Supporting Information for

Structure-Assisted Functional Anchor Implantation in Robust Metal–Organic Frameworks with Ultralarge Pores

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1. Materials and instrumentation

Materials

All starting materials and solvents were used as received without further purification from commercial suppliers. (Alfa Aesar, Sigma-Aldrich, TCI America, Cambridge Isotope, Oakwood Products) Silica gel (40 – 42 μm) was purchased from Silicycle Inc. The abbreviation for some solvents and reagents were listed here: 1,2-Dimethoxyethane (DME), CH_2Cl_2 (DCM), *N*,*N*-dimethylformamide (DMF), *N*,*N*-diethylformamide (DEF), dimethylsulfoxide (DMSO), and tetrahydrofuran (THF).

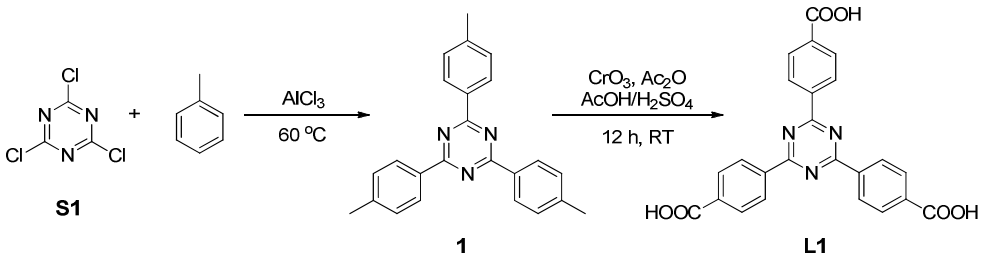
Instrumentation

Synthetic manipulations that required an inert atmosphere (where noted) were carried out under nitrogen using standard Schlenk techniques. Nuclear magnetic resonance (NMR) spectra were recorded on Mercury 300 spectrometer and Varian Inova 500 spectrometer. The chemical shifts are given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ (TMS) = 0, or referenced to the residual solvent resonances. Splitting patterns are denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Powder X-ray diffraction (PXRD) was carried out on a Bruker D8-Focus Bragg-Brentano X-ray powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178) at 40 kV and 40 mA. Thermogravimetric analyses (TGA) were conducted on a Shimadzu TGA-50 thermogravimetric analyzer from room temperature to 600 °C at a ramp rate of 2 °C/min in a flowing nitrogen atmosphere. Fourier transform infrared (IR) measurements were performed on a Shimadzu IR Affinity-1 spectrometer. Fluorescence spectra were recorded on PTI QuantaMaster series spectrofluorometer. N_2 adsorption-desorption isotherms at 77 K were measured by using a Micrometritics ASAP 2420 system. A high-purity grade (99.999%) of gases was used throughout the adsorption experiments. Prior to adsorption measurement, the sample was activated by solvent exchange (in several cycles using fresh acetone), followed by degassing at elevated temperature (150 °C) for 5 h.

2. Synthesis of organic compounds

Synthesis of ligands

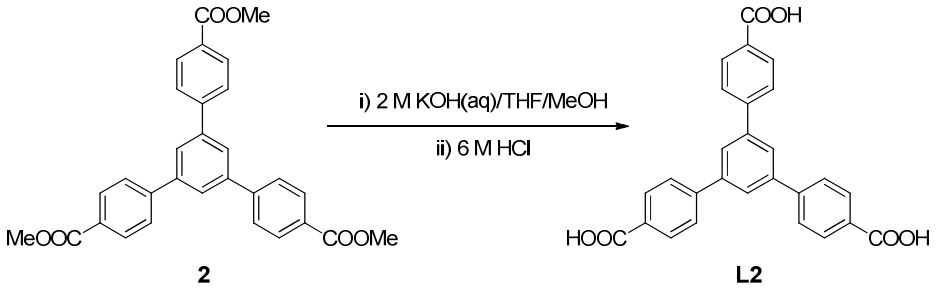
General procedure of hydrolysis: To a round bottomed flask, methyl ester compound (~500 mg) was dissolved in a mixture of THF and MeOH (100 mL, v/v = 1:1), and 50 mL 2 M KOH solution was added. The mixture was stirred and refluxed overnight at 40 °C. The organic phase was evaporated under reduced pressure. The resulting aqueous phase was diluted to ca. 100 mL and acidified with 6 M HCl. Resulting precipitates were collected, washed thoroughly with water, and dried to afford corresponding acid products.



Scheme S1. Synthetic scheme of **L1**

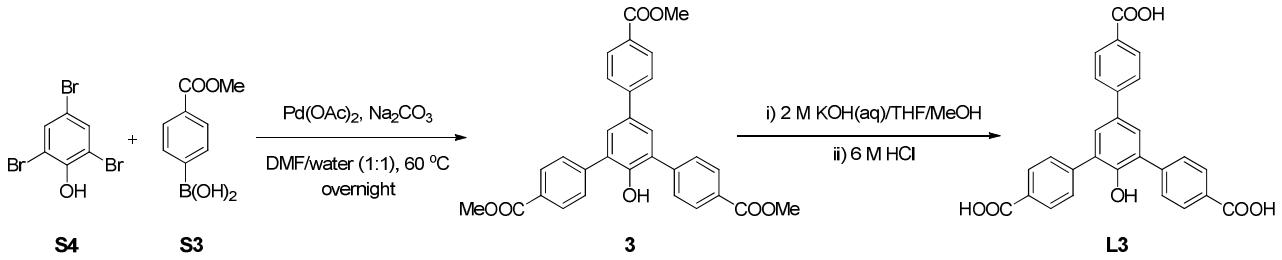
2,4,6-tri-p-tolyl-1,3,5-triazine (1). To a three neck flask, $AlCl_3$ (20 g) was dissolved in dry toluene and heated to 60 °C. $C_3N_3Cl_3$ (**S1**, 8.3 g) was then added portionwise for an hour and the mixture was stirred overnight. Then resulting red sticky oil was poured into a large amount of ice water to quench the catalyst and extracted with $CHCl_3$. After removing solvent, a crude product was precipitated out from methanol to yield a needle-like solid. Resulting solid was recrystallized from hot toluene to afford a white needle-like crystalline solid (10 g, 63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64 (d, 6 H), 7.35 (d, 6 H), 2.46 (s, 9 H).

4,4′,4″-s-triazine-2,4,6-triyl-tribenzoic acid (L1). To a 500 mL three-necked flask **1** (2.78 g) was dissolved in acetic acid (70 mL) and then 4.4 mL of H_2SO_4 was added. A solution of chromium oxide (7.2 g) in acetic anhydride (4.8 mL) was carefully added into the reaction flask with an ice bath. The resulting dark-green slurry was stirred overnight. The reaction mixture was poured into 250 mL cold water, stirred 1 h to well mixed, and filtered. The solids were washed with water to remove chromium acid. Dissolve the white solid in 200 mL 2 M NaOH solution. After the unreacted starting material was removed by filtration, the solution was acidified with 6 M HCl solution to give white crude product (until pH < 3). Resulting crude product was then filtered and dried. Recrystallization from DMF afforded pure product as a white solid (3.0 g, 86%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 13.35 (s, 3 H), 8.85 (d, 6 H), 8.20 (d, 6 H).



Scheme S2. Synthetic scheme of **L2**

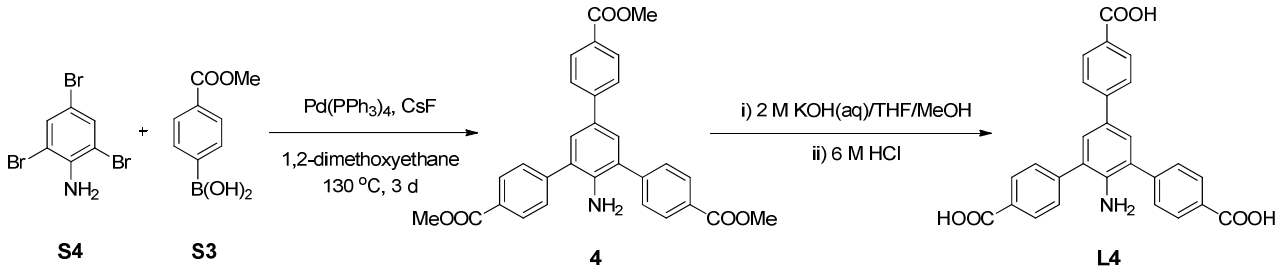
L2 was synthesized according to the literature procedure.[S1] ^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.09 (d, 6H), 8.06 (d, 6H), 8.04 (s, 3H).



Scheme S3. Synthetic scheme of **L3**

Dimethyl 2'-hydroxy-5'-(4-(methoxycarbonyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (3). A mixture of 2,4,6-tribromophenol (**S4**, 3 g, 9.06 mmol), (4-(methoxycarbonyl)phenyl)boronic acid (**S3**, 14.6 g, 91.1 mmol), Na_2CO_3 (6.7 g, 63.2 mmol), $Pd(OAc)_2$ (200 mg, 5 mol%) were dissolved in distilled water (100 mL) and degassed DMF (100 mL), and heated to 60 °C overnight under nitrogen atmosphere. Afterwards, the reaction mixture was poured into water, and pH value was adjusted to ~ 5. The resulting crude was filtered and washed with water. The crude product was purified by flash column chromatography on silica gel using progressively more polar to 1:1 mixture of hexanes : EtOAc as the mobile phase to afford **3** as a pale pink solid (3.6 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.17 (d, 4H), 8.10 (d, 2H), 7.68 (m, 6H), 7.59 (s, 2H), 3.95 (s, 9H).

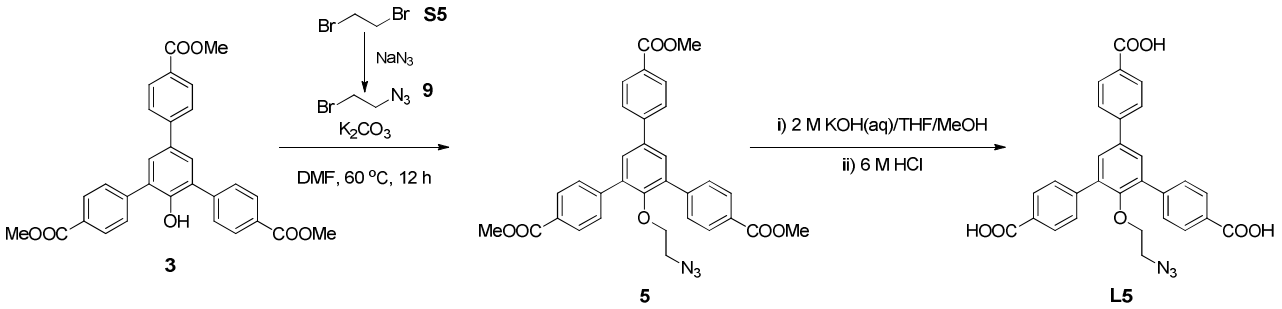
5'-(4-carboxyphenyl)-2'-hydroxy-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (L3). Compound **3** (500 mg) was hydrolyzed by following the *general procedure* described above to afford **L3** a light-brown solid (410 mg, 90%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 12.95 (s, 3H), 8.02 (d, 4H), 7.97 (d, 2H), 7.87 (d, 2H), 7.77 (d, 4H), 7.65 (s, 2H).



Scheme S4. Synthetic scheme of **L4**

Dimethyl 2'-amino-5'-(4-(methoxycarbonyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (4). A mixture of 2,4,6-tribromoaniline (**S4**, 3.3 g, 10.0 mmol), 4-(methoxycarbonyl)phenyl)boronic acid (**S3**, 7.2 g, 40.0 mmol), CsF (6.0 g, 40.0 mmol), $Pd(PPh_3)_4$ (578 mg, 5 mol%) were dissolved in degassed 1,2-dimethoxyethane (300 mL), and heated to 130 °C to reflux overnight for 3 d under nitrogen atmosphere. Afterward, the solvent was dried under reduced pressure. The residue was washed with distilled H_2O and then extracted with CH_2Cl_2 followed by drying with anhydrous $MgSO_4$. After the solvent was removed, the crude product was purified by flash column chromatography on a silica gel (hexanes: EtOAc = 5: 1) to afford **4** as a light brown solid (4.16 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (d, 4H), 8.08 (d, 2H), 7.66 (m, 6H), 7.45 (s, 2H), 3.96 (s, 9H).

2'-amino-5'-(4-carboxyphenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (L4). Compound **4** (500 mg) was hydrolyzed by following the *general procedure* described above to afford **L4** as a light-brown solid (435 mg, 95%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.10 (d, 4H), 7.98 (d, 2H), 7.85 (d, 2H), 7.74 (d, 4H), 7.52 (s, 2H), 4.74 (s, 2H).

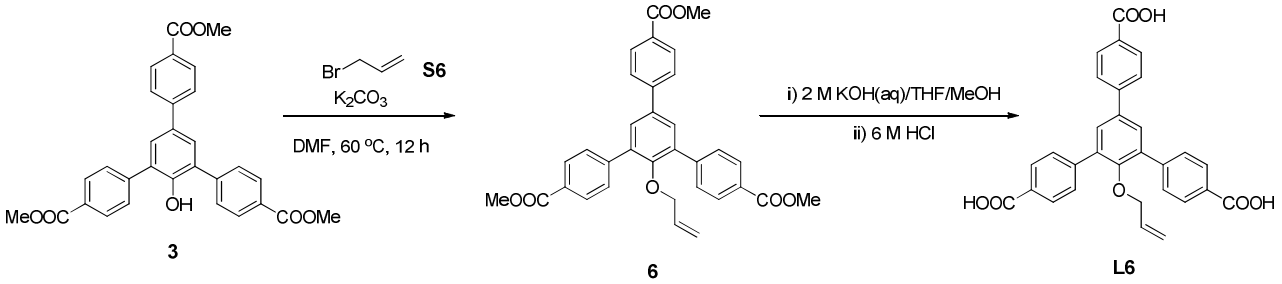


Scheme S5. Synthetic scheme of **L5**

1-azido-2-bromoethane (9). To dibromoethane (**S5**, 5 g, 27 mmol) dissolved in DMF (18 mL) sodium azide (1. 04 g, 16 mmol) was added portion-wise for 4 h. The reaction was then diluted with ether and the organic layer was washed with water. The organic layer was dried with $MgSO_4$ and concentrated under vacuum to afford **9** as a pale yellow oil (2.95 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.72-3.62 (m, 2H), 3.48 (t, 2H).

Dimethyl 2'-(2-azidoethoxy)-5'-(4-(methoxycarbonyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (5). To a solution of compound **3** (500 mg, 1.07 mmol) and K_2CO_3 (442.6 mg, 3.195 mmol) in DMF (8 mL) was added compound **9** (800 mg, 5.35 mmol). The mixture was stirred at 60 °C 12 hours, and water was added. Afterwards, the crude product was extracted with dichloromethane and dried under reduced pressure. The crude product was purified by flash column chromatography (hexanes: EtOAc = 6:1) to afford **5** as a pale yellow oil (574 mg, 95%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.08 (dd, 4H), 8.04 (d, 2H), 8.00 (d, 2H), 7.88 (dd, 4H), 7.83 (s, 2H), 3.96 (s, 9H), 3.13 (t, 2H), 3.05 (t, 2H).

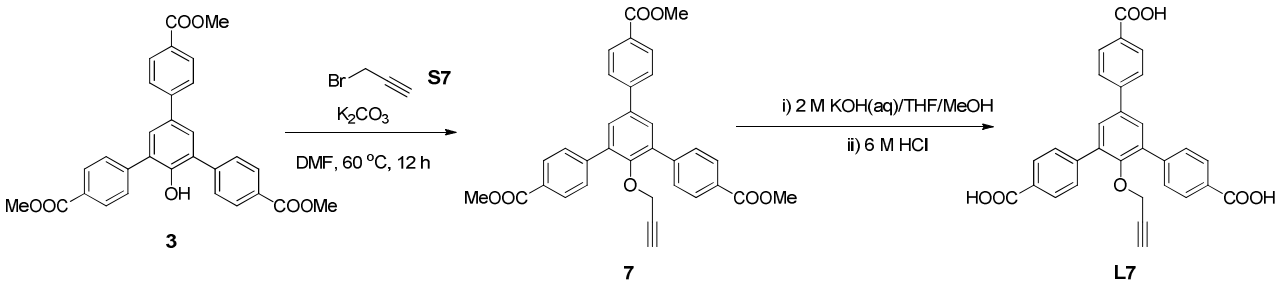
2'-(2-azidoethoxy)-5'-(4-carboxyphenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (L5).
Compound **5** (380 mg) was hydrolyzed by following the *general procedure* described above to afford **L5** as an ivory solid (350 mg, 99%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 13.04 (br, 3H), 8.05 (dd, 4H), 8.01 (d, 2H), 7.95 (d, 2H), 7.84 (dd, 4H), 7.79 (s, 2H), 3.52 (t, 1H), 3.32 (t, 1H), 3.13 (t, 1H), 3.05 (t, 1H).



Scheme S6. Synthetic scheme of **L6**

Dimethyl 2'-(allyloxy)-5'-(4-(methoxycarbonyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (6). To a solution of compound **3** (600 mg, 1.208 mmol) and K_2CO_3 (501 mg, 3.63 mmol) in DMF (8 mL) was added **S6** (365.4 mg, 3.02 mmol). The mixture was stirred at 65 °C 12 hours, and water was added. Afterwards, the crude product was extracted with dichloromethane and dried under reduced pressure. Resulting crude product was purified by flash column chromatography (hexanes: EtOAc = 6.5:1) to afford **7** as a white oil (520 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.11 (dd, 6H), 7.74 (d, 4H), 7.70 (d, 2H), 7.62 (d, 2H), 5.39 (qd, 1H), 4.89 (d, 1H), 4.84 (d, 1H), 3.96 (s, 9H), 3.74 (d, 2H).

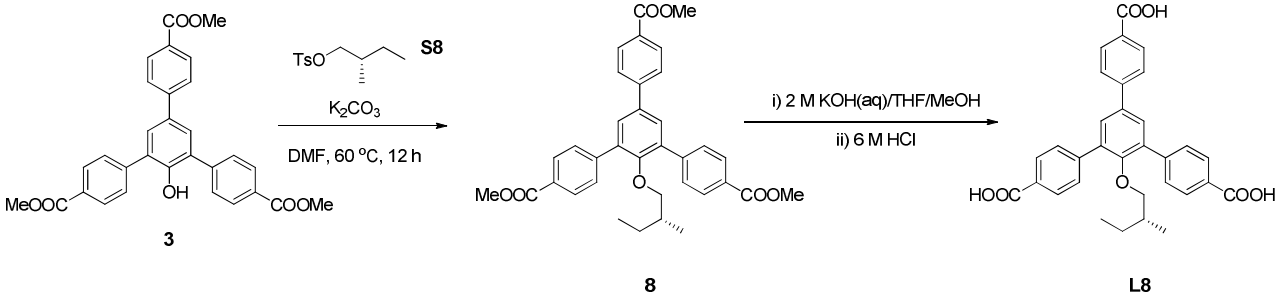
2'-(allyloxy)-5'-(4-carboxyphenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (L6).
Compound **6** (500 mg) was hydrolyzed by following the *general procedure* described above to afford **L6** a light-yellow solid (460 mg, 100%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 13.03 (br, 3H), 8.04 (d, 4H), 8.00 (dd, 2H), 7.95 (d, 2H), 7.83 (d, 4H), 7.78 (s, 2H), 5.40 (qd, 1H), 4.90 (d, 2H), 3.75 (d, 2H).



Scheme S7. Synthetic scheme of **L7**

Dimethyl 5'-(4-(methoxycarbonyl)phenyl)-2'-(prop-2-yn-1-yloxy)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (7). To a solution of compound **3** (500 mg, 1.07 mmol) and K_2CO_3 (414.6 mg, 3.21 mmol) in DMF (8 mL) was added **S7** (238 mg, 2.14 mmol). The mixture was stirred at 60 °C 12 hours, and water was added. Afterwards, the crude product was extracted with dichloromethane and dried under reduced pressure. Resulting crude product was purified by flash column chromatography (hexanes: EtOAc = 6:1) to afford **7** as a pale yellow oil (519 mg, 96%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.17-8.05 (m, 6H), 7.76 (d, 4H), 7.68 (d, 2H), 7.63 (d, 2H), 3.96 (s, 9H), 3.93 (s, 2H), 2.13 (s, 1H).

5'-(4-carboxyphenyl)-2'-(prop-2-yn-1-yloxy)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (L7). Compound **7** (510 mg) was hydrolyzed by following the *general procedure* described above to afford **L7** a light-yellow solid (465 mg, 99%). ^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.01 (m, 4H), 7.97 (d, 2H), 7.86 (d, 2H), 7.75 (d, 4H), 7.72 (s, 2H), 3.95 (d, 2H), 3.24 (t, 1H).

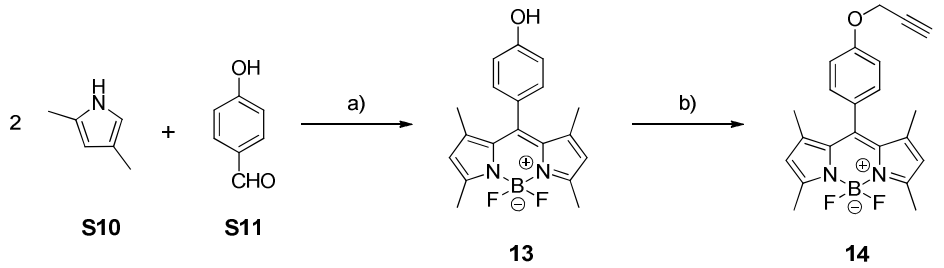


Scheme S8. Synthetic scheme of **L8**

(R)-dimethyl 5'-(4-(methoxycarbonyl)phenyl)-2'-(2-methylbutoxy)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate (8). To a solution of compound **3** (2.0 g, 4.28 mmol) and K_2CO_3 (0.7 g) in DMF (30 mL) was added **S8** (1.2 g). The resulting mixture was heated to 60 °C for 12h. The crude mixture was extracted with dichloromethane, washed thoroughly with water, and dried to afford **8** as an ivory powder (2.1 g, 93%). ^{1}H NMR ($CDCl_3$) δ = 8.11 (m, 6H), 7.72 (m, 6H), 7.61 (s, 2H), 3.95 (m, 9H), 3.05 (m, 2H), 1.24 (m, 1H), 1.01 (m, 1H), 0.78 (m, 1H), 0.49 (m, 6H).

(R)-5'-(4-carboxyphenyl)-2'-(2-methylbutoxy)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylic acid (L8). Compound **8** (500 mg) was hydrolyzed by following the *general procedure* described above to afford **L8** a white solid (400 mg, 86%). ^{1}H NMR (500 MHz, DMSO-d_6) = 13.01 (br, 3H), 8.02 (m, 6H), 7.94 (d, 2H), 7.81 (d, 4H), 7.78 (s, 2H), 3.05-2.98 (ddd, 2H), 0.95 (m, 1H), 0.76 (m, 2H) ,0.46 (d, 3H) ,0.37 (t, 3H).

(b) Synthesis of clickable dyes



Scheme S9. Synthetic scheme of **14**. Reagents and conditions a) i) TFA, THF, 12 h, r.t., ii) DDQ, CH_2Cl_2, 5 h, r.t., iii) TEA, $BF_3{\cdot}OEt_2$, 12 h, r.t., 49%; b) propargyl bromide, K_2CO_3, acetone, 12 h, reflux

5,5-difluoro-10-(4-hydroxyphenyl)-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (13). To a solution of **S11** (1 g, 8.19 mmol) and 2,4-dimethylpyrrole (1.85 mL, 18.02 mmol) in THF (150 mL) was added several drops of trifluoroacetic acid under a nitrogen atmosphere. The mixture was stirred at ambient temperature for 6 h, and the solution of 2,3-dichloride-5,6-dicyano-p-benzoquinone (2.05 g, 9.01 mmol) in THF (100 mL) was added. The resulting mixture was stirred continuously for another 5 h. After the addition of triethylamine (25 mL) and $BF_3{\cdot}OEt_2$ (31 mL) dropwise to the reaction mixture with an ice-water bath, the mixture was kept stirring at ambient temperature overnight, then filtered through Celite. The crude compound was washed with CH_2Cl_2 and the combined filtrate was evaporated to dryness. The residue was re-dissolved in CH_2Cl_2 and the solution was washed with 15% aqueous $NaHCO_3$ solution followed by water. The organic portion was dried over anhydrous $MgSO_4$, then evaporated. The crude product was purified by column chromatography on silica gel using progressively more polar 50:1 to 9:1 (hexanes: EtOAc) as a mobile phase to afford **13** as an orange solid (1.2 g, 43%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.15 (d, 2H), 6.97 (d, 2H), 5.99 (s, 2H), 4.95 (br, 1H), 2.56 (s, 6H), 1.45 (s, 6H).

5,5-difluoro-1,3,7,9-tetramethyl-10-(4-(prop-2-yn-1-yloxy)phenyl)-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (14). To a solution of compound **13** (300 mg, 0.882 mmol), K_2CO_3 (609.5 mg, 4.41 mmol) in dried acetone (100 mL) was added propargyl bromide (524 mg, 4.41 mmol). The mixture was heated to 55 °C and stirred for 12 h. Resulting mixture was evaporated to dryness and purified by column chromatography on silica gel using progressively more polar 50:1 to 15:1 (hexanes: EtOAc) as an eluent to afford **14** as a deep pink solid (175 mg, 53%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 (d, 2H), 7.09 (d, 2H), 5.98 (s, 2H), 4.76 (d, 2H), 2.55 (s, 6H), 2.17 (s, 1H), 1.42 (s, 6H).

3. Synthesis of PCN-333(M) (M = Fe, Sc)

Synthesis of PCN-333(Fe): To a mixture of H_3TATB (60 mg) and anhydrous $FeCl_3$ (60 mg) 10 mL DEF and trifluoroacetic acid (0.6 mL) were added. The mixture was heated to 150 °C in a pre-heated oven for 12 h until brown precipitate formed. Resulting brown precipitate was centrifuged and washed with fresh DMF for several times. Yield (based on ligand) = ~ 85%.

Synthesis of PCN-333(Sc): To a mixture of H_3TATB (80 mg) and anhydrous $ScCl_3{\cdot}6H_2O$ (200 mg) 10 mL DMF was added. The mixture was heated to 150 °C in a pre-heated oven for 2 h until white precipitate formed. Resulting precipitate was centrifuged and washed with fresh DMF for several times. Yield (based on ligand) = ~ 85%.

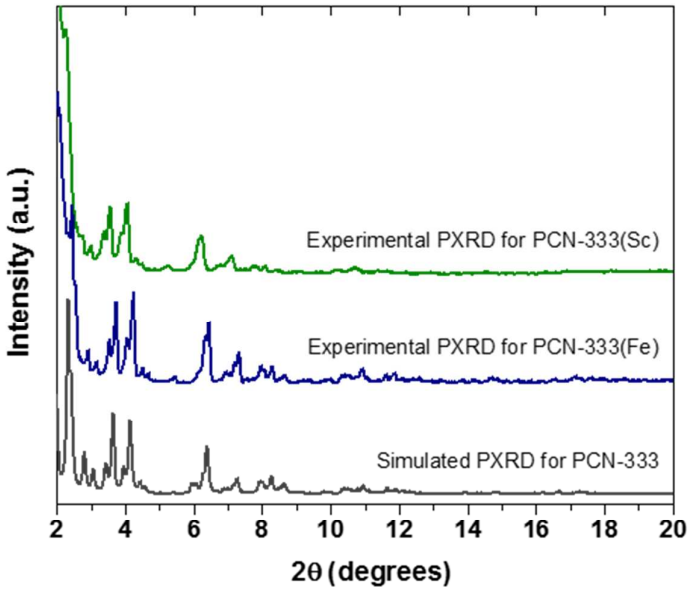


Figure S1. PXRD patterns of synthesized materials

4. Comparison of ligand exchange via ^{1}H NMR analysis

General procedure for digestion. Approximately 15 mg of each ligand exchanged PCN-333(Fe) sample was digested with 37% HCl, refluxed overnight, and washed with water until neutral pH. DMSO-d_6 (0.6 ml) was added to dissolve the ligands. ^{1}H NMR spectrum (500 MHz) of exchanged PCN-333(Fe) samples were collected at room temperature (~ 21 °C). The integration was done by setting aromatic hydrogen atoms in TATB as an absolute reference for BTB and BTB derivatives. The ratios between TATB and BTB were calculated by comparing the integrals of their aromatic hydrogens.

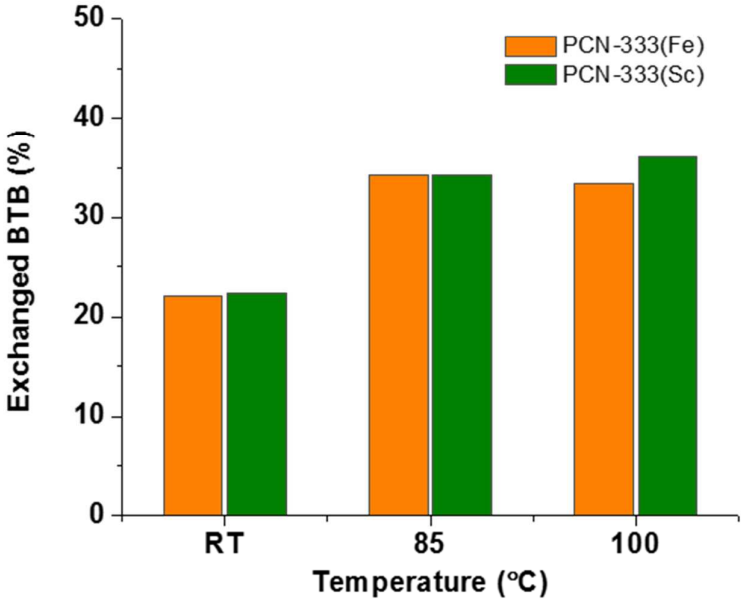


Figure S2. Comparison of BTB exchange ratio (%) in PCN-333(Fe) and PCN-333(Sc) incubated at different temperatures. Incubation time = 24 h. Data points are averages of three independent measurements.

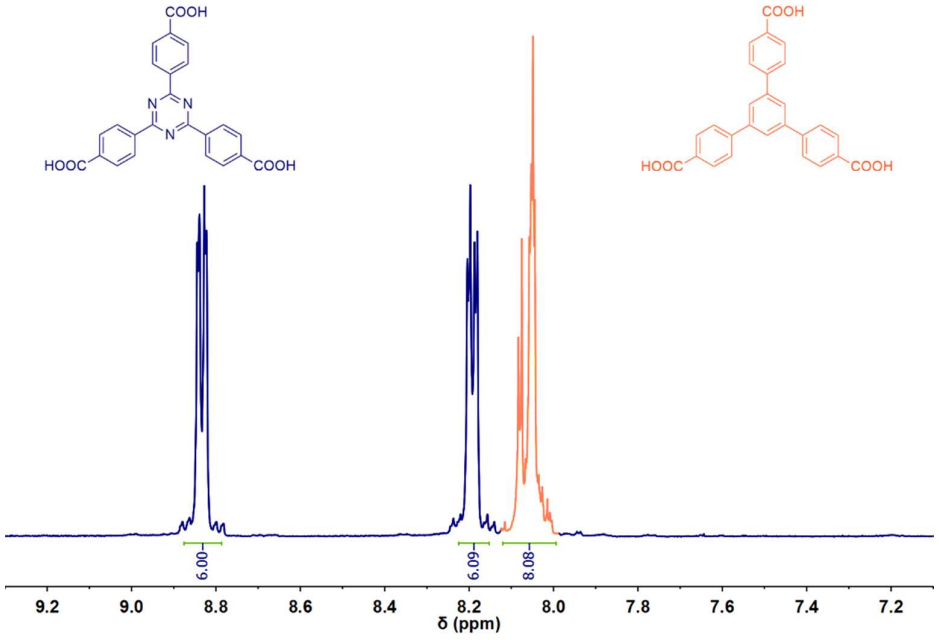


Figure S3. Partial ^{1}H NMR (DMSO-d_6) spectrum of digested MOF. (PCN-333(Fe) partially exchanged with BTB)

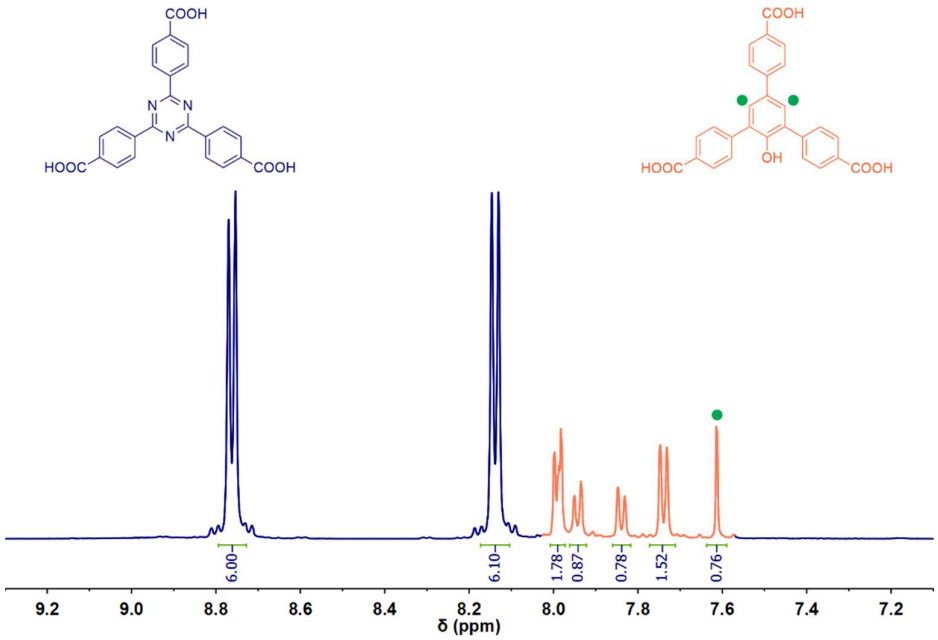


Figure S4. Partial ^{1}H NMR (DMSO-d_6) spectrum of digested MOF. (PCN-333(Fe) partially exchanged with OH-BTB)

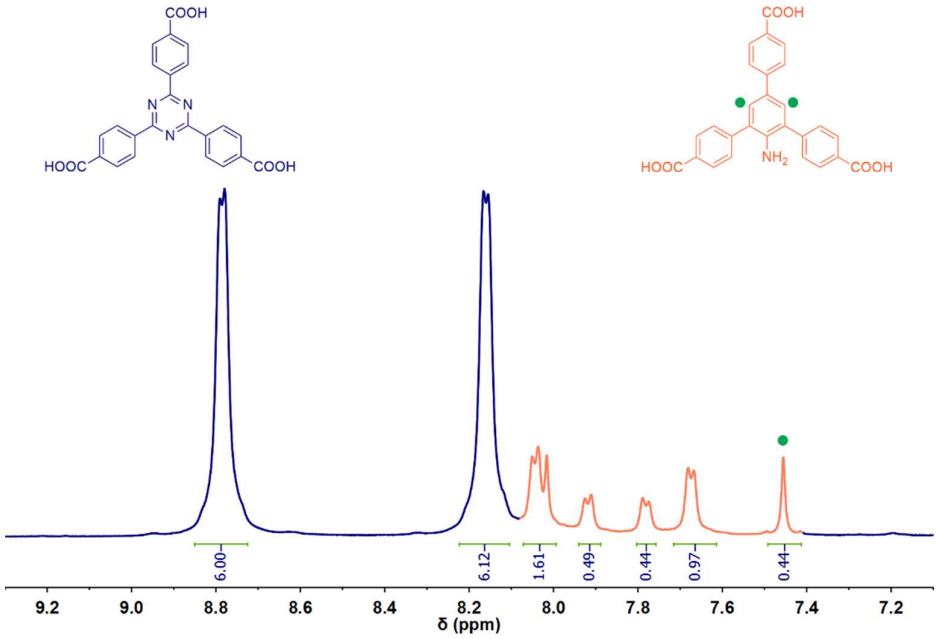


Figure S5. Partial ^{1}H NMR (DMSO-d_6) spectrum of digested MOF. (PCN-333(Fe) partially exchanged with NH_2-BTB)

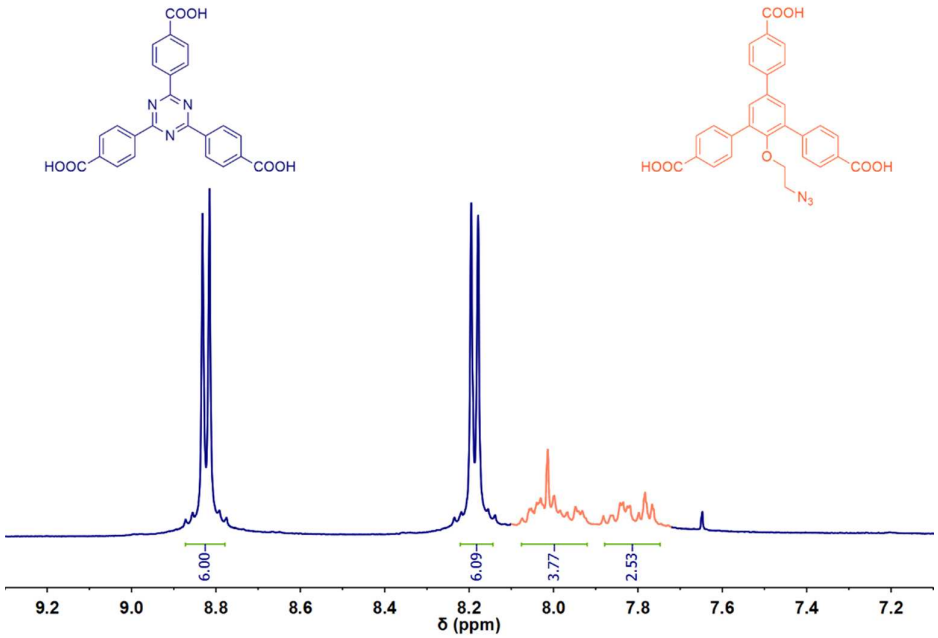


Figure S6. Partial ^{1}H NMR (DMSO-d_6) spectrum of digested MOF. (PCN-333(Fe) partially exchanged with azide-BTB)

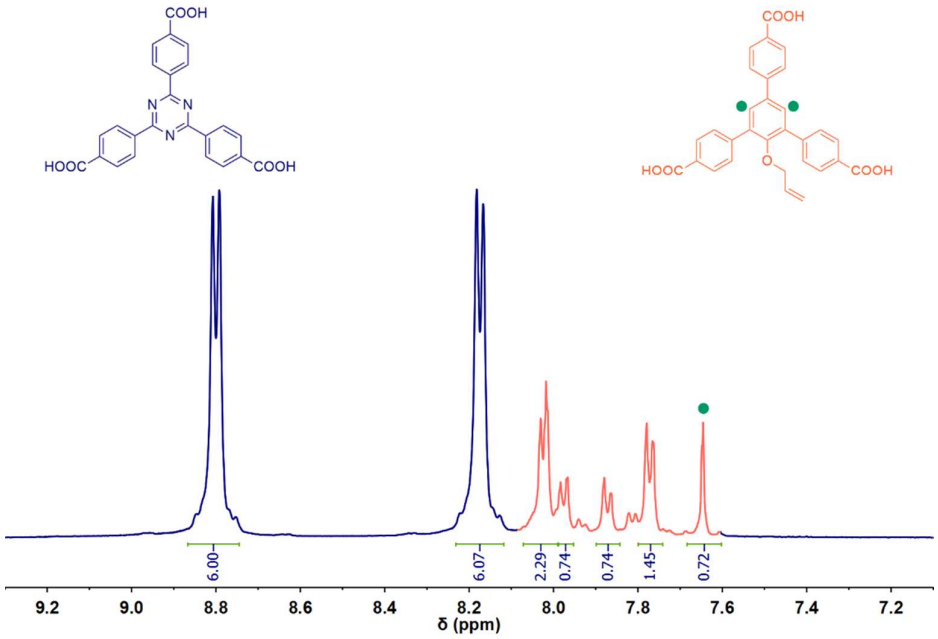


Figure S7. Partial ^{1}H NMR (DMSO-d_6) spectrum of digested MOF. (PCN-333(Fe) partially exchanged with alkene-BTB)

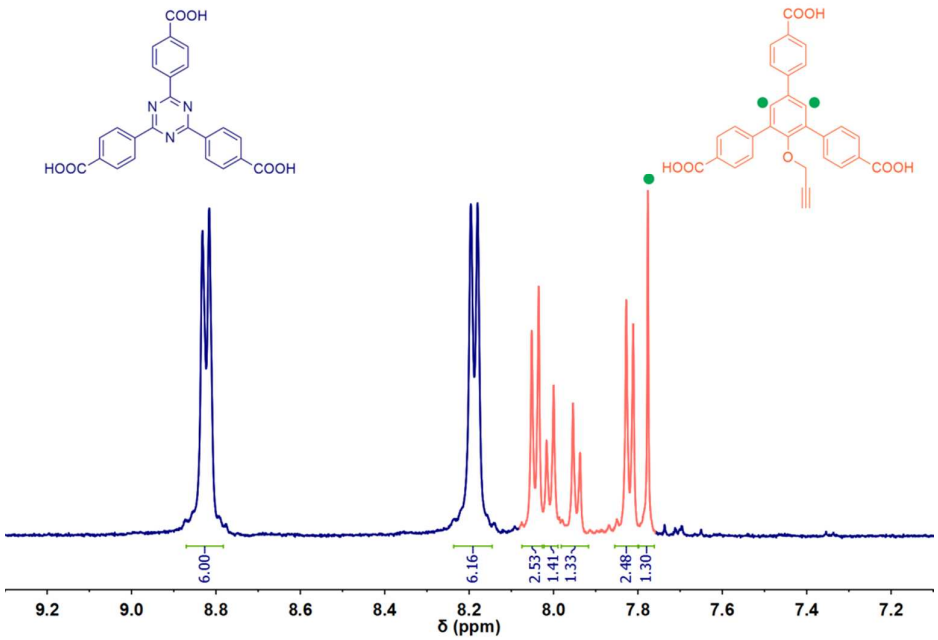


Figure S8. Partial ^{1}H NMR (DMSO-d_6) spectrum of digested MOF. (PCN-333(Fe) partially exchanged with alkyne-BTB)

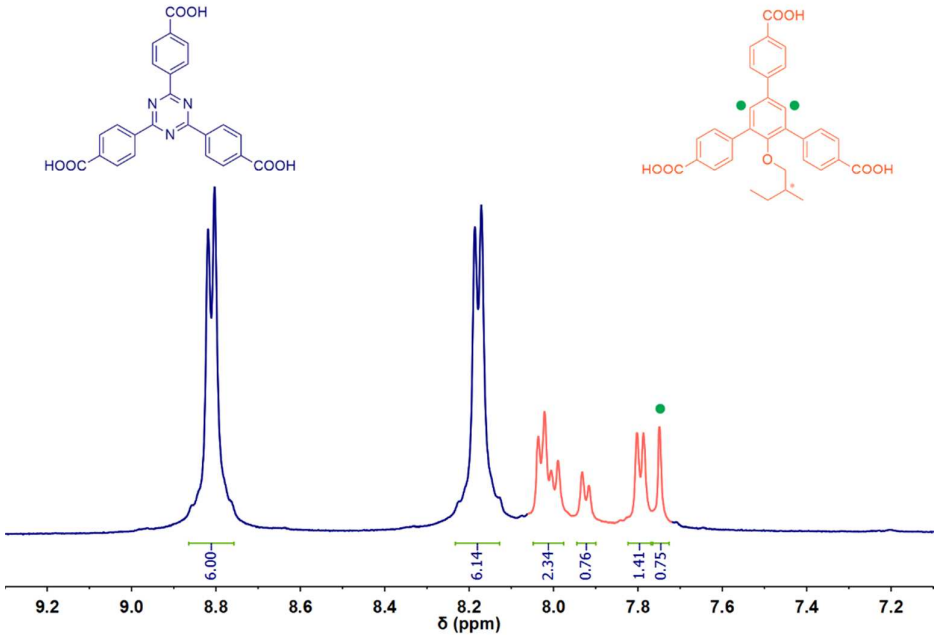


Figure S9. Partial ^{1}H-NMR (DMSO-d_6) spectrum of digested MOF. (PCN-333(Fe) partially exchanged with chiral-BTB)

5. Brunauer-Emmett-Teller (BET) surface area, pore volume, and pore size distribution calculation

Sample activation procedure. Thoroughly washed samples underwent solvent exchange with acetone several times and dried in a pre-heated 85 °C oven for 30 min. Resulting powder was then activated for BET measurement at 150 °C for 5 h.

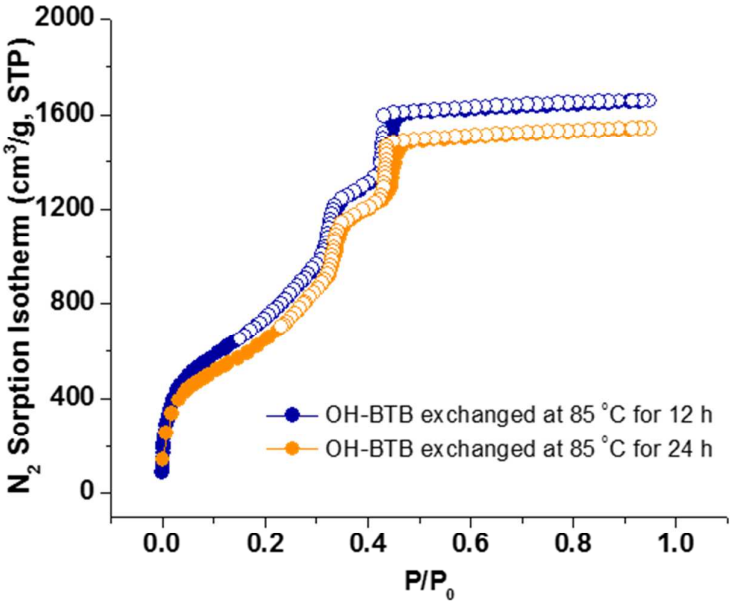


Figure S10. Nitrogen sorption isotherm of OH-BTB exchanged PCN-333(Fe) at 77 K. Ligand exchange was performed for different incubation time at 85 °C.

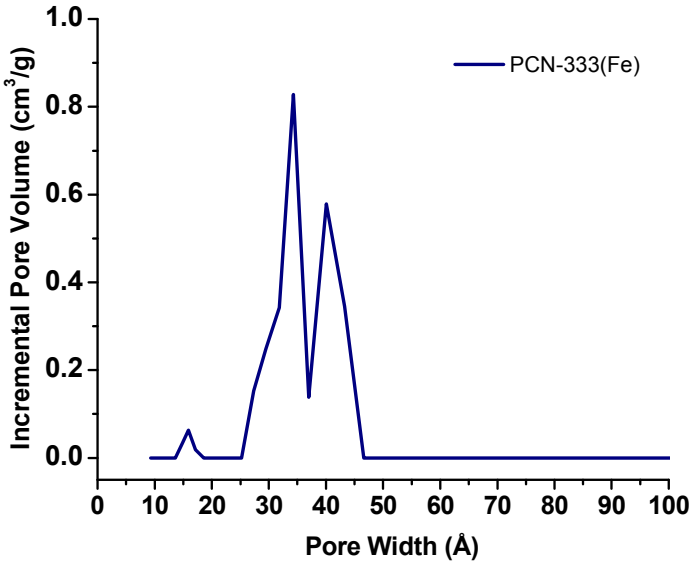


Figure S11. DFT pore size distribution for PCN-333(Fe) obtained from N_2 sorption isotherm at 77 K.

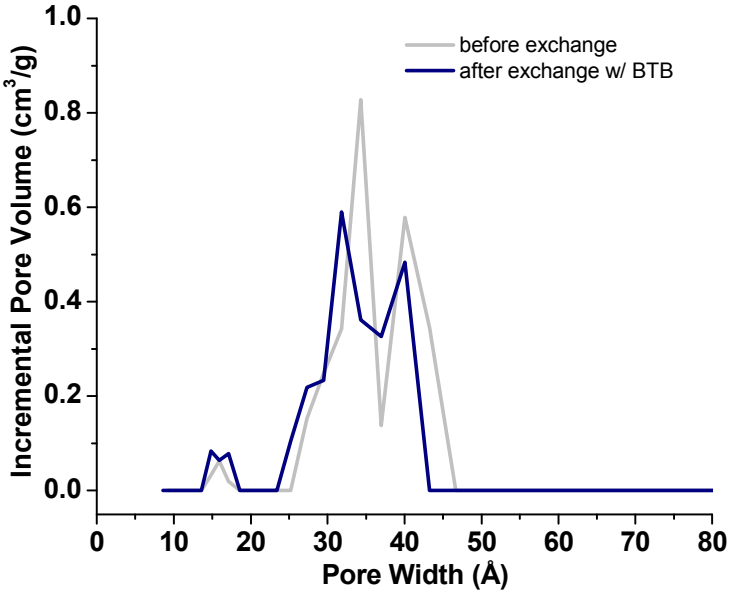


Figure S12. DFT pore size distribution for BTB exchanged PCN-333(Fe) obtained from N_2 sorption isotherm at 77 K.

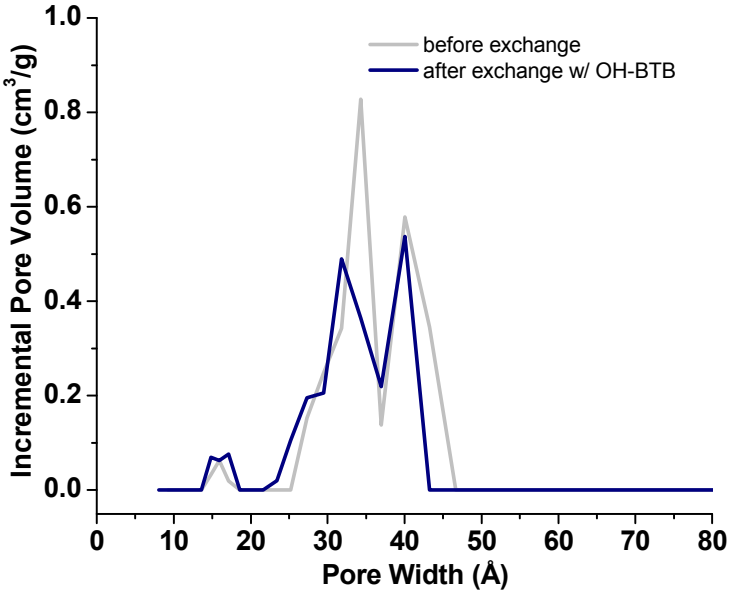


Figure S13. DFT pore size distribution for OH-BTB exchanged PCN-333(Fe) obtained from N_2 sorption isotherm at 77 K.

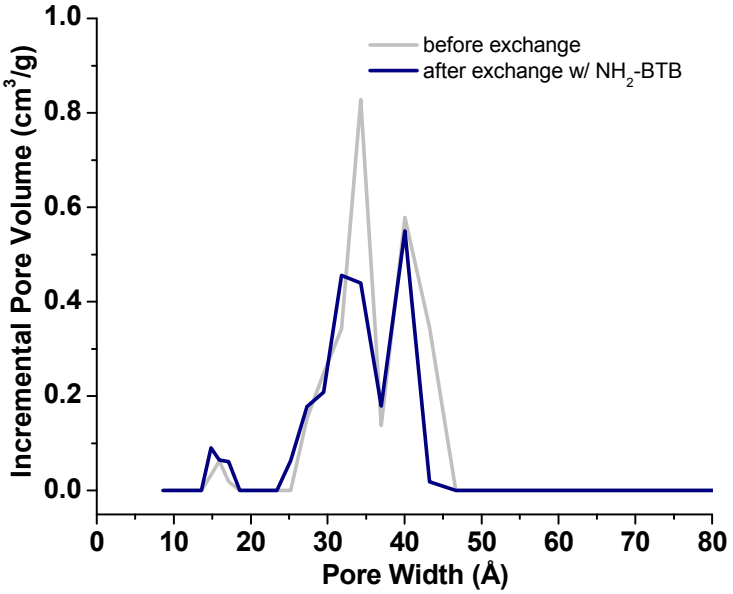


Figure S14. DFT pore size distribution for NH_2-BTB exchanged PCN-333(Fe) obtained from N_2 sorption isotherm at 77 K.

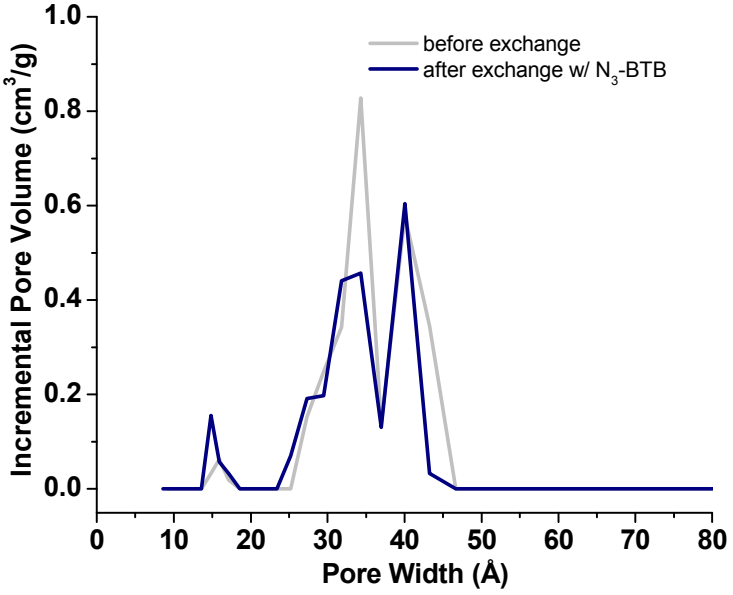


Figure S15. DFT pore size distribution for azide-BTB exchanged PCN-333(Fe) obtained from N_2 sorption isotherm at 77 K.

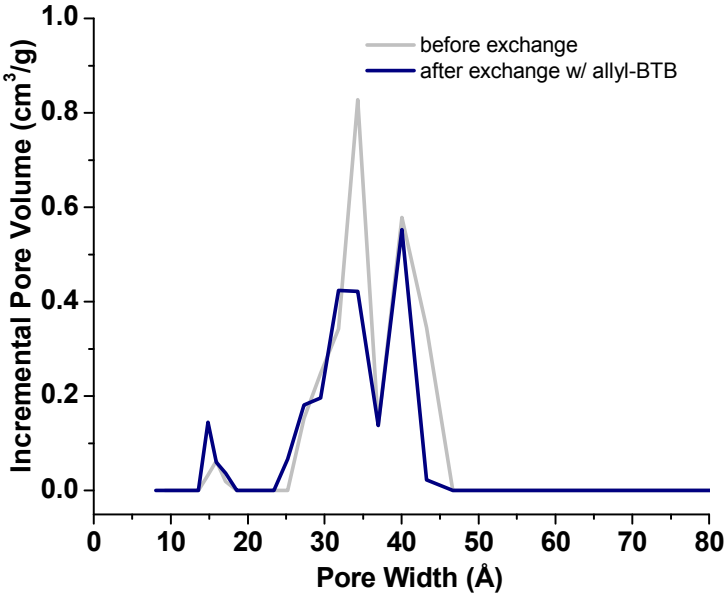


Figure S16. DFT pore size distribution for alkene-BTB exchanged PCN-333(Fe) obtained from N_2 sorption isotherm at 77 K.

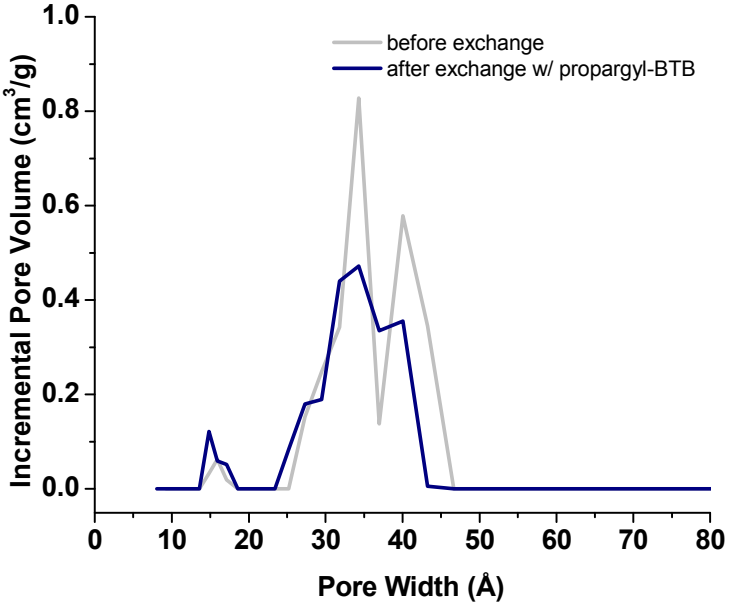


Figure S17. DFT pore size distribution for alkyne-BTB exchanged PCN-333(Fe) obtained from N_2 sorption isotherm at 77 K.

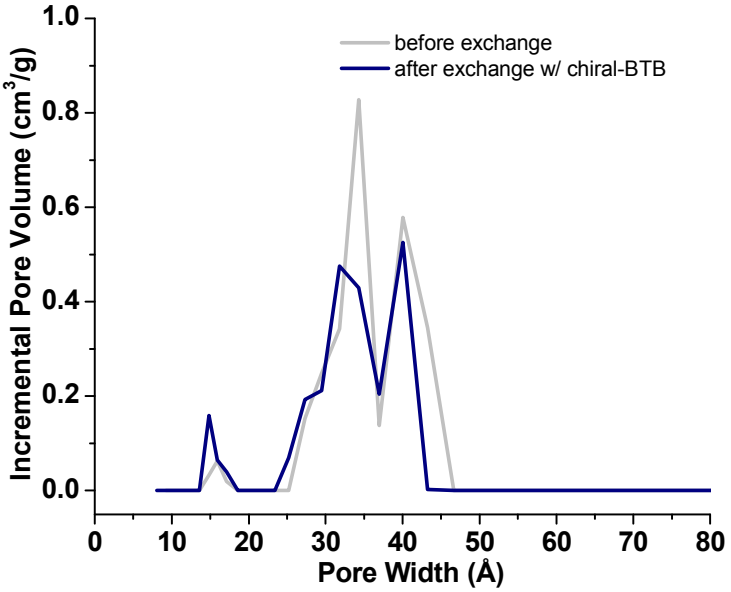


Figure S18. DFT pore size distribution for chiral-BTB exchanged PCN-333(Fe) obtained from N_2 sorption isotherm at 77 K.

Ligand	Theoretical pore volume (cm^3/g)	Experimental pore volume (cm^3/g)
TATB (PCN-333)	3.55	2.88
BTB	N/A	2.76
OH-BTB	N/A	2.49
NH_2-BTB	N/A	2.47
azide-BTB	N/A	2.53
alkene-BTB	N/A	2.39
alkyne-BTB	N/A	2.54
chiral-BTB	N/A	2.52

Table S1. Experimental pore volume obtained from N_2 sorption isotherm at 77 K.

6. IR spectra of ligand exchanged PCN-333(Fe)

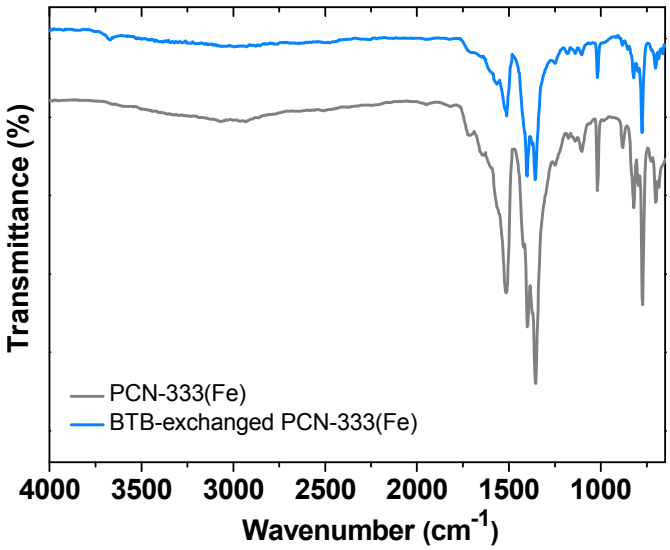


Figure S19. IR spectra of BTB exchanged PCN-333(Fe).

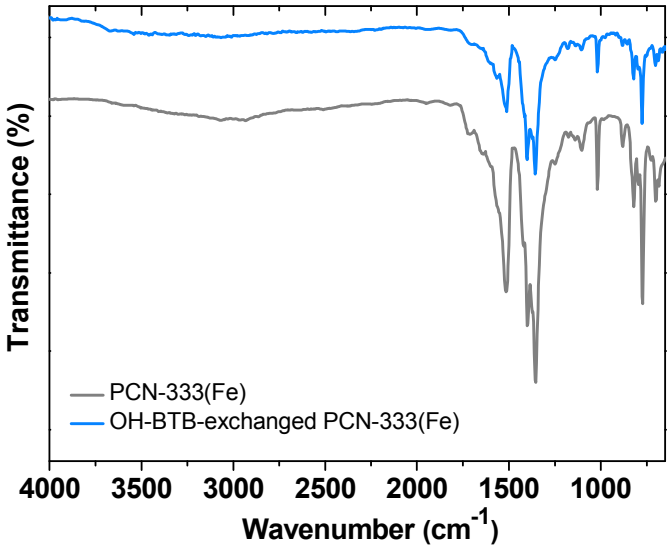


Figure S20. IR spectra of OH-BTB exchanged PCN-333(Fe).

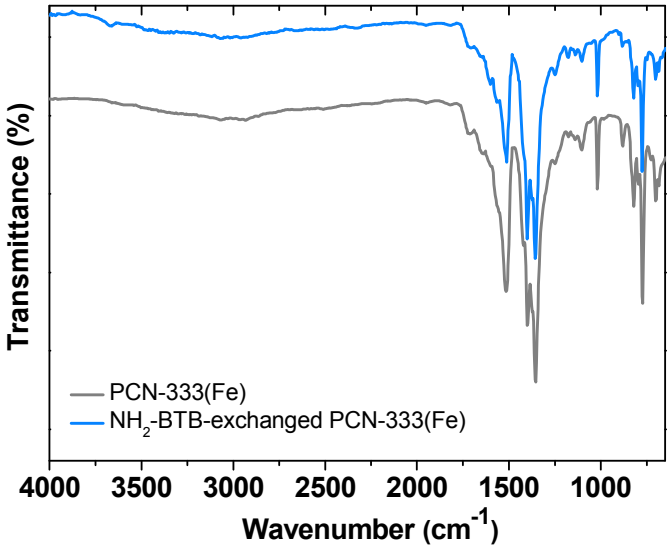


Figure S21. IR spectra of NH_2-BTB exchanged PCN-333(Fe).

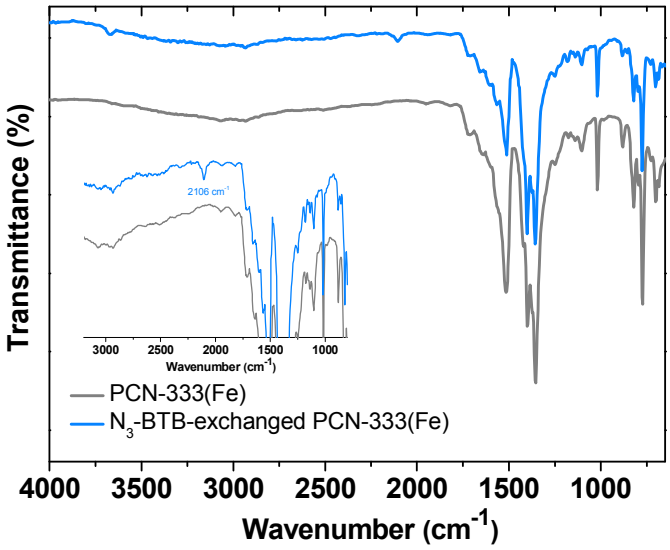


Figure S22. IR spectra of azide-BTB exchanged PCN-333(Fe). Inset: magnification of characteristic azide group stretching band at ~ 2100 cm^{-1}.

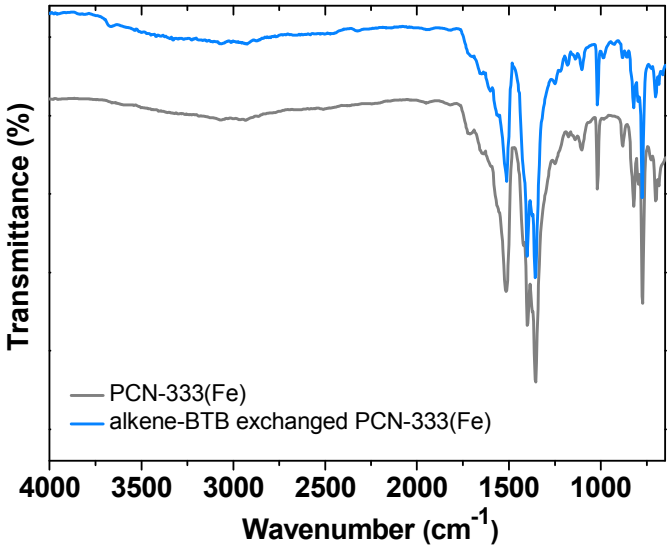


Figure S23. IR spectra of alkene-BTB exchanged PCN-333(Fe).

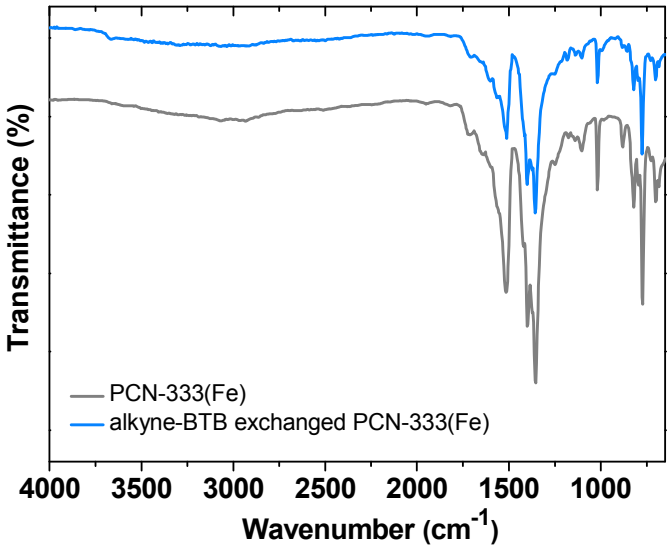


Figure S24. IR spectra of alkyne-BTB exchanged PCN-333(Fe).

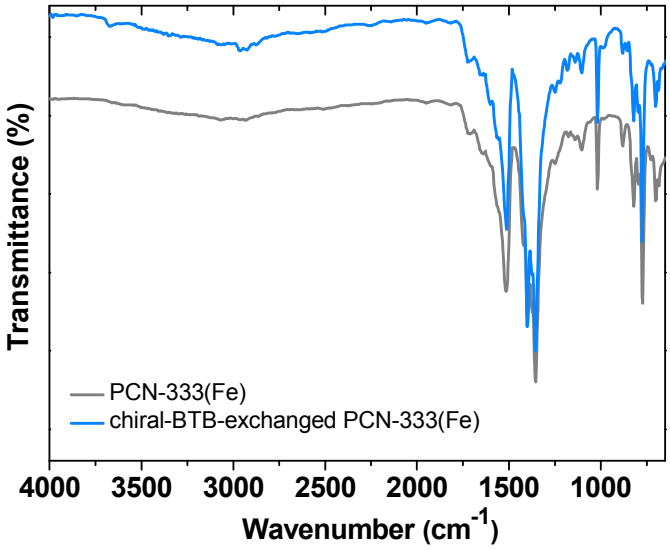


Figure S25. IR spectra of chiral-BTB exchanged PCN-333(Fe).

7. Click chemistry with azide-functionalized PCN-333(Fe)

Click Reaction with methyl propiolate: Methyl propiolate (200 μL) was added to a mixture of azide-BTB exchanged PCN-333(Fe) (6 mg) and CuI (0.5 mg) in DMF (2.0 ml) in a 4 mL vial. The reaction mixture was stirred at 60 °C for 20 h. The resulting precipitate was collected by centrifugation, washing thoroughly with DMF followed by acetone, and dried to afford light brown solid in quantitative yield.

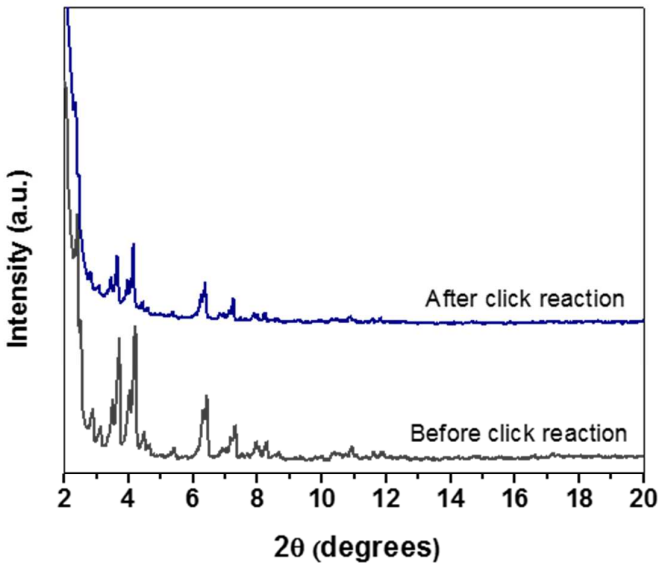


Figure S26. Comparison of PXRD patterns of before/after click reaction of methyl propiolate and azide-BTB exchanged PCN-333(Fe).

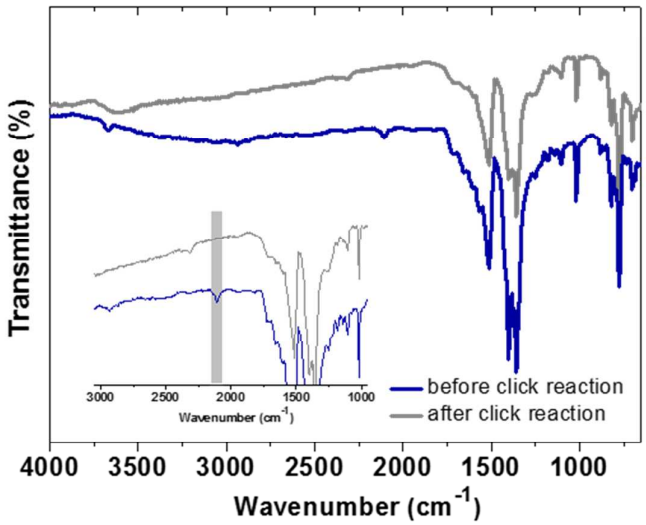


Figure S27. Full IR spectra of before/after click reaction of methyl propiolate and azide-BTB exchanged PCN-333(Fe)

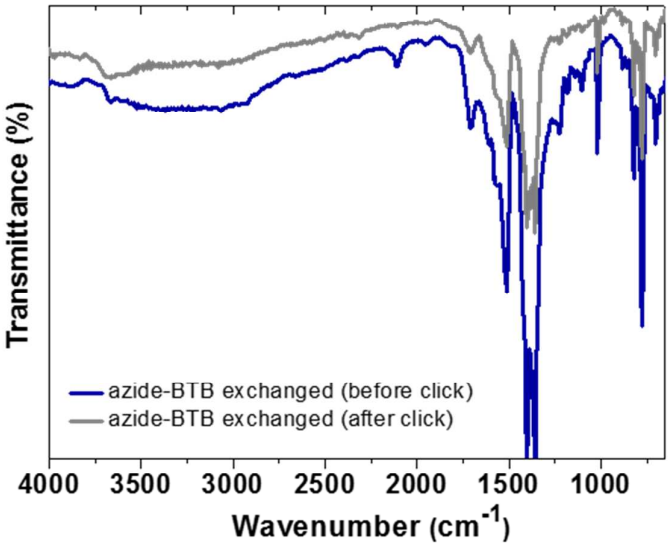


Figure S28. Full IR spectra of before/after click reaction of **14** and azide-BTB exchanged PCN-333(Fe)

8. Click chemistry with azide-functionalized PCN-333(Sc)

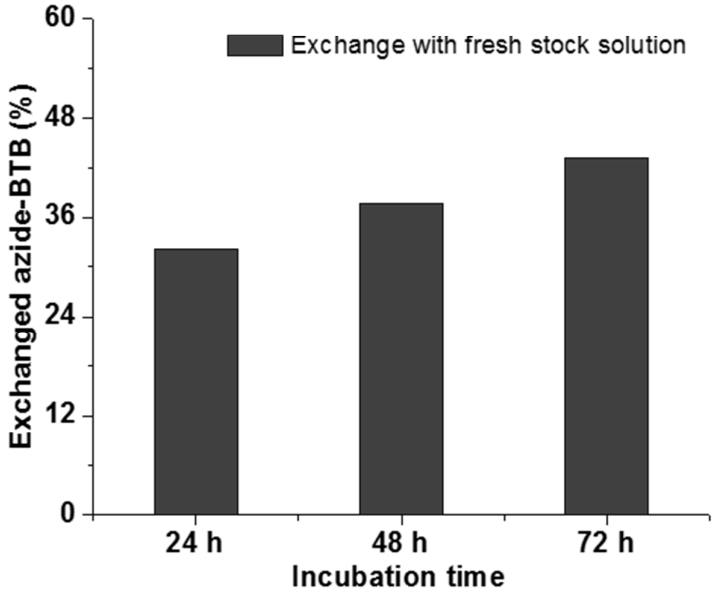


Figure S29. Azide-BTB exchange ratio (%) in PCN-333(Sc) for different incubation times.

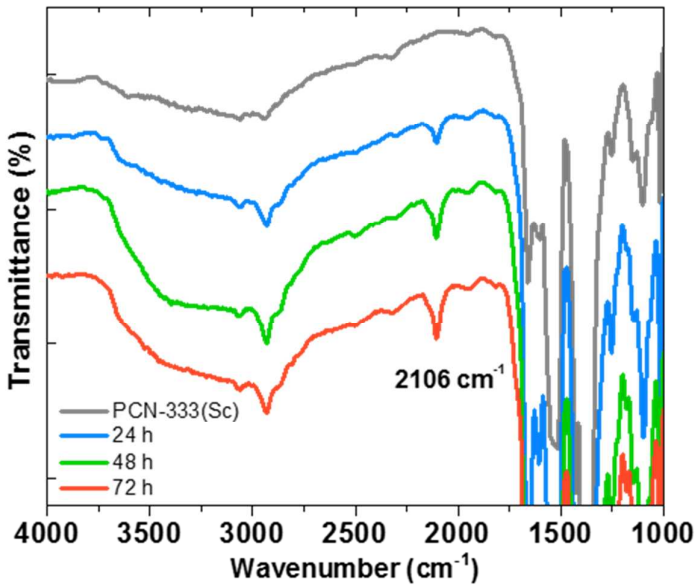


Figure S30. IR spectra of azide-BTB exchanged PCN-333(Sc) that having different ratios of azide-BTB.

Click Reaction with BODIPY: Compound **14** (5 mg) was added to a mixture of azide-BTB exchanged PCN-333(Sc) (10 mg) and CuI (0.5 mg) in THF (1.0 ml) in a 4 mL vial. The reaction mixture was stirred at 60 °C for 20 h. The resulting precipitate was collected by centrifugation, washing thoroughly with DMF followed by acetone, and dried to afford light brown solid in quantitative yield.

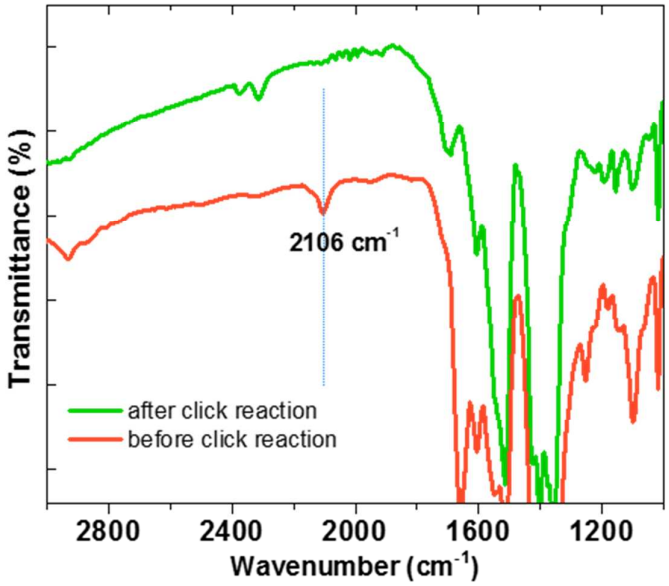


Figure S31. IR spectra of azide-BTB exchanged PCN-333(Sc) that having different ratios of N_3-BTB.

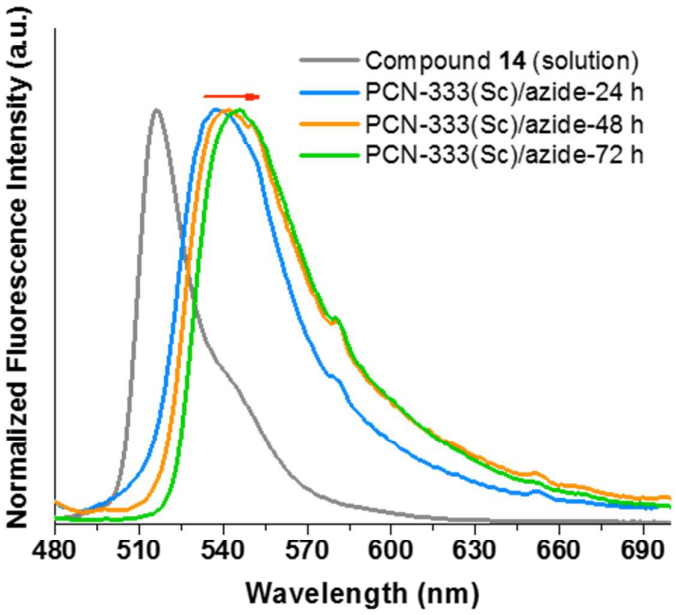


Figure S32. Fluorescence emission spectra of azide-BTB exchanged PCN-333(Sc) and **14** clicked MOFs in acetone. λ_{ex} = 450 nm.

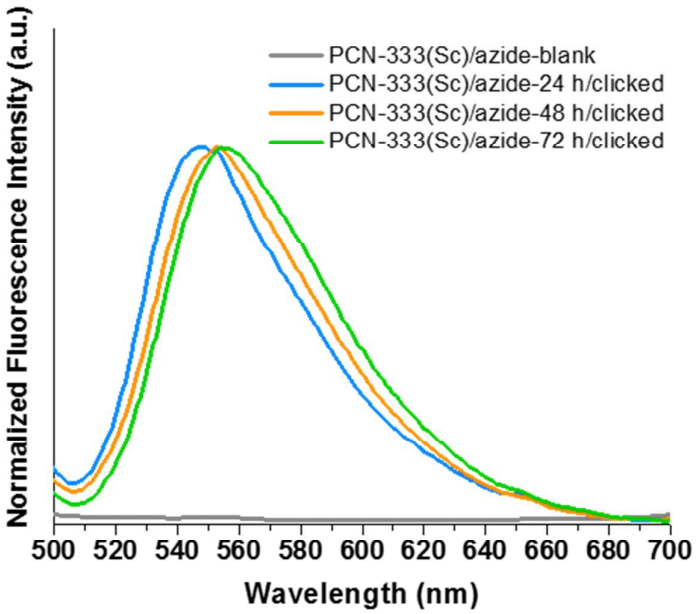


Figure S33. Solid-state fluorescence emission spectra of azide-BTB exchanged PCN-333(Sc) and **14** clicked MOFs. λ_{ex} = 450 nm.

9. Reversibility test

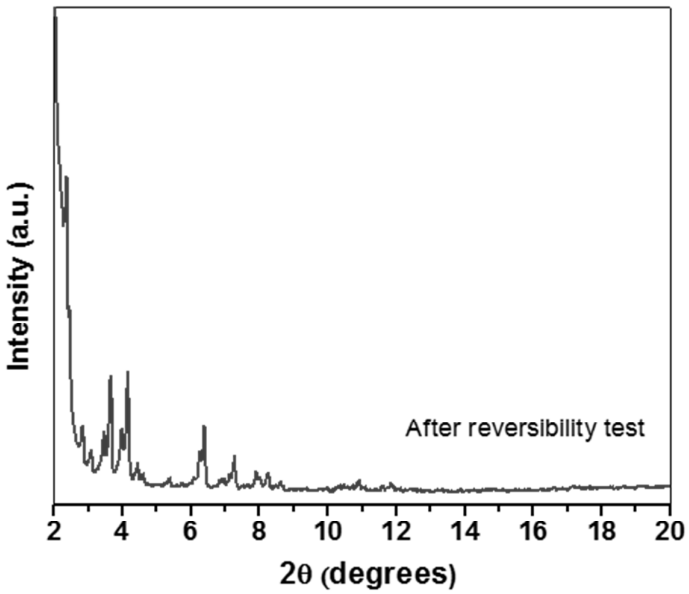


Figure S34. PXRD patterns of BTB exchanged PCN-333(Fe) after reversibility test with excess TATB.

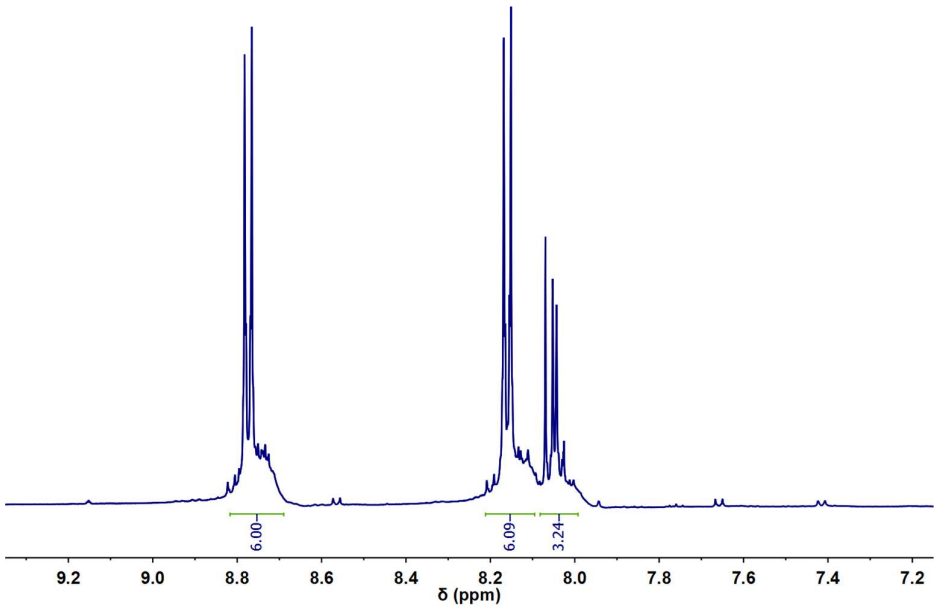


Figure S35. Partial ^{1}H NMR spectrum (DMSO-d_6) of supernatant from reversibility test.

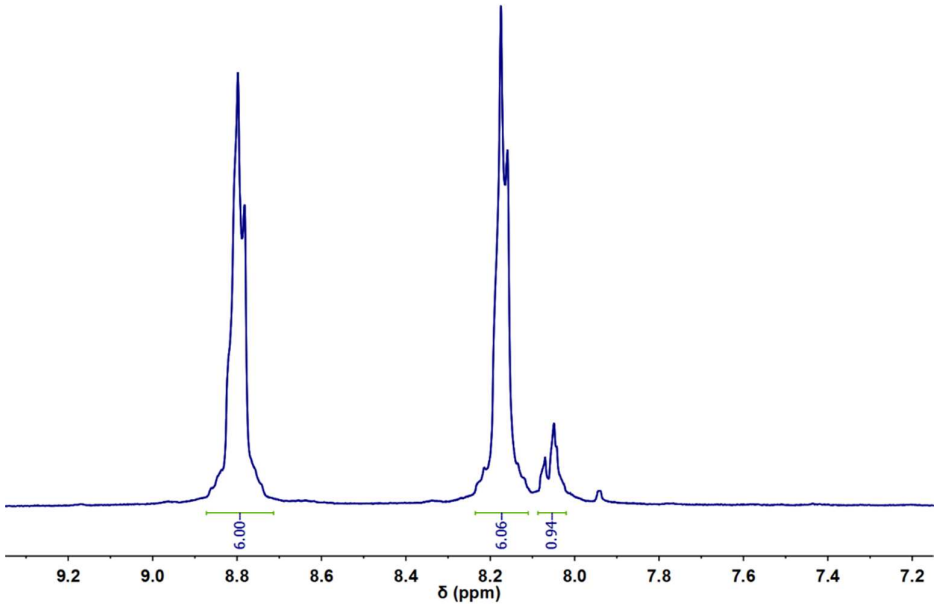


Figure S36. Partial ^{1}H NMR spectrum (DMSO-d_6) of digested MOF.

10. TGA trace of the samples

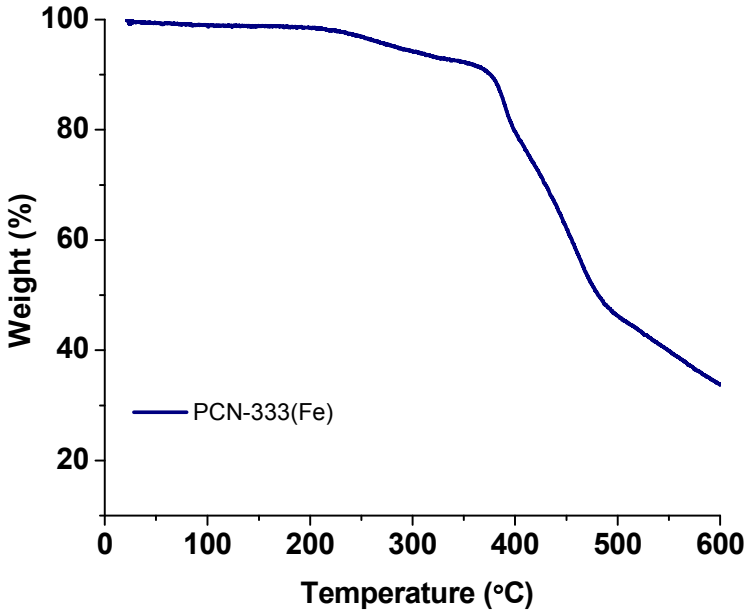


Figure S37. TGA trace for PCN-333(Fe).

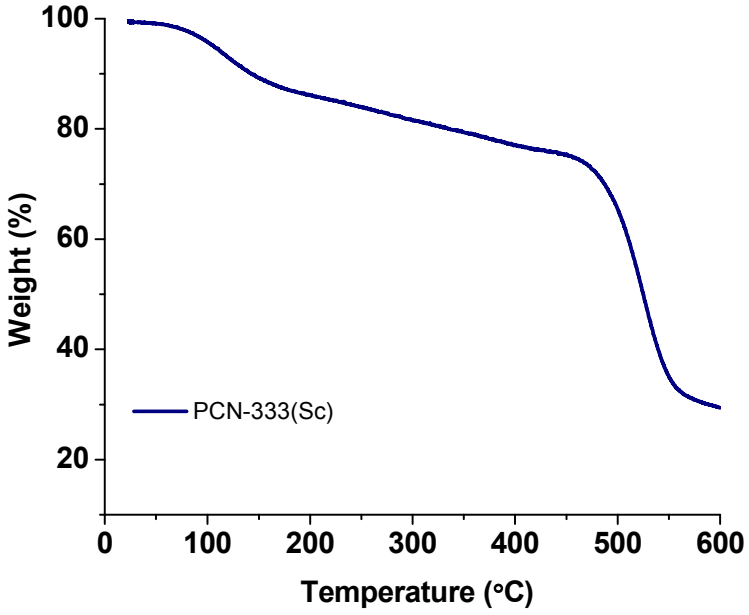


Figure S38. TGA trace for PCN-333(Sc).

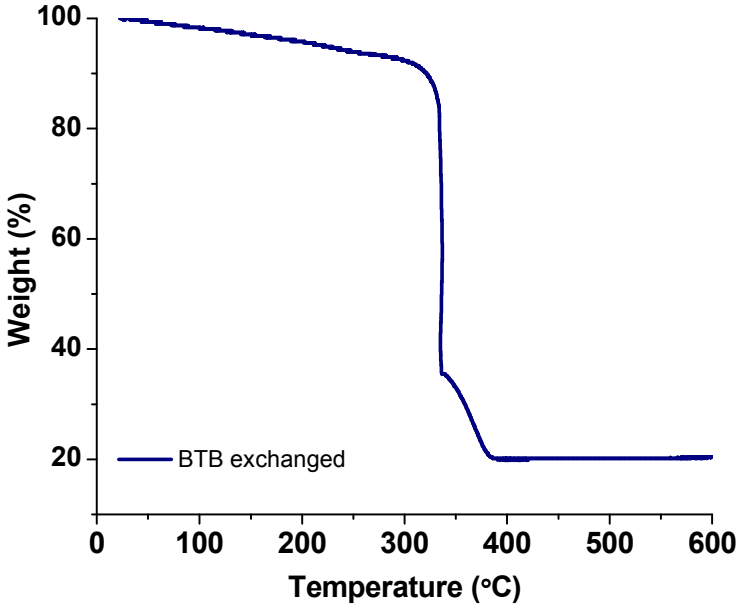


Figure S39. TGA trace for BTB exchanged PCN-333(Fe).

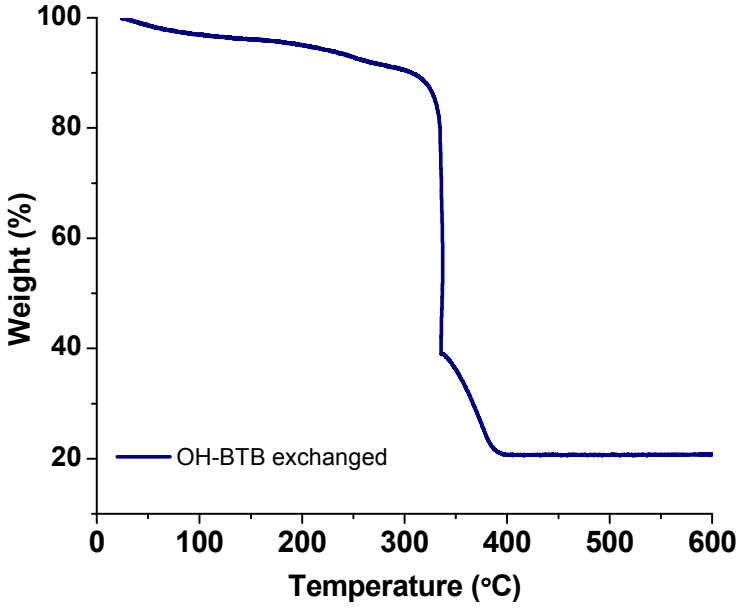


Figure S40. TGA trace for OH-BTB exchanged PCN-333(Fe).

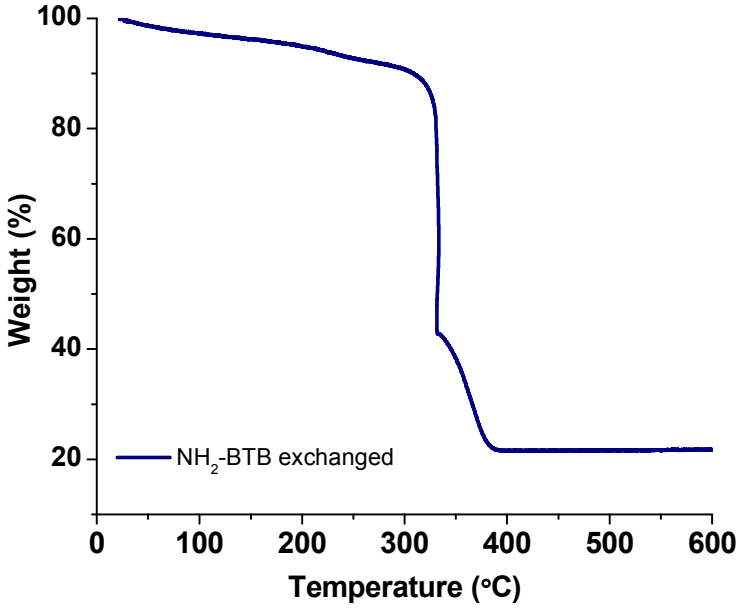


Figure S41. TGA trace for NH_2-BTB exchanged PCN-333(Fe).

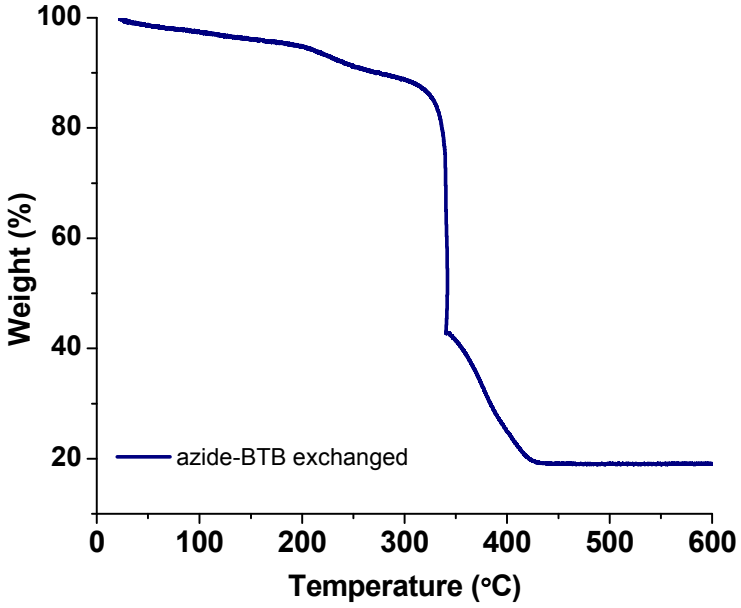


Figure S42. TGA trace for azide-BTB exchanged PCN-333(Fe).

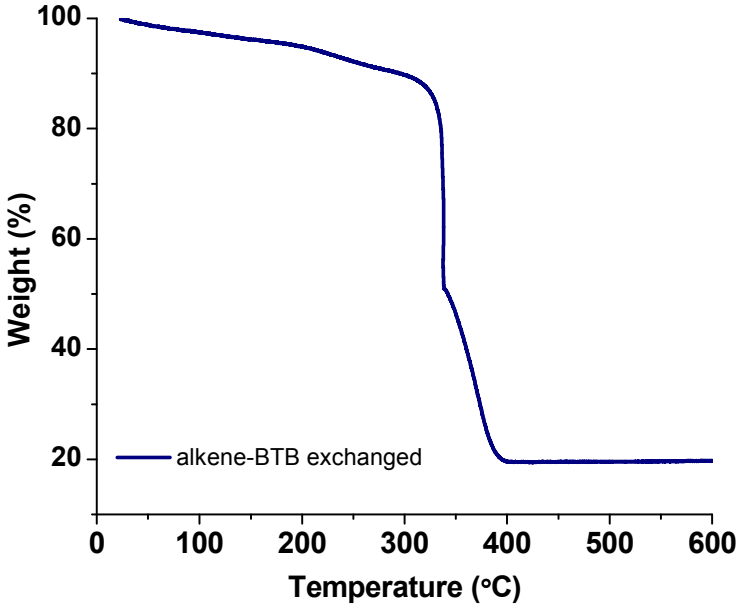


Figure S43. TGA trace for alkene-BTB exchanged PCN-333(Fe).

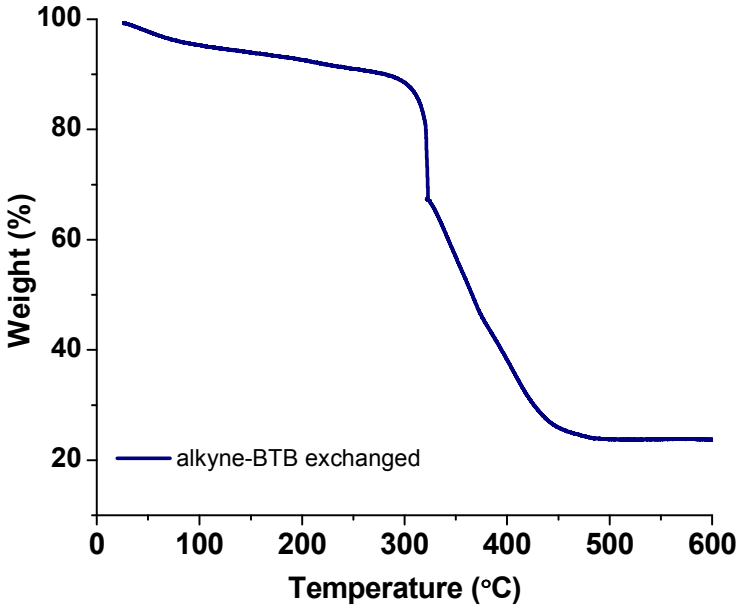


Figure S44. TGA trace for alkyne-BTB exchanged PCN-333(Fe).

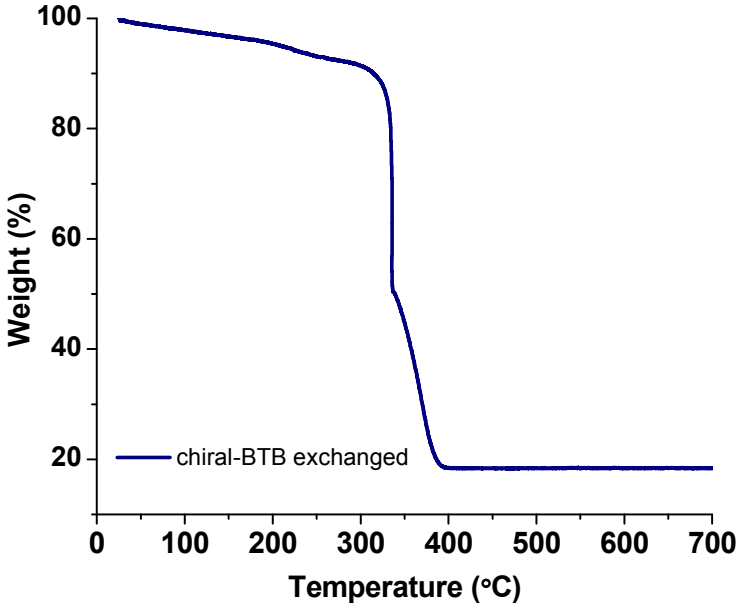


Figure S45. TGA trace for chiral-BTB exchanged PCN-333(Fe).

11. Thermodynamics behind in ligand exchange in PCN-333

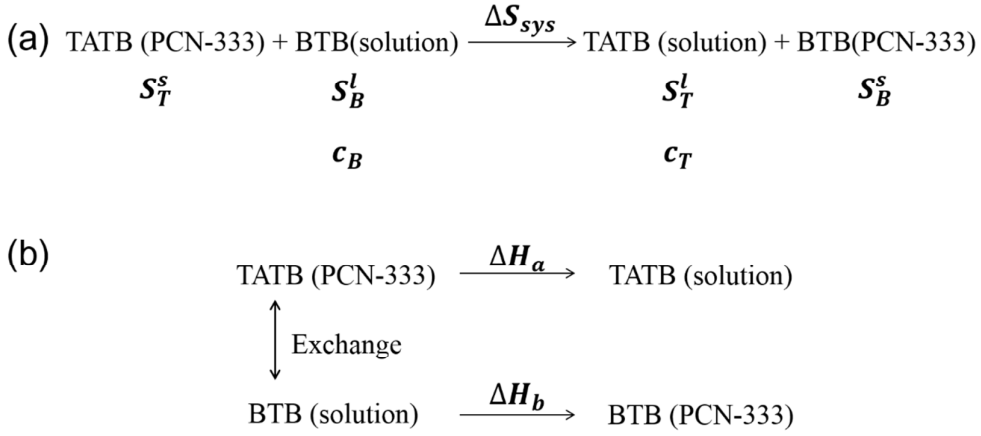


Figure S46. (a) Entropy change and (b) enthalpy change of the system during the ligand exchange.

When the solid state PCN-333 was mixed with BTB stock solution, both entropy and enthalpy of the system changed during the exchange process (Figure S46a). Here $S_T^s, S_B^l, S_T^l,$ and S_B^s represent entropy of TATB in solid phase (PCN-333), entropy of BTB in solution phase, entropy of TATB in solution phase, and entropy of BTB in solid phase, respectively. c_B and c_T are the concentrations of TATB and BTB in solution phase. Thus the entropy change for the ligand exchange process can be described as follows:

$$\Delta S_{sys} = \left(S_T^l + S_B^s\right) - \left(S_B^l + S_T^s\right)$$

After rearrangement,

$$\Delta S_{sys} = (S_B^s - S_T^s) + \left(S_T^l - S_B^l\right)$$

Compared to the entropy change in solution, the entropy change in solid is almost negligible. If we assume$(S_B^s - S_T^s) \approx 0$, then we have:

$$\Delta S_{sys} = S_T^l - S_B^l$$

$$\Delta S_{sys} = \left(S_T^{l,*} - \mathrm{Rln}c_T\right) - (S_B^{l,*} - Rlnc_B)$$

$$\Delta S_{sys} = \left(S_T^{l,*} - S_B^{l,*}\right) + Rln\frac{c_B}{c_T}$$

Here, $S_T^{l,*}$ and $S_B^{l,*}$ represent entropy of TATB and BTB in solution under standard conditions. Due to the resemblance between TATB and BTB, we can assume $S_T^{l,*} \approx S_B^{l,*}$. Therefore, the entropy change of the ligand exchange process is mainly determined by the concentrations of TATB and BTB in solution. In the initial stage of exchange, where $c_B \gg c_T$, $Rln\frac{c_B}{c_T}$ would be a very large positive value, which gives rise to an even larger positive ΔS_{sys}. The entropy increment (ΔS_{sys}), however would gradually become smaller as the concentration of TATB (c_T) increases in the solution phase.

In the meantime, during the dissociation of the bent TATB from the restricted supertetrahedral cage to the solution, it releases the strain energy. As a consequence, free TATB in the solution can adopt its lowest energy conformation and thus this process results in a negative value of enthalpy change, ΔH_a (Figure S46b). For the free BTB molecules to be exchanged into PCN-333, the ligands should take unfavorable D_{3h} symmetry (C_{3v} in the framework). In other words, BTB must place either three peripheral phenyl rings or carboxylates in the same plane. However, the first scenario gives rise to huge steric repulsions while the second case breaks the conjugation between carboxylates and phenyl rings, both of which are enthalpically highly unfavored. In addition, the inserted BTB has to be bent in the framework as TATB was to maintain the supertetrahedron. Consequently, a large positive enthalpy change, ΔH_b (Figure S46b), would take place when free BTBs are inserted into the framework. As the value of ΔH_b is larger than that of ΔH_a, the overall enthalpy change ($\Delta H_a + \Delta H_b$) for each set of individual TATB-BTB exchange can be considered as a positive constant value. Finally, the change in Gibbs free energy for the system can be described by,

$$\Delta G_{sys} = (\Delta H_a + \Delta H_b) - T\Delta S_{sys}$$

12. PXRD patterns of PCN-262

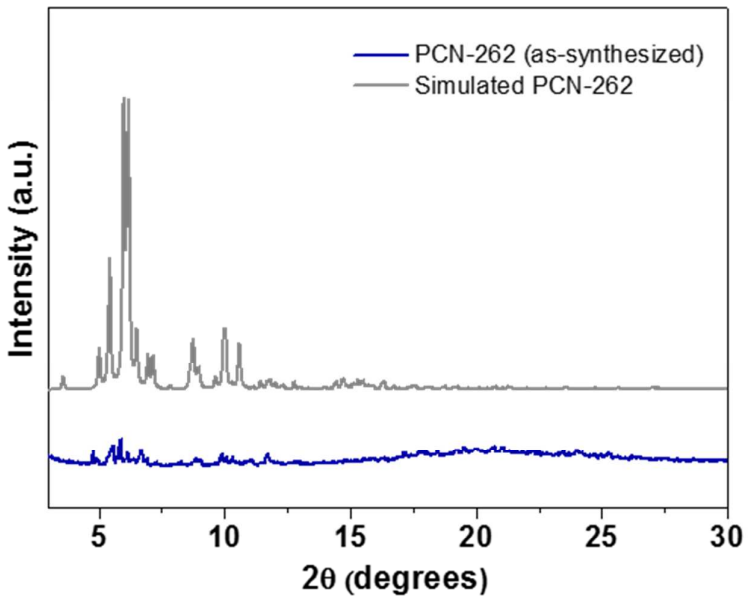


Figure S47. Comparison of simulated and experimental PXRD patterns of PCN-262.

13. References

S1. *Heckl et al. J. Phys. Chem. B* **2006,** *110,* 10829-10836.