Support Information for

Strain-promoted 'click' Modification of a Mesoporous Metal-Organic Framework

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Contents:

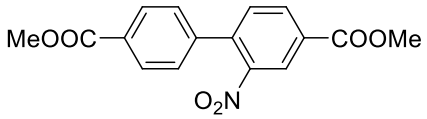
1. General procedures

All purchased chemicals were used without further purification. The elemental analyses (EA) were performed by the University of Illinois, Department of Chemistry Microanalysis Laboratory using an Exeter Analytical CE440. X-ray powder diffraction patterns were collected using a Bruker AXS D8 Discover powder diffractometer at 40 kV, 40 mA for Cu Kα, (λ = 1.5406 Å) with a scan speed of 0.20 sec/step from 2.5 to 20 º at a step size of 0.02 º. ^{1}H-NMR and ^{13}C-NMR spectra were obtained using a Bruker Avance III 400 MHz and 500 MHz spectrometers. Chemical shifts are in parts per million using the residual solvent peak (Chloroform-*d* and DMSO-d_6) as the reference value. Liquid chromatography-mass spectrometry (LCMS) analyses were performed on a Shimadzu LCMS-2020. Two LC methods were employed both using water and acetonitrile eluents. In the first method, the flow rate was held steady at 0.2 mL/min and acetonitrile was increased steadily from 10 % to 90 % over 0-9 min and then reduced to 10% acetonitrile for the final minute. In the second method, the flow rate was held steady at 0.2 mL/min and the acetonitrile:water ratio was held constant at 1:1 for the entire 6 min running time. The ionization interface was simultaneous ESI & APCI. FT-IR experiments were performed on Bruker Vertex-70LS FTIR spectrometer. About 2 mg of MOF sample was ground and mixed with ~250 mg KBr to make the sample pellets; the background pellet contained only 250 mg KBr. All spectra were collected using the Opus software interface from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1}; 16 scans were collected for both background and sample. Optical microscopic images of crystals were collected using an Olympus BH-2 microscope. Thermogravimetric analyses (TGA) were performed using a TGA Q500 thermal analysis system. All TGA experiments were performed under a N_2 atmosphere from about 20 °C to 600 °C at a rate of 5 °C /min. Data were analyzed using the TA Universal Analysis software package.

2. Synthesis of 2-azido-4,4'-biphenyl dicarboxylic acid

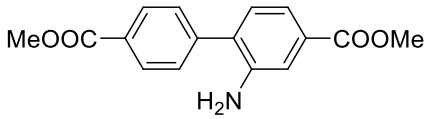
(note: the preparation of this compound follows reported procedures[2-5])

(1) Synthesis of dimethyl 2-nitro-4,4'-biphenyl dicarboxylate



Dimethyl 4,4'-biphenyl dicarboxylate (2.00 g ; 7.40 mmol) was dissolved in concentrated H_2SO_4 (15 mL) and cooled to below 5 °C in an ice-water bath. A mixture of 69 % HNO_3 (482 μL ; 7.40 mmol) and concentrated H_2SO_4 (3 mL) was added to the above solution, while maintaining the temperature of the reaction mixture between 2 °C and 5 °C. The reaction was allowed to proceed for 20 minutes below 5 °C. The resulting solution was poured onto ice (~ 300 mL), extracted with EtOAc (3X), washed with water until pH=7, dried over anhydrous $MgSO_4$, filtered, and concentrated to dryness to afford a white solid. Yield 1.98 g (85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 1.6 Hz, 1H), 8.29 (dd, J = 8.0, 1.7 Hz, 1H), 8.12 (m, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.40 (m, 2H), 4.00 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.68, 164.94, 149.17, 141.29, 139.72, 133.36, 132.34, 131.25, 130.72, 130.29 (2C), 128.11 (2C), 125.74, 53.12, 52.58.

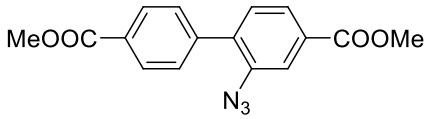
(2) Synthesis of dimethyl 2-amino-4,4'-biphenyl dicarboxylate



To a solution of dimethyl 2-nitro-4,4'-biphenyl dicarboxylate (2.00 g ; 6.35 mmol) in MeOH (80 mL) was first added Sn powder (4.40 g ; 36.67 mmol) with vigorous stirring and then 1M HCl (120 mL). The mixture was heated to reflux for 5 hours before it was cooled down to room temperature and poured onto ice. 1M NaOH was then added to adjust the pH to ~10. The mixture was then filtered through a Büchner funnel and the collected dried residue was re-dispersed in hot EtOAc, then filtered through Celite in a Büchner funnel. The clear filtrate was then concentrated *in vacuo* to afford a white solid. Yield 1.16 g (64 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (m, 2H), 7.55 (m, 2H), 7.48 (dd, J = 7.9, 1.6 Hz, 1H), 7.45 (d, J = 1.6 Hz, 1H), 7.18 (d, J = 7.9 Hz, 1H), 4.15 (s, 2H), 3.95 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (100

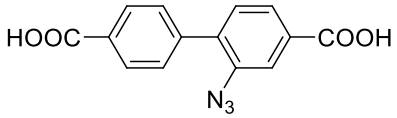
MHz, $CDCl_3$) δ 167.25, 166.98, 143.70, 143.58, 130.95, 130.74, 130.59, 130.46 (2C), 129.67, 129.11 (2C), 119.98, 116.92, 52.49, 52.39.

(3) Synthesis of dimethyl 2-azido-4,4'-biphenyl dicarboxylate



A mixture of dimethyl 2-amino-4,4'-biphenyl dicarboxylate (963 mg ; 3.38 mmol) in concentrated HCl (40 mL) and H_2O (30 mL) was kept stirring at room temperature for 2 hours before cooling to ~0°C. Then a solution of $NaNO_2$ (242 mg ; 3.50 mmol) in H_2O (5 mL) was added dropwise until the reaction mixture turned yellow and clear, indicating the formation of the diazonium salt. Subsequently, a solution of NaN_3 (227 mg ; 3.50 mmol) in H_2O (5 mL) was added dropwise to afford a white precipitate. The mixture was kept at ~0 °C for an additional 2 hours and at room temperature overnight before filtration. The residue was washed with H_2O and dried to afford an off-white solid. Yield 1.01 g (96 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (m, 2H), 7.92 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.52 (m, 2H), 7.40 (d, J = 8.0 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.74, 165.93, 141.74, 137.80, 136.73, 131.21, 131.16, 129.70, 129.47 (2C), 129.43 (2C), 126.03, 119.92, 52.51, 52.24.

(4) Synthesis of 2-azido-4,4'-biphenyl dicarboxylic acid



Dimethyl 2-azido-4,4'-biphenyl dicarboxylate (940 mg ; 3.02 mmol) was dissolved in THF (20 mL) then a solution of $LiOH{\cdot}H_2O$ (380 mg ; 9.06 mmol) in H_2O (10 mL) was added. The progress of the hydrolysis was monitored by either TLC or LC-MS. Upon completion, all volatiles were removed *in vacuo* and the remains were acidified with 1M HCl. The mixture was then filtered through a Büchner funnel and the residue was washed with H_2O before drying *in vacuo* to afford an off-white solid. Yield 819 mg (96 %). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.23 (s, 2H), 8.02 (m, 2H), 7.84 (s, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.64 (m,

2H), 7.56 (d, J = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.01, 166.27, 141.10, 137.15, 135.70, 131.88, 131.37, 130.22, 129.57 (2C), 129.18 (2C), 125.93, 119.86.

3. Synthesis of N_3-bio-MOF-100 and characterization

Stock solutions of the starting materials were prepared: 0.05 M Zinc acetate dihydrate in DMF (A); 0.05 M adenine in DMF (B); and 0.1 M 2-azido-4,4'-biphenyl dicarboxylic acid in DMF (C). In a glass tube, A (0.3 mL), B (0.1 mL), and C (0.1 mL) were mixed together and H_2O (0.05 mL) was added. The tube and its contents were in liquid N_2 and evacuated *in vacuo*. The tube was then sealed using a flame torch and kept in an 85 °C oven for 10-14 hours to yield polyhedral crystals. Thereafter, the tube was opened and the crystals were transferred to a microcentrifuge tube and washed with DMF (5X) and then DCM (10X).

The crystals were allowed to dry under Ar flow to yield approximately 2 mg (67%). CHN elemental analysis was performed, $C_{118.25}Cl_{12.5}H_{118.5}N_{42}O_{26}Zn_8$ = $Zn_8(adenine)_4(N_3\text{-}BPDC)_6O_2 \cdot 2Me_2NH_2$, $6.25CH_2Cl_2$. Calcd. *C*, 40.34; *H*, 2.56; *N*, 16.47. Found *C*, 40.44; *H*, 2.23; *N*, 16.04. TGA was performed. After extensive evacuation *in vacuo*, ^{1}H NMR and LC-MS were performed after acid digestion using a small amount of concentrated DCl/D_2O in DMSO-d_6 and FT-IR was performed using KBr pellet that contains dried MOF. X-ray powder diffraction and optical microscope experiments were performed when these crystals were re-dispersed in DMF. The ^{1}H-NMR spectrum (Figure **S1**) for the digested crystals confirms the presence of N_3-BPDC and the expected composition of the material. The ratio of hydrogens on adenine to the ones on N_3-BPDC is as expected based on the formula. As observed in the ^{1}H NMR (Figure S1) and in the LCMS trace Figure 2D, a small amount of impurity is present in the 2-azido-4,4'-biphenyl dicarboxylic acid sample and it also appears in the product MOF. Although we were not able to identify the impurity, we emphasize that its presence does not significantly affect the N_3-BPDC : adenine ratio in the MOF (the calculated and observed ratios are 1.5 and 1.47, respectively).

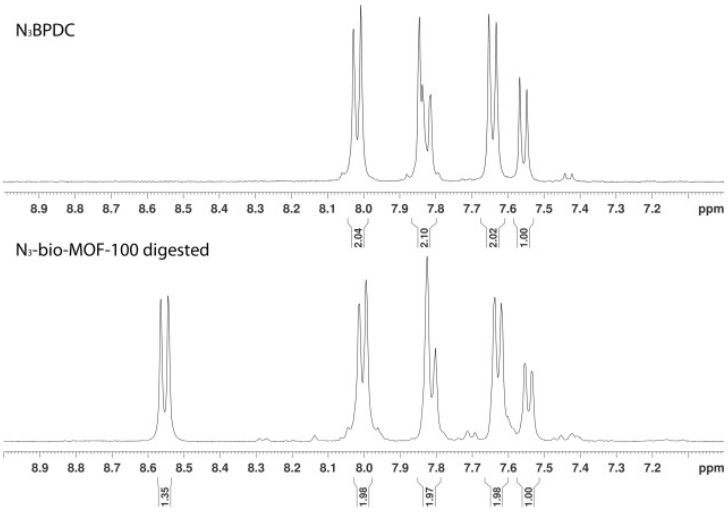


Figure S1. ^{1}H-NMR comparison between N_3BPDC and digested **N_3-bio-MOF-100**.

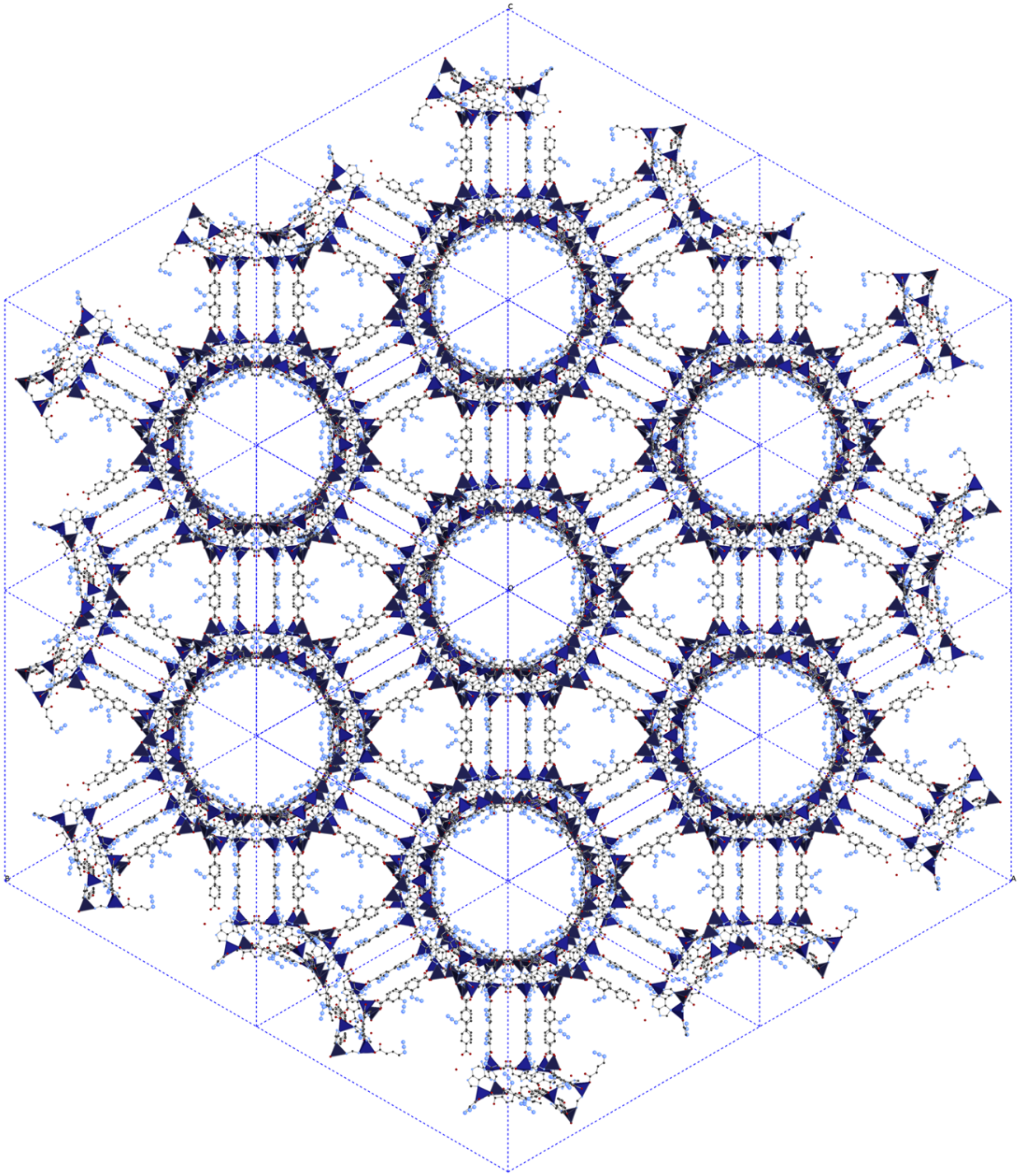


Figure S2. Structure of **N_3-bio-MOF-100**. This structure was generated from the single crystal X-ray diffraction data of **bio-MOF-100**. The purpose of this image is to show the azide-decorated channels (Zn^{2+}, dark blue tetrahedra; O, dark red spheres; N, light blue spheres; C, dark grey spheres; H atoms omitted for clarity).

4. Synthesis of DIBAC derivatives[6,7]

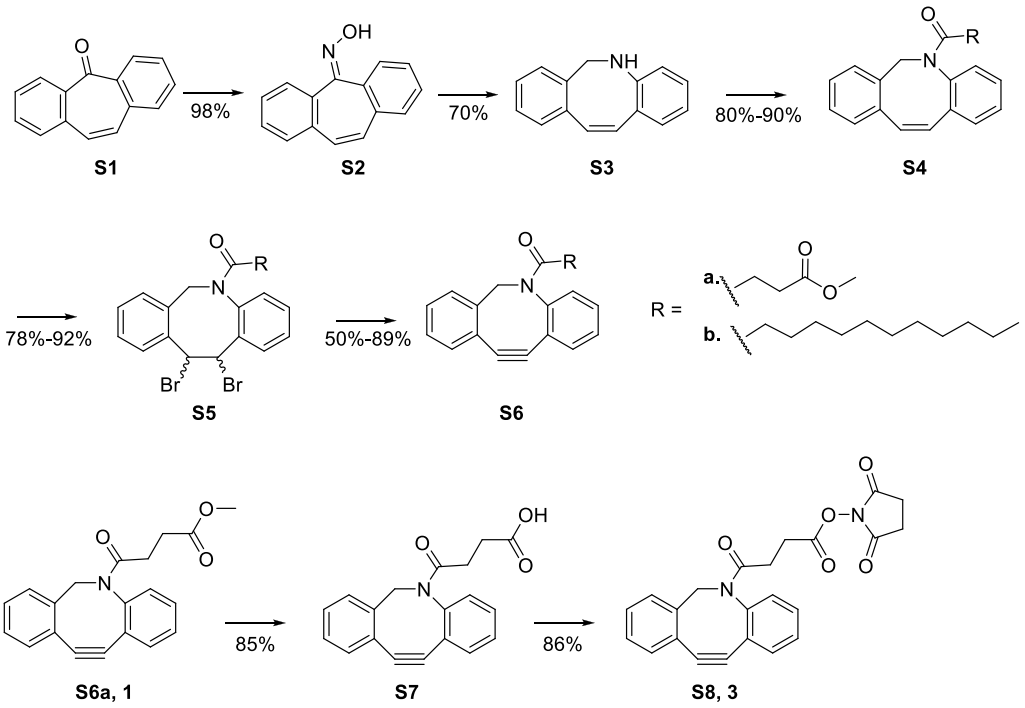
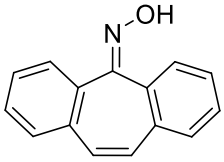


Figure S3. Synthesis route for compounds **1**, **2**, and **3**.

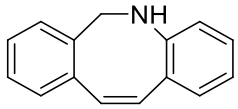
(1) 5*H*-dibenzo[7]annulen-5-one oxime (**S2**)



$NH_2OH{\cdot}HCl$ (1.04 g ; 14.97 mmol) was dissolved in a hot mixture of absolute EtOH (7 mL) and pyridine (5 mL). To this solution was added dibenzosuberenone (**S1**) (1 g ; 4.85 mmol) and pyridine (2 mL). The mixture was kept at reflux and monitored by TLC. When a complete disappearance of dibenzosuberenone was observed, all volatiles were removed *in vacuo*. The remains were re-dispersed between DCM and H_2O. The DCM phase was washed with another portion of H_2O, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to afford a pinkish white solid. Yield 1.12 g (98 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.67 – 7.66 (m, 1H), 7.62 – 7.55 (m, 1H), 7.49 – 7.32 (m, 6H), 6.98 – 6.84 (m,

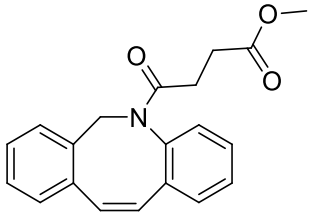
2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.62, 135.50, 134.62, 133.84, 130.87, 130.72, 130.56, 129.55, 129.23, 129.14, 129.04, 129.03, 128.92, 127.87, 127.74.

(2) 5,6-Dihydrodibenzo[*b*,*f*]azocine (**S3**)



To a cool (< 5°C) solution of oxime **S2** (2.26 mmol ; 500 mg) in dry DCM (28 mL) under Ar was added DIBAL-H (16.5 mL of a 1M solution in hexanes) via syringe while maintaining the temperature around 5 °C. The reaction mixture was kept at 5 °C for an additional 10 min and room temperature for 3 hours. The reaction completion was confirmed by TLC. Then the mixture was cooled to 0 °C followed by addition of NaF solid (3.38 g ; 80.5 mmol) and H_2O (1.1 mL). The slurry was stirred at 0 °C for another 30 min before filtering through Celite in a Büchner funnel. The residue was thoroughly washed with EtOAc. The combined organic solution was concentrated *in vacuo* to yield a bright yellow-green solid. Yield 328 mg (70 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 1H), 7.21 – 7.14 (m, 3H), 6.97 (dd, J = 7.8, 1.5 Hz, 1H), 6.88 (ddd, J = 7.7, 7.2, 1.2 Hz, 1H), 6.60 (ddd, J = 7.7, 7.2, 1.2 Hz, 1H), 6.54 (d, J = 13.1 Hz, 1H), 6.47 (dd, J = 8.1, 1.2 Hz, 1H), 6.36 (d, J = 13.1 Hz, 1H), 4.58 (s, 2H), 4.35 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.31, 139.47, 138.39, 134.94, 132.99, 130.38, 129.11, 128.20, 127.89, 127.64, 127.60, 122.01, 118.19, 117.98, 49.81.

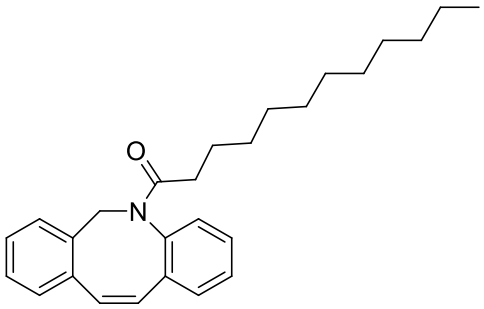
(3) Methyl 4-(dibenzo[*b*,*f*]azocin-5(6H)-yl)-4-oxobutanoate (**S4a**)



A solution of amine **S3** (200 mg ; 0.97 mmol) and triethylamine (267 µL ; 1.91 mmol) in DCM (6 mL) was cooled to 0 °C followed by careful addition of methyl succinyl chloride (178 µL, 1.44 mmol). The reaction mixture was kept at 0 °C for an additional 30 min. and then at room temperature overnight. Thereafter, it was quenched with H_2O and diluted with DCM. The organic phase was washed with saturated $NaHCO_3$ solution (2X), 1M HCl (2X), brine (2X) and dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Then it was purified

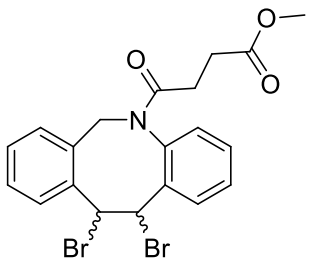
using column chromatography on 230-400 mesh silica (EtOAc:hexanes = 1:1) to yield a white solid. Yield 249 mg (80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 5H), 7.21 – 7.13 (m, 3H), 6.82 (d, J = 12.9 Hz, 1H), 6.65 (d, J = 12.9 Hz, 1H), 5.55 (d, J = 15.0 Hz, 1H), 4.29 (d, J = 15.0 Hz, 1H), 3.65 (s, 3H), 2.68 – 2.60 (m, 1H), 2.55 – 2.40 (m, 2H), 2.11 – 1.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.44, 170.87, 140.53, 136.50, 135.85, 134.60, 132.67, 131.83, 130.88, 130.18, 128.57, 128.28, 128.04, 127.31, 126.97, 54.50, 51.65, 29.57, 29.05.

(4) N-dodecanoyl 5,6-dihydrodibenzo[*b*,*f*]azocine (**S4b**)



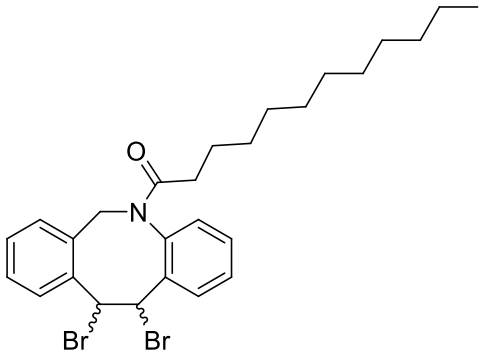
A solution of amine **S3 (**605 mg ; 2.92 mmol) in DCM (15 mL) was cooled to 0°C followed by careful addition of lauroyl chloride (810 µL, 3.50 mmol). Then triethylamine (610 µL ; 4.38 mmol) was added once solid precipitation was observed. Another 5 mL of DCM was added and the precipitation gradually disappeared. The reaction was allowed to stir at room temperature for 3 hours and TLC and LC-MS was used to monitor the reaction until complete conversion. The reaction was diluted with DCM and quenched by adding 1M NaOH solution and stirring for 20 min. The mixture was separated and the organic layer was washed with 1M NaOH solution (2X), 1M HCl (3X), brine (3X), dried over anhydrous $MgSO_4$, filtered, and then concentrated *in vacuo* before purification by column chromatography on 230-400 mesh silica (EtOAc:hexanes = 1:2) to afford a yellow oil. Yield 1024 mg (90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.19 (m, 4H), 7.19 – 7.07 (m, 4H), 6.75 (d, J = 13.2 Hz, 1H), 6.56 (d, J = 13.2 Hz, 1H), 5.45 (d, J = 14.8 Hz, 1H), 4.18 (d, J = 14.8 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.90 – 1.82 (m, 1H), 1.49 – 1.37 (m, 2H), 1.31 – 0.95 (m, 16H), 0.86 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.96, 141.40, 136.16, 135.86, 135.00, 132.47, 132.11, 131.38, 130.48, 128.26, 128.16, 127.69, 127.28, 127.27, 126.94, 54.61, 34.53, 31.89, 29.58, 29.55, 29.40, 29.31, 29.25, 29.01, 25.25, 22.67, 14.12.

(5) Methyl 4-(11,12-dibromo-11,12-dihydrodibenzo[*b*,*f*]azocin-5(6H)-yl)-4-oxobutanoate (**S5a**)



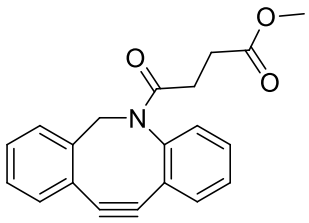
Amide **S4a** (317 mg ; 0.99 mmol) was dissolved in DCM (16 mL) and cooled to 0 °C followed by careful addition of a solution of Br_2 (0.16 g, 0.99 mmol) in 5 mL DCM under Ar, while maintaining the temperature around 0 °C. The reaction mixture was stirred at 0 °C for 2 hours and quenched with saturated Na_2SO_3 solution (stirring for 20 min). The mixture was separated and the organic layer was washed with saturated Na_2SO_3 solution (3X), H_2O (2X), brine (1X), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* before purification by column chromatography on 230-400 mesh silica (EtOAc:hexanes = 1:2 to 1:1.5) to yield a yellow-white solid (NMR showed that the product is actually a mixture of two stereoisomers with a ratio close to 9:1). Yield 370 mg (78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.8 Hz, 1H), 7.30 – 6.97 (m, 6H), 6.87 (d, J = 7.4 Hz, 1H), 5.90 (d, J = 9.9 Hz, 1H), 5.80 (d, J = 14.9 Hz, 1H), 5.14 (d, J = 10.0 Hz, 1H), 4.17 (d, J = 14.9 Hz, 1H), 3.67 (s, 3H), 2.90 – 2.80 (m, 1H), 2.67 – 2.54 (m, 2H), 2.51 – 2.42 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.58, 171.99, 138.32, 137.06, 136.94, 132.78, 130.81, 130.70, 130.65, 129.65, 129.49, 128.97, 128.90, 128.59, 60.10, 55.55, 52.56, 51.77, 30.65, 29.22.

(6) N-dodecanoyl 5,6,11,12-tetrahydro-11,12-dibromodibenzo[*b*,*f*]azocine (**S5b**)



Amide **S4b** (1.016 g ; 2.61 mmol) was dissolved in DCM (15 mL) and cooled to 0 °C followed by careful addition of a solution of Br_2 (0.418 g, 2.61 mmol) in 4 mL under Ar, while maintaining the temperature around 0 °C. The reaction mixture was stirred at 0 °C and monitored by LC-MS; additional Br_2 was added when necessary. After 12 hours, the reaction was quenched with saturated Na_2SO_3 solution (stirring for 20 min). The mixture was then separated and the organic layer was washed with saturated Na_2SO_3 solution (3X), H_2O (2X), brine (1X), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* before it was purified using column chromatography on 230-400 mesh silica (EtOAc:hexanes = 1:4) to yield a yellow oil (NMR showed that the product is a mixture of two stereoisomers, but one of them is of only trace amount). Yield 1.315 g (92 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.7 Hz, 1H), 7.23 – 7.08 (m, 3H), 7.07 – 6.98 (m, 2H), 6.95 (d, J = 7.7 Hz, 1H), 6.86 (d, J = 7.4 Hz, 1H), 5.92 (d, J = 9.9 Hz, 1H), 5.80 (d, J = 14.9 Hz, 1H), 5.13 (d, J = 9.9 Hz, 1H), 5.13 (d, J = 9.9 Hz, 1H), 4.14 (d, J = 14.9 Hz, 1H), 2.32 – 2.21 (m, 1H), 2.11 – 1.99 (m, 1H), 1.68 – 1.63 (m, 2H), 1.32 – 1.10 (m, 16H), 0.85 (t, J = 6.8 Hz, 3H)..^{13}C NMR (100 MHz, $CDCl_3$) δ 173.80, 138.20, 137.45, 137.11, 133.09, 130.67, 130.46, 130.37, 129.58, 129.30, 128.90, 128.79, 128.60, 60.04, 55.71, 52.43, 35.98, 31.89, 29.59, 29.44, 29.40, 29.32, 25.24, 22.68, 14.12.

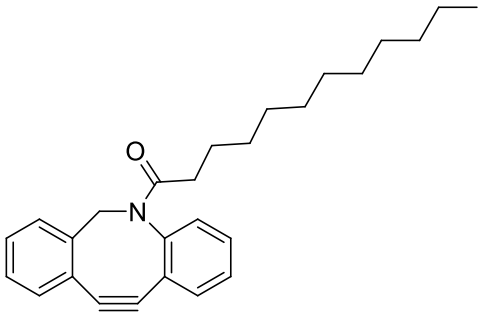
(7) Methyl 4-(11,12-didehydrodibenzo[*b*,*f*]azocin-5(6H)-yl)-4-oxobutanoate (**S6a, Compound 1**)



Compound **S5a** (101 mg ; 0.21 mmol) was dissolved in anhydrous THF (10 mL) under Ar and cooled to around -40 °C in a dry ice-acetonitrile bath followed by careful addition of a solution of tBuOK (0.4 mL ; 0.4 mmol ; 1 M in THF) via syringe. After 2 hours at -40 °C, another 0.16 mL of tBuOK (1M in THF) was added dropwise via syringe. After another hour, LC-MS showed complete conversion. The reaction mixture was then poured into brine (25 mL) and extracted with DCM (3X). The combined organic phase was washed with brine (2X), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* before purification by column

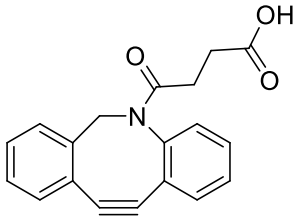
chromatography on 230-400 mesh silica (EtOAc:hexanes = 1:2) to yield a yellow-white solid. Yield 34 mg (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.5 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.42 – 7.20 (m, 6H), 5.15 (d, J = 13.9 Hz, 1H), 3.66 (d, J = 13.8 Hz, 1H), 3.54 (s, 3H), 2.71 (ddd, J = 16.4, 8.2, 6.2 Hz, 1H), 2.59 (ddd, J = 17.2, 8.2, 6.1 Hz, 1H), 2.32 (dt, J = 17.1, 6.2 Hz, 1H), 1.94 (dt, J = 16.3, 6.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.31, 171.67, 151.45, 148.00, 132.26, 129.28, 128.51, 128.29, 128.11, 127.72, 127.09, 125.46, 123.13, 122.67, 114.93, 107.68, 55.46, 51.62, 29.51, 29.06.

(8) N-dodecanoyl 5,6-dihydro-11,12-didehydrodibenzo[*b*,*f*]azocine (**S6b, Compound 2**)



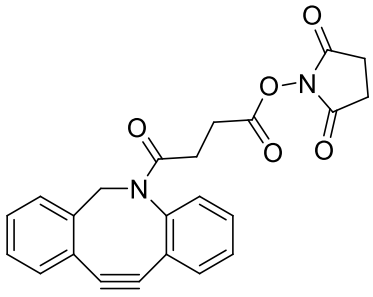
Compound **S5b** (500 mg ; 0.91 mmol) was dissolved in anhydrous THF (10 mL) under Ar and cooled to around -40 °C in a dry ice-acetonitrile bath followed by careful addition of a solution of tBuOK (1.82 mL ; 1.82 mmol ; 1 M in THF) via syringe. After 2 hours at -40 °C, another 0.6 mL of tBuOK (1M in THF) was added dropwise via syringe. After another hour, LC-MS showed complete reaction. The reaction mixture was then poured into brine (20 mL) and extracted with DCM (3X). The combined organic phase was washed with brine (2X), H_2O (1X), dried over anhydrous $MgSO_4$, and then concentrated *in vacuo* before purification by column chromatography on 230-400 mesh silica (EtOAc:hexanes = 1:4) to yield a yellow-green oil. Yield 314 mg (89 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 1H), 7.51 – 7.19 (m, 7H), 5.19 (d, J = 13.8 Hz, 1H), 3.67 (d, J = 13.7 Hz, 1H), 2.18 (dt, J = 14.8, 7.3 Hz, 1H), 1.96 (dt, J = 15.1, 7.5 Hz, 1H), 1.47 – 1.36 (m, 2H), 1.34 – 0.96 (m, 16H), 0.90 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.66, 152.13, 148.15, 132.38, 128.94, 128.26, 128.21, 127.82, 127.62, 127.02, 125.37, 123.15, 122.62, 115.15, 107.90, 55.20, 34.79, 31.91, 29.58, 29.51, 29.38, 29.31, 29.15, 28.83, 25.37, 22.68, 14.12.

(9) 4-(11,12-didehydrodibenzo[*b*,*f*]azocin-5(6H)-yl)-4-oxobutanoic acid (**S7**)



A solution of compound **S6a (**40 mg ; 0.12 mmol) in anhydrous THF (2.5 mL) was added to a solution of $LiOH{\cdot}H_2O$ (6.4 mg ; 0.15 mmol) in H_2O (0.5 mL). The reaction was allowed to proceed under stirring at room temperature and monitored by TLC. Upon complete conversion, it was diluted with H_2O and subsequently adjusted to pH~14 using 2M NaOH solution. The mixture was washed with DCM (2X), acidified to pH~2 using 2M HCl solution and then extracted using DCM (4X). The combined organic phase was dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to yield a yellow-white solid. Yield 33 mg (85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.4 Hz, 1H), 7.47 – 7.19 (m, 7H), 5.14 (d, J = 13.9 Hz, 1H), 3.68 (d, J = 13.8 Hz, 1H), 2.70 (ddd, J = 16.5, 8.9, 5.2 Hz, 1H), 2.58 (ddd, J = 16.9, 8.9, 5.1 Hz, 1H), 2.34 (ddd, J = 16.9, 6.4, 5.3 Hz, 1H), 1.96 (ddd, J = 16.5, 6.3, 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.21, 172.36, 151.00, 147.68, 132.26, 129.10, 128.57, 128.41, 128.34, 127.87, 127.21, 125.58, 123.00, 122.67, 115.04, 107.45, 55.67, 29.49, 29.46.

(10) 2,5-dioxopyrrolidin-1-yl 4-(didehydrodibenzo[*b*,*f*]azocin-5(6H)-yl)-4-oxobutanoate (**S8**, **Compound 3**)



To a solution of compound **S7** (12.6 mg ; 0.043 mmol) in DCM (2 mL) was added *N*-hydroxysuccinimide (5.4 mg ; 0.047 mmol) and a solution of EDC·HCl (9 mg ; 0.047 mmol) in 1 mL of DCM. The reaction was allowed to proceed under stirring at room temperature and monitored by TLC. Upon complete conversion, it was diluted with DCM, washed with saturated NaCl solution (3X), dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to

yield a yellow solid. The product was used without further purification. Yield 14.3 mg (86 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 1H), 7.43 – 7.24 (m, 7H), 5.16 (d, J = 13.9 Hz, 1H), 3.67 (d, J = 13.9 Hz, 1H), 2.95 (dt, J = 17.5, 7.6 Hz, 1H), 2.84 – 2.77 (m, 1H), 2.77 (s, 4H), 2.65 – 2.58 (m, 1H), 2.06 (ddd, J = 16.8, 7.8, 5.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.26, 168.84, 168.29, 151.01, 147.77, 132.27, 129.09, 128.62, 128.36, 127.83, 127.23, 125.54, 123.03, 122.73, 115.01, 107.53, 55.58, 29.18, 26.42, 25.51.

5. Strain-promoted click reactions for 1 & 2 and characterization

Adenine (5×10^{-6} mol) is the limiting reagent in a typical synthesis of **N_3-bio-MOF-100**. Assuming 100% conversion, there should be a total of 7.5×10^{-6} mol of N_3BPDC (7.5×10^{-6} mol azide groups) in the resulting product, based on the ratio of adenine:N_3BPDC (4:6). Since the product yield is approximately 67%, we should expect approximately 5×10^{-6} mol azide groups in the final product. Based on this, we used 5×10^{-6} mol, or one equivalent, of either **1** or **2** for our PSM reactions

In a typical strain-promoted click reaction, 5×10^{-6} mol of **1** or **2** (1.6 mg and 1.9 mg, respectively) was added to a microcentrifuge tube containing pre-washed MOF crystals in DCM (see Section 3 for details). After vortexing for a few seconds, the tube was allowed to sit overnight. Then, the supernatant was removed and the crystals were washed with DCM (10X) to remove any unreacted **1** or **2**. Solvent was slowly removed by Ar flow. CHN elemental analysis was performed: $C_{240}Cl_{16}H_{224}N_{48}O_{44}Zn_8$ = Zn_8(adenine)$_4$(N_3-BPDC + **1**)$_6O_2$ • $2Me_2NH_{22}$, $8CH_2Cl_2$. Calcd. *C*, 56.83; *H*, 4.94; *N*, 10.97. Found *C*, 57.08; *H*, 5.11; *N*, 11.02.

$C_{285}Cl_{22}H_{326}N_{48}O_{32}Zn_8$ = Zn_8(adenine)$_4$(N_3-BPDC + **2**)$_6O_2$ • $2Me_2NH_{22}$, $11CH_2Cl_2$. Calcd. *C*, 50.17; *H*, 3.49; *N*, 11.26. Found *C*, 50.24; *H*, 3.51; *N*, 11.27.

After evacuation *in vacuo*, LC-MS (negative mode) was performed after acid digestion using acetonitrile and a small amount of concentrated HCl. FT-IR was performed using KBr pellet that contains dried crystals. X-ray powder diffraction and optical microscope experiments were performed when these crystals were re-dispersed in DMF.

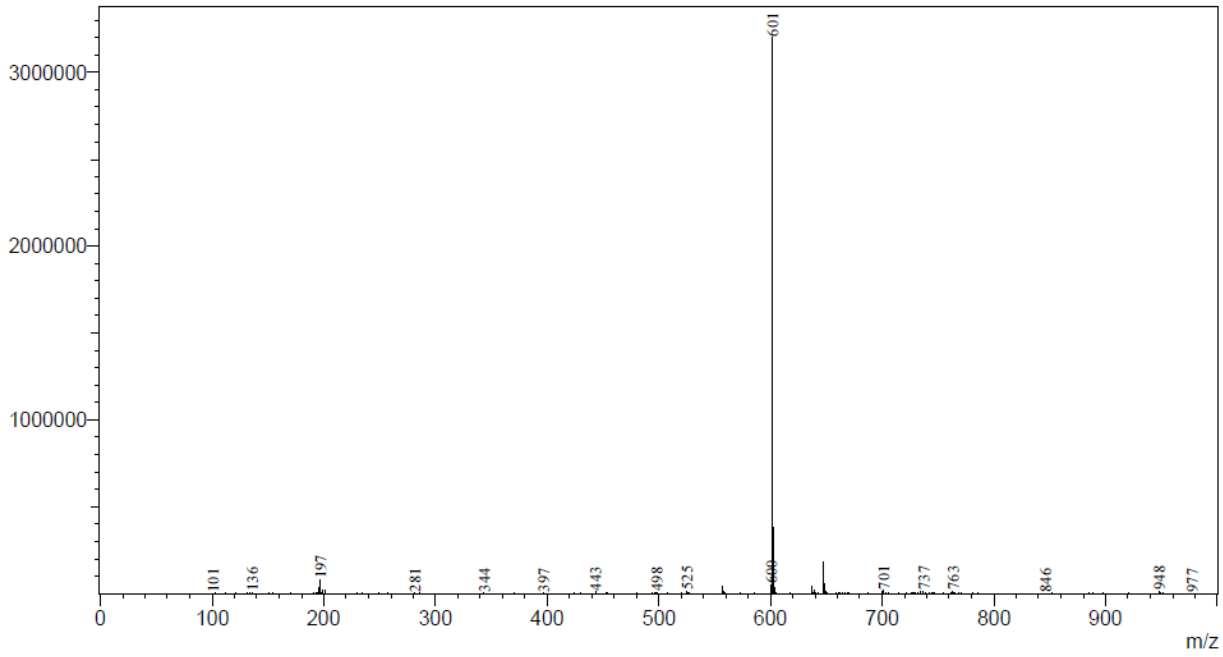


Figure S4. MS spectrum for **1-bio-MOF-100** digested in HCl/MeCN.

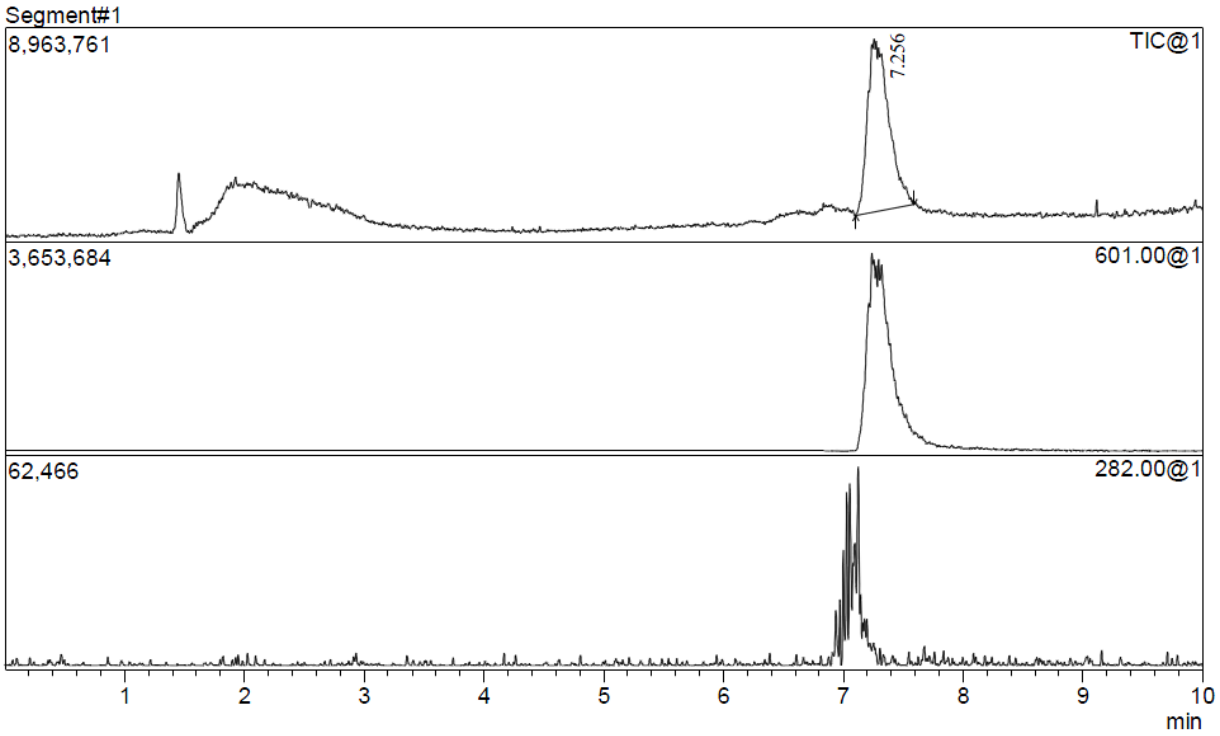


Figure S5. TIC chromatogram for **1-bio-MOF-100** digested in HCl/MeCN (top: all ions; middle: m/z=601; bottom: m/z=282).

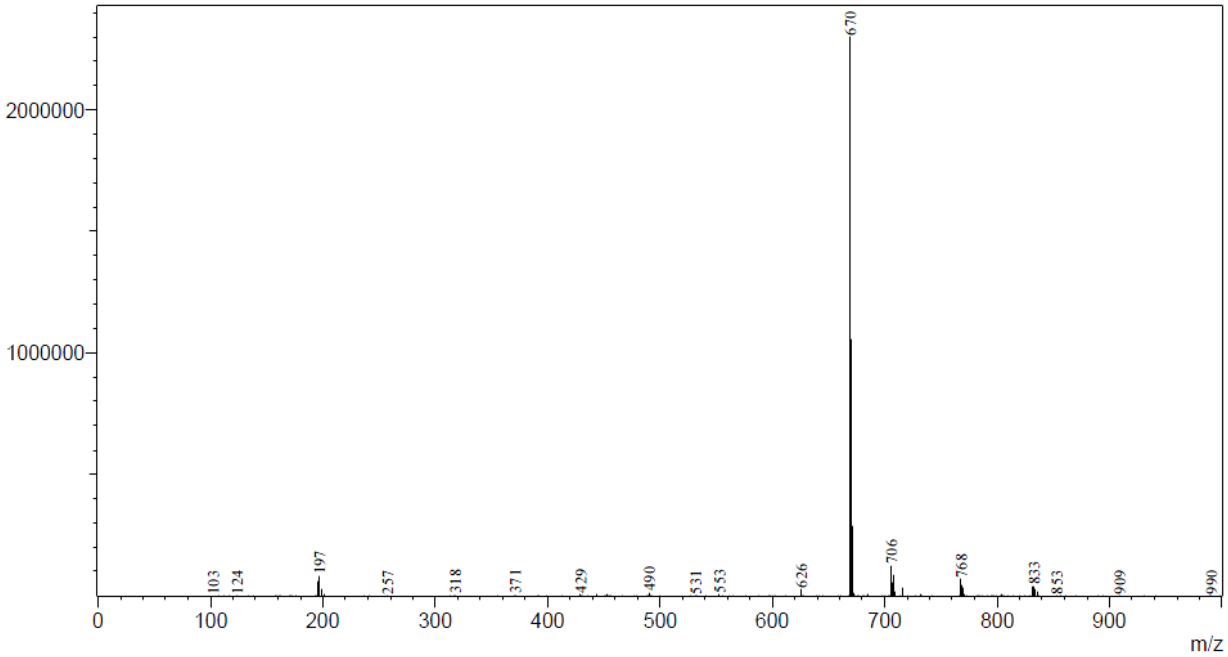


Figure S6. MS spectrum for **2-bio-MOF-100** digested in HCl/MeCN.

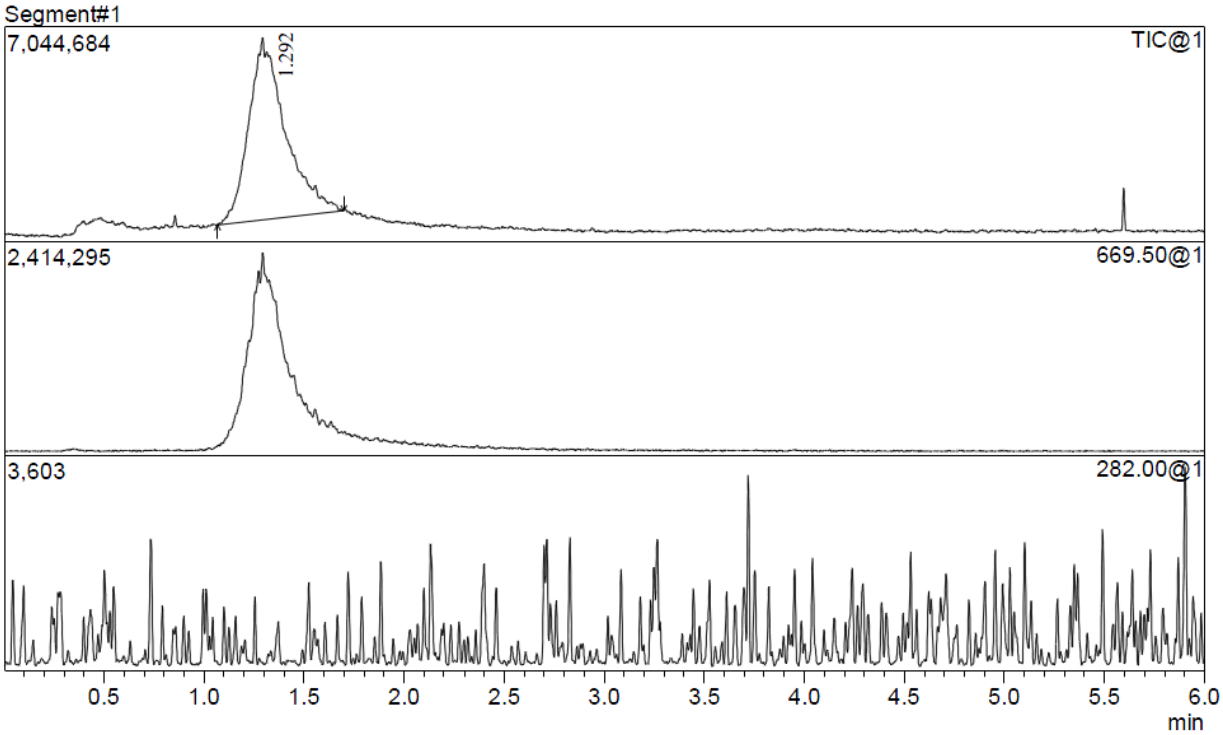


Figure S7. TIC chromatogram for **2-bio-MOF-100** digested in HCl/MeCN (top: all ions; middle: m/z=669.5; bottom: m/z=282).

6. Thermogravimetric (TGA) analysis

5-7 mg of samples of **bio-MOF-100**, **N_3-bio-MOF-100**, **1-bio-MOF-100**, and **2-bio-MOF-100** were dried with Ar before TGA analysis. Each sample was soaked in dichloromethane prior to analysis to fully remove and replace any included solvent with dichloromethane.

The data clearly shows that the MOFs remain porous after reactions with 1 and 2. As expected, after the PSM reaction, the amount of solvent within the pores decreases.

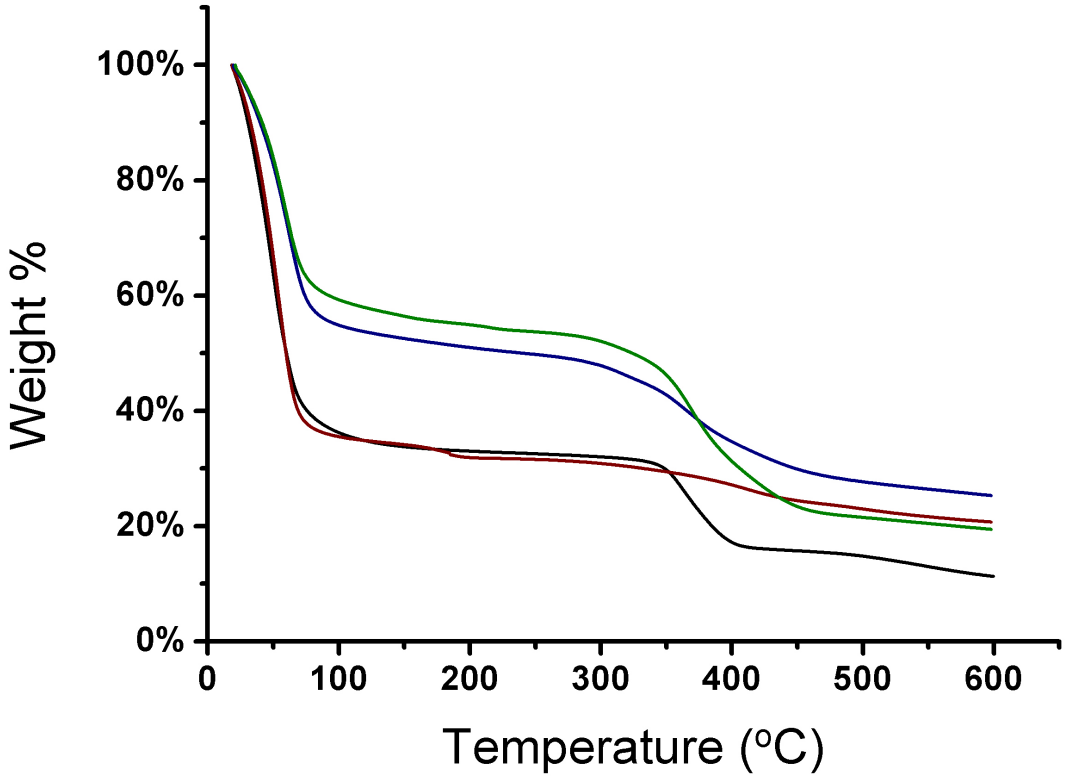


Figure S8. TGA for **bio-MOF-100** (black), **N_3-bio-MOF-100** (dark red), **1-bio-MOF-100** (navy), and **2-bio-MOF-100** (green)

7. Copper-catalyzed click reactions for 1-hexyne and characterization

In a copper-catalyzed click reaction, $2 \times (5\times10^{-6})$ mol (two equivalents to azide groups in MOF crystals) or $50 \times (5\times10^{-6})$ mol (fifty equivalents to azide groups in MOF crystals) of 1-hexyne was added to a microcentrifuge tube that contains pre-washed MOF crystals soaked in DCM (handled via same procedure described in section **3**). Then, a visible amount of CuI was added. After vortexing for a few seconds, the tube was allowed to sit for 48 hours. Thereafter, the supernatant was removed and the crystals were washed by DCM (10X) to get remove any unreacted 1-hexyne. After removal of solvent using Ar flow, LC-MS was performed after acid digestion using acetonitrile and a small amount of concentrated HCl. FT-IR was performed using a KBr pellet that contains ground dried crystals.

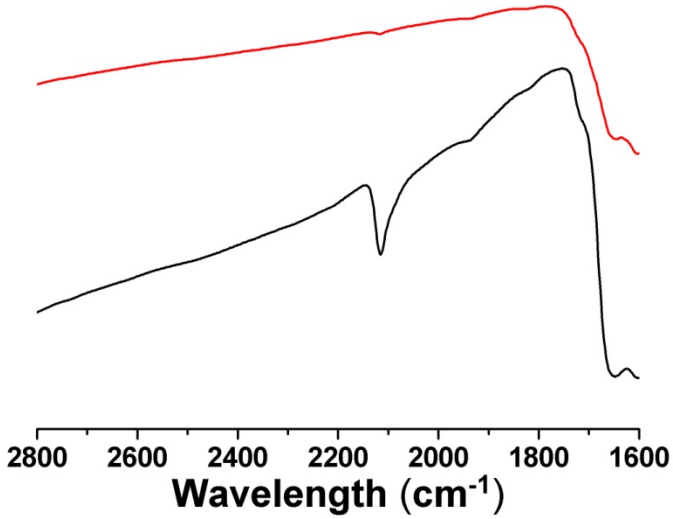
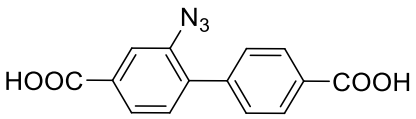
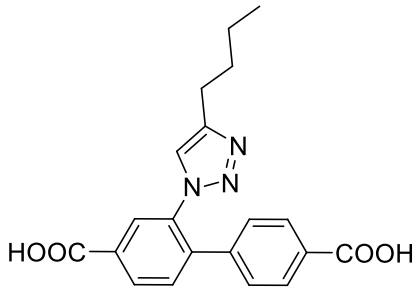


Figure S9. FT-IR spectra for **N_3-bio-MOF-100** + 2 equiv. or 50 equiv. of 1-hexyne (**N_3-bio-MOF-100** + 50 equiv. of 1-hexyne, red; **N_3-bio-MOF-100** + 2 equiv. 1-hexyne, black)

LC-MS TIC chromatogram and MS peak search results (negative mode):

m/z = 281.6 corresponds to the anion of: 

m/z = 363.7 and m/z= 729.6 correspond to $[M-H]^-$ and $[2M-H]^-$ of:



(1) CuI catalyzed, 2 equiv. of 1-hexyne used.

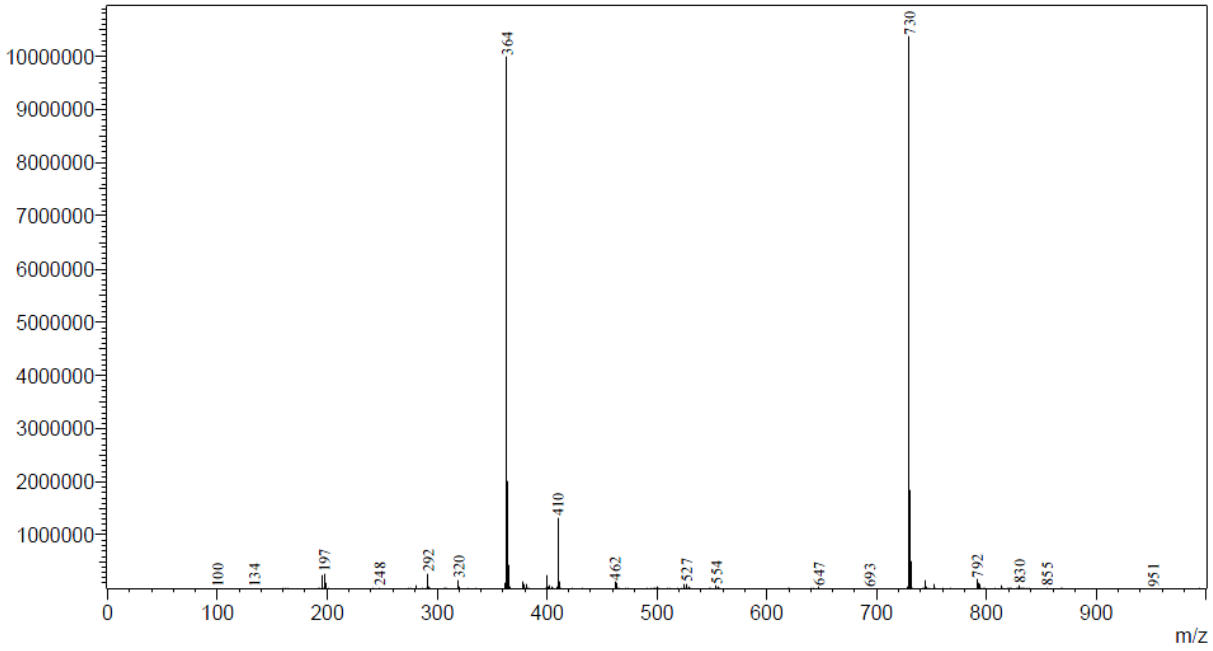


Figure S10. MS spectrum for **N_3-bio-MOF-100** + 2 equiv. of 1-hexyne digested in HCl/MeCN.

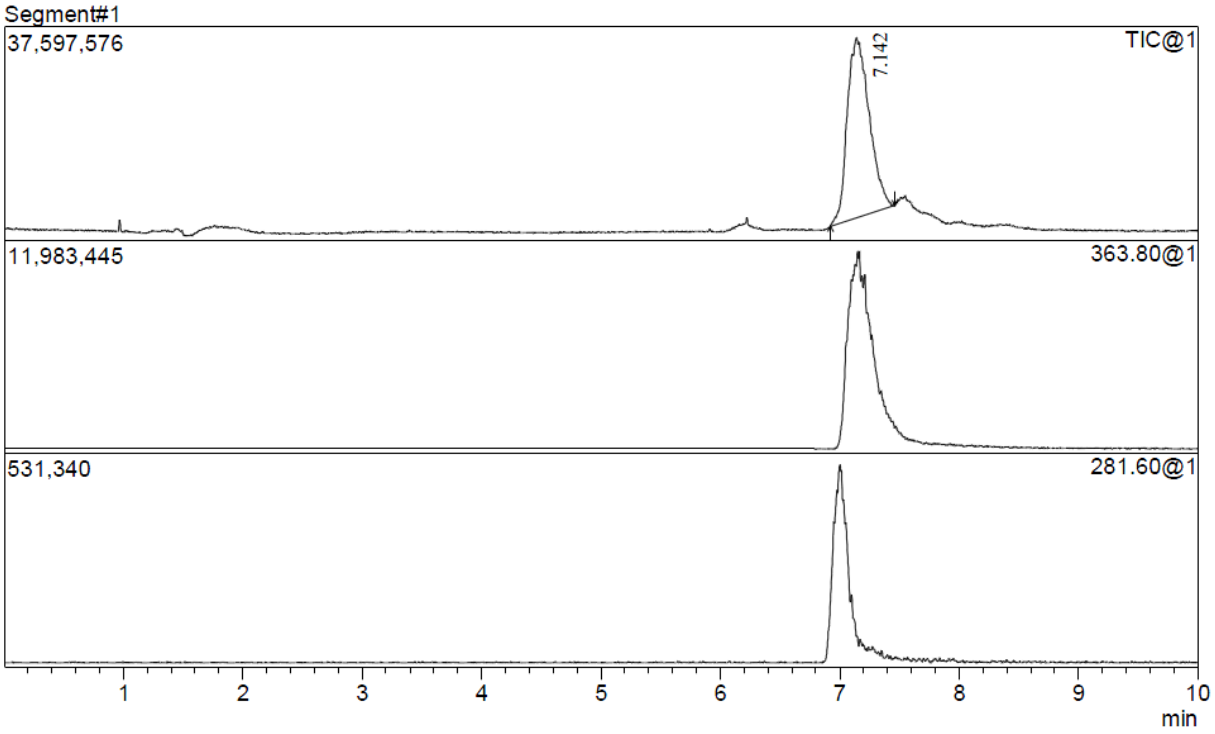


Figure S11. TIC chromatogram for **N_3-bio-MOF-100** + 2 equiv. of 1-hexyne digested in HCl/MeCN (top: all ions; middle: m/z=363.8; bottom: m/z=281.6).

(2) CuI catalyzed, 50 equiv. of 1-hexyne used.

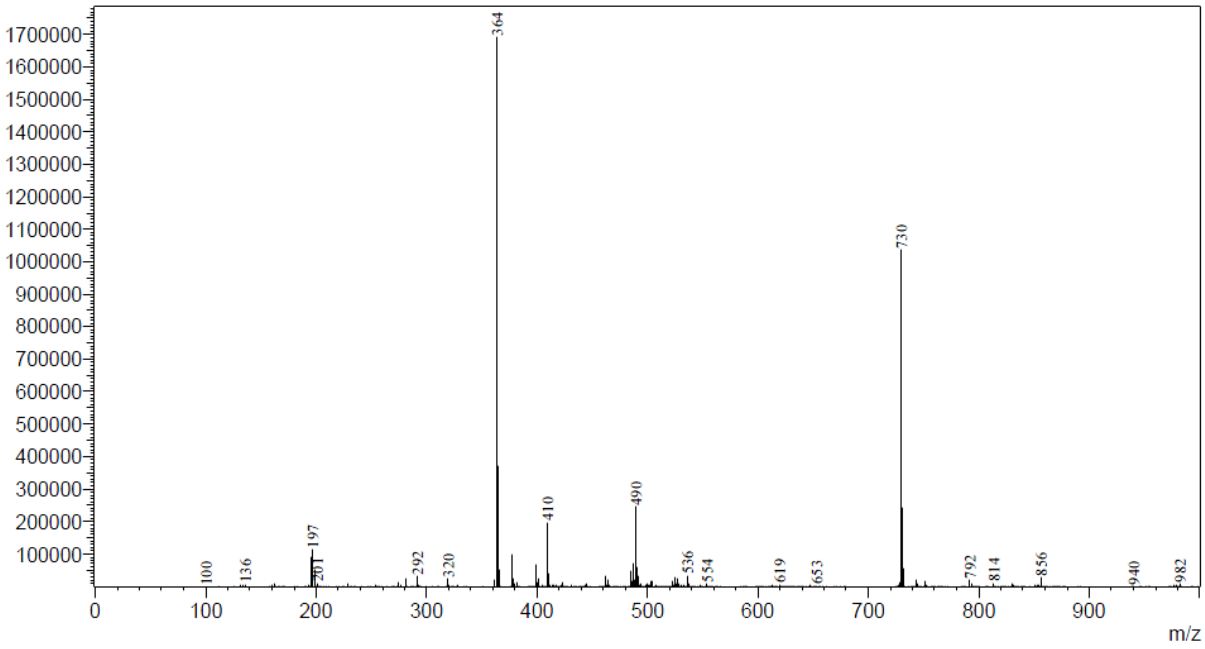


Figure S12. MS spectrum for **N_3-bio-MOF-100** + 50 equiv. of 1-hexyne digested in HCl/MeCN.

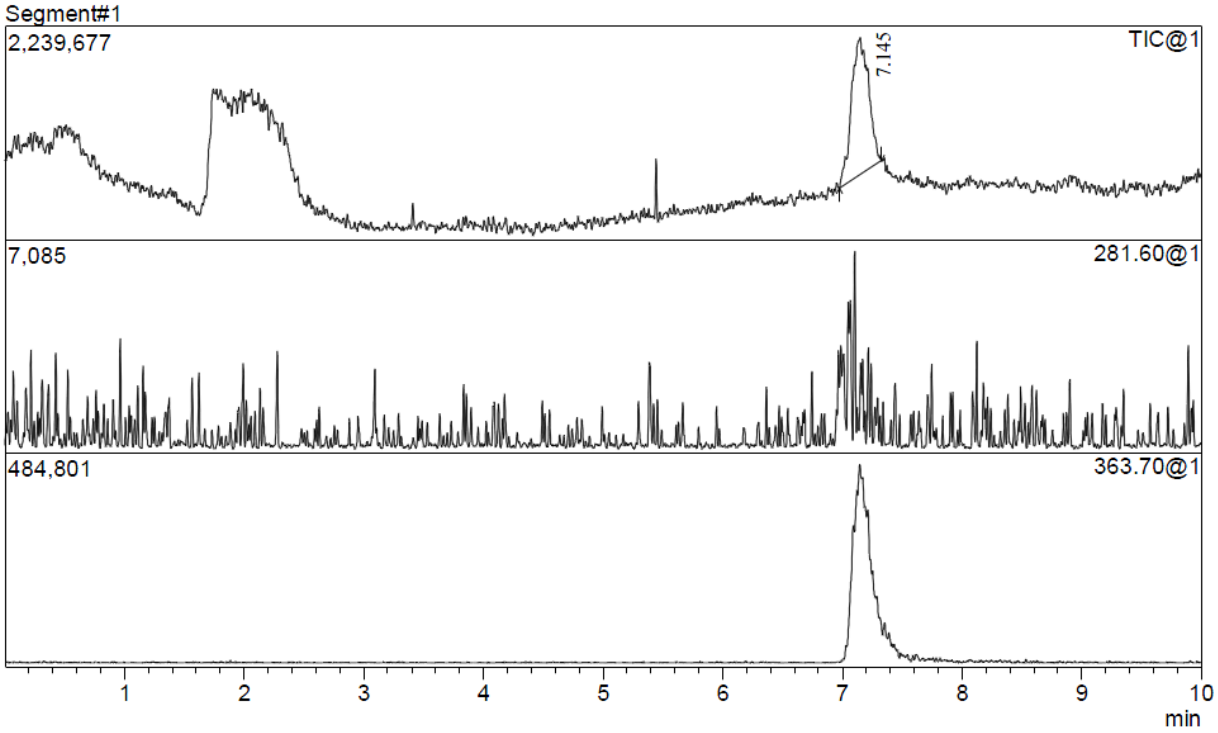
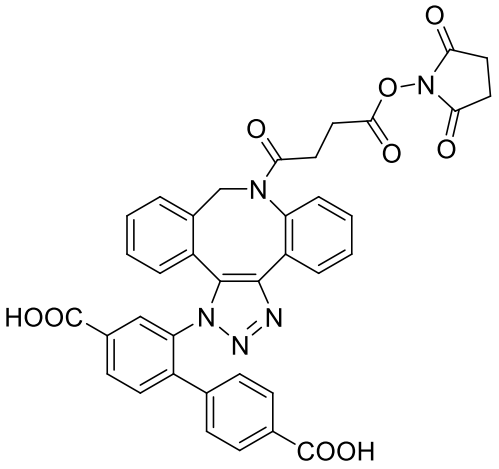


Figure S13. TIC chromatogram for **N_3-bio-MOF-100** + 50 equiv. of 1-hexyne digested in HCl/MeCN (top: all ions; middle: m/z=281.6; bottom: m/z=363.7).

8. Strain-promoted 'click' reaction for 3 and peptide coupling

Because of the limited amount of **3** available, less than 5×10^{-6} mol was used for these reactions. Pre-washed N_3-bio-MOF-100 crystals were soaked in DCM containing about 1 mg of **3** and were allowed to sit overnight. Then, a portion of the crystals were digested in 150 μL DMF containing 1 μL of conc. HCl. The resulting clear solution was subjected to LC-MS analysis (positive mode).

m/z = 686.00 and m/z = 708.00 correspond to the $[M+H]^+$ and $[M+Na]^+$ of the following compound, respectively:



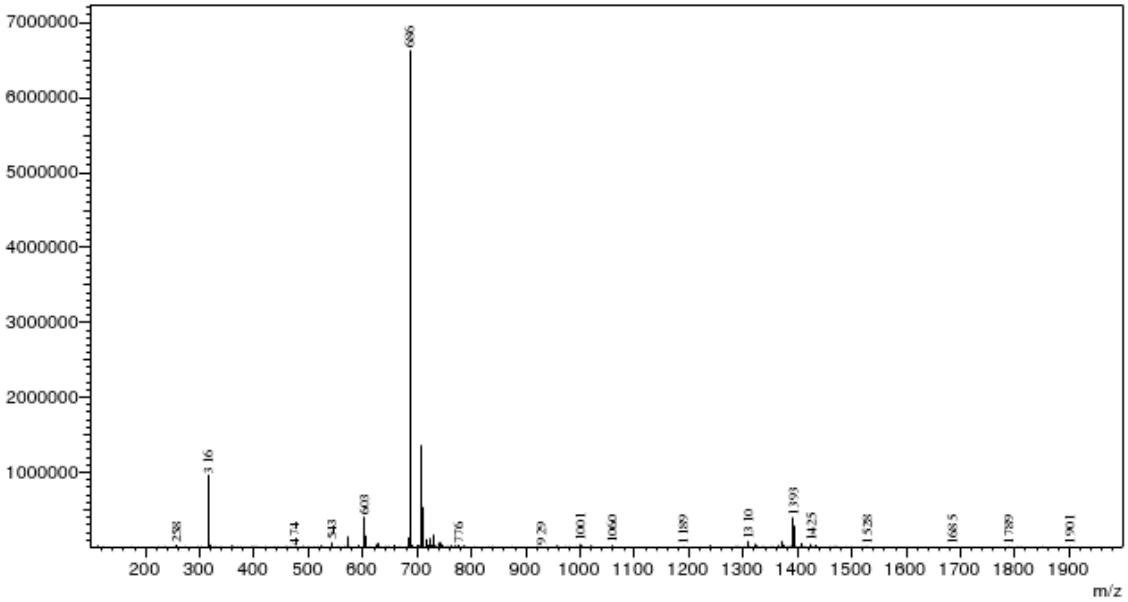


Figure S14. MS spectrum for **3-bio-MOF-100** digested in HCl/DMF.

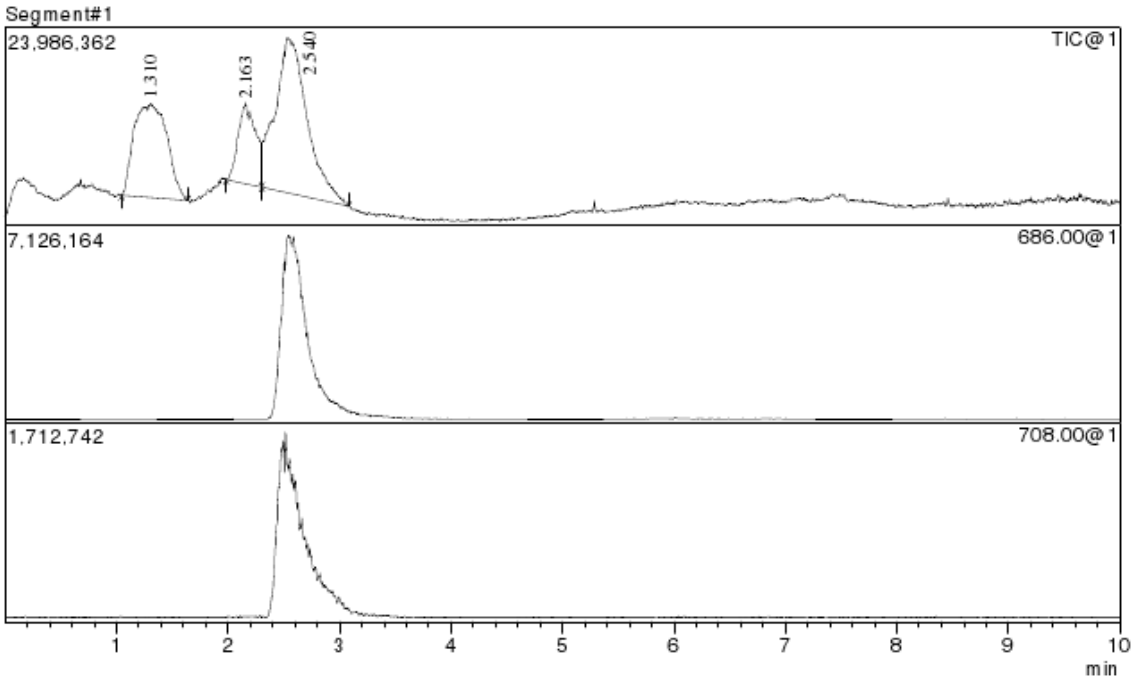
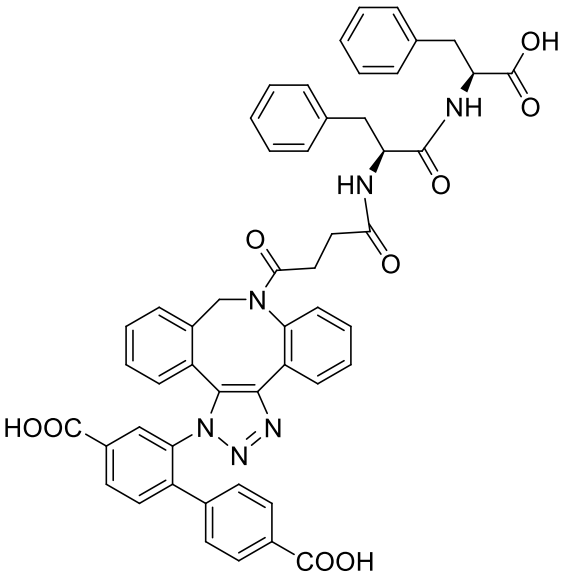


Figure S15. TIC chromatogram for **3-bio-MOF-100** digested in HCl/DMF (top: all ions; middle: m/z=686; bottom: m/z=708).

MOF crystals decorated by **3** were washed with DMF and then soaked in a DMF solution of dipeptide Phe-Phe. The molar amount of the peptide used was calculated to be equal to the amount of **3** used in the previous step. After reaction overnight, a portion of the crystals were digested using 150 μL DMF containing 1 μL of conc. HCl. The resulted clear solution was subjected to LC-MS analysis (positive mode).

m/z = 883.00 and m/z = 905.00 correspond to the $[M+H]^+$ and $[M+Na]^+$ of the following compound, respectively:



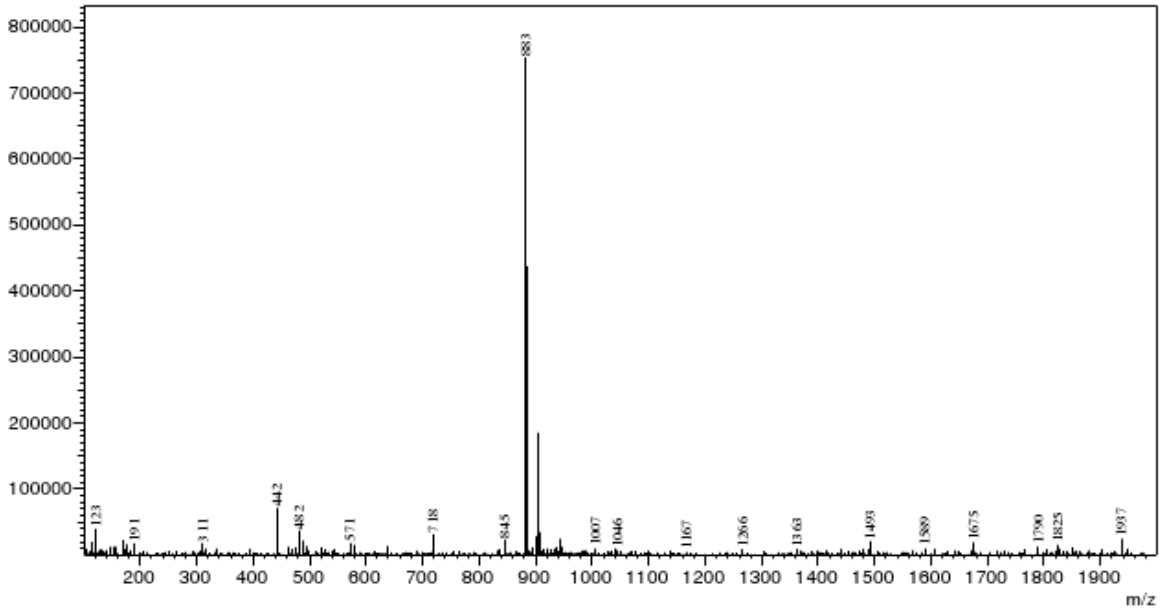


Figure S16. MS spectrum for **Phe$_2$-bio-MOF-100** digested in HCl/DMF.

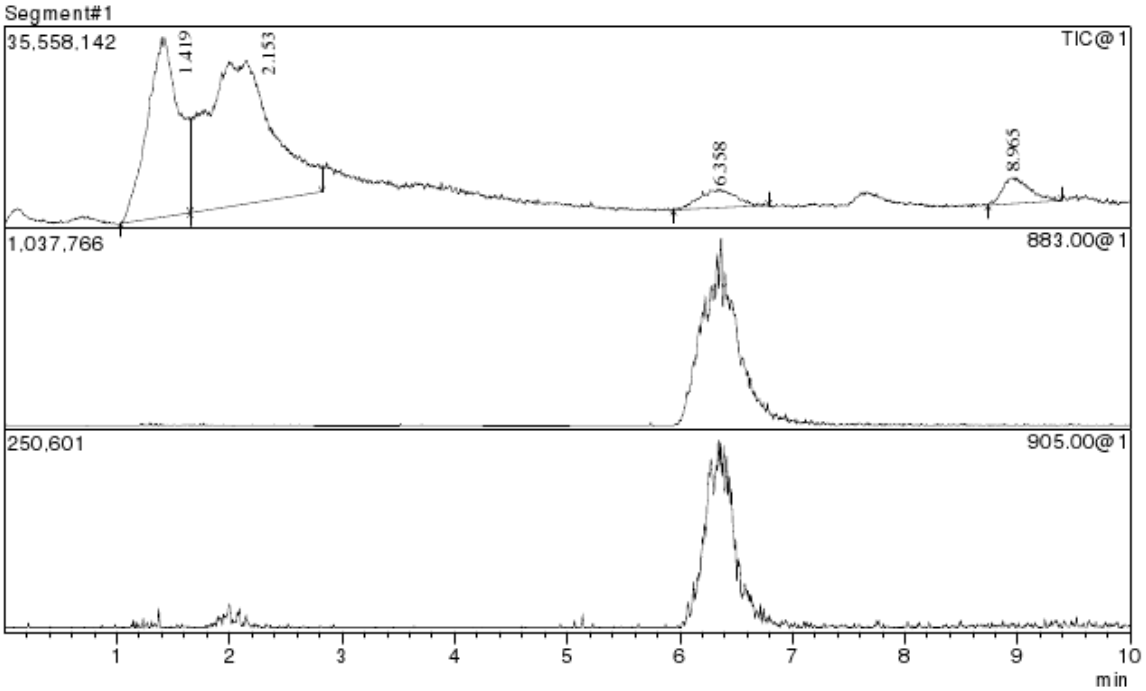


Figure S17. TIC chromatogram for **Phe$_2$-bio-MOF-100** digested in HCl/DMF (top: all ions; middle: m/z=883; bottom: m/z=905).

9. Additional images

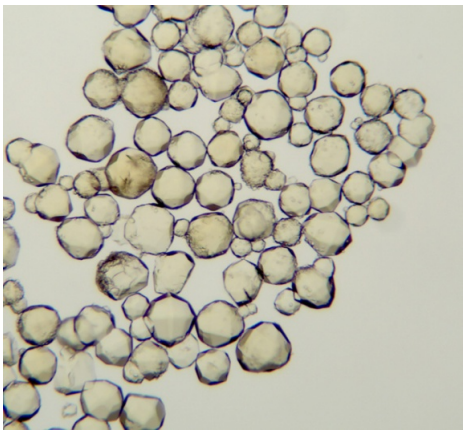


Figure S18. N_3-bio-MOF-100.

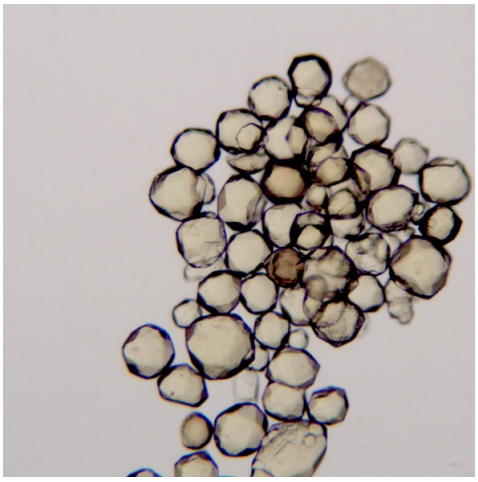


Figure S19. 1-bio-MOF-100.

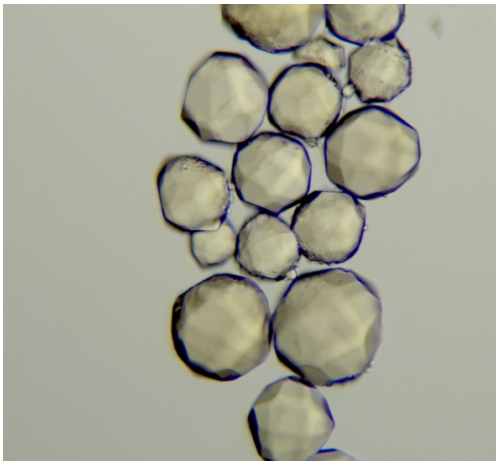


Figure S20. 2-bio-MOF-100.

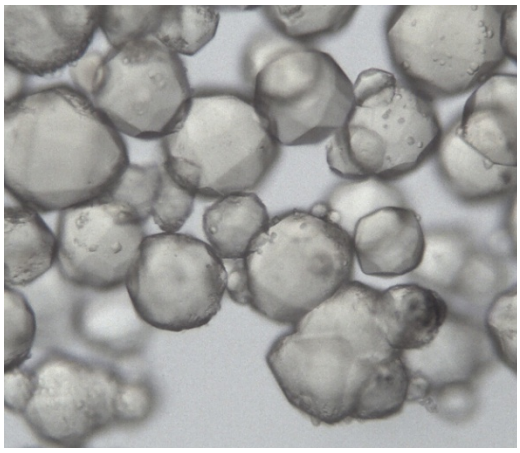


Figure S21. 3-bio-MOF-100.

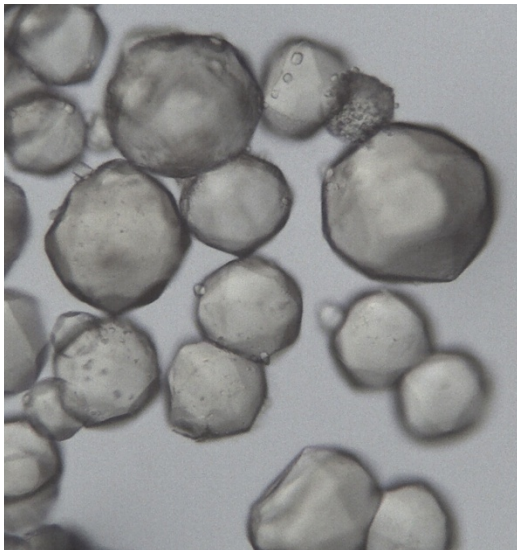


Figure S22. Phe_2-bio-MOF-100.

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