Supporting Information

Precisely Embedding Active Sites into a Mesoporous Zr-Framework through Linker Installation for High-efficiency Photocatalysis

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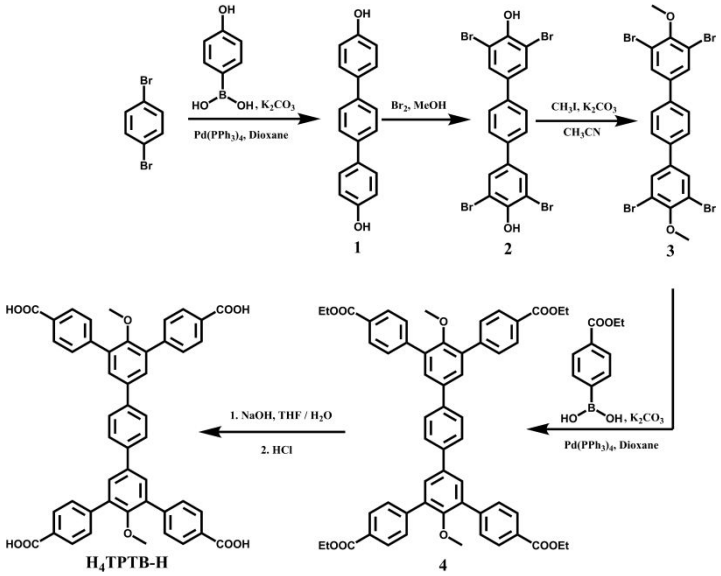
Materials and Instrumentation

All reagents and solvents used in synthetic studies were commercially available and used as supplied without further purification. The ligands were synthesized through the routines in Supplementary Schemes S1 to S3. ^{1}H NMR spectra were obtained on a Mercury 500 MHz spectrometer. Gas sorption measurements were conducted on a Micromeritics ASAP 2020 system. Single crystal X-ray diffraction experiments were carried on a Bruker D8-Venture diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å). Powder X-ray diffraction (PXRD) was carried out with a Bruker D8-Focus Bragg-Brentano X-ray powder diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at 40 kV and 40 mA. Simulations of the PXRD spectrum are attained from the single-crystal data and diffraction-crystal module of the Mercury program available free of charge via http://www.ccdc.cam.ac.uk/products/mercury/.

Ligand Syntheses

(1) Synthesis of H_4TPTB-H



Scheme S1. Synthesis of H_4TPTB-H.

Synthesis of dimethyl [1,1':4',1''-terphenyl]-4,4''-diol (**1**). 1,4-dibromobenzene (4.72 g, 20 mmol), (4-hydroxyphenyl)boronic acid (8.28 g, 60 mmol), K_2CO_3 (11 g, 80 mmol), tetrakis(triphenylphosphine)palladium (0.46 g, 0.4 mmol) were added to a 500-mL Schlenk flask charged with a stir bar. The flask was pumped under vacuum and refilled with N_2 three times before 300 mL degassed 1,4-dioxane was transferred to the system. The reaction mixture was heated to 85 °C for 72 h under a N_2 atmosphere. After the reaction mixture cooled to room temperature, the organic solvent was removed using a rotary evaporator, and the resulting mixture was poured into water and extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and then the solvent was removed again using a rotary evaporator. After purification by column chromatography on silica gel using dichloromethane/hexane (1:1 v/v) as eluent and evaporation of the fraction containing the product, compound **1** was obtained as a white solid (3.93 g, yield: 75 %). ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.80 (d, 4H), 7.46 (d, 4H), 7.58 (s, 4H) ppm.

Synthesis of 3,3'',5,5''-tetrabromo-[1,1':4',1''-terphenyl]-4,4''-diol (**2**). Bromine (2.4 mL, 50 mmol) was added to a solution of compound **1** (2.62 g, 10 mmol) in methanol (100 mL). After 5 h of stirring, the resulting precipitate was filtered and washed sequentially with aqueous solutions of $NaHCO_3$, Na_2SO_3 and water. The resulting white powder was dissolved in acetone and dried over anhydrous Na_2SO_4. Pure compound **2** was obtained by recrystallization in acetone (2.91 g, 50 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.72 (s, 4H), 7.89 (s, 4H), 10.08 (s, 2H) ppm.

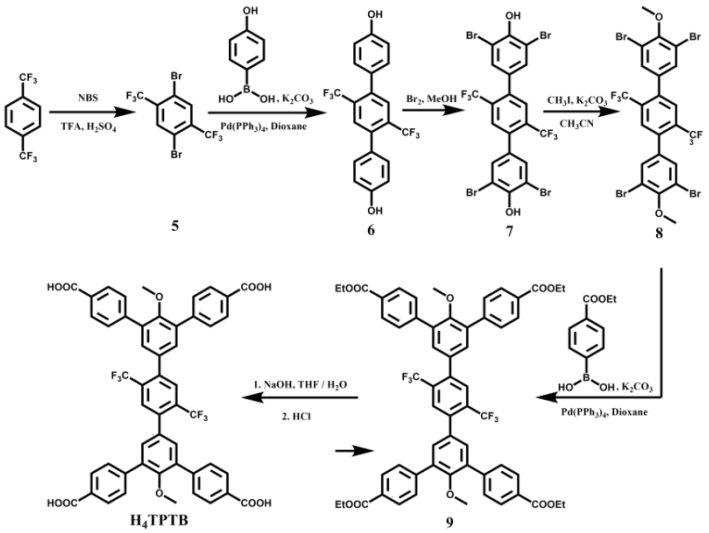
Synthesis of 3,3'',5,5''-tetrabromo-4,4''-dimethoxy-1,1':4',1''-terphenyl (**3**). Compound **2** (2.89 g, 5 mmol), methyl iodide (4.26 g, 30 mmol), and K_2CO_3 (2.1 g, 15 mmol) were dissolved into acetonitrile (100 mL). The reaction mixture was heated at reflux for 18 h under argon atmosphere and then cooled to room temperature. Acetonitrile was removed using rotary evaporation and the resulting mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over

anhydrous $MgSO_4$, and then the solvent was removed again using a rotary evaporator. After purification by column chromatography on silica gel using dichloromethane/hexane (1:3 v/v) as eluent and evaporation of the fraction containing the product, compound **3** was obtained as a white powder (2.18 g, yield: 72 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (s, 6H), 7.58 (s, 4H), 7.75 (s, 4H) ppm.

Synthesis of diethyl 5',5'''-bis(4-(ethoxycarbonyl)phenyl)-4''',6'-dimethoxy-[1,1':3',1'':4'',1''':3''',1''''-quinquephenyl]-4,4''''-dicarboxylate (**4**). Compound **3** (1.5g, 2.5 mmol), (4-(ethoxycarbonyl)phenyl)boronic acid (2.91 g, 15 mmol), K_2CO_3 (2.76 g, 20 mmol), and tetrakis(triphenylphosphine)palladium (0.116 g, 0.1 mmol) were added to a 250-mL Schlenk flask charged with a stir bar. The flask was pumped under vacuum and refilled with N_2 three times before 150 mL degassed 1,4-dioxane was transferred to the system. The reaction mixture was heated to 85 °C for 72 h under a N_2 atmosphere. After the reaction mixture cooled to room temperature, the organic solvent was removed using a rotary evaporator, and the resulting mixture was poured into water and extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and then the solvent was removed again using a rotary evaporator. After purification by column chromatography on silica gel using ethyl acetate/hexane (1:4 v/v) as eluent and evaporation of the fraction containing the product, compound **4** was obtained as a pale yellow solid (1.63 g, yield: 74 %). ^{1}H NMR (500 MHz, $CDCl_3$): *δ* 1.43 (t, 12H), 3.19 (s, 6H), 4.43 (q, 8H), 7.64 (s, 4H), 7.72 (s, 4H), 7.76 (d, 8H), 8.14 (d, 8H) ppm.

Synthesis of 5',5'''-bis(4-carboxyphenyl)-4''',6'-dimethoxy-[1,1':3',1'':4'',1''':3''',1''''-quinquephenyl]-4,4''''-dicarboxylic acid (**H_4TPTB-H**). Compound **4** (1.63 g, 1.4 mmol) was dissolved in 20 mL of THF, to which 30 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux for 10 h, and then the organic solvent was removed using a rotary evaporator. The aqueous phase was acidified to pH = 2 using 6 M HCl aqueous solution. The resulting precipitate was collected via filtration, washed with water (200 mL), and dried under vacuum to afford **H_4TPTB** (1.03 g, 96 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.12 (s, 6H), 7.74 (s, 4H), 7.81 (d, 8H), 7.88 (s, 4H), 8.07 (d, 8H) ppm.

(2) Synthesis of H_4TPTB:



Scheme S2. Synthesis of H_4TPTB.

Synthesis of 1,4-dibromo-2,5-bis(trifluoromethyl)benzene (**5**).[1] In a 250 mL flask, 1,4-bis(trifluoromethyl)benzene (9.5 g, 44 mmol) was dissolved in 125 mL trifluoroacetic acid and 30 mL concentrated sulfuric acid and reflux for 10 min under stirring. The temperature was allowed to cool to 60 ^{o}C before N-bromosuccinimide (23.7 g, 133 mmol) was added to the reaction mixture slowly in 5 h. The reaction mixture was heated at 60 ^{o}C for 48 h and then cooled to room temperature. The flask was placed into ice bath for 5 h where the product precipitated. Compound **5** was obtained by filtering and drying under vacuum overnight (12.6 g, 77 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 2H) ppm.

Synthesis of 2',5'-bis(trifluoromethyl)-[1,1':4',1''-terphenyl]-4,4''-diol (**6**). Compound **5** (7.44 g, 20 mmol), (4-hydroxyphenyl)boronic acid (8.28 g, 60 mmol), K_2CO_3 (11 g, 80 mmol), tetrakis(triphenylphosphine)palladium (0.46 g, 0.4 mmol) were added to a 500-mL Schlenk flask charged with a stir bar. The flask was pumped under vacuum and refilled with N_2 three times before 300 mL degassed 1,4-dioxane was transferred to the system. The reaction mixture was heated to 85 ^{o}C for 72 h under a N_2 atmosphere. After the reaction mixture cooled to room temperature, the organic solvent was removed using a rotary evaporator, and the resulting mixture was poured into water and extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and then the solvent was removed again using a rotary evaporator. After purification by column chromatography on silica gel using dichloromethane/hexane (1:1 v/v) as eluent and evaporation of the fraction containing the product, compound **6** was obtained as a white solid (5.82 g, yield: 73 %). ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.85 (d, 4H), 7.21 (d, 4H), 7.69 (s, 2H), 9.71 (s, 2H) ppm.

Synthesis of 3,3'',5,5''-tetrabromo-2',5'-bis(trifluoromethyl)-[1,1':4',1''-terphenyl]-4,4''-diol (**7**). Bromine (4.22 mL, 88 mmol) was added to a solution of compound **6** (7 g, 17.6 mmol) in methanol (200 mL). After 5 h of stirring, the resulting precipitate was filtered and washed sequentially with aqueous solutions of $NaHCO_3$, Na_2SO_3 and water. The resulting white powder was dissolved in acetone and dried over anhydrous Na_2SO_4. Pure compound **7** was obtained by recrystallization in acetone (8.8 g, 70 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.58 (s, 4H), 7.87 (s, 2H), 10.29 (s, 2H) ppm.

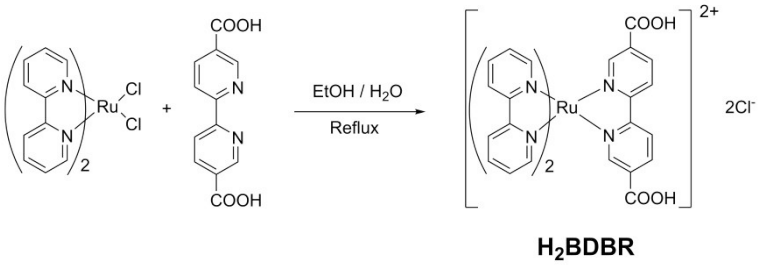
Synthesis of 3,3'',5,5''-tetrabromo-4,4''-dimethoxy-2',5'-bis(trifluoromethyl)-1,1':4',1''-terphenyl (**8**). Compound **7** (8.8 g, 12.3 mmol), methyl iodide (10.5 g, 74 mmol), and K_2CO_3 (5.2 g, 37 mmol) were dissolved into acetonitrile (200 mL). The reaction mixture was heated at reflux for 18 h under argon atmosphere and then cooled to room temperature. Acetonitrile was removed using rotary evaporation and the resulting mixture was poured into water and extracted with dichloromethane (3 × 80 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and then the solvent was removed again using a rotary evaporator. After purification by column chromatography on silica gel using dichloromethane/hexane (1:3 v/v) as eluent and evaporation of the fraction containing the product, compound **8** was obtained as a white powder (7.42 g, yield: 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97 (s, 6H), 7.52 (s, 4H), 7.70 (s, 2H) ppm.

Synthesis of diethyl 5',5'''-bis(4-(ethoxycarbonyl)phenyl)-4''',6'-dimethoxy-2'',5''-bis(trifluoromethyl)-[1,1':3',1'':4'',1''':3''',1''''-quinquephenyl]-4,4''''-dicarboxylate (**9**). Compound **8** (3.71 g, 5 mmol), (4-(ethoxycarbonyl)phenyl)boronic acid (5.82 g, 30 mmol), K_2CO_3 (5.52 g, 40 mmol), and tetrakis(triphenylphosphine)palladium (0.232 g, 0.2 mmol) were added to a 500-mL Schlenk flask charged

with a stir bar. The flask was pumped under vacuum and refilled with N_2 three times before 300 mL degassed 1,4-dioxane was transferred to the system. The reaction mixture was heated to 85 °C for 72 h under a N_2 atmosphere. After the reaction mixture cooled to room temperature, the organic solvent was removed using a rotary evaporator, and the resulting mixture was poured into water and extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and then the solvent was removed again using a rotary evaporator. After purification by column chromatography on silica gel using ethyl acetate/hexane (1:4 v/v) as eluent and evaporation of the fraction containing the product, compound **9** was obtained as a pale yellow solid (4.03 g, yield: 79%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43 (t, 12H), 2.31 (s, 6H), 4.41 (q, 8H), 7.41 (s, 4H), 7.74 (d, 8H), 7.85 (s, 2H), 8.13 (d, 8H) ppm.

Synthesis of 5',5'''-bis(4-carboxyphenyl)-4''',6'-dimethoxy-2'',5''-bis(trifluoromethyl)-[1,1':3',1'':4'',1''':3''',1''''-quinquephenyl]-4,4''''-dicarboxylic acid (**H_4TPTB**). Compound **9** (4.03 g, 4 mmol) was dissolved in 30 mL of THF, to which 100 mL of 10 M NaOH aqueous solution was added. The mixture was stirred under reflux for 10 h, and then the organic solvent was removed using a rotary evaporator. The aqueous phase was acidified to pH = 2 using 6 M HCl aqueous solution. The resulting precipitate was collected via filtration, washed with water (300 mL), and dried under vacuum to afford **H_4TPTB** (3.19 g, 88 %). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.15 (s, 6H), 7.50 (s, 4H), 7.77 (d, 8H), 8.06 (t, 10H), 13.03 (s, 4H) ppm.

(3) Synthesis of H_2BDBR:



Scheme S3. Synthesis of H_2BDBR.

The ruthenium containing linear linker **H_2BDBR** ([bis(2,2'-bipyridine,N_1,N_1')(5,5'-dicarboxy-2,2'-bipyridine-)ruthenium(II)] dichloride) was synthesized according to a literature procedure.[2]

MOF Syntheses

(1) Synthesis of PCN-808

$ZrCl_4$ (20 mg), H_4TPTB (10 mg), benzoic acid (800 mg), and DMF (3 mL) were charged in a Pyrex vial. The mixture was heated in a 120 ºC oven for 72 h. After cooling down to room temperature, the colorless crystals of PCN-808 were harvested (yield: 58 %).

(2) Synthesis of PCN-808-BPDC

PCN-808 (100 mg), H_2BPDC (200 mg) and DMF (40 mL) were charged in a Pyrex vial. The mixture was heated in a 100 ºC oven for 24 h. After cooling down to room temperature, the crystals of PCN-808-BPDC were harvested (yield: 97 %).

(3) Synthesis of PCN-808-BDBR

PCN-808 (100 mg), H_2BDBR (80 mg) and DMF (40 mL) were charged in a Pyrex vial. The mixture was heated in a 100 ºC oven for 24 h. After cooling down to room temperature, the crystals of PCN-808-BDBR were harvested (yield: 94 %).

(4) Synthesis of UiO-67-Ru

$ZrCl_4$ (10 mg), H_2BPDC (9 mg), H_2BDBR (2 mg) acetic acid (82 μL), and DMF (1.5 mL) were charged in a Pyrex vial. The mixture was heated in a 100 ºC oven for 24 h. After cooling down to room temperature, the resulting yellow solid was isolated by centrifugation, and washed with DMF and methanol (yield: 75 %).

Single-crystal X-ray Crystallography

Crystals of PCN-808, PCN-808-BPDC and PCN-808-BDBR were taken directly from the mother liquid without further treatment, transferred to oil, and mounted onto a loop for single crystal X-ray data collection. Single crystal X-ray diffraction experiments were carried on a Bruker Smart Apex diffractometer equipped with a Cu-Kα sealed-tube X-ray source (λ = 1.54178 Å, graphite monochromated) under 100 K by using a ω scan mode. The data frames were recorded using the program APEX3 and processed using the program SAINT routine within APEX3. The data were corrected for absorption and beam corrections based on the multi-scan technique as implemented in SADABS. The structures were solved by direct methods using SHELXS and refined by full-matrix least-squares on F^2 using SHELXL software.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on the aromatic rings were located at geometrically calculated positions and refined by riding. However, the hydrogen atoms for the coordinated molecules cannot be found from the residual electron density peaks and the attempt of theoretical addition was not done. The free solvent molecules are highly disordered in MOFs, and attempts to locate and refine the solvent peaks were unsuccessful. The diffused electron densities resulting from these solvent molecules were removed using the SQUEEZE routine of PLATON; structures were then refined again using the data generated.[4] Crystal data are summarized in Table S2 and S3. CCDC 1896946-1896949 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

N_2 Sorption Isotherms

N_2 adsorption measurements were performed using a Micromeritics ASAP 2020 surface area and pore size analyser. Before sorption experiments, as-synthesized samples were washed with DMF several times to remove unreacted starting ligands and inorganic species. Afterwards, the crystals were carefully decanted and washed with DMF and acetone several times. Then the samples were activated under vacuum at 80 ^{o}C for 10 h. Low-pressure N_2 adsorption isotherms were measured at 77 K in a liquid nitrogen bath. The specific surface areas were determined using the Brunauer-Emmett-Teller model from the N_2 sorption data. For the N_2 sorption isotherms, please see Figure 3.

Photocatalytic Activity Tests

As-synthesized PCN-808-BDBR was washed three times with DMF, solvent exchanged with acetone for 3 days and dried in oven before photocatalytic testing. To a flame-dried 4 mL vial equipped with a magnetic stir bar were added $Ru(bpy)_3Cl_2$ or PCN-808-BDBR (0.50 μmol, 0.01 equiv), tetrahydroisoquinoline derivative (0.05 mmol, 1.0 equiv), and nitromethane (2 mL). The reaction mixture was stirred at room temperature under 450 nm LED lamp (100 mW/cm^2) in open air. After the reaction was completed (~12 hours), the catalyst was removed by centrifugation, and the supernatant was dried under vacuum. Conversion yields of the aza-Henry reaction catalyzed by $Ru(bpy)_3Cl_2$ or PCN-808-BDBR were determined by ^{1}H NMR of the crude product.

Photocatalytic oxidation of dihydroartemisinic acid to artemisinin. The synthesis of artemisinin was conducted using PCN-808-BDBR as photocatalyst under a 450 nm LED lamp (100 mW/cm^2) in the presence of O_2. In a typical reaction, dihydroartemisinic acid (25 mg, 0.106 mmol), MOF catalyst (0.002 mmol based on Ru) and trifluoroacetic acid (8 μL) were dispersed in dichloromethane (5 mL) and slowly bubbled with O_2 under the irradiation of LED lamps (150 W) at 5-10°C for 3 hours. After removal of dichloromethane, conversion and selectivity to artemisinin was measured by ^{1}H-NMR in $CDCl_3$ using biphenyl (16.3 mg, 0.106 mmol) as an internal standard.

^{1}H NMR Spectroscopy

For ^{1}H NMR spectroscopy, the activated samples (around 5 mg) in 4 mL vials were digested with one drop of D_2SO_4-d_2. About 0.5 mL DMSO-d_6 was added to the vial and the mixture was sonicated for 5 minutes before the upper clear solution was collected for NMR measurement. ^{1}H NMR spectra for PCN-808, PCN-808-BPDC, PCN-808-BDBR are presented below.

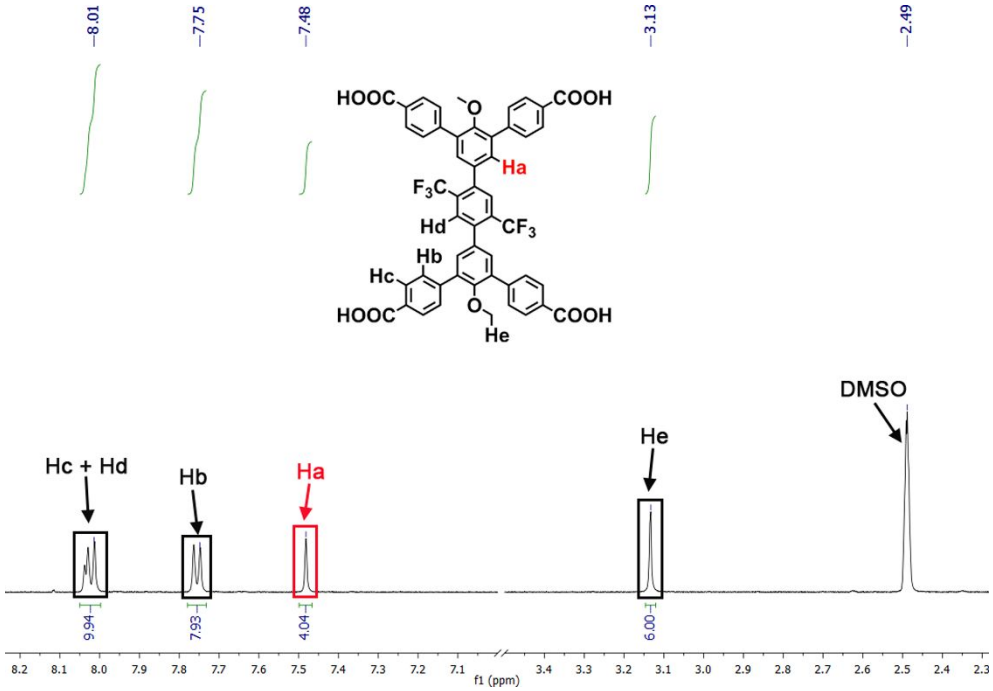


Figure S1. ^{1}H NMR spectroscopy of PCN-808.

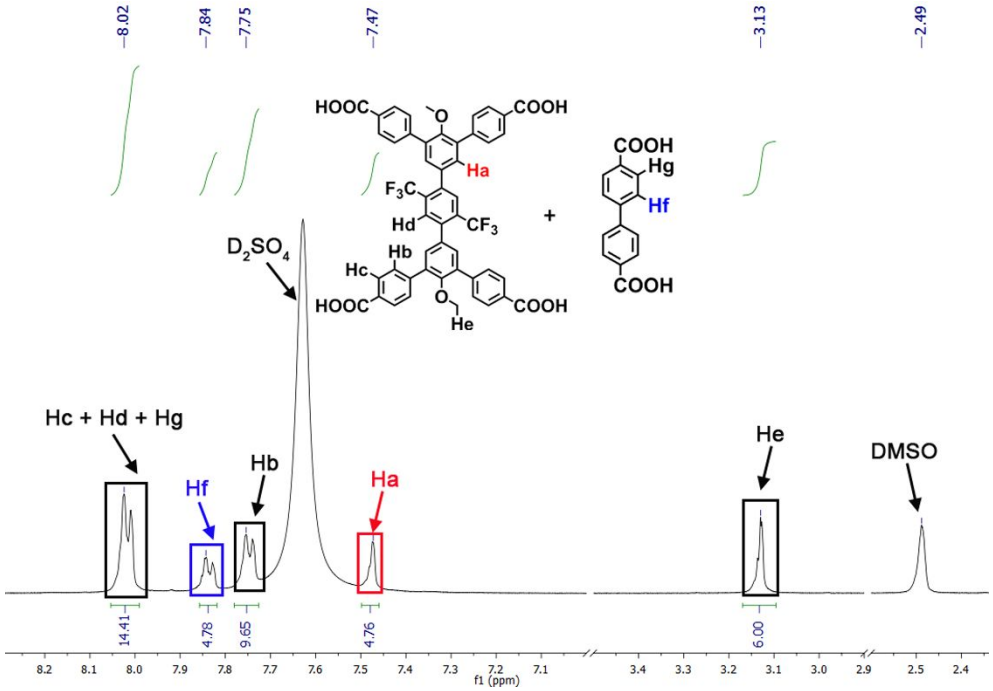


Figure S2. ^{1}H NMR spectroscopy of PCN-808-BPDC.

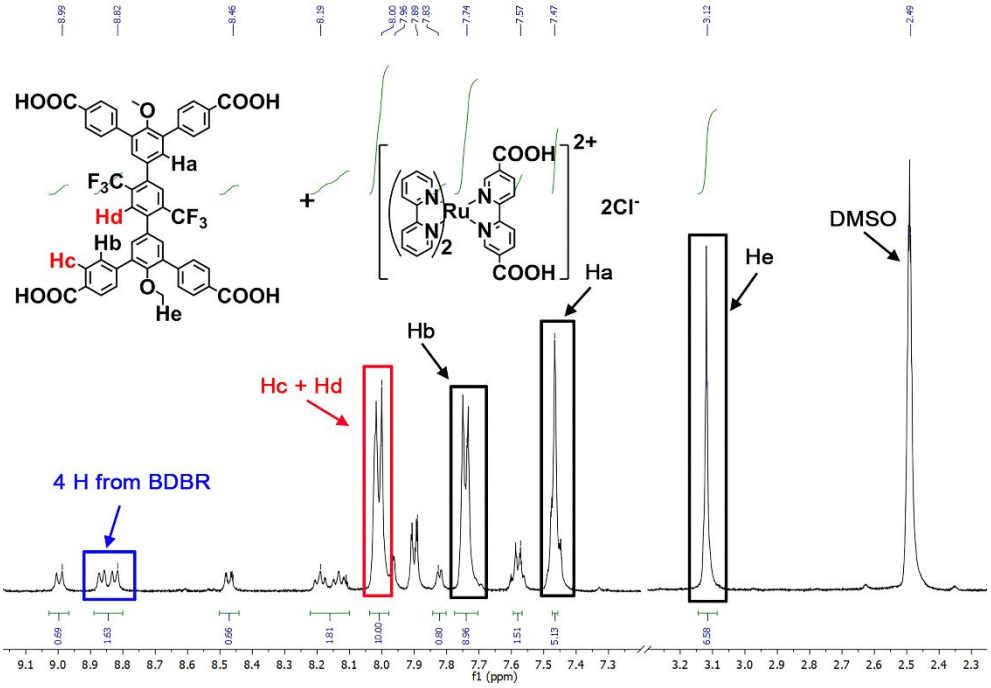


Figure S3. [1]H NMR spectroscopy of PCN-808-BDBR.

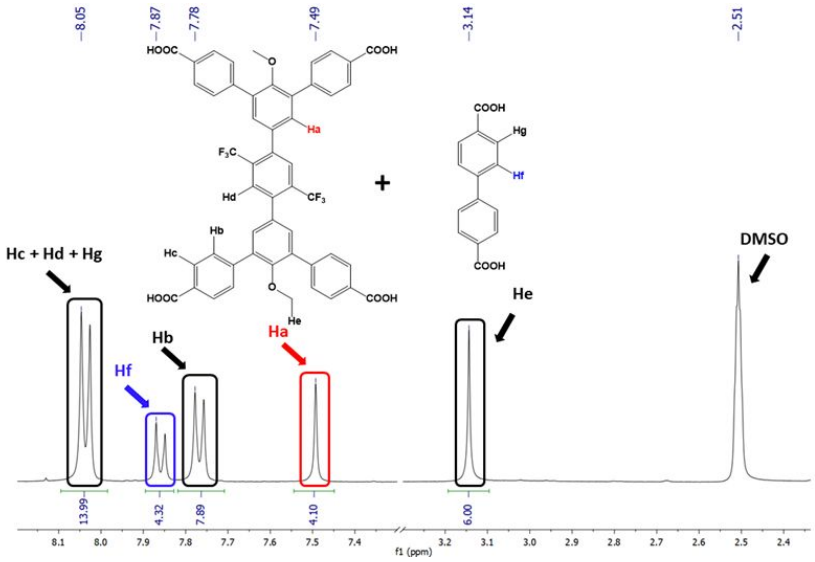


Figure S4. [1]H NMR spectroscopy of PCN-808-BPDC after heated for 24 hrs in DMF at 85 [o]C.

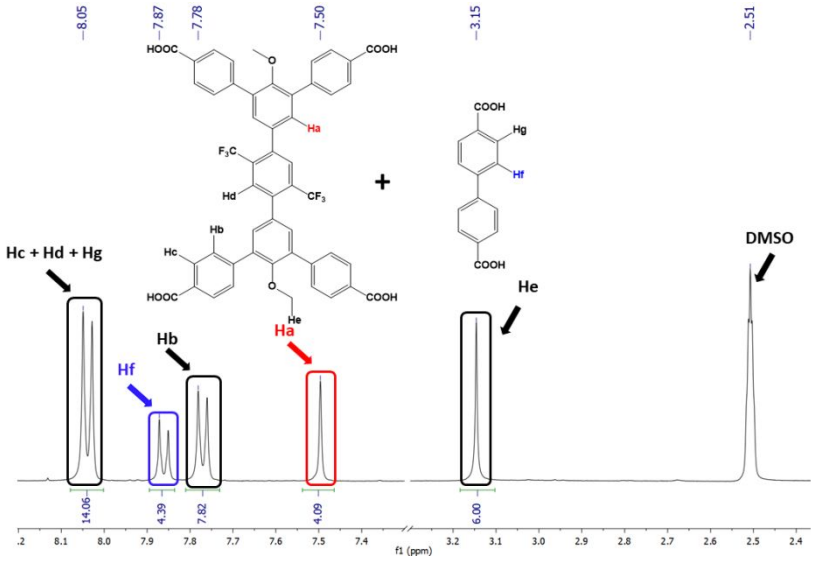


Figure S5. ^{1}H NMR spectroscopy of PCN-808-BPDC after heated for 48 hrs in DMF at 85 ^{o}C.

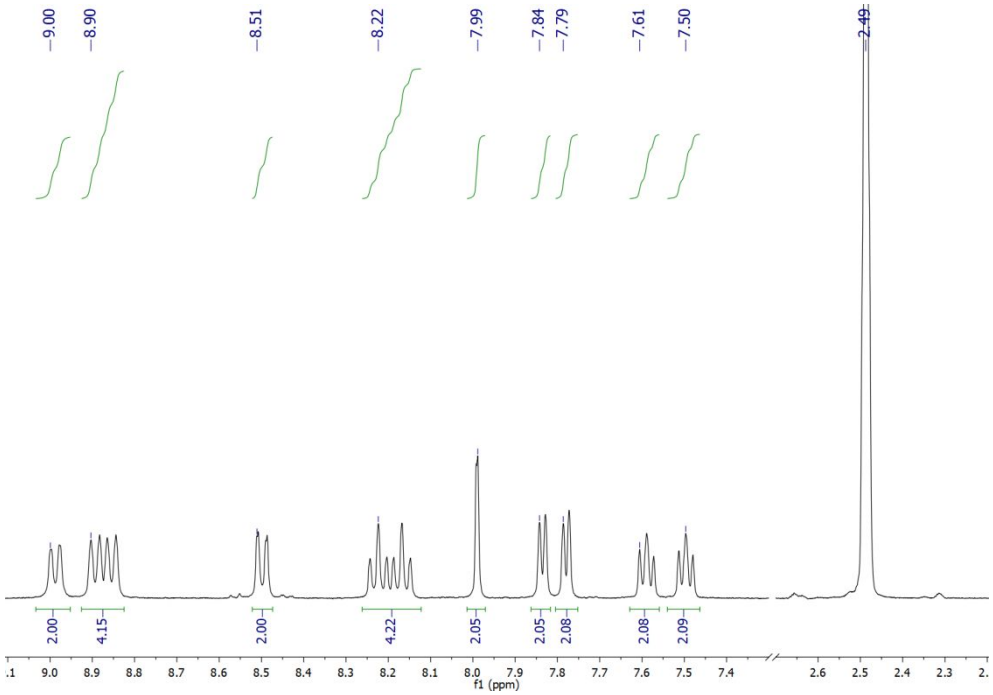


Figure S6. ^{1}H NMR spectroscopy of the pure linker H_2BDBR.

Table S1. Linker ratios from single crystal structure and from ^{1}H NMR of digested samples.

MOF	Linker ratios from single crystal structure	Linker ratios from ^{1}H NMR of digested sample
PCN-808	100 % H_4TPTB	100 % H_4TPTB (Figure S1)
PCN-808-BPDC	H_4TPTB : H_2BPDC = 2:1	H_4TPTB : H_2BPDC = 4.76/4 : 4.78/4 ≈ 1:1 (Figure S2)
PCN-808-BDBR	H_4TPTB : H_2BDBR = 2:1	H_4TPTB : H_2BDBR = 10/10 : 1.63/4 ≈ 8:3 (Figure S3)
PCN-808-BPDC heated	H_4TPTB : H_2BPDC = 2:1	H_4TPTB : H_2BPDC = 4.10/4 :

in DMF for 24 hrs		4.32/4 ≈ 1:1 (Figure S4)
PCN-808-BPDC heated in DMF for 48 hrs	H_4TPTB : H_2BPDC = 2:1	H_4TPTB : H_2BPDC = 4.09/4 : 4.39/4 ≈ 1:1 (Figure S5)

Additional Figures

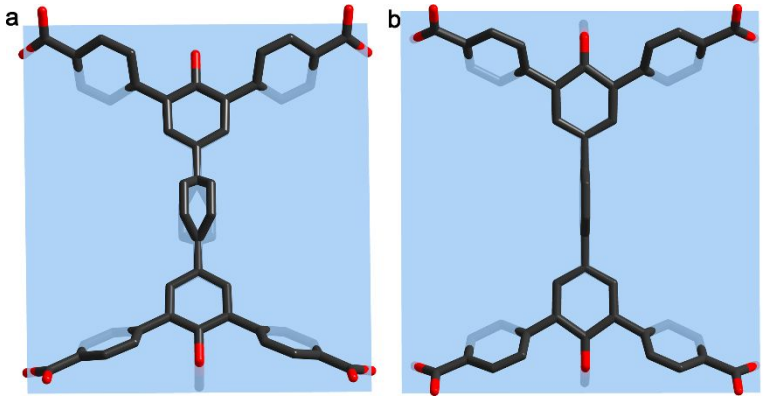


Figure S7. Configuration of the TPTB ligand in (a) PCN-808, and (b) PCN-808-BPDC.

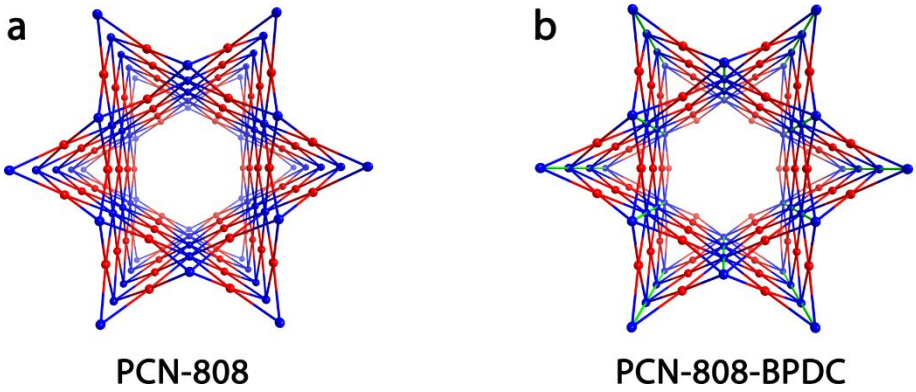


Figure S8. The {4,8}-c **csq** topology of PCN-808 with the topological point symbol of $\{4^{16}.6^{12}\}\{4^4.6^2\}_2$ (a), and the {4,10}-c topology of PCN-808-BPDC with the topological point symbol of $\{3^2.4^2.5^2\}_2\{3^8.4^{16}.5^8.6^{13}\}$ (b). Blue balls represent the Zr_6 clusters, red balls represent the tetratopic carboxylate ligands and the green sticks represent the installed BPDC ligands.

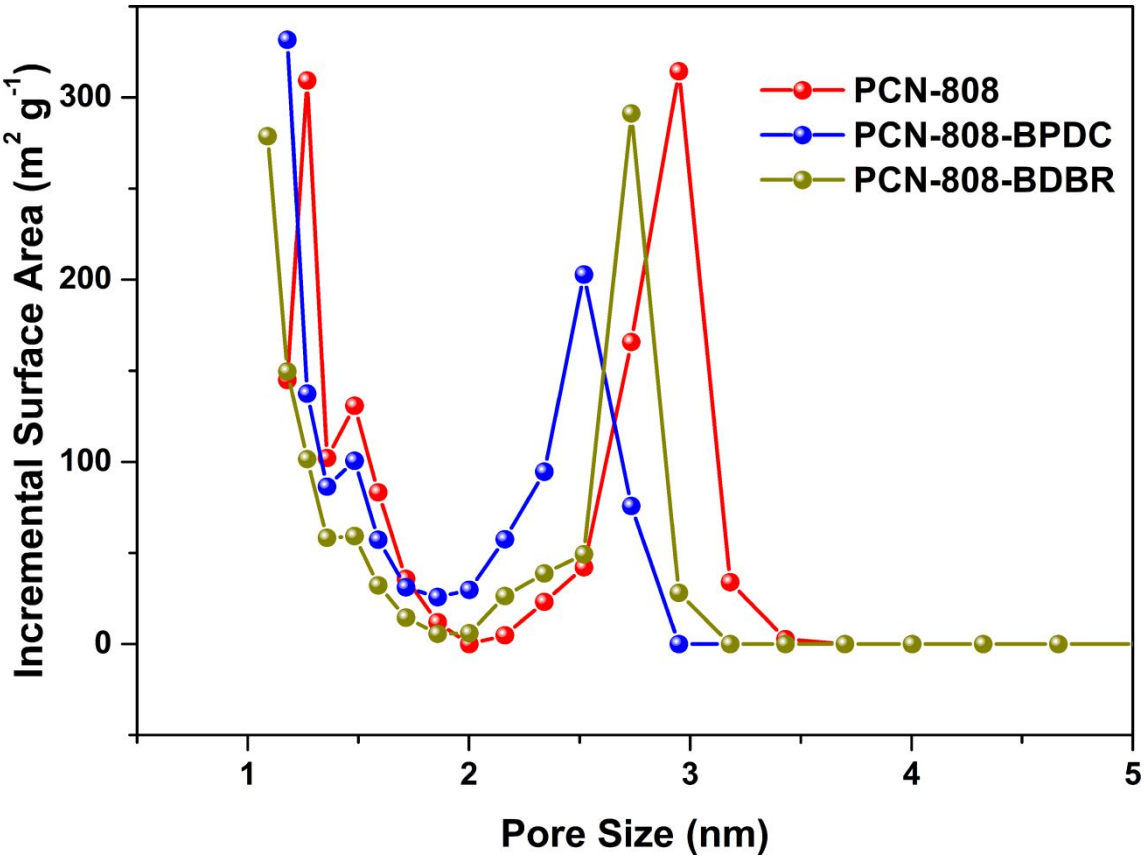


Figure S9. Pore size distributions of PCN-808, PCN-808-BPDC, and PCN-808-BDBR analyzed by NLDFT methods based on the N_2 adsorption isotherms.

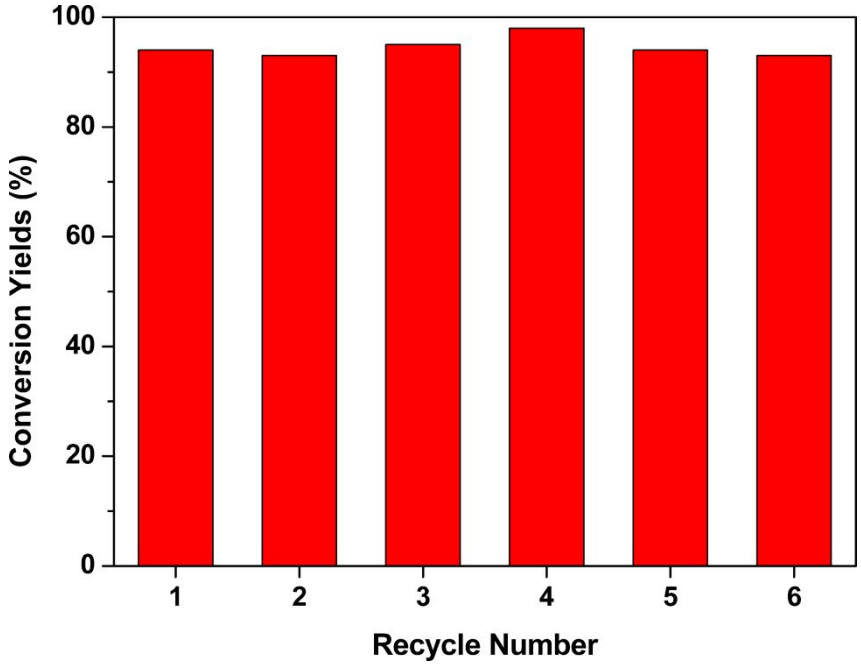


Figure S10. Catalytic cycling experiments for aza-Henry reaction (substrate **1b**, R = Br) catalyzed by PCN-808-BDBR.

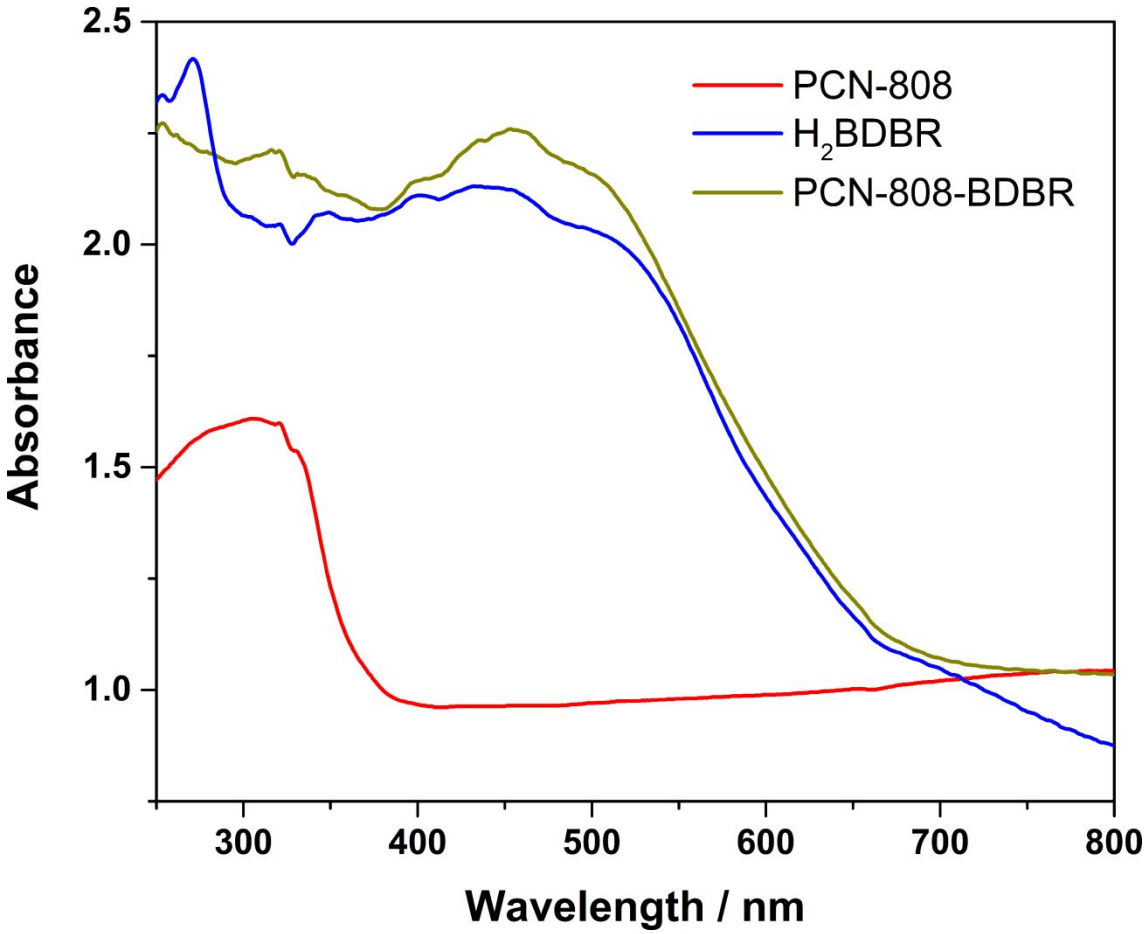


Figure S11. DR-UV-Vis spectra of PCN-808, H_2BDBR, and PCN-808-BDBR.

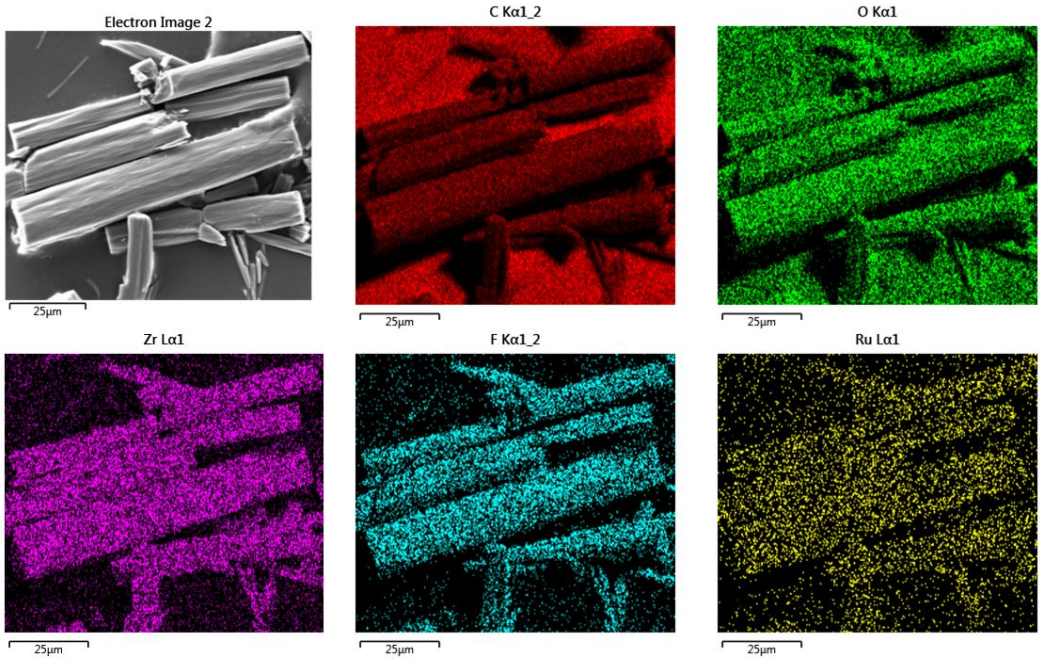


Figure 12. SEM images and eds mappings for C, O, Zr, F, and Ru in PCN-808-BDBR.

Additional Tables

Table S2. Crystal data and structure refinements for PCN-808 and PCN-808-BPDC.

code	PCN-808	PCN-808-BPDC
CCDC	1896949	1896948
formula	$C_{96}H_{52}O_{36}Zr_6$	$C_{14.25}H_{10}F_{1.50}O_{4.50}Zr_{0.75}$
*M*r	2328.69	350.14
T / K	100(2)	100(2)
Crystal system	hexagonal	hexagonal
Space group	P_6/mmm	P_6/mmm
a / Å	40.5456(7)	41.321(4)
c / Å	19.6333(4)	19.208(2)
V / Å^3	27951.9(11)	28403(6)
Z	3	24
D_c / g cm^{-3}	0.415	0.491
μ (mm^{-1})	1.518	1.574
F (000)	3468	4200
Completeness	0.996	0.923
Collected reflections	8210	8479
Unique reflections	5837	5184
Parameters	168	183
R_{int}	0.0613	0.0948
R_1[I＞2σ]	0.0477	0.0589
wR_2[I＞2σ]	0.1471	0.1622
R_1 (all data)	0.0612	0.0854
wR_2 (all data)	0.1547	0.1712
GOF on F^{20}	1.079	1.110

Table S3. Crystal data and structure refinements for PCN-808-BDBR and BDBR.

code	PCN-808-BDBR	BDBR
CCDC	1896947	1896946
formula	$C_{14.65}H_8N_{0.45}O_{4.75}Ru_{0.13}Zr_{0.75}$	$C_{256}H_{176}O_{32}N_{48}Ru_8$
*M*r	347.56	5245.08
T / K	100(2)	100(2)
Crystal system	hexagonal	orthorhombic
Space group	P_6/mmm	*Pcab*
a / Å	40.8928(8)	14.4913(4)
b / Å	40.8928(8)	18.0990(5)
c / Å	19.2023(4)	25.5467(7)
V / Å^3	27808.5(12)	6700.3(3)
Z	24	1
D_c / g cm^{-3}	0.498	1.300
μ (mm^{-1})	1.878	0.542
F (000)	4146	83
Completeness	0.999	0.998
Collected reflections	7699	6637
Unique reflections	4484	6310
Parameters	178	389
R_{int}	0.1180	0.0363
R_1[I＞2σ]	0.1002	0.0401
wR_2[I＞2σ]	0.3012	0.0415
R_1 (all data)	0.1354	0.1040
wR_2 (all data)	0.3272	0.1049
GOF on F^{20}	1.337	0.903

References

[1] P. Horcajada, F. Salles, S. Wuttke, T. Devic, D. Heurtaux, G. Maurin, A. Vimont, M. Daturi, O. David, E. Magnier, N. Stock, Y. Filinchuk, D. Popov, C. Riekel, G. Ferey, C. Serre, *J. Am. Chem. Soc.* **2011**, *133*, 17839-17847.

[2] C. Wang, Z. Xie, K. E. deKrafft, W. Lin, *J. Am. Chem. Soc.* **2011**, *133*, 13445-13454.

[3] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112-122.

[4] A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7-13.