m), 1715 (s), 1604 (s), 1563 (m), 1507 (w), 1433 (m), 1350 (w), 1284 (s), 1228 (s), 1191 (s), 1099 (s), 1046 (s), 975 (m), 812 (m),

772 (m), 695 (m), 614 (w) cm^{-1} . GPC: $M_n = 12,200$ Da, $M_w = 22,243$ Da, PDI = 1.8, degree of polymerization = 31.



Synthesis of Polymer 2'

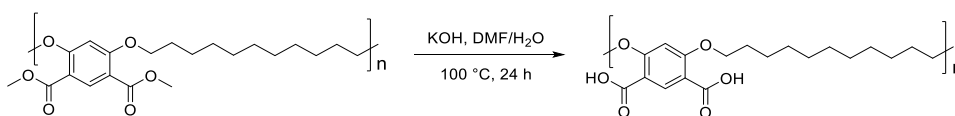
Dimethyl 4,6-dihydroxy-isophthalate (500 mg, 2.2 mmol), 1,11-dibromoundecane (690 mg, 2.2 mmol), and K_2CO_3 (1.2 g, 8.8 mmol) were added into 10 mL of DMF. The suspension was stirred for overnight and then heated at 100 °C for 24 h. After cooling down, 50 mL of water was added to the mixture and the precipitate was washed with water and methanol (MeOH), then isolated by centrifugation. The residue was dried in a 60 °C oven to obtain solid product. Yield: 518 mg (62%). ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 8.16 (s, 1H, ArH), 6.53 (s, 1H, ArH), 3.98 (br t, 4H, CH_2), 3.66 (s, 6H, CH_3), 1.58 (br t, 4H, CH_2), 1.32 (br t, 4H, CH_2), 1.14 (m, 10H, CH_2). FT-IR: $\tilde{\nu} = 2922$ (m), 2852 (m), 1701 (s), 1604 (s), 1562 (m), 1507 (w), 1447 (m), 1460 (m), 1420 (m), 1390 (m), 1288 (s), 1224 (s), 1190 (s), 1104 (s), 999 (s), 820 (m), 773 (m), 691 (m), 617 (m) cm^{-1} . Due to the low solubility of polymer in organic solvents, the GPC result is not available.



Synthesis of Polymer 1

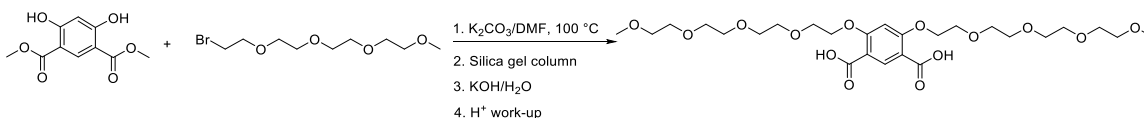
The ester precursor (600 mg, 1.6 mmol) were placed in a 1:1 mixture of water and DMF (30 mL total) with 1.0 g of KOH. The mixture was heated at 100 °C for 24 h to produce a clear solution. After cooling down, the solution was acidified to a pH value of ~2 with a 1.0 M HCl solution. Solvents were removed by rotary evaporation and more 1.0 M HCl solution was added to the resulting mixture. The mixture was filtered and washed with water, then dried at 80 °C in vacuo to obtain offwhite solids. Yield: 540 mg (95%). ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 8.18 (s, 1H, ArH), 6.74 (s, 1H, ArH), 4.25 (t, 4H, CH_2 , $J = 4.8$ Hz), 3.77 (t, 4H, CH_2 , $J = 4.8$ Hz), 3.61 (t, 4H, CH_2 , $J = 4.8$ Hz), 3.51 (t, 4H, CH_2 , $J = 4.8$ Hz). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$): 165.8, 162.5, 136.0, 112.2, 99.0, 70.1, 69.9, 68.8, 68.7. FT-IR: $\tilde{\nu} = 3265$ (m), 2870 (m), 1708 (s), 1605 (s), 1567 (m), 1499 (w), 1447 (m), 1348 (m), 1282 (s), 1104 (s), 1067 (s), 1034 (s), 943 (m), 910 (m),

843 (m), 774 (w), 728 (w), 646 (m), 617 (m) cm^{-1} . GPC: $M_n = 9,667$ Da, $M_w = 17,756$ Da, PDI = 1.8, degree of polymerization = 27.



Synthesis of Polymer 2

The ester precursor (500 mg, 1.3 mmol) were placed in a 1:1 mixture of water and DMF (100 mL total) with 4.0 g of KOH. The mixture was heated at 100 °C for 2 d to produce a clear solution. The solution was acidified to a pH value of ~2 with a 1.0 M HCl solution. The mixture was concentrated by rotary evaporation, then added 10 mL of 1.0 M HCl solution. The resulting precipitate was collected by centrifugation, and subsequently washed with water (3×20 mL) and MeOH (3×20 mL). The isolated polyacid polymers were dried at 60 °C oven overnight. Yield: 380 mg (83%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.18 (s, 1H, ArH), 6.64 (s, 1H, ArH), 4.09 (t, 4H, CH_2 , $J = 6.0$ Hz), 1.69 (t, 4H, CH_2 , $J = 6.0$ Hz), 1.42 (t, 4H, CH_2 , $J = 6.0$ Hz), 1.25 (m, 10H, CH_2 , $J = 4.8$ Hz). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$): 166.0, 162.8, 136.2, 111.7, 98.1, 68.5, 29.1, 29.0, 28.8, 28.5, 25.4. FT-IR: $\tilde{\nu} = 2923$ (m), 2852 (m), 1686 (s), 1602 (s), 1560 (m), 1461 (m), 1401 (m), 1278 (s), 1243 (s), 1208 (s), 1106 (s), 1070 (s), 992 (m), 945 (m), 819 (m), 775 (w), 722 (w), 668 (w), 611 (w) cm^{-1} . GPC: $M_n = 4,000$ Da, $M_w = 9,900$ Da, PDI = 2.5, degree of polymerization = 12.



Synthesis of Compound 3 (4,6-Bis[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]isophthalic acid)

4,6-dihydroxy-isophthalate (200 mg, 0.88 mmol), K_2CO_3 (486 mg, 3.5 mmol), and 2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]ethyl bromide (950 mg, 3.5 mmol) were dissolved in 10 mL of DMF. The mixture was heated at 100 °C overnight and was then filtered to remove K_2CO_3 . DMF in the mixture was removed in vacuo by rotary evaporation. The remainder was purified by silica gel column chromatography (MeOH/ CH_2Cl_2 gradient: 0 to 20/80) and the solvent was removed under vacuum by rotary evaporation. Water (50

mL) and KOH (500 mg) were added to the resulting solid and the solution was heated to reflux overnight. After cooling down to room temperature, the solution was acidified with 1M HCl solution to pH~2 in an ice bath. Water was removed by rotary evaporation. The mixture was dissolved in ethyl acetate and filtered, then the solution was dried to obtain oil product. Yield: 488 mg (96%). ^1H NMR (400 MHz, DMSO- d_6): δ 8.18 (s, 1H, ArH), 6.78 (s, 1H, ArH), 4.28 (t, 4H, CH₂, J = 4.8 Hz), 3.79 (t, 4H, CH₂, J = 4.8 Hz), 3.63 (t, 4H, CH₂, J = 4.8 Hz), 3.50 (m, 16H, CH₂), 3.41 (q, 4H, CH₂, J = 3.2 Hz), 3.22 (t, 6H, CH₃, J = 3.2 Hz). ^{13}C NMR (125 MHz, DMSO- d_6): 165.8, 162.5, 136.0, 112.2, 99.1, 71.3, 70.1, 69.9, 69.8, 69.8, 69.6, 68.8, 68.7, 58.1. FT-IR: $\tilde{\nu}$ = 3398 (s), 2928 (m), 2778 (m), 1708 (s), 1606 (s), 1567 (m), 1467 (m), 1350 (m), 1285 (m), 1249 (m), 1201 (m), 1074 (s), 1022 (s), 946 (m), 888 (m), 845 (m), 542 (m) cm^{-1} . ESI-MS: $[\text{M-H}]^-$ 577.11.

Synthesis of MOP-H [Cu₂₄(*m*-bdc)₂₄(S)₂₄]. (S = terminal solvent molecule) Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10^{-2} mmol) and isophthalic acid (H₂*m*-bdc, 6.8 mg, 4.1×10^{-2} mmol) were dissolved in 0.75 mL of DMF and 0.25 mL of ethanol (EtOH) in a 4 mL scintillation vial. The vial was placed in a sand bath in a preheated isothermal oven at 80 °C for 16 h. The isolated product (52% based on Cu) was washed with DMF (3×5 mL) and EtOH (3×5 mL), and then air-dried for 5 min. FT-IR: $\tilde{\nu}$ = 1606 (s), 1535 (s), 1482 (m), 1442 (m), 1382 (s), 1276 (m), 1161 (w), 1078 (w), 1039 (w), 739 (s), 719 (s), 660 (m), 485 (m) cm^{-1} .

Synthesis of MOP-OH [Cu₂₄(5-OH-*m*-bdc)₂₄(S)₂₄]. Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10^{-2} mmol) and 5-hydroxyisophthalic acid (5-OH-H₂*m*-bdc, 7.5 mg, 4.1×10^{-2} mmol) were dissolved in 0.75 mL of *N,N*-diethylformamide (DEF) and 0.25 mL of MeOH in a 4 mL scintillation vial. The vial was placed in a sand bath in a preheated isothermal oven at 80 °C for 16 h. The isolated product (36% based on Cu) was washed with DEF (3×5 mL) and CH₂Cl₂ (3×5 mL), and then air-dried for 5 min. FT-IR: $\tilde{\nu}$ = 1610 (s), 1573 (s), 1508 (m), 1376 (s), 1273 (m), 1210 (m), 1127 (w), 1001 (m), 979 (m), 899 (w), 809 (m), 770 (s), 731 (s), 481 (m) cm^{-1} .

Synthesis of MOP-NO₂ [Cu₂₄(5-NO₂-*m*-bdc)₂₄(S)₂₄]. Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10^{-2} mmol) and 5-nitroisophthalic acid (5-NO₂-H₂*m*-bdc, 8.7 mg, 4.1×10^{-2} mmol) were dissolved in 0.40 mL of DMF and 0.60 mL of MeOH in a 4 mL scintillation vial. The vial was placed in a sand bath in a preheated isothermal oven at 60 °C for 2 d. The

isolated product (55% based on Cu) was washed with DMF (3×5 mL) and MeOH (3×5 mL), and then air-dried for 5 min. FT-IR: $\tilde{\nu}$ = 3088 (w), 1625 (m), 1534 (m), 1459 (m), 1375 (s), 1341 (s), 1086 (m), 1038 (w), 925 (m), 782 (m), 723 (s), 480 (m) cm^{-1} .

Synthesis of MOF-CH₃-*m*-bdc [Cu(5-CH₃-*m*-bdc)(H₂O)]_n. Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10⁻² mmol) and 5-methylisophthalic acid (5-CH₃-H₂*m*-bdc, 7.4 mg, 4.1×10⁻² mmol) were dissolved in 0.40 mL of DMF and 0.40 mL of MeOH in a 4 mL scintillation vial. The vial was placed in a sand bath in a preheated isothermal oven at 60 °C for 2 d. The isolated product (55% based on Cu) was washed with DMF (3×5 mL) and MeOH (3×5 mL), and then air-dried for 5 min. FT-IR: $\tilde{\nu}$ = 3416 (m), 1627 (s), 1588 (s), 1420 (m), 1375 (m), 1249 (m), 1113 (w), 792 (m), 770 (s), 731 (s), 495 (m) cm^{-1} .

Synthesis of MOF-NH₂-*m*-bdc [Cu(5-NH₂-*m*-bdc)(DMF)]_n. Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10⁻² mmol) and 5-aminoisophthalic acid (5-NH₂-H₂*m*-bdc, 7.4 mg, 4.1×10⁻² mmol) were dissolved in 0.75 mL of DMF and 0.25 mL of MeOH in a 4 mL scintillation vial. The vial was placed in a sand bath in a preheated isothermal oven at 60 °C for 2 d. The isolated product (51% based on Cu) was washed with DMF (3×5 mL) and MeOH (3×5 mL), and then air-dried for 5 min. FT-IR: $\tilde{\nu}$ = 3440 (m), 3353 (m), 1657 (m), 1579 (s), 1480 (m), 1418 (m), 1388 (s), 1250 (m), 1150 (w), 1103 (m), 1060 (w), 1000 (m), 896 (m), 784 (s), 727 (s), 669 (m), 526 (m), 480 (s) cm^{-1} .

Synthesis of pm-MOP-H [Cu₂₄(*m*-bdc)₂₄(S)₂₄]. Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10⁻² mmol), isophthalic acid (H₂*m*-bdc, 5.8 mg, 3.5×10⁻² mmol), and polymer **1** (2.0 mg, 5.6×10⁻³ mmol) were dissolved in 0.75 mL of DMF and 0.25 mL of EtOH in a 4 mL scintillation vial. The vial was placed in a sand bath in a preheated isothermal oven at 80 °C for 16 h. The isolated product (43% based on Cu) was washed with DMF (3×5 mL) and EtOH (3×5 mL), and then air-dried for 5 min. FT-IR: $\tilde{\nu}$ = 1604 (s), 1534 (s), 1481 (m), 1438 (m), 1375 (s), 1276 (m), 1160 (m), 1076 (m), 1039 (w), 935 (w), 825 (w), 717 (s), 659 (m), 487 (m) cm^{-1} .

Synthesis of pm-MOP-OH [Cu₂₄(5-OH-*m*-bdc)₂₄(S)₂₄]. Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10⁻² mmol), 5-hydroxyisophthalic acid (5-OH-H₂*m*-bdc, 6.8 mg, 3.7×10⁻² mmol), and polymer **1** (1.2 mg, 3.5×10⁻³ mmol) were dissolved in 0.75 mL of DEF and 0.25 mL of MeOH in a 4 mL scintillation vial. The vial was placed in a sand bath in a preheated isothermal oven at 80 °C for 16 h. The isolated product (36% based on Cu) was washed

with DMF (3×5 mL) and CH₂Cl₂ (3×5 mL), and then air-dried for 5 min. FT-IR: $\tilde{\nu}$ = 1625 (s), 1588 (s), 1388 (s), 1268 (m), 1209 (m), 1122 (m), 1002 (m), 977 (m), 776 (s), 734 (s), 670 (m), 646 (m), 486 (m) cm⁻¹.

Synthesis of pm-MOP-NO₂ [Cu₂₄(5-NO₂-*m*-bdc)₂₄(S)₂₄]. Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10⁻² mmol), 5-nitroisophthalic acid (5-NO₂-H₂*m*-bdc, 7.9 mg, 3.7×10⁻² mmol), and polymer **1** (1.2 mg, 3.5×10⁻³ mmol) were dissolved in 0.40 mL of DMF and 0.60 mL of MeOH in a 4 mL scintillation vial. The vial was placed in a sand bath in a preheated isothermal oven at 60 °C for 2 d. The isolated product (59% based on Cu) was washed with DMF (3×5 mL) and MeOH (3×5 mL), and then air-dried for 5 min. FT-IR: $\tilde{\nu}$ = 3089 (w), 1624 (s), 1532 (s), 1457 (m), 1343 (s), 1083 (m), 924 (m), 782 (m), 724 (s), 468 (m) cm⁻¹.

Synthesis of pm-MOP-CH₃ [Cu₂₄(5-CH₃-*m*-bdc)₂₄(S)₂₄]. Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10⁻² mmol), 5-methylisophthalic acid (5-CH₃-H₂*m*-bdc, 6.8 mg, 3.7×10⁻² mmol), and polymer **1** (1.2 mg, 3.5×10⁻³ mmol) were dissolved in 0.40 mL of DMF and 0.40 mL of MeOH in a 4 mL scintillation vial. The vial was placed in a sand bath in a preheated isothermal oven at 60 °C for 2 d. The isolated product (55% based on Cu) was washed with DMF (3×5 mL) and MeOH (3×5 mL), and then air-dried for 5 min. FT-IR: $\tilde{\nu}$ = 2916 (w), 1610 (m), 1541 (s), 1422 (s), 1371 (s), 1276 (m), 1112 (w), 933 (w), 769 (s), 727 (s), 495 (m) cm⁻¹.

Synthesis of pm-MOP-NH₂ [Cu₂₄(5-NH₂-*m*-bdc)₂₄(S)₂₄][Cu_{0.5}(S')(S'')]₈ (*S*, *S'*, and *S''* are unassigned solvent molecules). Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10⁻² mmol), 5-aminoisophthalic acid (5-NH₂-H₂*m*-bdc, 6.8 mg, 3.7×10⁻² mmol), and polymer **1** (1.2 mg, 3.5×10⁻³ mmol) were dissolved in 0.75 mL of DMF and 0.25 mL of MeOH in a 4 mL scintillation vial. The vial was placed in a sand bath in a preheated isothermal oven at 60 °C for 2 d. The isolated product (61% based on Cu) was washed with DMF (3×5 mL) and MeOH (3×5 mL), and then air-dried for 5 min. FT-IR: $\tilde{\nu}$ = 3258 (w), 3119 (w), 1619 (m), 1546 (s), 1476 (m), 1364 (s), 1103 (m), 1001 (m), 957 (m), 772 (s), 725 (s), 670 (m), 457 (m) cm⁻¹.

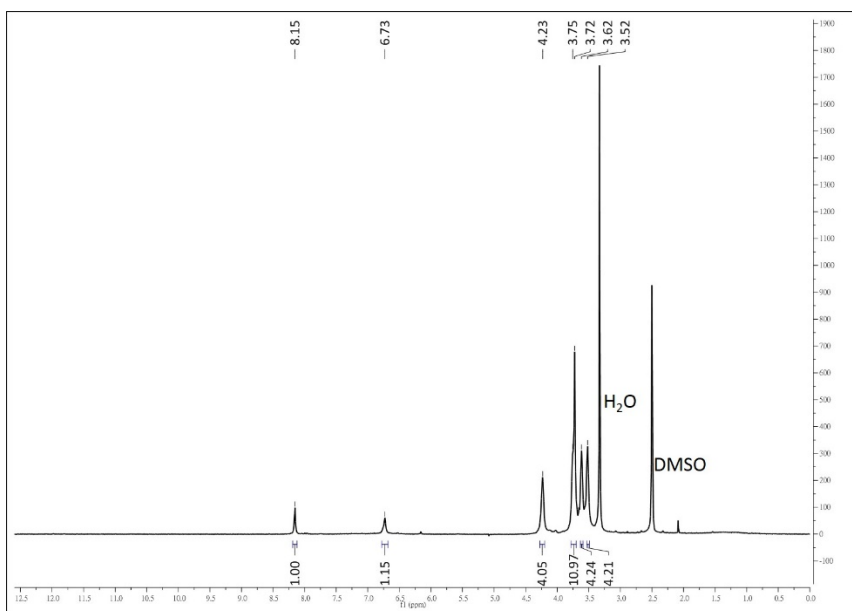


Figure S1. ¹H NMR spectrum of polymer **1'**.

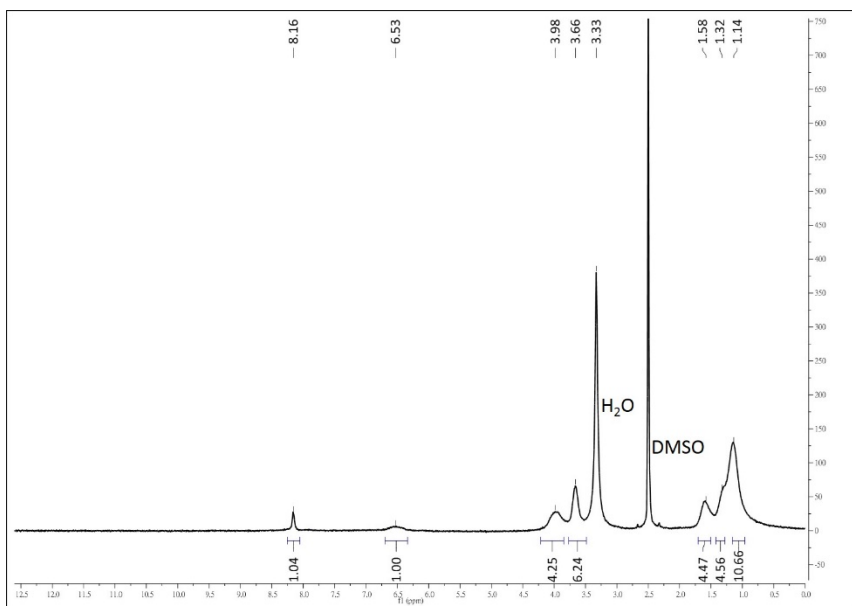


Figure S2. ¹H NMR spectrum of **2'**.

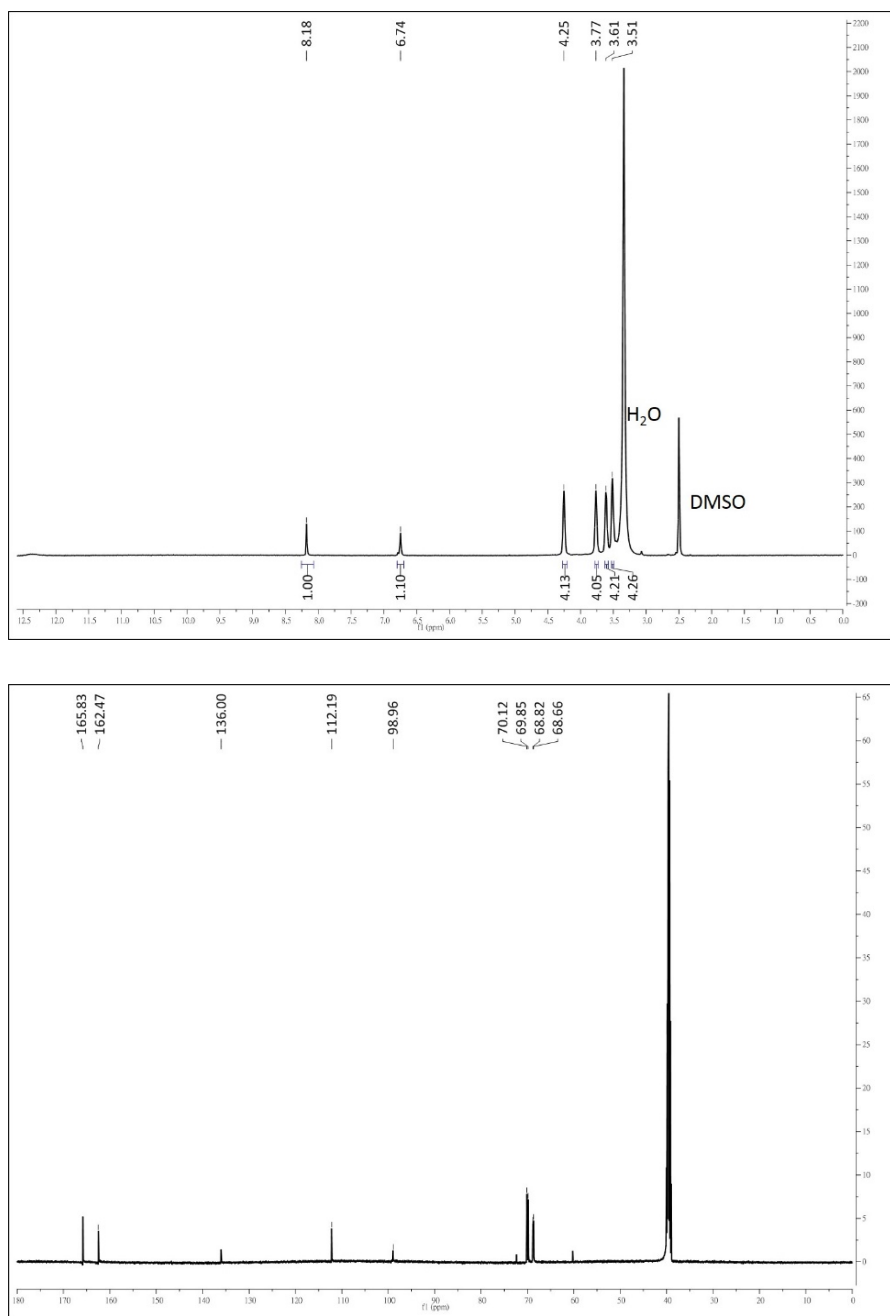


Figure S3. ^1H NMR and ^{13}C NMR spectrum of polymer 1.

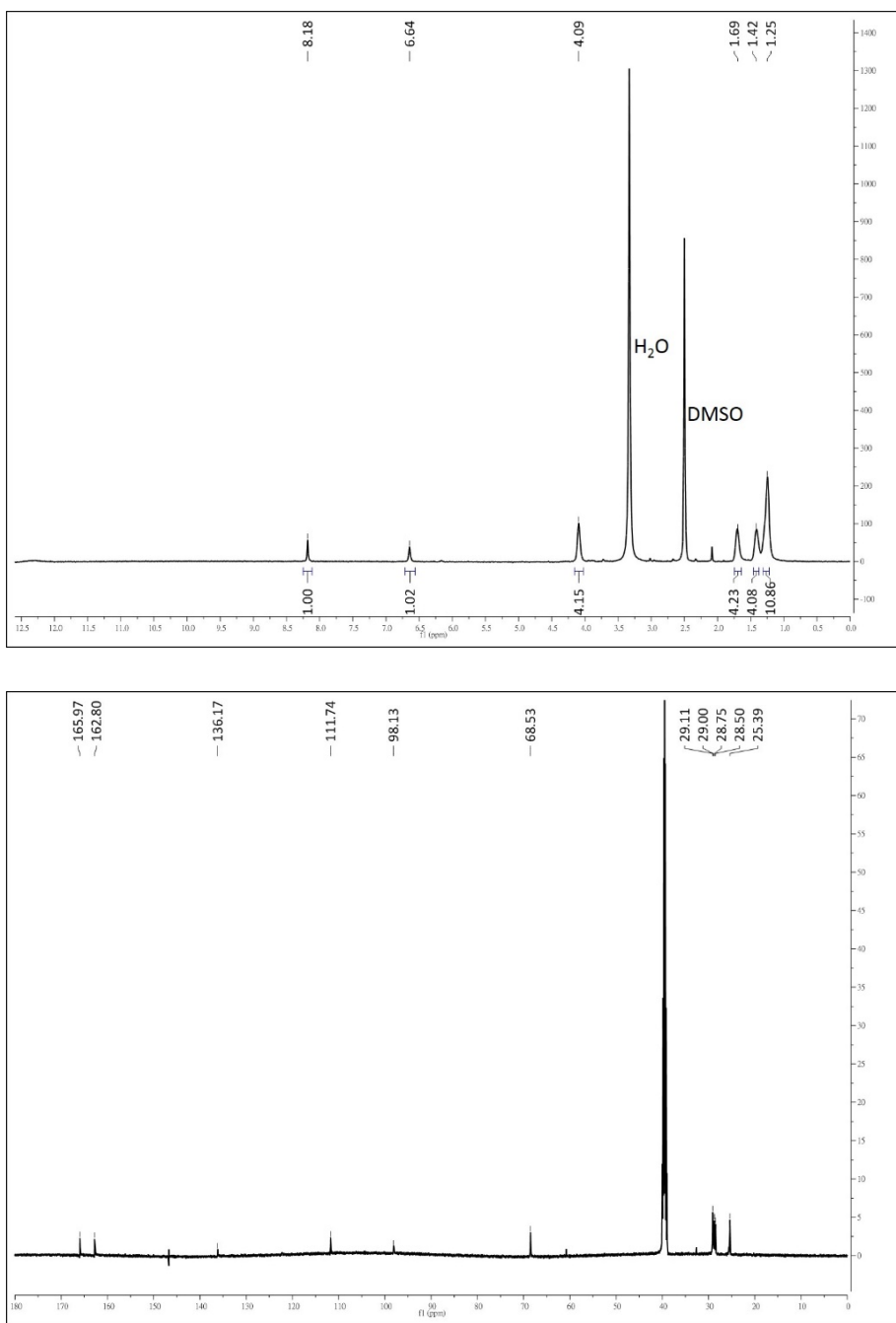


Figure S4. ^1H NMR and ^{13}C NMR spectrum of polymer 2.

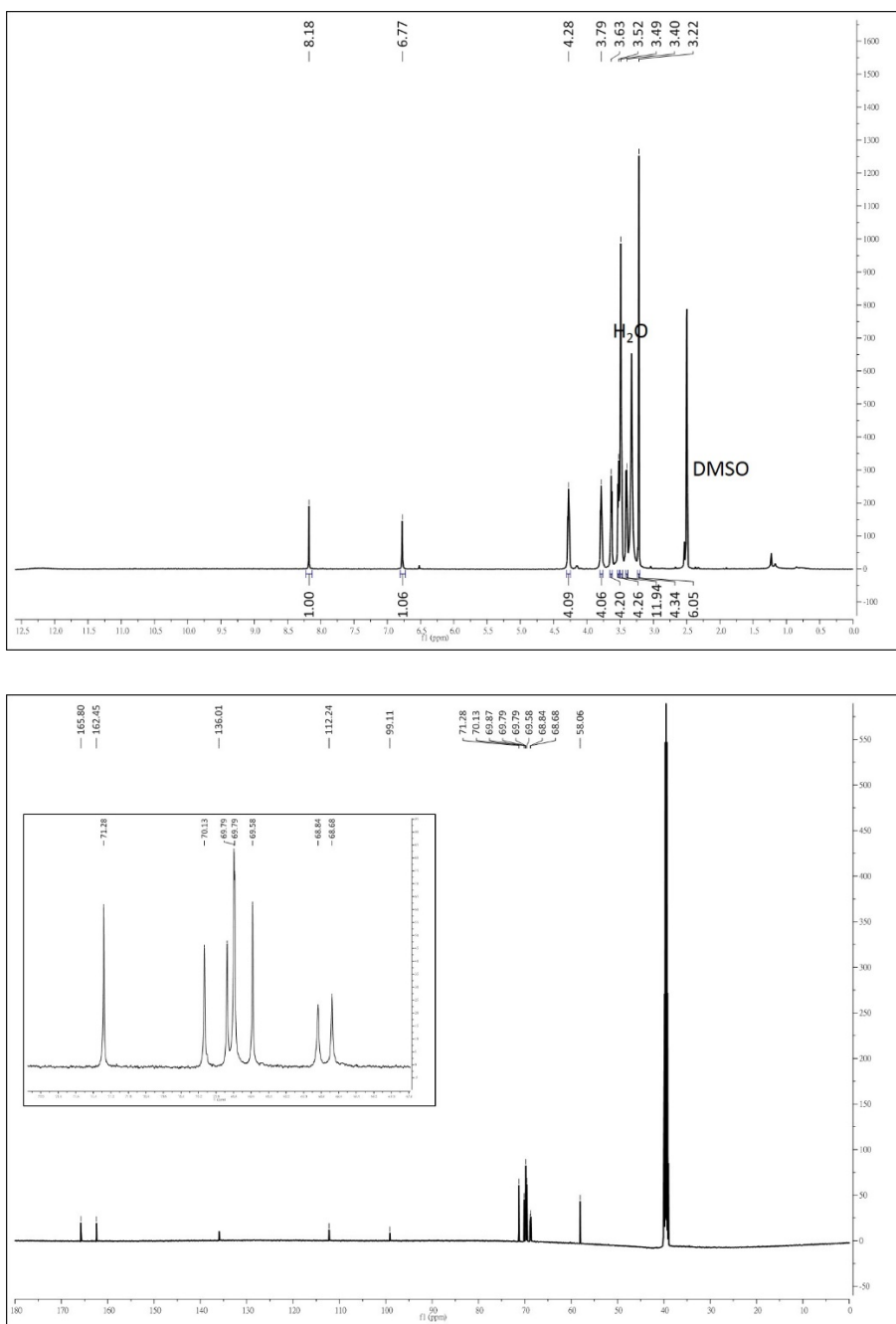


Figure S5. ^1H NMR and ^{13}C NMR spectrum of compound **3**.

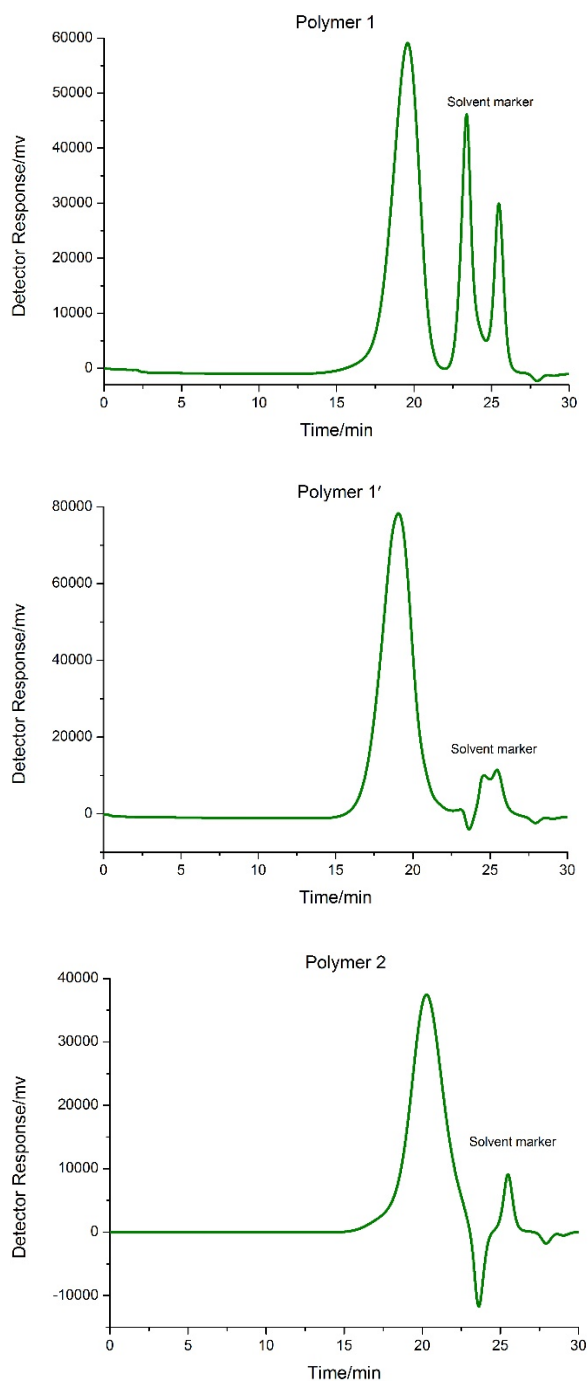


Figure S6. GPC traces of polymer 1, 1', and 2.

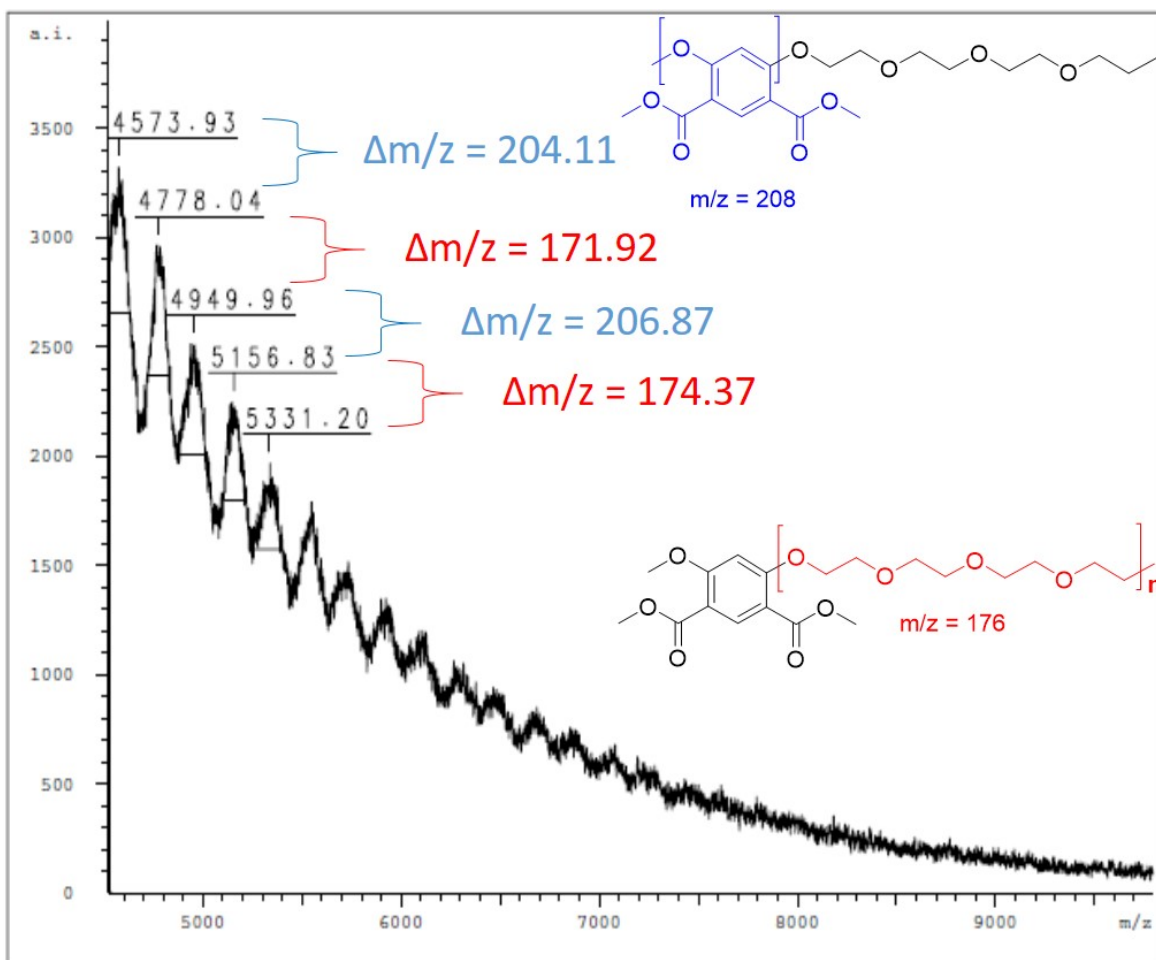


Figure S7. MALDI-TOF mass spectrum of polymer 1'. Polymer 1' was dissolved in THF and α -cyano-4-hydroxycinnamic acid (HCCA) was used as the matrix. The low resolution of spectrum is due to the low solubility of polymer 1' and only shorter chains were detected (e.g. 5331.20 g/mol corresponding to a degree of polymerization of ~14 repeat units). The $\Delta m/z$ numbers at ~176 and ~208 g/mol are highly characteristic of the repeating units of the polymer.

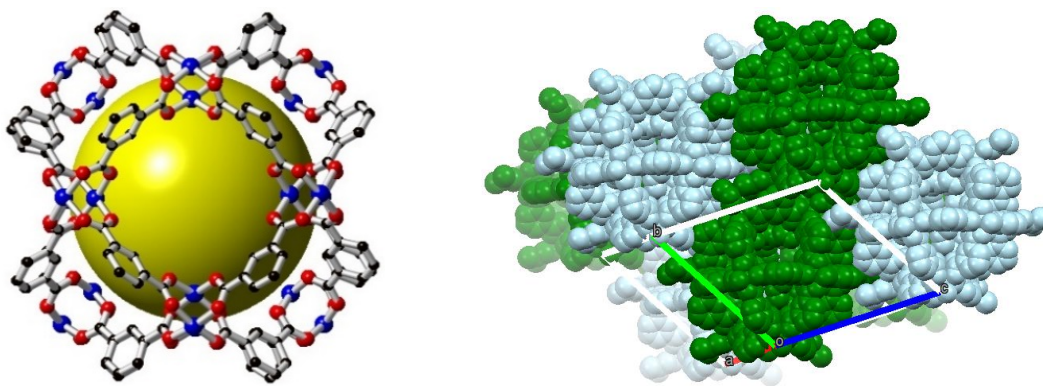


Figure S8. *Left:* Crystal structure of MOP-H (terminal DMF and H₂O ligands have been omitted for clarity). Cu, blue; O, red; C, black. The yellow sphere serves to highlight the void space within the cage. *Right:* Molecular packing of MOP-H. The lines represent the unit cell of the crystal structure. The packed MOP molecules are presented in different colors for clarity.

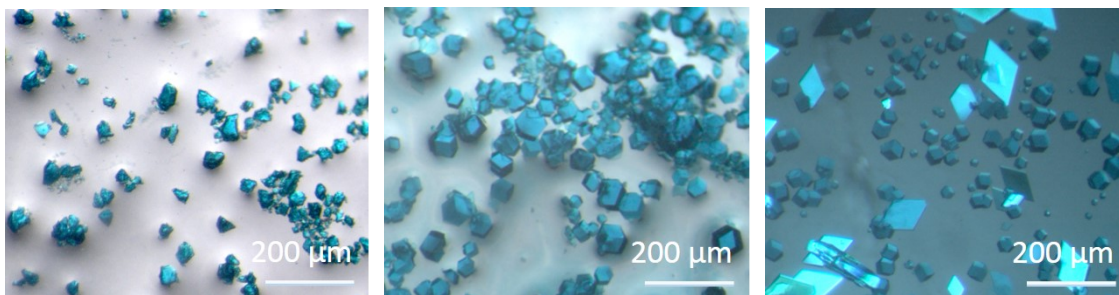


Figure S9. Optical images of products from the solutions containing 0.027 mmol of H₂*m*-bdc and 0.014 mmol of polymer **1** (2:1 ratio, *left*), 0.031 mmol of H₂*m*-bdc and 0.010 mmol of polymer **1** (3:1 ratio, *middle*), and 0.039 mmol of H₂*m*-bdc and 0.002 mmol of polymer **1** (20:1 ratio, *right*) under identical reaction conditions (0.75 mL DMF/0.25 mL EtOH at 80 °C for 16 h).

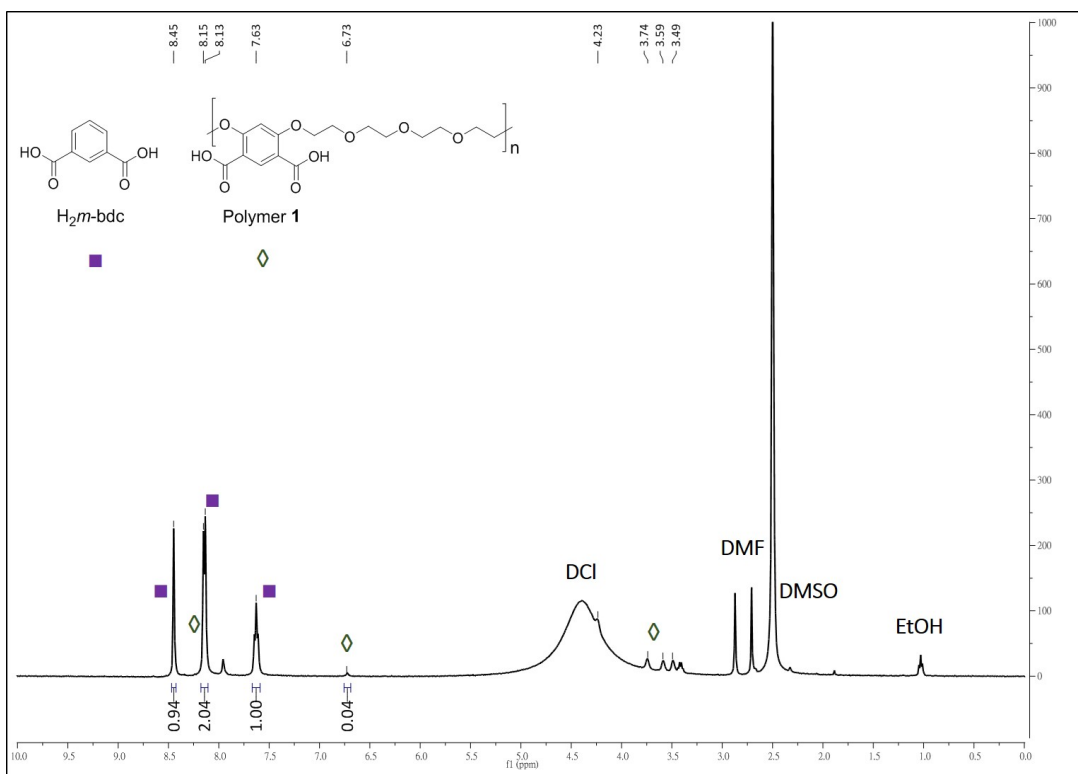


Figure S10. ^1H NMR spectrum of digested pm-MOP-H that shows the molar ratio of $\text{H}_2\text{m-bdc}$ to polymer **1** is $\sim 25:1$.

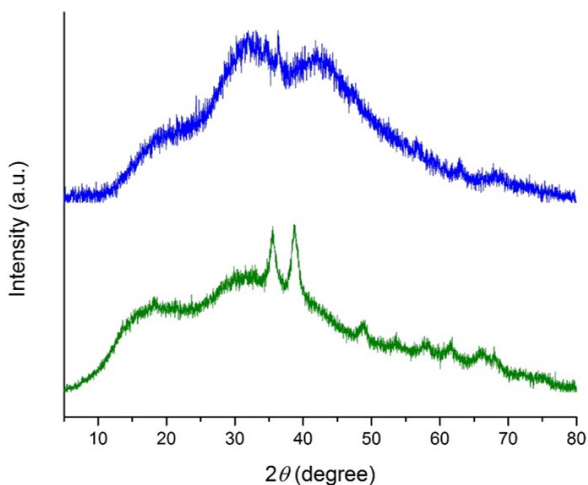


Figure S11. PXRD patterns of amorphous solid (*blue*) obtained from the reaction of 0.04 mmol of polymer **1** and $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$. A combination of amorphous solid and CuO (*green*) obtained from the reaction of 0.04 mmol of polymer **1** and 0.12 mmol of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$. Identical reaction conditions were used as for the preparation of pm-MOP-H (0.75 mL DMF/0.25 mL EtOH at 80 °C for 16 h).

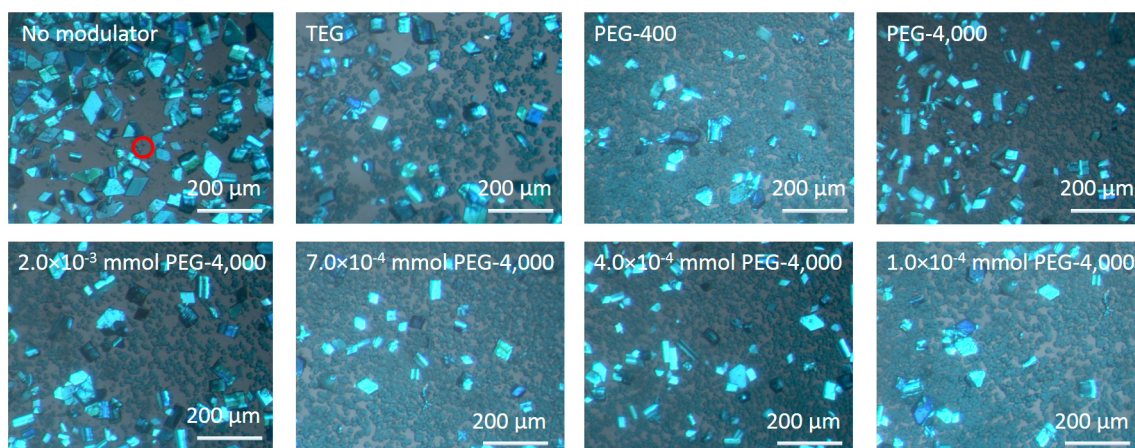


Figure S12. *Top:* Optical images of MOP-H (*left to right*) using no modulator, TEG, PEG-400, and PEG-4000. These additives increase the abundance of the smaller, cubic crystals (see red circle), but still result in a mixed phase and do not increase the physical dimensions of these crystals significantly. *Bottom:* Optical images of products with difference concentrations of PEG-4000 (*left to right:* 2.0×10^{-3} , 7.0×10^{-4} , 4.0×10^{-4} , and 1.0×10^{-4} mmol), which again, increase the abundance of the smaller, cubic crystals, but still result in a mixed phase and do not increase the physical dimensions of these crystals significantly. The reaction conditions for all samples were 0.75 mL DMF/0.25 mL EtOH at 80 °C for 16 h.

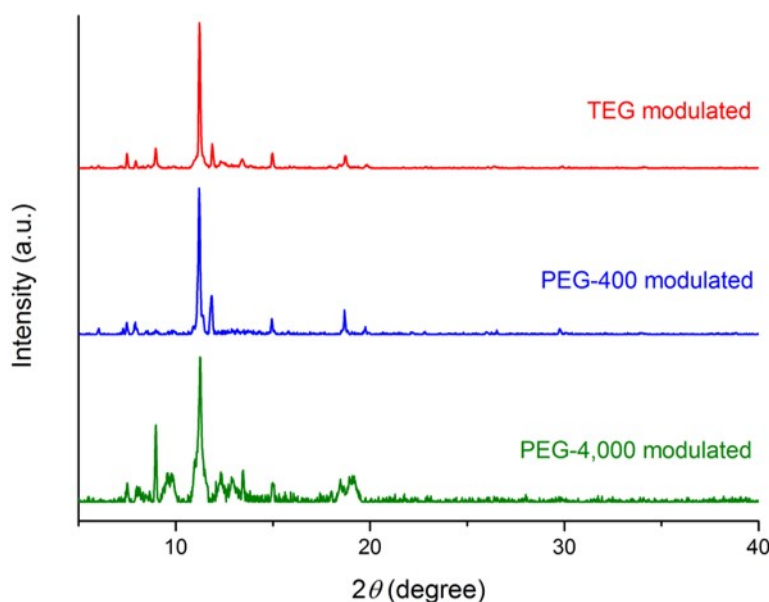


Figure S13. PXRD patterns of products using TEG, PEG-400, and PEG-4000 (2.0×10^{-3} mmol) as modulators under identical reaction conditions as that of pm-MOP-H synthesis (0.75 mL DMF/0.25 mL EtOH at 80 °C for 16 h).

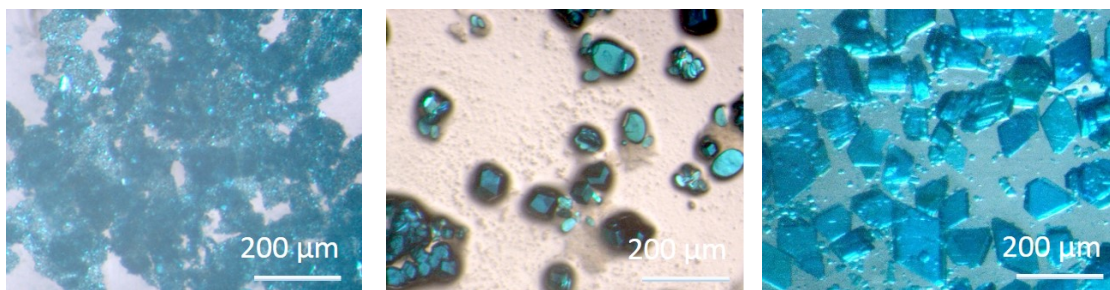


Figure S14. Optical images of products using polymer **1'** (*left*), polymer **2** (*middle*), and compound **3** (*right*) as modulators under identical reaction conditions as that of pm-MOP-H synthesis (0.75 mL DMF/0.25 mL EtOH at 80 °C for 16 h).

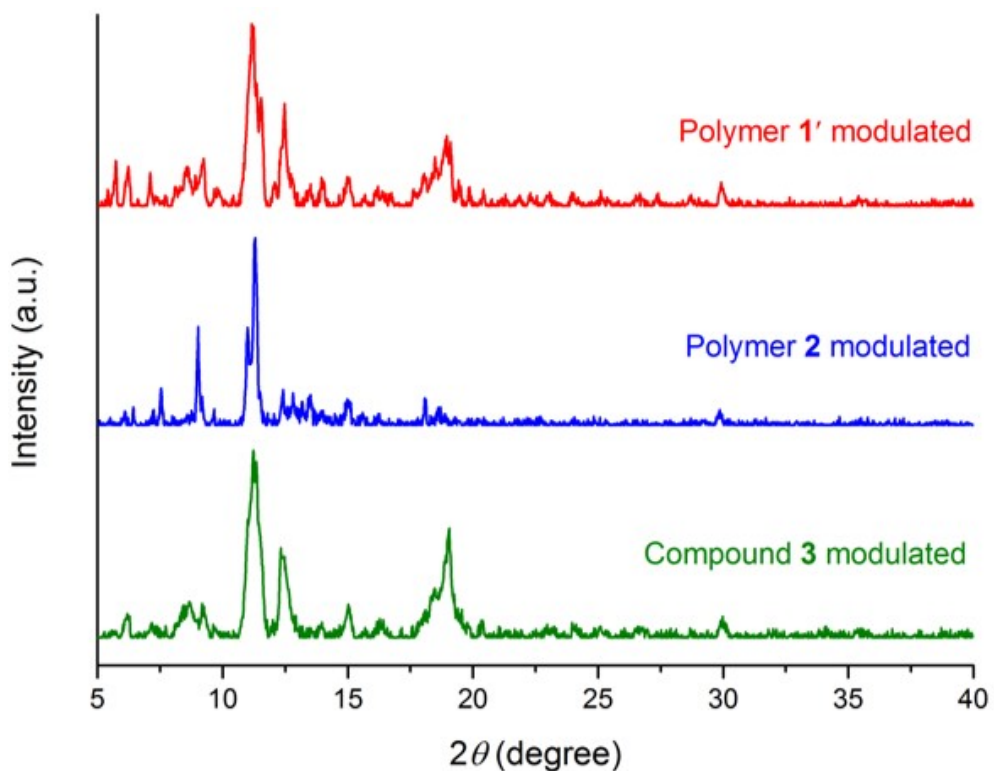


Figure S15. PXRD patterns of products using polymer **1'**, polymer **2**, and compound **3** (6.0×10^{-3} mmol) as modulators under the same reaction condition as that of pm-MOP-H synthesis.

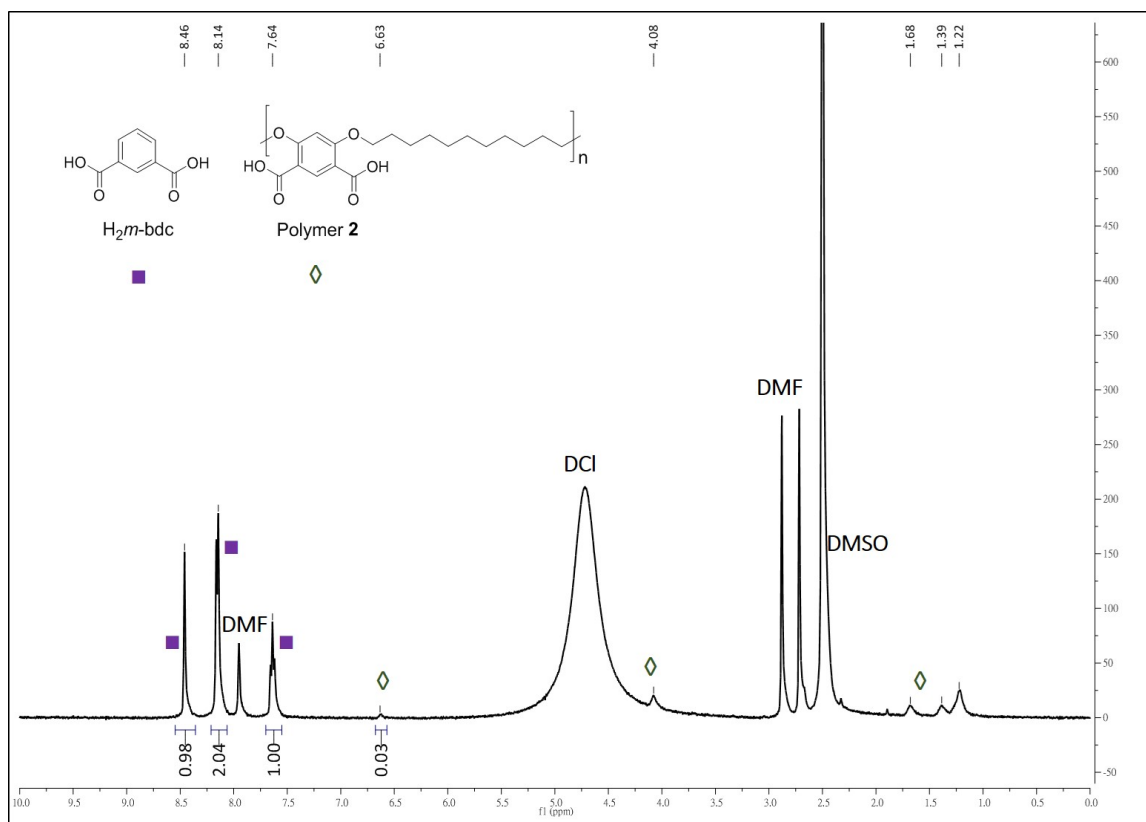


Figure S16. ^1H NMR spectrum of digested MOP-H that shows the molar ratio of $\text{H}_2\text{m-bdc}$ to polymer **2** is $\sim 33:1$.

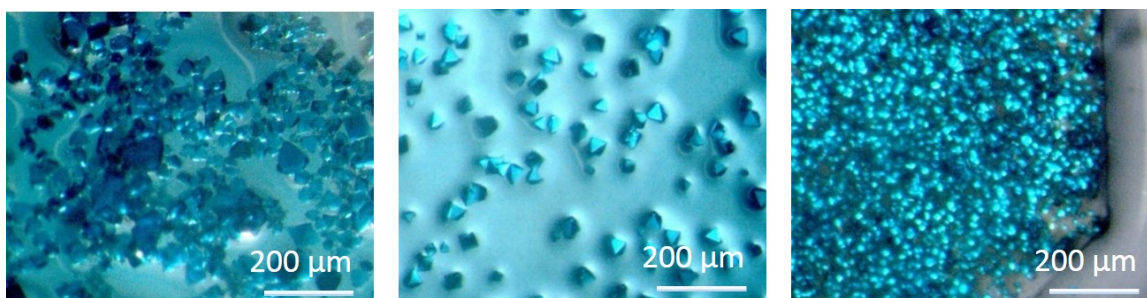


Figure S18. Images of MOP-OH (*left*), pm-MOP-OH (*middle*), and pm-MOP-OH deposited on a glass surface (*right*).

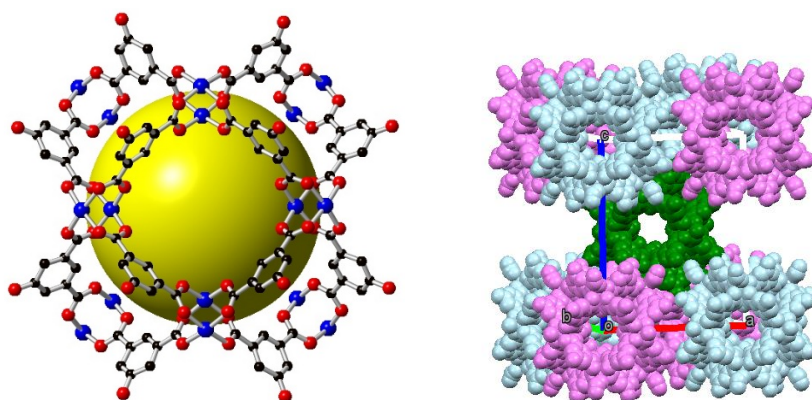


Figure S19. *Left:* Crystal structure of MOP-OH (terminal H₂O ligands have been omitted for clarity). Cu, blue; O, red; C, black. The yellow sphere serves to highlight the void space within the cage. *Right:* Molecular packing of MOP-OH. The lines represent the unit cell of the crystal structure. The packed MOP molecules are presented in different colors for clarity.

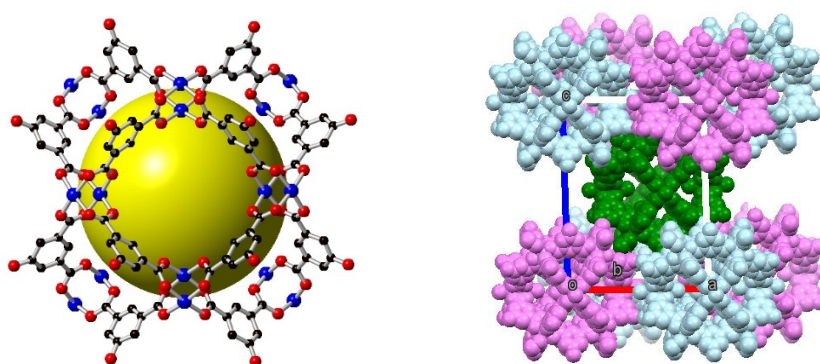


Figure S20. *Left:* Crystal structure of pm-MOP-OH (terminal H₂O ligands have been omitted for clarity). Cu, blue; O, red; C, black. The yellow sphere serves to highlight the void space within the cage. *Right:* Molecular packing of pm-MOP-OH. The lines represent the unit cell of the crystal structure. The packed MOP molecules are presented in different colors for clarity.

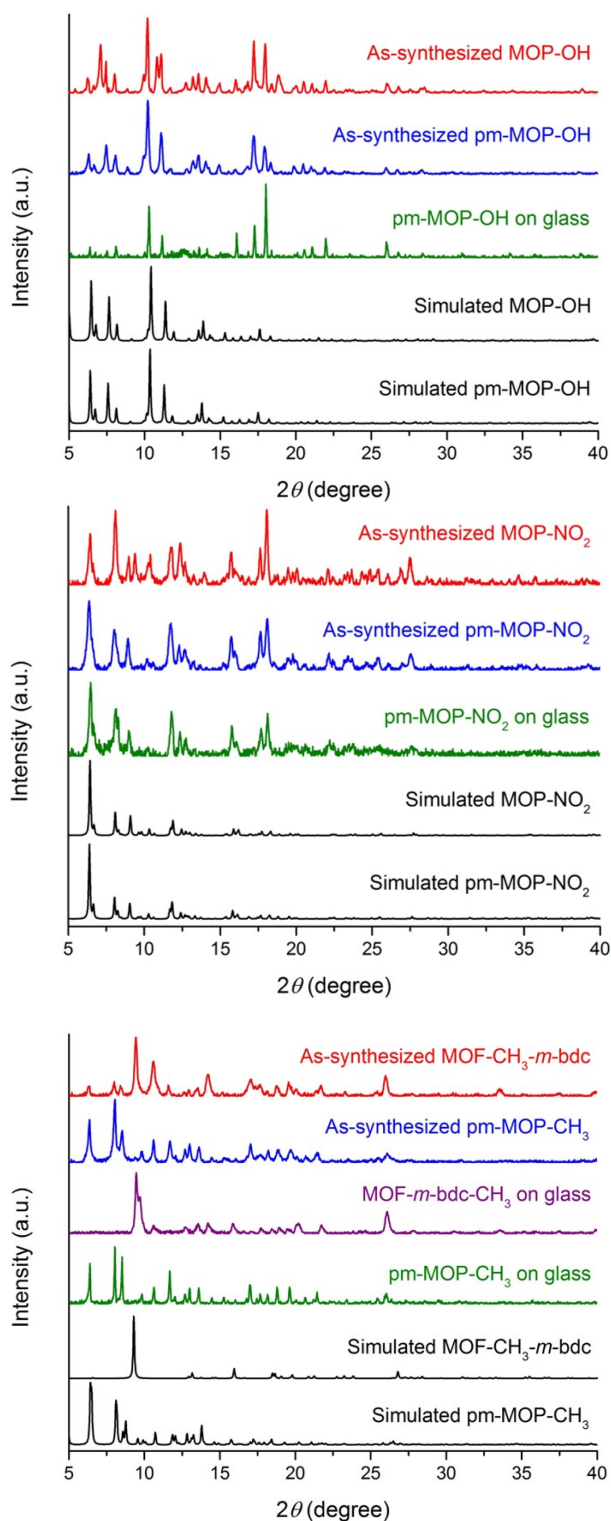


Figure S21. PXRD patterns of materials synthesized from 5-OH-H₂*m*-bdc, 5-NO₂-H₂*m*-bdc, and 5-CH₃-H₂*m*-bdc as free-standing crystals and as films on glass.

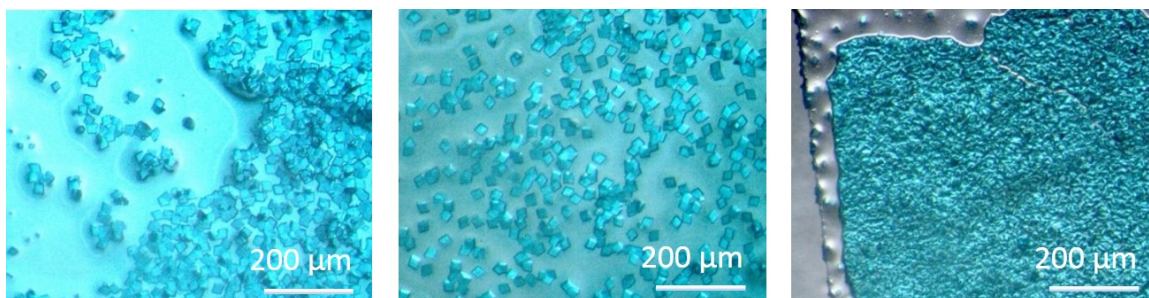


Figure S22. Images of MOP-NO₂ (*left*), pm-MOP-NO₂ (*middle*), and pm-MOP-NO₂ deposited on a glass surface (*right*).

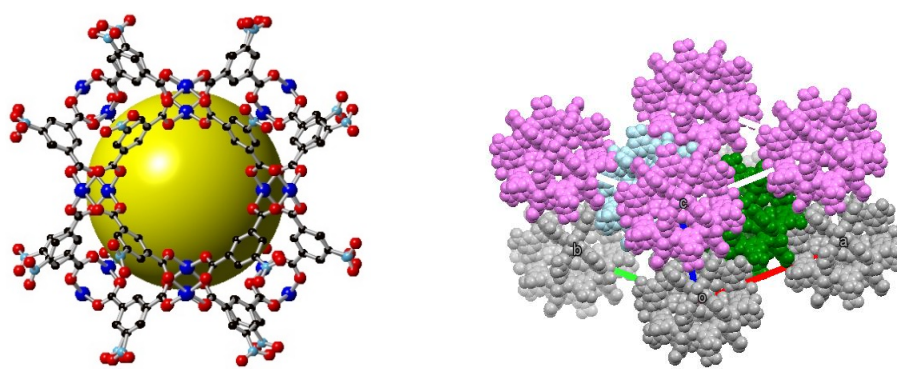


Figure S23. *Left:* Crystal structure of MOP-NO₂ (terminal H₂O ligands have been omitted for clarity). Cu, blue; O, red; C, black; N, light blue. The yellow sphere serves to highlight the void space within the cage. *Right:* Molecular packing of MOP-NO₂. The lines represent the unit cell of the crystal structure. The packed MOP molecules are presented in different colors for clarity.

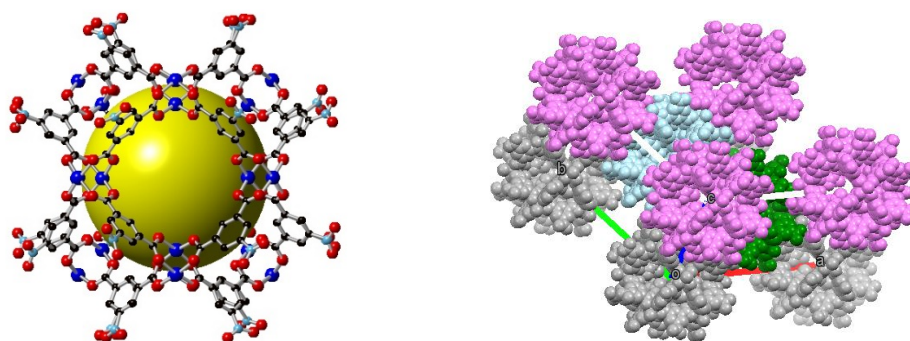


Figure S24. *Left:* Crystal structure of pm-MOP-NO₂ (terminal MeOH and H₂O ligands have been omitted for clarity). Cu, blue; O, red; C, black; N, light blue. The yellow sphere serves to highlight the void space within the cage. *Right:* Molecular packing of pm-MOP-NO₂. The lines represent the unit cell of the crystal structure. The packed MOP molecules are presented in different colors for clarity.



Figure S25. Images of MOF-CH₃-*m*-bdc (*left*), pm-MOP-CH₃ (*middle*), and pm-MOP-CH₃ deposited on glass surface (*right*).

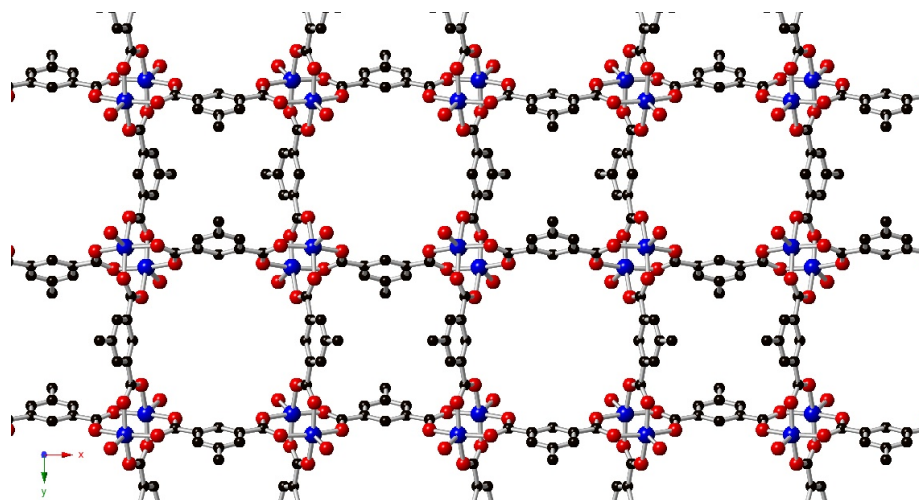


Figure S26. Crystal structure of MOF-CH₃-*m*-bdc.⁴ Cu, blue; O, red; C, black. Hydrogen atoms have been omitted for clarity.

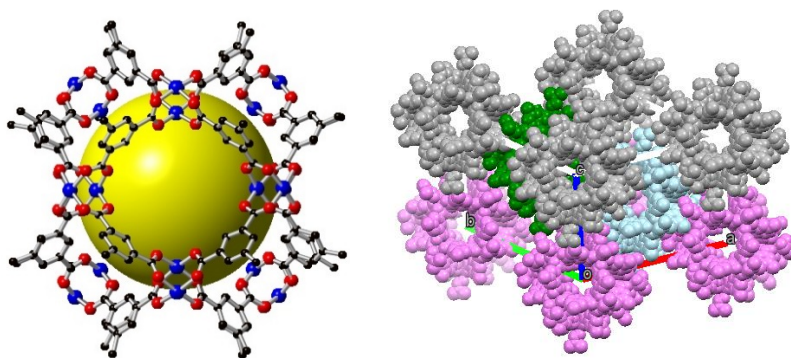


Figure S27. *Left:* Crystal structure of pm-MOP-CH₃ (terminal H₂O ligands have been omitted for clarity). Cu, blue; O, red; C, black. The yellow sphere serves to highlight the void space within the cage. *Right:* Molecular packing of pm-MOP-CH₃. The lines represent the unit cell of the crystal structure. The packed MOP molecules are presented in different colors for clarity.

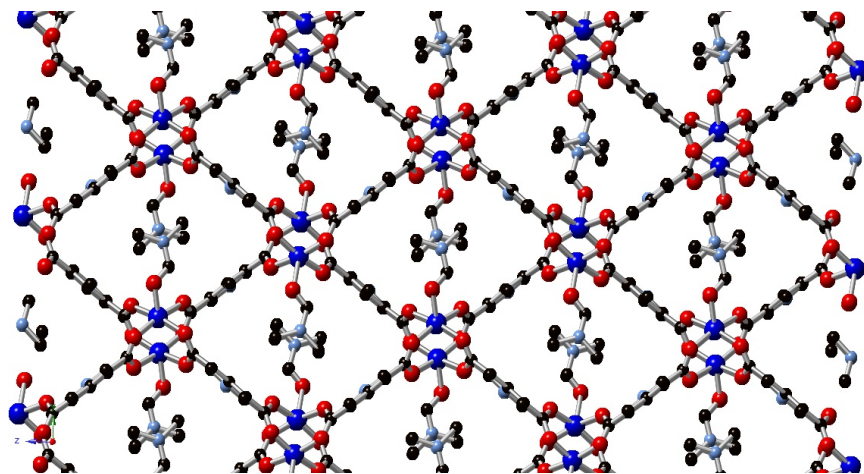


Figure S28. Crystal structure of MOF-NH₂-*m*-bdc.⁵ Cu, blue; O, red; C, black; N, light blue. Hydrogen atoms have been omitted for clarity.

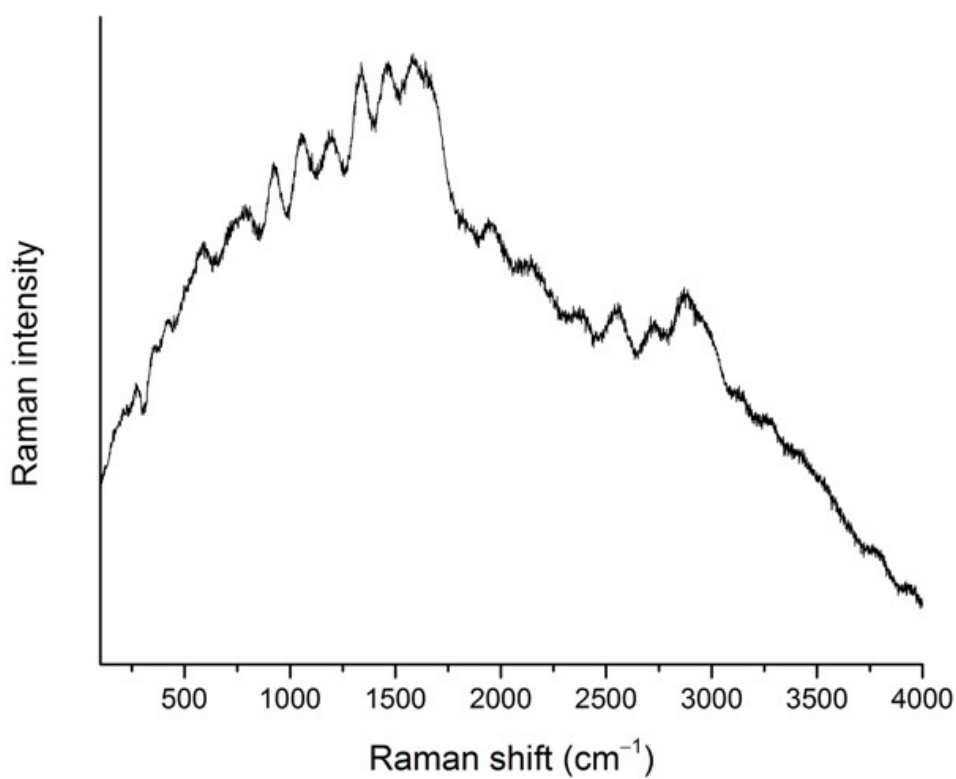
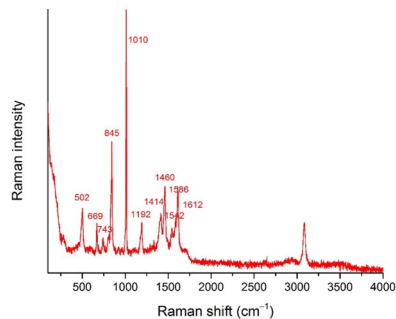
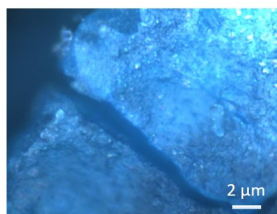


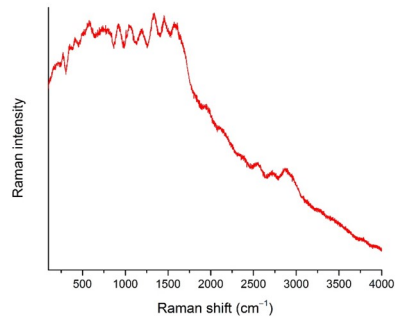
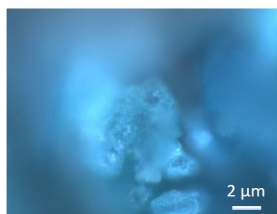
Figure S29. Raman spectrum of polymer 1.

(a) MOP-H

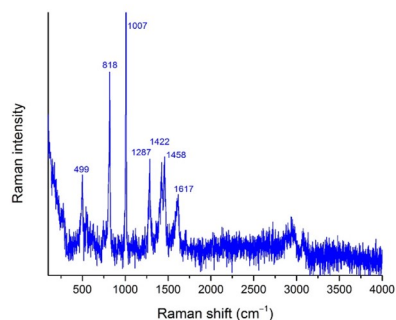
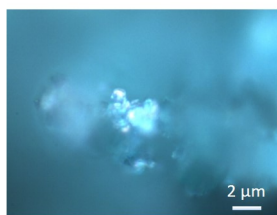


Raman shift (cm ⁻¹)	Assignment	References
502	Cu-O	6,7
669	ν(COO)	8,9
743	out of plane ring bending	6
743	COO of Isophthalate	9
845	out of plane CH bending, CC stretching	6,9
1010	C=C stretching, CC stretching	6,9,8
1192		
1414	COO symmetric stretch	7
1460	symmetric COO stretch	6,7
1460	CC stretching	9
1542	asymmetric COO stretching	6,7
1586	asymmetric stretching CC	9
1612	CC, C=C stretching	6,7,8,9

(b) pm-MOP-H



(c) MOP-OH



Raman shift (cm ⁻¹)	Assignment	References
499	Cu-O	6,7
818	out of plane CH bending	6,10
1007	C=C stretching, CC stretching	6,8,9
1287		
1422	COO symmetric stretch	7
1458	COO stretch	6,7
1458	CC	9
1617	C=O	8

(d) pm-MOP-OH

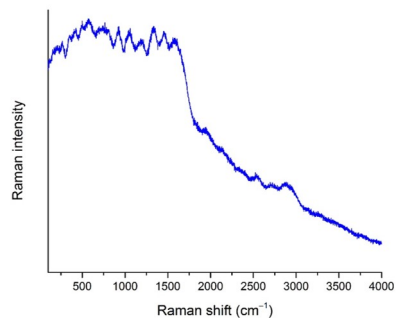
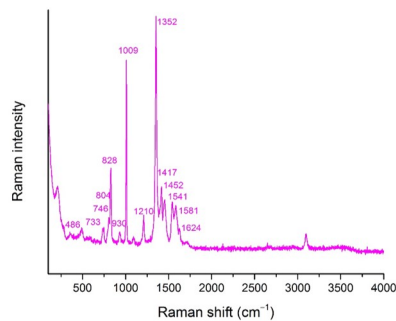
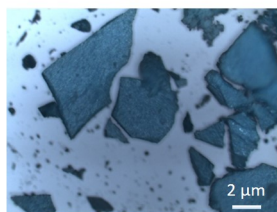
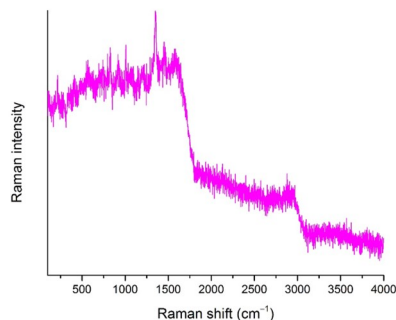
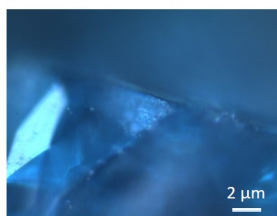
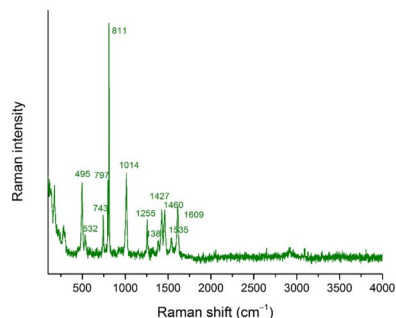
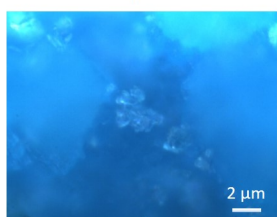


Figure S30. Confocal microscopic images (*left*), Raman spectra (*middle*), and peak assignments (*right*) for MOPs (a, c, e), MOFs (g, i), and pm-MOPs (b, d, f, h, j). No peak assignment for pm-MOPs are provided due to the absence of characteristic peaks.

(e) MOP-NO₂

Raman shift (cm ⁻¹)	Assignment	References
486	Cu-O	6,7
733	NO ₂ wagging	11
746	out of plane ring bending	6
804	symmetric stretch CN	12
828	out of plane CH bending, scissoring of NO ₂	6,11
930	CH	11
1009	C=C stretching, CC stretching	6,8,9
1210		
1352	symmetric stretch NO ₂	11
1417	COO symmetric stretch	7
1452	COO stretch	6,7
1452	CC	9
1541	COO and asymmetric NO ₂	11,12
1581	C-C stretch	11
1624	C=O	8

(f) pm-MOP-NO₂(g) MOF-CH₃-*m*-bdc

Raman shift (cm ⁻¹)	Assignment	References
495	Cu-O	6,7
532	ring deformation	13
743	out of plane ring bending	6
797	ring deformation	13
811	out of plane CH bending	6
1014	C=C stretching, CC stretching	6,8,9
1255		
1381	CH bend (methyl)	13
1427	COO symmetric stretch	7
1460	COO stretch	6,7
1460	CC	9
1535	CC	9
1609	CC, C=C	6,7,8,9

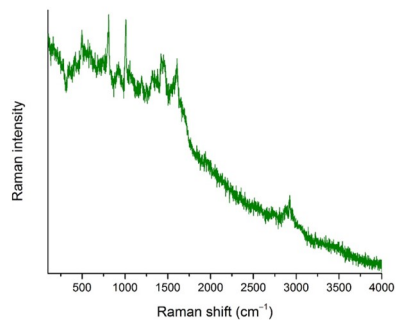
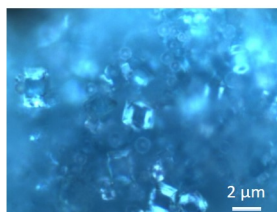
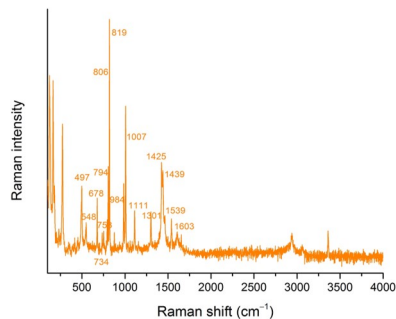
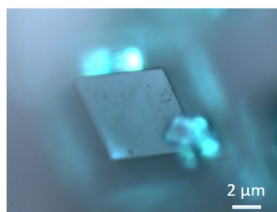
(h) pm-MOP-CH₃

Figure S30 (cont). Confocal microscopic images (*left*), Raman spectra (*middle*), and peak assignments (*right*) for MOPs (a, c, e), MOFs (g, i), and pm-MOPs (b, d, f, h, j). No peak assignment for pm-MOPs are provided due to the absence of characteristic peaks.

(i) MOF-NH₂-*m*-bdc



Raman shift (cm ⁻¹)	Assignment	References
497	Cu-O	6,7
548		
678	out of plane ring deformation	13
734	out of plane CH bending	6
753		
794	ring deformation	13
806	symmetric stretch CN	12
819	out of plane CH bending	6
984	ring breathing	13
1007	C=C stretching, CC stretching	6,8,9
1111		
1301		
1425	COO symmetric stretch	7
1439	COO stretch	6,7
1439	CC	9
1539	CC	9
1603	CC, C=C	6,7,8,9

(j) pm-MOP-NH₂

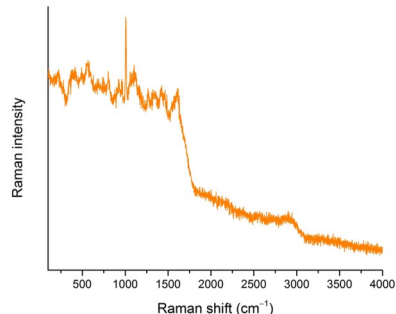
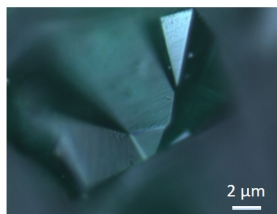


Figure S30 (cont). Confocal microscopic images (*left*), Raman spectra (*middle*), and peak assignments (*right*) for MOPs (a, c, e), MOFs (g, i), and pm-MOPs (b, d, f, h, j). No peak assignment for pm-MOPs are provided due to the absence of characteristic peaks.

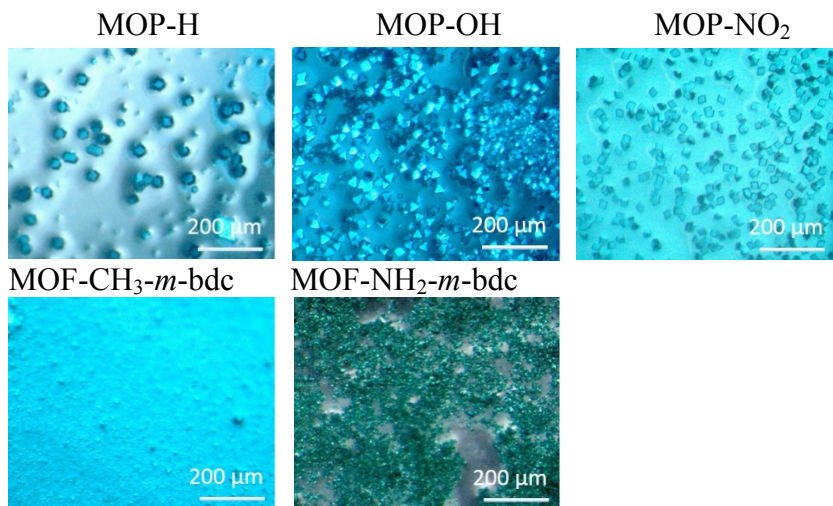


Figure S31. Optical images of reaction products on glass using PEG-4000 as a modulator to produce thin films. PEG-4000 was unable to induce thin film formation in these materials.

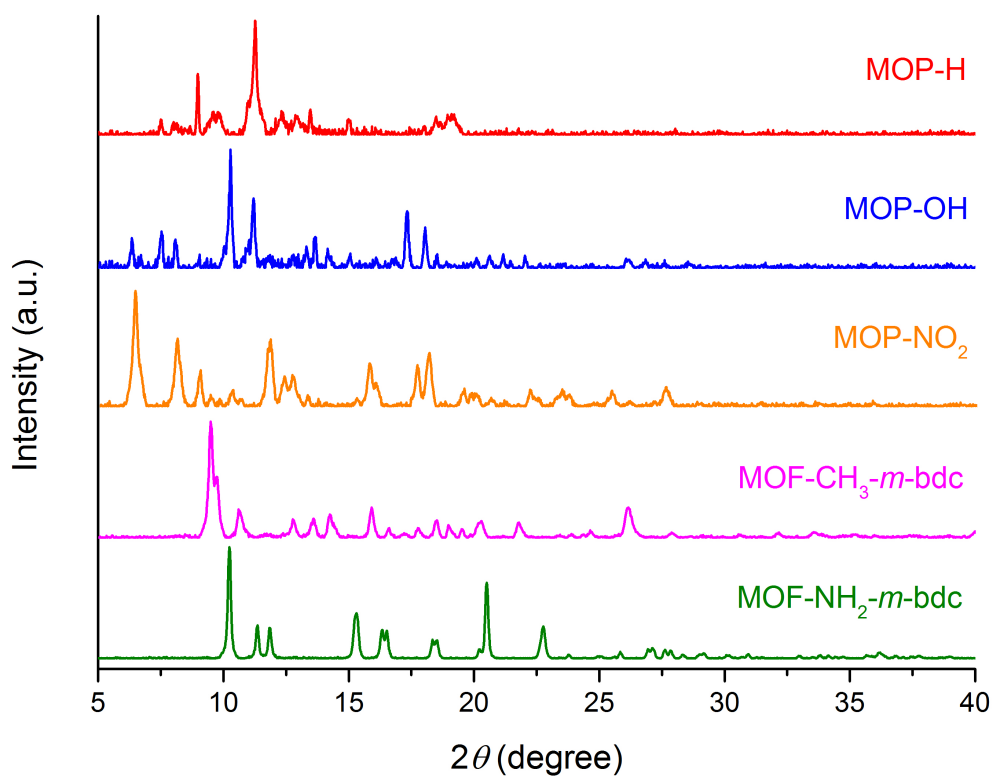


Figure S32. PXRD patterns of products using PEG-4000 as a modulator.

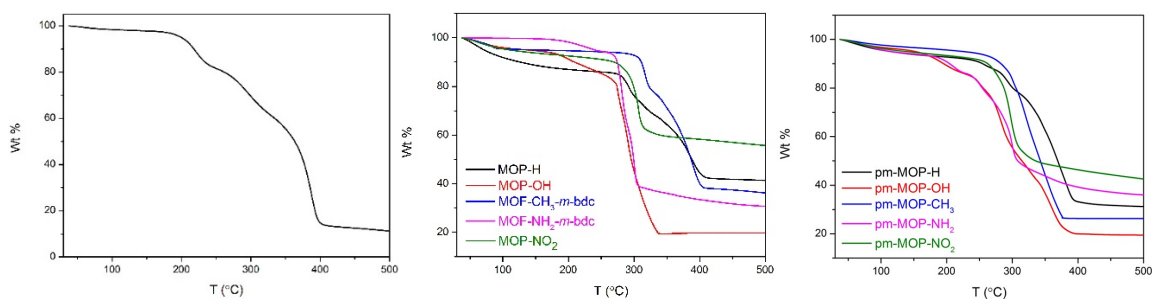


Figure S33. TGA traces for polymer **1** (*left*), activated MOPs and MOFs (*middle*), and pm-MOPs (*right*). The samples were analyzed under a stream of N₂ (80 mL/min) from 30 to 500 °C with a ramping rate of 5 °C/min.

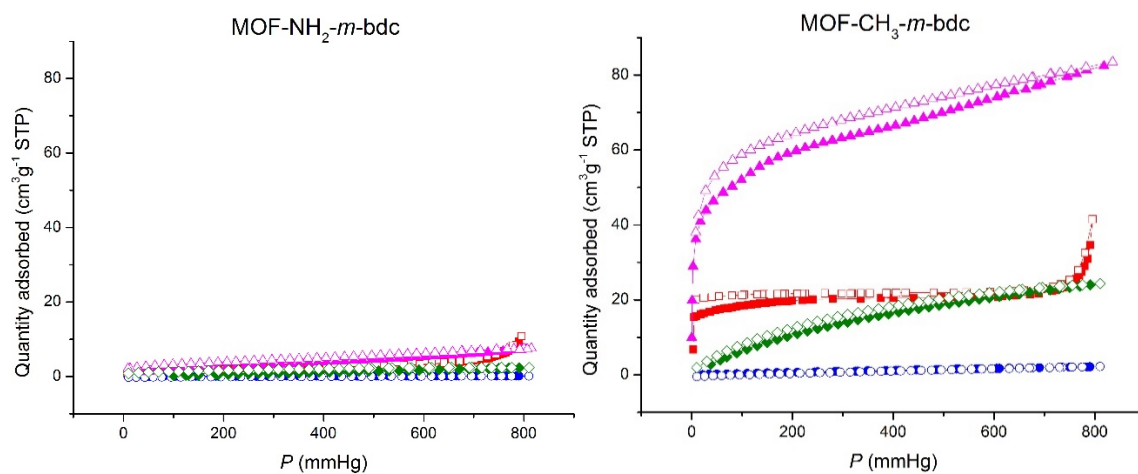


Figure S34. N₂ (77 K: red; 298 K: blue) and CO₂ (195 K: magenta, 298 K: green) sorption isotherms of activated MOF-NH₂-*m*-bdc and MOF-CH₃-*m*-bdc. Filled shape: adsorption; open shape: desorption.

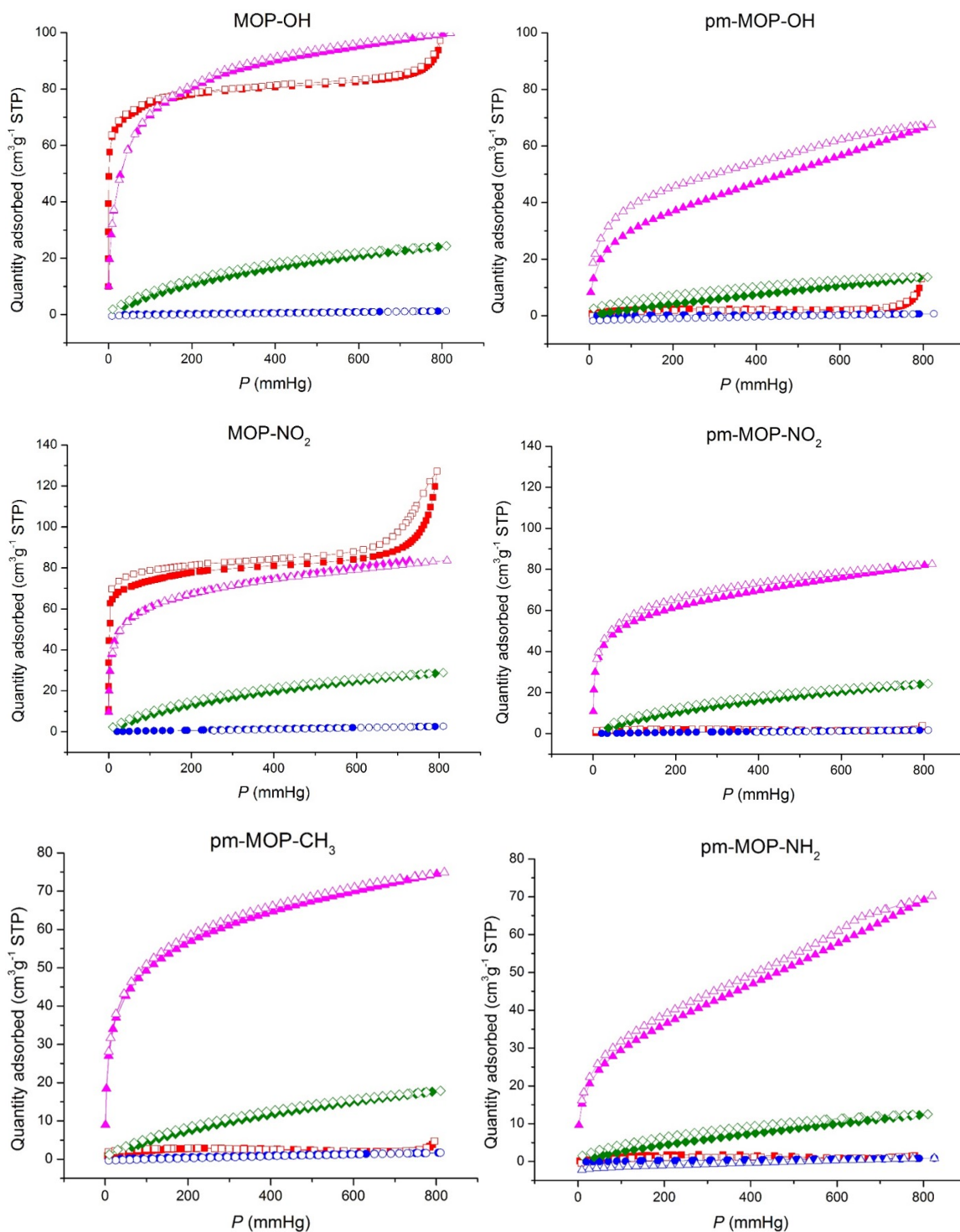


Figure S35. N₂ (77 K: red; 298 K: blue) and CO₂ (195 K: magenta, 298 K: green) sorption isotherms of activated MOP-OH, pm-MOP-OH, MOP-NO₂, pm-MOP-NO₂, pm-MOP-CH₃, and pm-MOP-NH₂. Filled symbols: adsorption; open symbols: desorption.

Table S1. Reactions to explore conditions for preparing uniform cubic MOP-H crystals. Reactions include Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10⁻² mmol) and 0.75 mL DMF/0.25 mL EtOH at 80 °C for 16 h. Products were characterized by PXRD and ¹H NMR.

H ₂ <i>m</i> -bdc	Polymers	Additives	Results
4.5 mg, 2.7×10 ⁻² mmol	Polymer 1 (4.8 mg, 1.4×10 ⁻² mmol)	—	Cubic crystals with no clear shape; <i>m</i> -bdc: 1 = 2:1
5.1 mg, 3.1×10 ⁻² mmol	Polymer 1 (3.6 mg, 1.0×10 ⁻² mmol)	—	Cubic crystals with non-uniform size; <i>m</i> -bdc: 1 = 8:1
6.5 mg, 3.9×10 ⁻² mmol	Polymer 1 (0.7 mg, 2.0×10 ⁻³ mmol)	—	A mixture of cubic and prismatic crystals; <i>m</i> -bdc: 1 = 25:1
4.5 mg, 2.7×10 ⁻² mmol	Polymer 1' (5.4 mg, 1.4×10 ⁻² mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
5.1 mg, 3.1×10 ⁻² mmol	Polymer 1' (3.9 mg, 1.0×10 ⁻² mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
5.8 mg, 3.5×10 ⁻² mmol	Polymer 1' (2.3 mg, 6.0×10 ⁻³ mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.5 mg, 3.9×10 ⁻² mmol	Polymer 1' (0.8 mg, 2.0×10 ⁻³ mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
4.5 mg, 2.7×10 ⁻² mmol	Polymer 2 (4.9 mg, 1.4×10 ⁻² mmol)	—	A mixture of cubic and prismatic crystals; <i>m</i> -bdc: 2 = 25:1
5.8 mg, 3.5×10 ⁻² mmol	Polymer 2 (2.0 mg, 6.0×10 ⁻³ mmol)	—	A mixture of cubic and prismatic crystals; <i>m</i> -bdc: 2 = 33:1
6.5 mg, 3.9×10 ⁻² mmol	Polymer 2 (0.7 mg, 2.0×10 ⁻³ mmol)	—	A mixture of cubic and prismatic crystals; <i>m</i> -bdc: 2 = 33:1
5.1 mg, 3.1×10 ⁻² mmol	—	Compound 3 (5.8 mg, 1.0×10 ⁻² mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
5.8 mg, 3.5×10 ⁻² mmol	—	Compound 3 (3.5 mg, 6.0×10 ⁻³ mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.5 mg, 3.9×10 ⁻² mmol	—	Compound 3 (1.2 mg, 2.0×10 ⁻³ mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.8 mg, 4.1×10 ⁻² mmol	—	Tetraethylene glycol (8.0 mg, 4.1×10 ⁻² mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.8 mg, 4.1×10 ⁻² mmol	—	Tetraethylene glycol (2.6 mg, 1.4×10 ⁻² mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.8 mg, 4.1×10 ⁻² mmol	—	Tetraethylene glycol (1.4 mg, 7.0×10 ⁻³ mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.8 mg, 4.1×10 ⁻² mmol	—	Tetraethylene glycol (0.4 mg, 2.0×10 ⁻³ mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.8 mg, 4.1×10 ⁻² mmol	PEG-400 ^a (8.0 mg, 2.0×10 ⁻² mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10 ⁻² mmol	PEG-400 (2.6 mg, 7.0×10 ⁻³ mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10 ⁻² mmol	PEG-400 (1.4 mg, 4.0×10 ⁻³ mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10 ⁻² mmol	PEG-400 (0.4 mg, 1.0×10 ⁻³ mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10 ⁻² mmol	PEG-4,000 ^b (8.0 mg, 2.0×10 ⁻³ mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated

6.8 mg, 4.1×10^{-2} mmol	PEG-4,000 (2.6 mg, 7.0×10^{-4} mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PEG-4,000 (1.4 mg, 4.0×10^{-4} mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PEG-4,000 (0.4 mg, 1.0×10^{-4} mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP ^c (0.5 mg, 1.3×10^{-5} mmol)	TMDP ^d (1.0 mg, 5.0×10^{-3} mmol)	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP (1.0 mg, 2.5×10^{-5} mmol)	TMDP (1.0 mg, 5.0×10^{-3} mmol)	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP (0.5 mg, 1.3×10^{-5} mmol)	TMDP (2.1 mg, 1.0×10^{-2} mmol)	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP (1.0 mg, 2.5×10^{-5} mmol)	TMDP (2.1 mg, 1.0×10^{-2} mmol)	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP (0.5 mg, 1.3×10^{-5} mmol)	N(CH ₃) ₄ NO ₃ (0.7 mg, 5.0×10^{-3} mmol)	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP (1.0 mg, 2.5×10^{-5} mmol)	N(CH ₃) ₄ NO ₃ (0.7 mg, 5.0×10^{-3} mmol)	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP (0.5 mg, 1.3×10^{-5} mmol)	N(CH ₃) ₄ NO ₃ (1.4 mg, 1.0×10^{-2} mmol)	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP (1.0 mg, 2.5×10^{-5} mmol)	N(CH ₃) ₄ NO ₃ (1.4 mg, 1.0×10^{-2} mmol)	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	—	TMDP (1.0 mg, 5.0×10^{-3} mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.8 mg, 4.1×10^{-2} mmol	—	TMDP (2.1 mg, 1.0×10^{-2} mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.8 mg, 4.1×10^{-2} mmol	—	TMDP (4.2 mg, 2.0×10^{-2} mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP (0.5 mg, 1.3×10^{-5} mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP (1.0 mg, 2.5×10^{-5} mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	PVP (2.0 mg, 5.0×10^{-5} mmol)	—	A mixture of cubic and prismatic crystals; no polymer incorporated
6.8 mg, 4.1×10^{-2} mmol	—	N(CH ₃) ₄ NO ₃ (0.7 mg, 5.0×10^{-3} mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.8 mg, 4.1×10^{-2} mmol	—	N(CH ₃) ₄ NO ₃ (1.4 mg, 1.0×10^{-2} mmol)	A mixture of cubic and prismatic crystals; no additive incorporated
6.8 mg, 4.1×10^{-2} mmol	—	N(CH ₃) ₄ NO ₃ (2.8 mg, 2.0×10^{-2} mmol)	A mixture of cubic and prismatic crystals; no additive incorporated

^a PEG-400 = polyethylene glycol, average molecular weight 400 Da; ^b PEG-4000 = polyethylene glycol, average molecular weight 4000 Da; ^c PVP = polyvinylpyrrolidone, average molecular weight 40,000 Da; ^d TMDP = 4,4'-trimethylenedipiperidine

Table S2. Reaction conditions with Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10⁻² mmol) for deposition of crystals on a glass surface. All products were characterized by PXRD.

	H₂<i>m</i>-bdc Derivatives	Polymer 1	Reaction Conditions	Results
MOP-H	H ₂ <i>m</i> -bdc 6.8 mg, 4.1×10 ⁻² mmol	—	DMF/EtOH 0.56 mL/0.19 mL 80°C, 16 h	No deposition
MOP-OH	5-OH-H ₂ <i>m</i> -bdc 7.5 mg, 4.1×10 ⁻² mmol	—	DEF/MeOH 0.56 mL/0.19 mL 80°C, 16 h	No deposition
MOP-NO ₂	5-NO ₂ -H ₂ <i>m</i> -bdc 8.7 mg, 4.1×10 ⁻² mmol	—	DMF/MeOH 0.30 mL/0.45 mL 60°C, 2 d	A layer of crystals
MOF-CH ₃ - <i>m</i> - bdc	5-CH ₃ -H ₂ <i>m</i> -bdc 7.4 mg, 4.1×10 ⁻² mmol	—	DMF/MeOH 0.30 mL/0.30 mL 60°C, 2 d	A layer of crystals
MOF-NH ₂ - <i>m</i> - bdc	5-NH ₂ -H ₂ <i>m</i> -bdc 7.4 mg, 4.1×10 ⁻² mmol	—	DMF/MeOH 0.56 mL/0.19 mL 60°C, 2 d	No deposition
pm-MOP-H	H ₂ <i>m</i> -bdc 5.8 mg, 3.5×10 ⁻² mmol	1.9 mg, 6.0×10 ⁻³ mmol	DMF/EtOH 0.56 mL/0.19 mL 80°C, 16 h	A layer of crystals
pm-MOP-OH	5-OH-H ₂ <i>m</i> -bdc 6.8 mg, 3.7×10 ⁻² mmol	1.2 mg, 3.7×10 ⁻³ mmol	DEF/MeOH 0.56 mL/0.19 mL 80°C, 16 h	A layer of crystals
pm-MOP-NO ₂	5-NO ₂ -H ₂ <i>m</i> -bdc 7.9 mg, 3.7×10 ⁻² mmol	1.2 mg, 3.7×10 ⁻³ mmol	DMF/MeOH 0.30 mL/0.45 mL 60°C, 2 d	A layer of crystals
pm-MOP-CH ₃	5-CH ₃ -H ₂ <i>m</i> -bdc 6.8 mg, 3.7×10 ⁻² mmol	1.2 mg, 3.7×10 ⁻³ mmol	DMF/MeOH 0.30 mL/0.30 mL 60°C, 2 d	A layer of crystals
pm-MOP-NH ₂	5-NH ₂ -H ₂ <i>m</i> -bdc 6.8 mg, 3.7×10 ⁻² mmol	1.2 mg, 3.7×10 ⁻³ mmol	DMF/MeOH 0.56 mL/0.19 mL 60°C, 2 d	A layer of crystals

Table S3. Control experiments with Cu(NO₃)₂·2.5H₂O (9.5 mg, 4.1×10⁻² mmol) and PEG-4000 for deposition of crystals on a glass surface. All products were characterized by PXRD.

H ₂ <i>m</i> -bdc Derivatives	PEG-4000	Reaction Conditions		Results
H ₂ <i>m</i> -bdc 5.8 mg, 3.5×10 ⁻² mmol	9.0 mg, 2.3×10 ⁻³ mmol 1.5 mg, 3.8×10 ⁻⁴ mmol 0.9 mg, 2.3×10 ⁻⁴ mmol	DMF/EtOH 0.56 mL/0.19 mL 80°C, 16 h		MOP-H No deposition
5-OH-H ₂ <i>m</i> -bdc 7.5 mg, 3.7×10 ⁻² mmol	9.0 mg, 2.3×10 ⁻³ mmol 1.5 mg, 3.8×10 ⁻⁴ mmol 0.9 mg, 2.3×10 ⁻⁴ mmol	DEF/MeOH 0.56 mL/0.19 mL 80°C, 16 h		MOP-OH No deposition
5-NO ₂ -H ₂ <i>m</i> -bdc 8.7 mg, 3.7×10 ⁻² mmol	9.0 mg, 2.3×10 ⁻³ mmol 1.5 mg, 3.8×10 ⁻⁴ mmol 0.9 mg, 2.3×10 ⁻⁴ mmol	DMF/MeOH 0.30 mL/0.45 mL 60°C, 2 d		MOP-NO ₂ A layer of crystals
5-CH ₃ -H ₂ <i>m</i> -bdc 7.4 mg, 3.7×10 ⁻² mmol	9.0 mg, 2.3×10 ⁻³ mmol 1.5 mg, 3.8×10 ⁻⁴ mmol 0.9 mg, 2.3×10 ⁻⁴ mmol	DMF/MeOH 0.30 mL/0.30 mL 60°C, 2 d		MOF-CH ₃ - <i>m</i> -bdc A layer of crystals
5-NH ₂ -H ₂ <i>m</i> -bdc 7.4 mg, 3.7×10 ⁻² mmol	9.0 mg, 2.3×10 ⁻³ mmol 1.5 mg, 3.8×10 ⁻⁴ mmol 0.9 mg, 2.3×10 ⁻⁴ mmol	DMF/MeOH 0.56 mL/0.19 mL 60°C, 2 d		MOF-NH ₂ - <i>m</i> -bdc No deposition

Table S4. Crystallographic Data for MOP-H.

Identification code	MOP-H
Empirical formula	C ₁₉₆ Cu ₂₄ O ₁₂₀
Formula weight	5799.16
Temperature/K	296.15
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	24.3070(19)
<i>b</i> /Å	24.5206(18)
<i>c</i> /Å	25.3072(18)
α /°	118.393(2)
β /°	111.787(2)
γ /°	93.769(2)
Volume/Å ³	11767.2(16)
<i>Z</i>	1
ρ_{calc} g/cm ³	0.8183
μ /mm ⁻¹	1.109
<i>F</i> (000)	2841.8
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	2.06 to 47.66
Index ranges	-27 \leq h \leq 27, -27 \leq k \leq 27, -28 \leq l \leq 19
Reflections collected	114820
Independent reflections	35288 [<i>R</i> _{int} = 0.0871, <i>R</i> _{sigma} = 0.1679]
Data/restraints/parameters	35288/72/1530
Goodness-of-fit on <i>F</i> ²	0.8030
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0603, w <i>R</i> ₂ = 0.1582
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1153, w <i>R</i> ₂ = 0.1721
Largest diff. peak/hole / e Å ⁻³	1.83/-0.99

Table S5. Crystallographic Data for MOP-OH.

Identification code	MOP-OH
Empirical formula	C ₁₉₂ Cu ₂₄ O ₁₄₄
Formula weight	6135.12
Temperature/K	296(2)
Crystal system	Tetragonal
Space group	<i>I4/m</i>
<i>a</i> /Å	27.401(11)
<i>b</i> /Å	27.401(11)
<i>c</i> /Å	35.409(14)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	26585(18)
<i>Z</i>	2
ρ_{calc} g/cm ³	0.7664
μ /mm ⁻¹	0.987
<i>F</i> (000)	6020.2
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	2.98 to 31.1
Index ranges	-15 ≤ <i>h</i> ≤ 20, -20 ≤ <i>k</i> ≤ 16, -26 ≤ <i>l</i> ≤ 20
Reflections collected	9448
Independent reflections	3090 [<i>R</i> _{int} = 0.0934, <i>R</i> _{sigma} = 0.1160]
Data/restraints/parameters	3097/234/411
Goodness-of-fit on <i>F</i> ²	0.9139
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0529, <i>wR</i> ₂ = 0.1339
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0808, <i>wR</i> ₂ = 0.1406
Largest diff. peak/hole / e Å ⁻³	0.44/-0.57

Table S6. Crystallographic Data for MOP-NO₂.

Identification code	MOP-NO ₂
Empirical formula	C ₁₉₂ Cu ₂₄ N ₂₄ O ₁₆₈
Formula weight	6855.36
Temperature/K	100(2)
Crystal system	Trigonal
Space group	<i>R</i> -3
<i>a</i> /Å	36.076(2)
<i>b</i> /Å	36.076(2)
<i>c</i> /Å	29.2307(19)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	32946(3)
<i>Z</i>	3
ρ_{calc} g/cm ³	1.0365
μ /mm ⁻¹	1.206
<i>F</i> (000)	10111.2
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	1.9 to 33.08
Index ranges	-28 ≤ <i>h</i> ≤ 28, -25 ≤ <i>k</i> ≤ 28, -23 ≤ <i>l</i> ≤ 23
Reflections collected	23188
Independent reflections	3936 [<i>R</i> _{int} = 0.0625, <i>R</i> _{sigma} = 0.0523]
Data/restraints/parameters	3936/360/606
Goodness-of-fit on <i>F</i> ²	1.022
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0797, <i>wR</i> ₂ = 0.2159
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0989, <i>wR</i> ₂ = 0.2353
Largest diff. peak/hole / e Å ⁻³	1.33/-0.67

Table S7. Crystallographic Data for pm-MOP-H.

Identification code	pm-MOP-H
Empirical formula	C ₁₉₂ H ₉₆ Cu ₂₄ O ₁₂₀
Formula weight	5847.89
Temperature/K	296.15
Crystal system	Cubic
Space group	<i>Im-3m</i>
<i>a</i> /Å	27.570(2)
<i>b</i> /Å	27.570(2)
<i>c</i> /Å	27.570(2)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	20957(3)
<i>Z</i>	2
ρ_{calc} g/cm ³	0.9267
μ /mm ⁻¹	1.245
<i>F</i> (000)	5827.7
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	2.08 to 46.56
Index ranges	-21 \leq h \leq 30, -29 \leq k \leq 30, -30 \leq l \leq 30
Reflections collected	33648
Independent reflections	1496 [<i>R</i> _{int} = 0.0955, <i>R</i> _{sigma} = 0.0355]
Data/restraints/parameters	1496/12/73
Goodness-of-fit on <i>F</i> ²	0.9908
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0618, w <i>R</i> ₂ = 0.1657
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0828, w <i>R</i> ₂ = 0.1773
Largest diff. peak/hole / e Å ⁻³	0.76/-2.10

Table S8. Crystallographic Data for pm-MOP-OH.

Identification code	pm-MOP-OH
Empirical formula	C ₂₀₀ Cu ₂₄ O ₁₄₅
Formula weight	6247.20
Temperature/K	100(2)
Crystal system	Tetragonal
Space group	<i>I4/m</i>
<i>a</i> /Å	27.571(4)
<i>b</i> /Å	27.571(4)
<i>c</i> /Å	35.456(5)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	26952(6)
<i>Z</i>	2
ρ_{calc} g/cm ³	0.7697
μ /mm ⁻¹	0.975
<i>F</i> (000)	6132.3
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	2.08 to 39.78
Index ranges	-19 \leq h \leq 25, -24 \leq k \leq 25, -26 \leq l \leq 33
Reflections collected	16595
Independent reflections	5033 [<i>R</i> _{int} = 0.0535, <i>R</i> _{sigma} = 0.0841]
Data/restraints/parameters	5033/234/422
Goodness-of-fit on <i>F</i> ²	0.9157
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0661, w <i>R</i> ₂ = 0.1831
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0911, w <i>R</i> ₂ = 0.1935
Largest diff. peak/hole / e Å ⁻³	0.61/-0.73

Table S9. Crystallographic Data for pm-MOP-NO₂.

Identification code	pm-MOP-NO ₂
Empirical formula	C ₂₉₇ Cu ₃₆ N ₃₆ O ₂₅₂
Formula weight	6565.56
Temperature/K	100(2)
Crystal system	Trigonal
Space group	<i>R</i> -3
<i>a</i> /Å	36.173(7)
<i>b</i> /Å	36.173(7)
<i>c</i> /Å	29.289(6)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	33190(11)
<i>Z</i>	2
ρ_{calc} g/cm ³	1.0397
μ /mm ⁻¹	1.198
<i>F</i> (000)	10188.0
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	2.26 to 40
Index ranges	-34 ≤ <i>h</i> ≤ 34, -34 ≤ <i>k</i> ≤ 34, -28 ≤ <i>l</i> ≤ 28
Reflections collected	13020
Independent reflections	6892 [<i>R</i> _{int} = 0.0633, <i>R</i> _{sigma} = 0.1531]
Data/restraints/parameters	6699/336/601
Goodness-of-fit on <i>F</i> ²	1.02
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0857, w <i>R</i> ₂ = 0.1988
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1442, w <i>R</i> ₂ = 0.2186
Largest diff. peak/hole / e Å ⁻³	1.23/-0.82

Table S10. Crystallographic Data for pm-MOP-CH₃.

Identification code	pm-MOP-CH ₃
Empirical formula	C ₃₆ Cu ₄ O ₂₀
Formula weight	1006.57
Temperature/K	100.0
Crystal system	Trigonal
Space group	<i>R</i> -3
<i>a</i> /Å	35.660(3)
<i>b</i> /Å	35.660(3)
<i>c</i> /Å	30.219(3)
α /°	90
β /°	90
γ /°	120
Volume/Å ³	33279(5)
<i>Z</i>	18
ρ_{calc} g/cm ³	0.9040
μ /mm ⁻¹	1.178
<i>F</i> (000)	8885.7
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	1.88 to 30.04
Index ranges	-25 \leq <i>h</i> \leq 12, 0 \leq <i>k</i> \leq 26, 0 \leq <i>l</i> \leq 21
Reflections collected	2974
Independent reflections	2974 [<i>R</i> _{int} = 0.0000, <i>R</i> _{sigma} = 0.0485]
Data/restraints/parameters	2974/330/540
Goodness-of-fit on <i>F</i> ²	1.026
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0713, <i>wR</i> ₂ = 0.1872
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0921, <i>wR</i> ₂ = 0.2031
Largest diff. peak/hole / e Å ⁻³	0.89/-0.42

Table S11. Crystallographic Data for pm-MOP-NH₂.

Identification code	pm-MOP-NH ₂
Empirical formula	C ₁₉₂ Cu ₂₈ N ₂₄ O ₁₃₂
Formula weight	6533.56
Temperature/K	100(2)
Crystal system	Tetragonal
Space group	<i>I4/mmm</i>
<i>a</i> /Å	26.217(2)
<i>b</i> /Å	26.217(2)
<i>c</i> /Å	44.813(5)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	30801(5)
<i>Z</i>	2
ρ_{calc} g/cm ³	0.7044
μ /mm ⁻¹	0.987
<i>F</i> (000)	6398.7
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	2.86 to 41.66
Index ranges	-26 ≤ <i>h</i> ≤ 13, -25 ≤ <i>k</i> ≤ 24, -44 ≤ <i>l</i> ≤ 26
Reflections collected	33610
Independent reflections	4507 [<i>R</i> _{int} = 0.0630, <i>R</i> _{sigma} = 0.0501]
Data/restraints/parameters	4507/69/235
Goodness-of-fit on <i>F</i> ²	0.979
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0967, <i>wR</i> ₂ = 0.2659
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.1303, <i>wR</i> ₂ = 0.2954
Largest diff. peak/hole / e Å ⁻³	1.69/-0.58

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