

Supporting Information

Highly Porous Zirconium Metal-Organic Frameworks with β -UH₃-Like Topology Based on Elongated Tetrahedral Linkers

Xin Zhang,[†] Xu Zhang,[†] Jacob A. Johnson,[†] Yu-Sheng Chen,[‡] and Jian Zhang^{*,†}

[†]Department of Chemistry, University of Nebraska–Lincoln, Lincoln, Nebraska 68588, United States

[‡]ChemMatCARS, Center for Advanced Radiation Sources, The University of Chicago, 9700 South Cass Avenue, Argonne, Illinois 60439, United States

*To whom correspondence should be addressed: Email, jzhang3@unl.edu

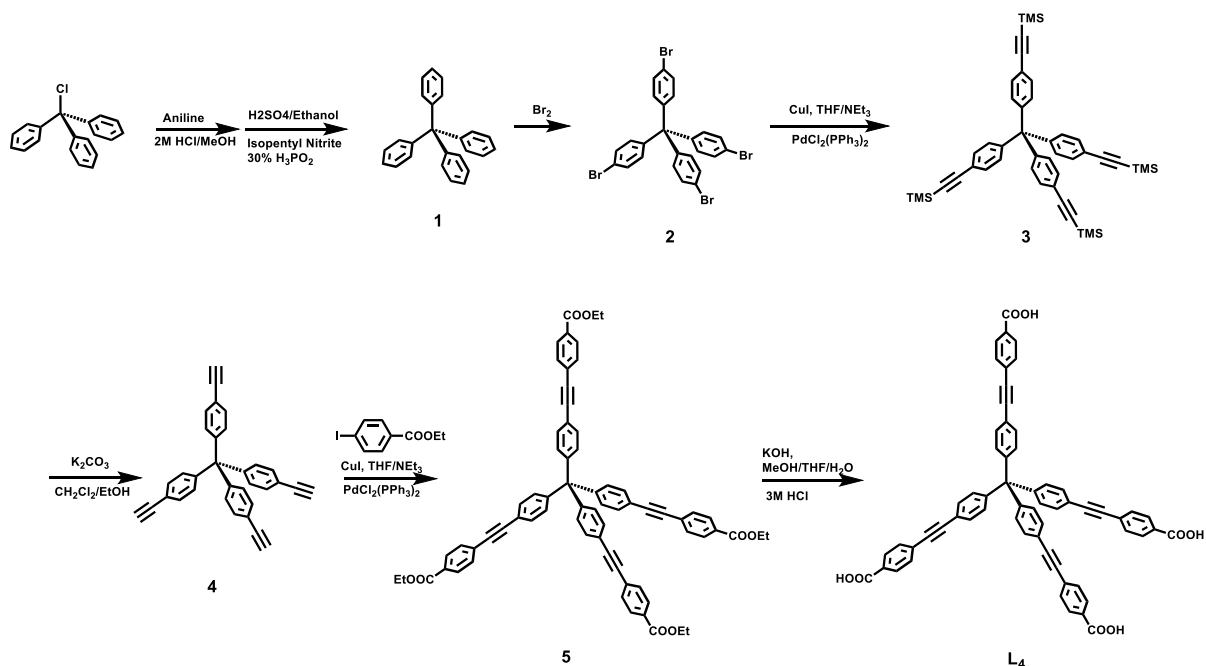
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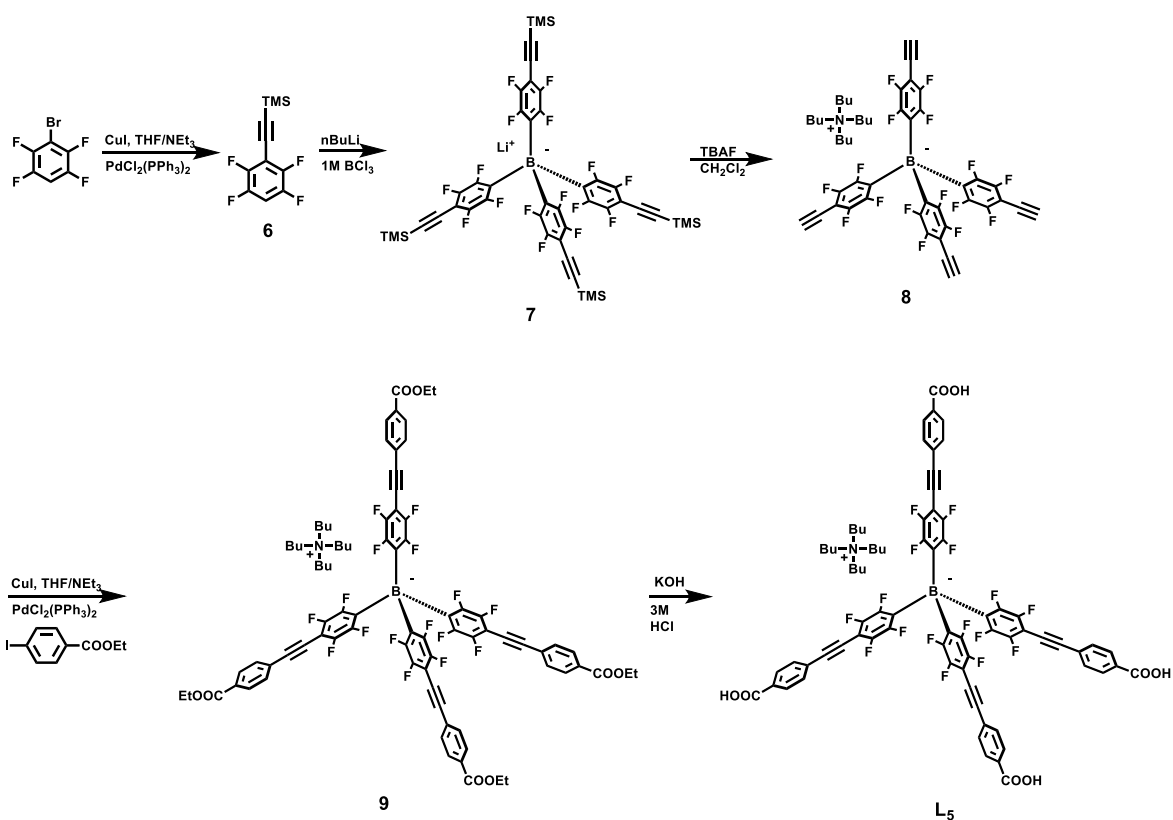
S-1 Materials and General Procedures

All solvents and reagents were purchased and commercially available and, unless otherwise noted, used without further purification. NMR was performed on either a Bruker FT-NMR spectrometer (400 MHz) or a Bruker FT-NMR spectrometer (300 MHz). Thermogravimetric Analysis (TGA) was performed on a Perkin Elmer STA 6000 Thermogravimetric Analyzer, heated from 30°C to 700°C at a rate of 3°C/minute under N₂ atmosphere. PXRD data was taken with a PANalytical Empyrean diffractometer with a PIXcel 3D detector. The copper target X-ray tube was set to 45 kV and 40 mA. Gas adsorption isotherms were collected using the surface area analyzer ASAP-2020. N₂ gas adsorption isotherms were measured at 77 K using a liquid N₂ bath.

S-2 Synthesis of Ligands



Scheme S1. Synthesis of Ligand L_4



Scheme S2. Synthesis of Ligand L_5

Ligand **L₄** was synthesized according to previous literature with slight modifications¹. Compound **4** was synthesized based on reported method²⁻⁴ with similar yield. Ligand **L₅** was synthesized based on a reported compound **8**⁵, followed by sonogashira cross coupling⁶ and hydrolysis to obtain the final product.

Tetraethyl4,4',4'',4'''-((methanetetrayltetrakis(benzene-4,1-diyl))tetrakis(ethyne-2,1-diyl))tetrabenzoate (5)

Compound **4** (1.5g, 3.6 mmol), and ethyl 4-iodobenzoate(4.969g, 18 mmol) were dissolved in a mixture of triethylamine/THF (90mL/150mL). The solution was bubbled with argon for 30 mins to remove dissolved oxygen. Then Pd(PPh₃)₂Cl₂ (81.36mg, 0.116 mmol) and CuI (22mg, 0.116mmol) were quickly added into the solution. Under argon, the reaction mixture was stirred at rt for 24 h, then filter out insoluble salt. Solvent was removed by rotavapor and crude product was run through a column with dichloromethane: hexane= 1: 2 then 2:1 to get pure white solid product (2.21g 60.8%).

¹H NMR (DMSO, 400 MHz, ppm): δ 8.02 (d, J = 8.5 Hz, 8H), 7.57 (d, J = 8.5 Hz, 8H), 7.48 (d, J = 8.6 Hz, 8H), 7.22 (d, J = 8.6 Hz, 8H), 4.39 (q, J = 7.1 Hz, 8H), 1.40 (t, J = 7.1 Hz, 12H).

4,4',4'',4'''-((methanetetrayltetrakis(benzene-4,1-diyl))tetrakis(ethyne-2,1-diyl)) tetrabenzoic acid (L₄)

Compound **10** (2.21g, 2.2mmol) was suspended in a mixture of 120 mL THF, 120 mL methanol and 120 mL 1M KOH aqueous solution. The resulting suspension was bubbled with argon for 20 min to remove dissolved oxygen and then heat to reflux under argon for 3 days. Solvent was removed by rotavapor, and 3M HCl was added to adjust the pH to 1. White precipitate was formed and filtered under

vacuum filtration. After dried in vacuum oven overnight, white solid product was obtained with yield close to 100%.

^1H NMR (DMSO, 400 MHz, ppm) δ 13.15 (s, 4H), 7.97 (d, J = 8.1 Hz, 8H), 7.66 (d, J = 8.0 Hz, 8H), 7.60 (d, J = 7.9 Hz, 8H), 7.24 (d, J = 8.1 Hz, 8H).

Trimethyl((2,3,5,6-tetrafluorophenyl)ethynyl)silane (6)

3-bromo-1,2,4,5-tetrafluorobenzene (6 g, 26.19 mmol) and triphenylphosphine (687mg, 2.62 mmol) were dissolved in a mixture of triethylamine/ toluene (45mL/45mL). The solution was bubbled with argon for 30 mins to remove dissolved oxygen. Then $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (921mg, 1.311 mmol), CuI (249mg, 1.311mmol) and ethynyltrimethylsilane (3.85g, 39.285 mmol) were quickly added into the solution. After heating the reaction mixture at 80 $^\circ\text{C}$ for 12 h, solvent was removed by rotavapor. 100 mL of hexane was added to the residue and filter out the insoluble solid. The filtrate was then dried and yellow oil product was obtained. The crude product was purified by column with hexane as eluent to get pure product (light yellow oil, 6.21g, 96.4% yield).

^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.03 (tt, J =9.7, 7.3 Hz, 1H), 0.29 (s, 9H)

^{19}F NMR (CDCl_3 , 400 MHz, ppm): δ -136.51 (m, 2F), -139.10 (m, 2F)

Lithium tetrakis(2,3,5,6-tetrafluoro-4-((trimethylsilyl)ethynyl)phenyl)borate (7)

Compound **6** (3g 12.2mmol) was dissolved in freshly distilled diethyl ether (16 mL) under argon. After cooling down to -78 $^\circ\text{C}$ by acetone-dry ice bath, $n\text{BuLi}$ (2.5M in hexane, 4.64mL) was injected into the solution dropwisely. The resulting solution was stirred at the same temperature for another hour, and then BCl_3 (1M in hexane, 2.69 mL) was injected. After slowly increased to rt overnight, solution was filtered through frit funnel with silica gel, wash by 50 mL acetone. After the filtrate is dried,

remaining solid was dissolved in dichloromethane, and white solid product (1.71g, 56.2%) was precipitated out by adding hexane.

^1H NMR (CDCl_3 , 400 MHz, ppm): δ 0.24 (s, 9H)

^{19}F NMR (CDCl_3 , 376 MHz, ppm): δ -133.04 (s, 8F), -141.27 (s, 8F)

^{11}B NMR (CDCl_3 , 128 MHz, ppm): δ -16.28 (s, 1B)

Tetrabutylammonium, tetrakis(4-ethynyl-2,3,5,6-tetrafluorophenyl)borate (8)

Under argon protection, compound **7** (2g, 2mmol) was dissolved in 80mL of THF.

Tetrabutylammonium (1M in THF, 10mL) was added into the solution and stirred at rt for 2h. Then solvent was removed and crude product was dissolved in dichloromethane and washed by water twice. Dichloromethane layer was collected and dried by MgSO_4 . After removal of dichloromethane, pure compound **3** (1.74g, 92%) was obtained as white powder.

^1H NMR (CDCl_3 , 300 MHz, TMS, ppm): δ 3.45 (s, 4H) δ 2.96 (m, 8H) δ 1.53 (m, 8H) δ 1.31 (dq, $J=14.5, 7.3\text{Hz}$, 8H) δ 0.93 (t, $J=7.3\text{ Hz}$, 12H)

^{19}F NMR (CDCl_3 , 376 MHz, ppm): δ -131.77 (s, 8F), -141.18 (s, 8F)

^{11}B NMR (CDCl_3 , 128 MHz, ppm): δ -16.19 (s, 1B)

Tetrabutylammonium tetraethyl4,4',4'',4'''-(((λ^4 -boranetetrayl)tetrakis(2,3,5,6-tetrafluorobenzene-4,1-diyl))tetrakis(ethyne-2,1-diyl))tetrabenzoate (9)

Compound **8** (1.1g, 1.16mmol) and ethyl 4-iodobenzoate (1.6g, 5.82 mmol) were dissolved in a mixture of triethylamine/THF (30mL/50mL). The solution was bubbled with argon for 30 mins to remove dissolved oxygen. Then $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (81.36mg, 0.116 mmol) and CuI (22mg, 0.116mmol) were quickly added into the solution. Under argon, the reaction mixture was stirred at rt for 24 h, then

filter out insoluble salt. Solvent was removed by rotavapor and crude product was run through a column with dichloromethane:hexane= 3:1 then pure dichloromethane. Light yellow product was collected (1.05g, 61%).

^1H NMR (CDCl_3 , 300 MHz, ppm): 8.01 (d, $J = 8.4$ Hz, 8H), 7.57 (d, $J = 8.4$ Hz, 8H), δ 4.38 (q, $J=7.1$ Hz, 8H) δ 2.98 (m, 8H) δ 1.54 (m, 8H), δ 1.40 (t, $J = 7.1$ Hz, 12H), δ 1.33 (dq, $J=14.5, 7.3$ Hz, 8H) δ 0.93 (t, $J=7.3$ Hz, 12H)

^{19}F NMR (CDCl_3 , 376 MHz, ppm): δ -131.79 (s, 8F), -140.78 (s, 8F)

^{11}B NMR (CDCl_3 , 128 MHz, ppm): δ -16.02 (s, 1B)

Tetrabutylammonium 4',4'',4'''-(((14-borane-tetrayl)tetrakis(2,3,5,6-tetrafluorobenzene-4,1-diyl))tetrakis(ethyne-2,1-diyl))tetrabenzoate (L_5)

Compound **9** (1.4g, 0.945mmol) was dissolved in 100 mL THF, then 50 mL 3M KOH aqueous solution was added. The resulting solution was bubbled with argon for 20 min to remove dissolved oxygen. After reflux for 10 h under argon, the reaction was stopped and THF was removed by rotavapor. 3M HCl was added to adjust the pH to 1, and precipitate was filtered and dried in vacuum oven overnight to get yellow product with close to 100% yield.

^1H NMR (DMSO , 400 MHz, ppm): δ 13.23 (s, 4H), 7.99 (d, $J = 8.3$ Hz, 8H), 7.70 (d, $J = 8.3$ Hz, 8H), 3.15 (m, 8H), 1.55 (m, 8H), 1.30 (m, 8H), 0.92 (t, $J = 7.3$ Hz, 12H).

^{19}F NMR (CDCl_3 , 282 MHz, ppm): δ -131.80 (s, 8F), -140.40 (s, 8F)

^{11}B NMR (CDCl_3 , 128 MHz, ppm): δ -16.15 (s, 1B)

MS: 1667.71, theoretical: 1667.67 (with two tetrabutyl ammonium cations)

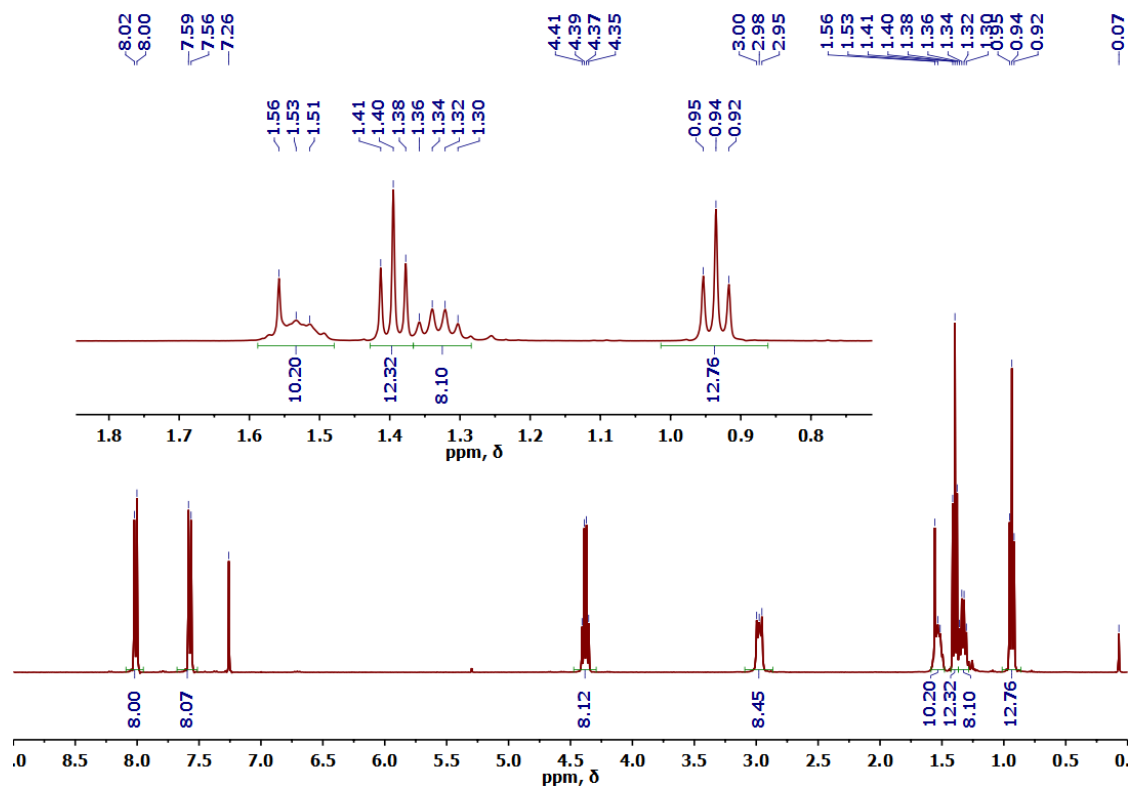


Figure S1. ¹H NMR Spectrum of compound **9**

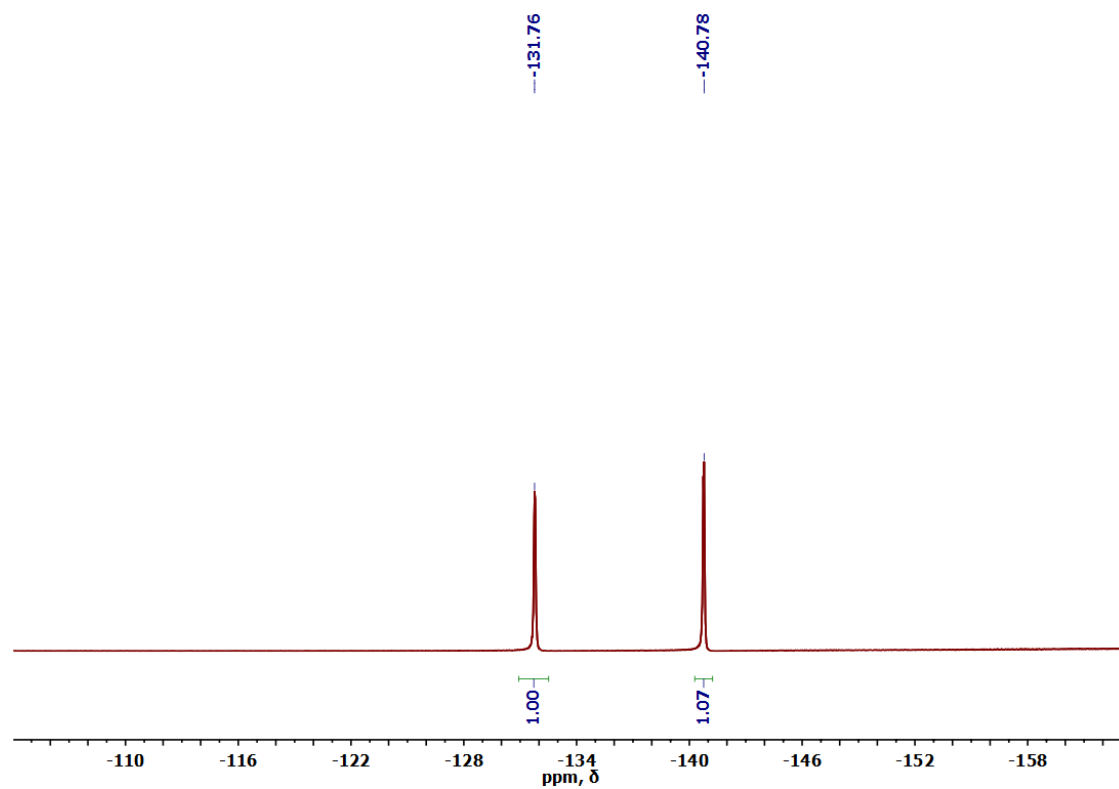


Figure S2. ¹⁹F NMR Spectrum of compound **9**

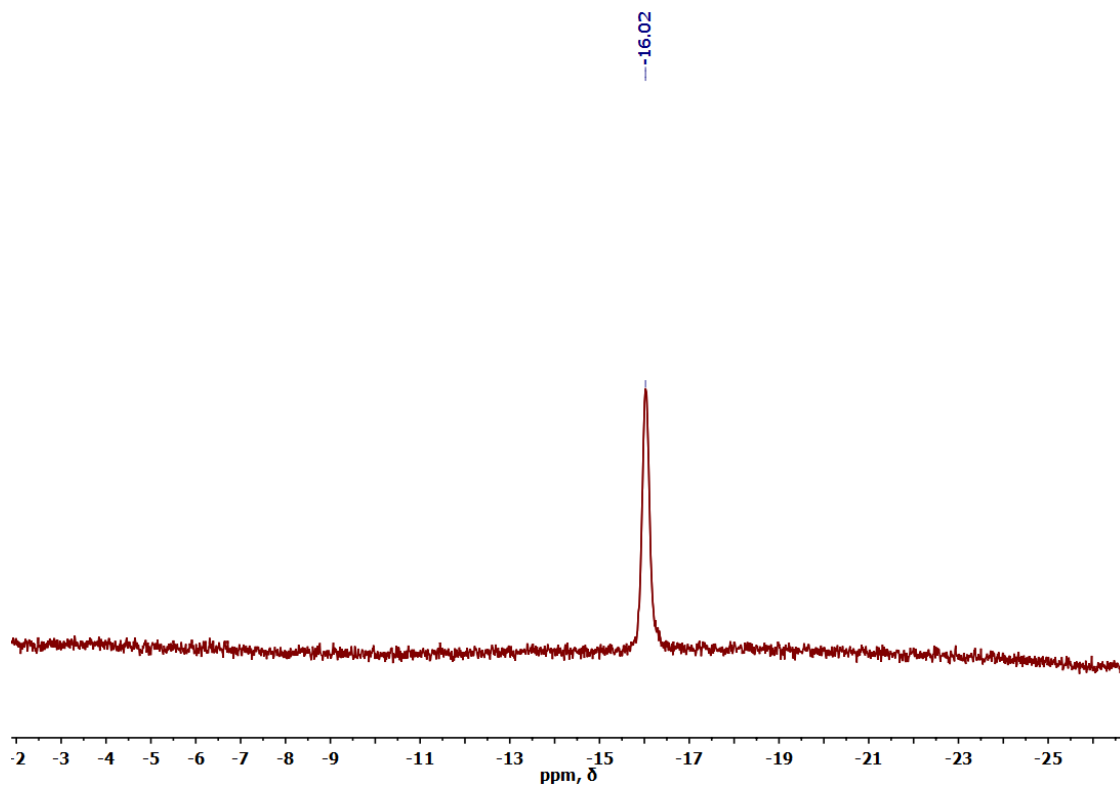


Figure S3. ^{11}B NMR Spectrum of compound **9**

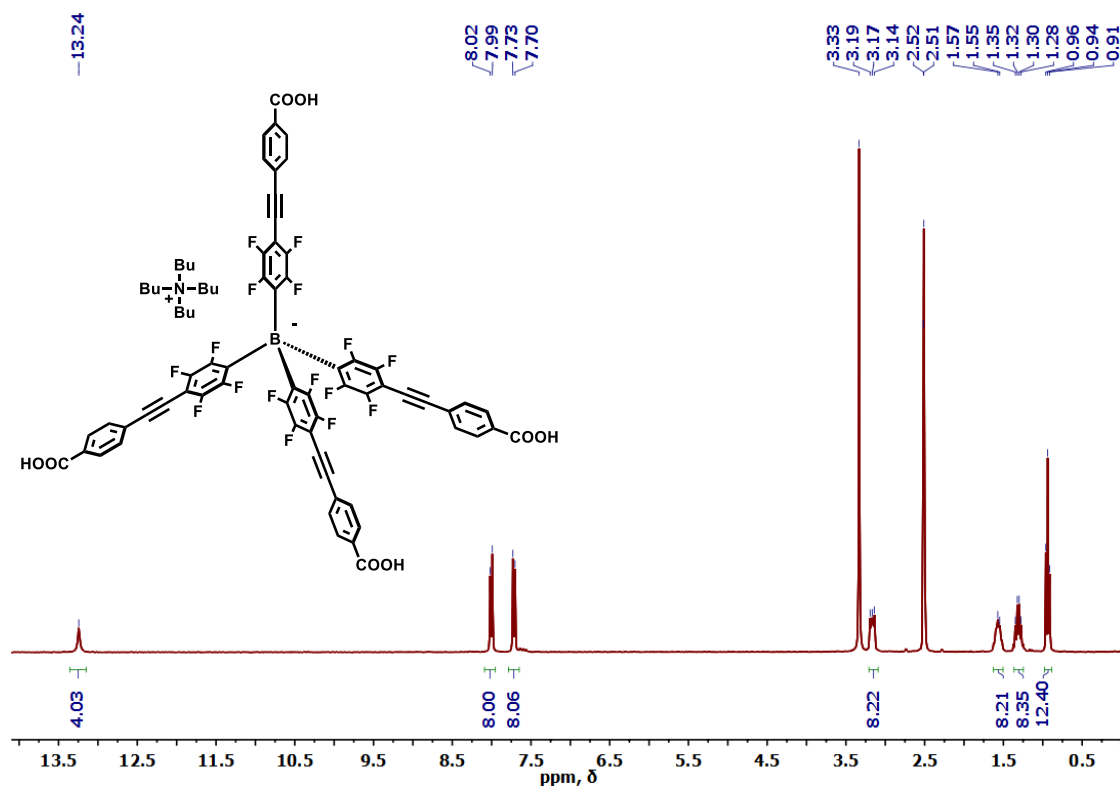


Figure S4. ^1H NMR Spectrum of compound **L₅**

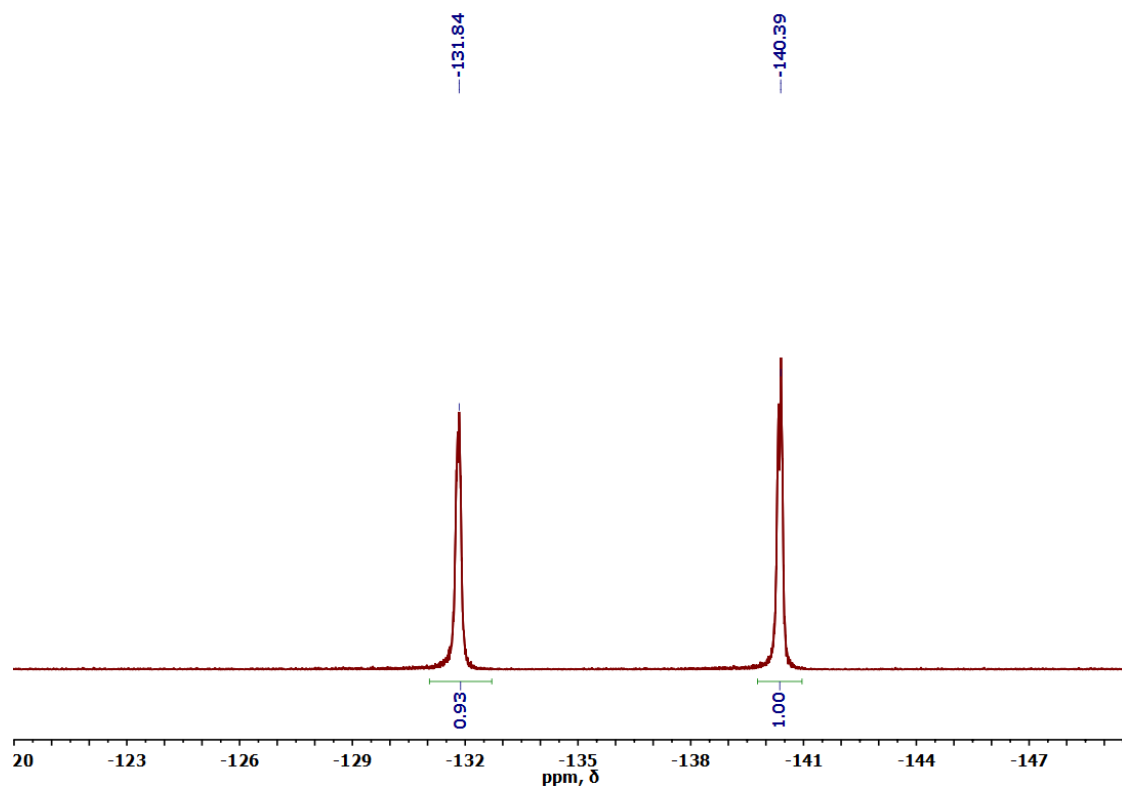


Figure S5. ^{19}F NMR Spectrum of compound L_5

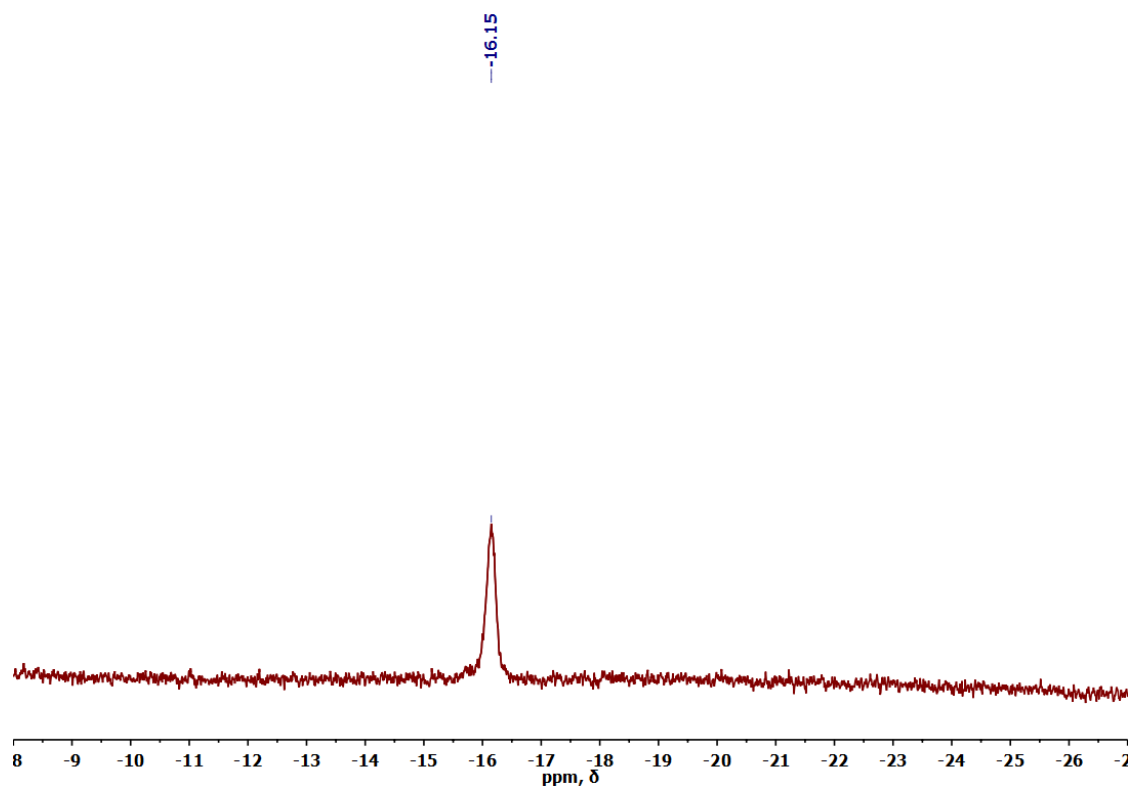


Figure S6. ^{11}B NMR Spectrum of compound L_5

S-3 Synthesis of MOFs

NPF-200

12mg (0.0133 mmol) **L**₄ ligand, 14 mg (0.06 mmol) of ZrCl₄ and 250 mg (2.05 mmol) of benzoic acid were mixed in 2.2 mL of DMF in a 4mL glass vial and ultrasonically dissolved. The clear solution was heated in an oven at 120°C for 48h. After cooling down to room temperature, colorless truncated octahedral shape single crystals were present on the vial bottom and wall (yield ~11mg 73%).

NPF-201

20mg (0.0133 mmol) **L**₅ ligand, 14 mg (0.06 mmol) of ZrCl₄ and 180 mg (1.48 mmol) of benzoic acid were mixed in 2.2 mL of DMF in a 4mL glass vial and ultrasonically dissolved. The clear solution was heated in an oven at 120°C for 48h. After cooling down to room temperature, colorless truncated octahedral shape single crystals were present on the vial bottom and wall (yield ~18mg 84%).

Ru@NPF-201

22 mg of NPF-201 crystals were submerged in 4 mL 3mM Ru(bpy)₃(PF₆)₂ DMF solution for 12 hours. Then the solution was removed and resulting crystals were washed by fresh DMF for 24 hours to obtain Ru@NPF-201, which is used for photocatalysis study. The sample was digested in DMSO-d₆ with concentrated D₂SO₄. NMR of the digested sample showed [Ru(bpy)₃]²⁺:ligand= 0.37, which is close to theoretical ration 0.5.

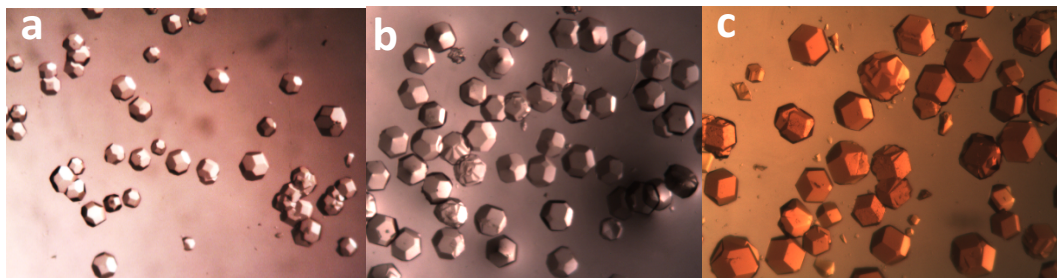


Figure S7. Photograph of single crystals: a) NPF-200, b) NPF-201 and c) Ru@NPF-201.

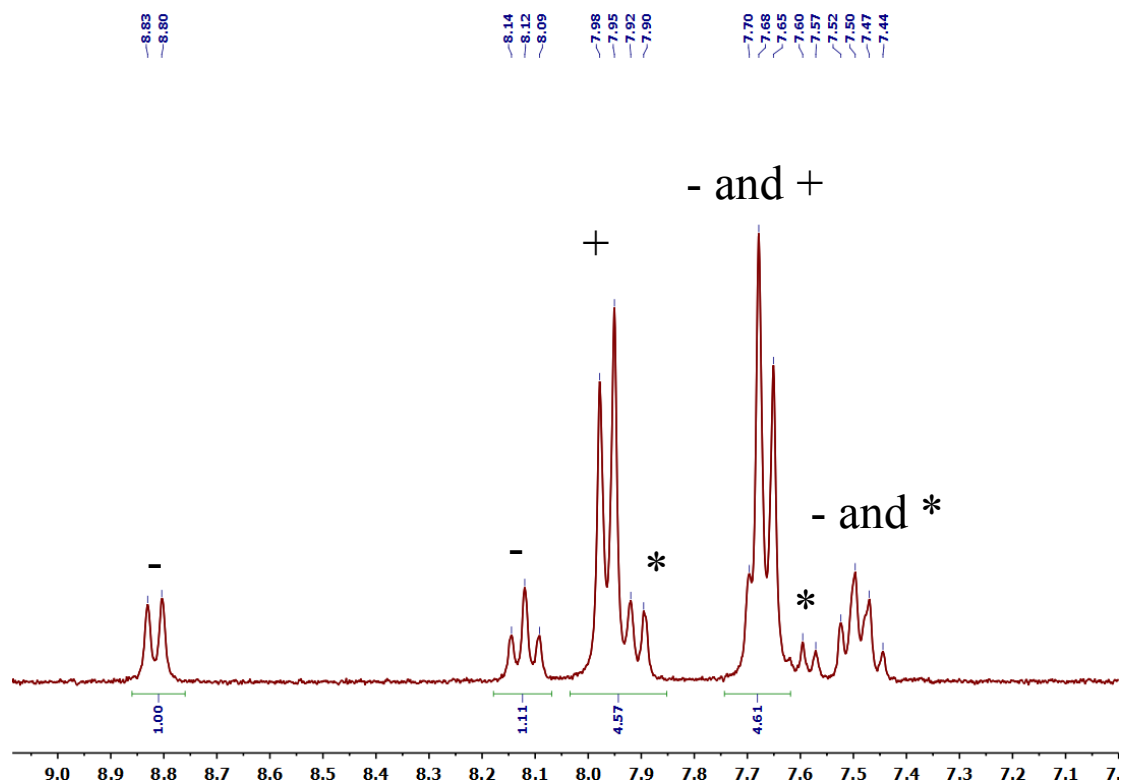


Figure S8. ^1H NMR Spectrum of digested Ru@NPF-201 in DMSO- d_6 . ‘-’: peaks from bipyridine; ‘+’: peaks from L_5 ; ‘*’: peaks from benzoic acid.

S-4 Crystallographic Data

Single crystal X-ray diffraction data was collected using synchrotron radiation, $\lambda = 0.41325 \text{ \AA}$, at the Advanced Photon Source, Chicago, IL. Indexing was performed using APEX2 (Difference Vectors method)⁷. Data integration and reduction were performed using SaintPlus 6.0⁸. Absorption correction was performed by multi-scan method implemented in SADABS⁹. Space groups were determined using XPREP implemented in APEX2⁷. The structure was solved using SHELXS-97 (direct methods)¹⁰ and refined using SHELXL-97 (full-matrix least-squares on F^2)^{11,12}. Zr, B, C, O, F atoms were refined with anisotropic displacement parameters and H atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: $U_{iso}(H) = 1.2U_{eq}(-CH)$. The contribution of disordered solvent molecules was treated as diffuse using the SQUEEZE procedure implemented in PLATON¹³. Crystal data and refinement conditions are shown in Table S1. CCDC 1471480 and 1471526 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for NPF-200 and NPF-201.

Compound name	NPF-200	NPF-201
CCDC number	1471480	1471526
Empirical formula	C ₃₆₆ H ₁₉₂ O ₆₆ Zr ₁₃	C ₃₆₀ H ₉₆ B ₆ F ₈₄ O ₆₀ Zr ₁₃
Formula weight	6831.06	8227.09
Temperature	296(2) K	296(2) K
Wavelength	0.41328 Å	0.41328 Å
Crystal system	Cubic	Cubic
Space group	Pm-3n	Pm-3n
a, b, c	48.842(8) Å	49.365(3) Å
α , β , γ	90°	90°
Volume	116512(35) Å ³	120297(11) Å ³
Z	4	4
Density (calculated)	0.389 Mg/m ³	0.454 Mg/m ³
Absorption coefficient	0.392 mm ⁻¹	0.175 mm ⁻¹
F(000)	13744	16168
Crystal size	0.5 x 0.5 x 0.3 mm ³	0.50 x 0.50 x 0.50 mm ³
Theta range for data collection	0.77 to 11.92°.	0.59 to 10.82°.
Index ranges	-48<= <i>h</i> <=47, -35<= <i>k</i> <=48, -48<= <i>l</i> <=33	-41<= <i>h</i> <=44, -40<= <i>k</i> <=44, -44<= <i>l</i> <=29
Reflections collected	302130	385503
Independent reflections	10577 [R(int) = 0.1087]	8236 [R(int) = 0.1654]
Completeness to theta = 11.92°	99.20%	99.30%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	10577 / 270 / 341	8236 / 336 / 413
Goodness-of-fit on F ²	1.325	1.412
Final R indices [I>2sigma(I)]	R ₁ = 0.1200, wR ₂ = 0.3423	R ₁ = 0.1422, wR ₂ = 0.3537
R indices (all data)	R ₁ = 0.1585, wR ₂ = 0.3640	R ₁ = 0.1854, wR ₂ = 0.3858
Extinction coefficient	0.0051(6)	0.00080(18)
Largest diff. peak and hole	1.216 and -0.531 e.Å ⁻³	0.736 and -0.982 e.Å ⁻³

S-5 Powder X-Ray Diffraction

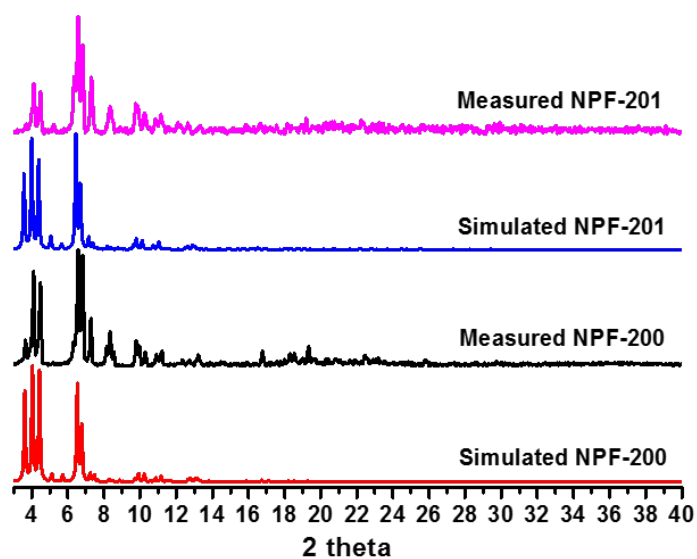


Figure S9. PXRD of NPF-200 and NPF-201

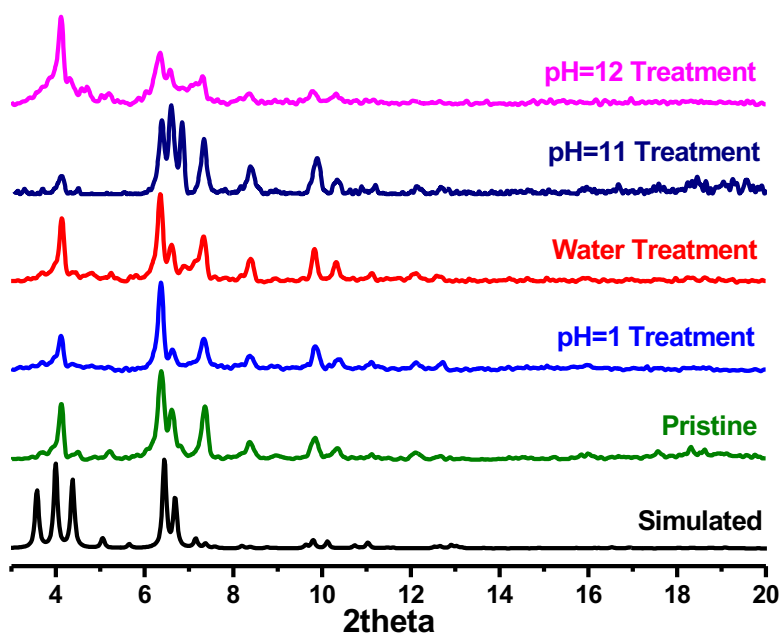


Figure S10. PXRD of NPF-201 after different treatment

S-6 MOF Activation and Gas Adsorption

As synthesized NPF-200 (~40mg) samples were washed by 20 mL DMF for 3 days (change fresh DMF every 12h), to remove unreacted ligand, metal salt and benzoic acid. Then the samples were washed by 20 mL 200 proof ethanol for 3 days (change fresh ethanol every 12h), to exchange all DMF out of MOFs. Afterwards, supercritical CO₂ treatment was performed to dry the samples prior to gas adsorption/desorption measurement. The BET surface area of NPF-200 is 5,463 m² g⁻¹. To examine water stability of NPF-200, activated samples were soaked in DI water for 24 hours followed by ethanol exchange and supercritical CO₂ treatment. The N₂ adsorption showed slight deviation with a BET surface area of 4799 m²/g, as shown in Figure S11.

NPF-201 was activated by the same procedures as NPF-200. The BET surface area of NPF-201 is 534 m² g⁻¹, probably due to framework collapse induced by electrostatic attraction between counter cations and frameworks, as shown in Figure S12, the pores size of NPF-201 is much smaller than that in NPF-200 (Figure 2c).

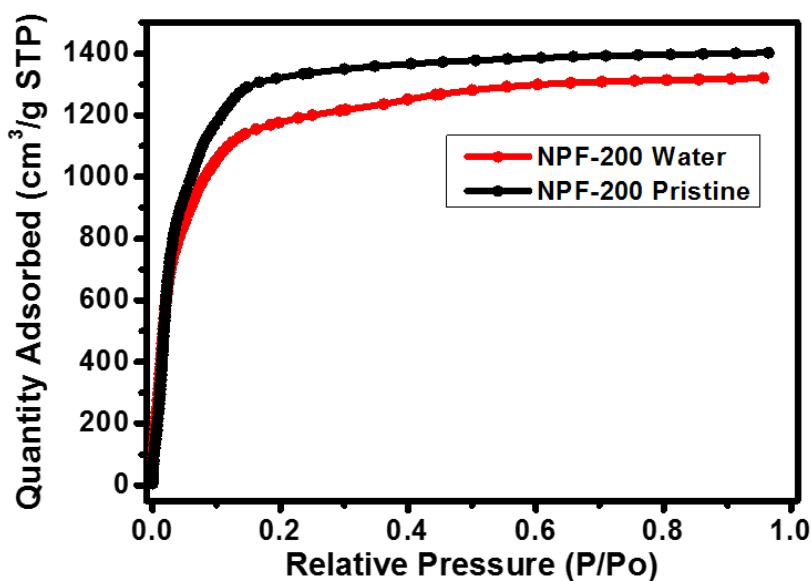


Figure S11. N₂ Adsorption isotherm of NPF-200 before and after water treatment.

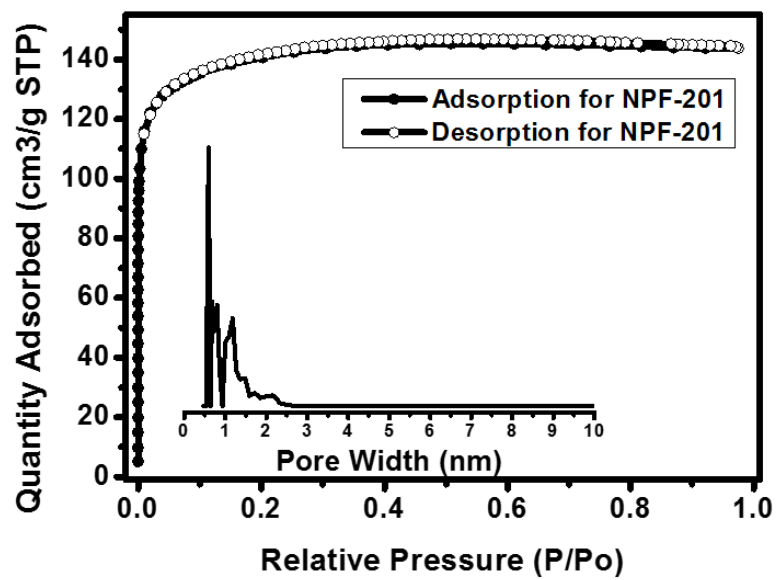


Figure S12. N₂ Adsorption isotherm and DFT pore size distribution of NPF-201

S-7 Topology and Cage Type Analysis

The Zr_6 and Zr_8 clusters in NPF-200 (and NPF-201) can be conceived as the topological close packing phase A15. In a unit cell, Zr_6 clusters adopt the body center cubic occupancy and Zr_6 clusters occupy the two positions in each cube face. Zr_8 clusters lie in the 12-fold distorted icosahedra, which is composed of 20 tetrahedra. The packing of icosahedrons leaves 2 tetrahedral cavities on each face of the unit cell, as shown in blue color. In each unit cell, there are 2 Zr_8 clusters (one in body center and eight on cell vertices, $1 + 8 \times 1/8 = 2$) which means 2 icosahedral or 40 tetrahedra. Meanwhile, on each face, there is $2 \times 1/2 = 1$ tetrahedron, which gives 6 tetrahedra on all faces. In total, there are 40 (from icosahedra) + 6 (from each face) = 46 tetrahedra. The blue tetrahedra are void without any ligand. In each icosahedron, only tetrahedra composed with two Zr_6 clusters in the same face of unit cell will be filled in with ligands, as shown in Figure S14, tetrahedra composed of light blue triangle and central Zr_8 cluster will be filled in with ligands. Thus, there are 12 ligands in each icosahedron and $12 \times 2 = 24$ ligands in a unit cell.

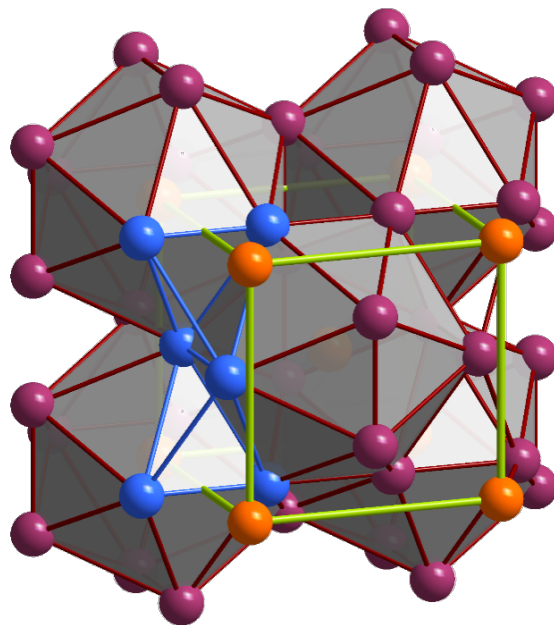


Figure S13. Icosahedra (on body center and vertices) and tetrahedral cavities (on faces) packing in simplified NPF-200. Four icosahedra in the front face are omitted for clarity. Orange atom represents Zr_8 clusters, and dark red and blue atom represents Zr_6 clusters. 6 blue atoms represent two tetrahedral cavities on each face.

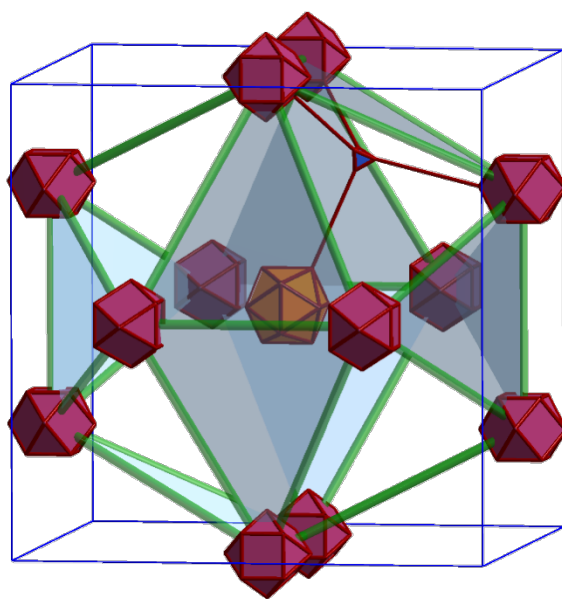


Figure S14. Ligand connection with central Zr_8 cluster and surrounding Zr_6 clusters.

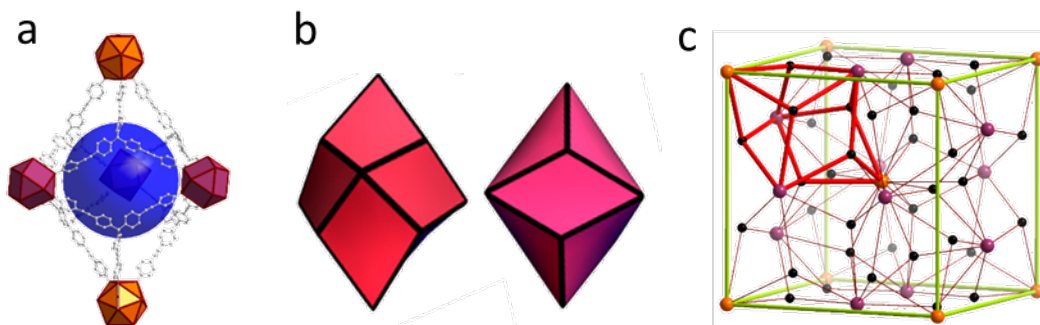


Figure S15. Cage1 with capped trigonal bipyramidal shape. a) A sphere of diameter 20 Å can be fit in;
b) Natural tiling of cage 1; c) Position of cage 1 in unit cell;

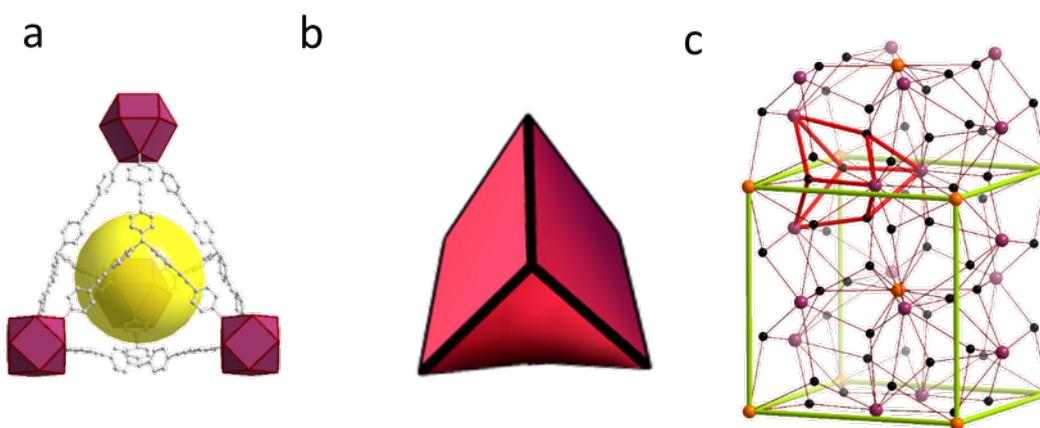


Figure S16. Cage2 with capped tetrahedral shape. a) A sphere of diameter 15 Å can be fit in; b) Natural
tiling of cage 2; c) Position of cage 2 in unit cell;

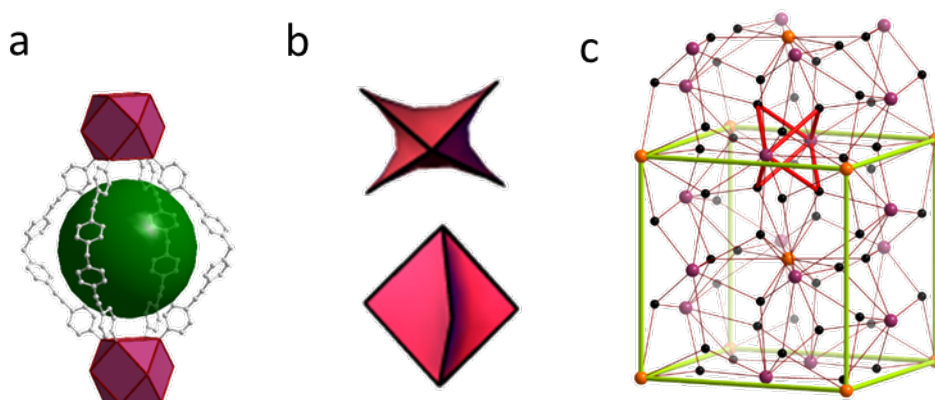


Figure S17. Cage3 with octahedral shape. a) A sphere of diameter 14 Å can be fit in; b) Natural tiling of
cage 3; c) Position of cage 3 in unit cell;

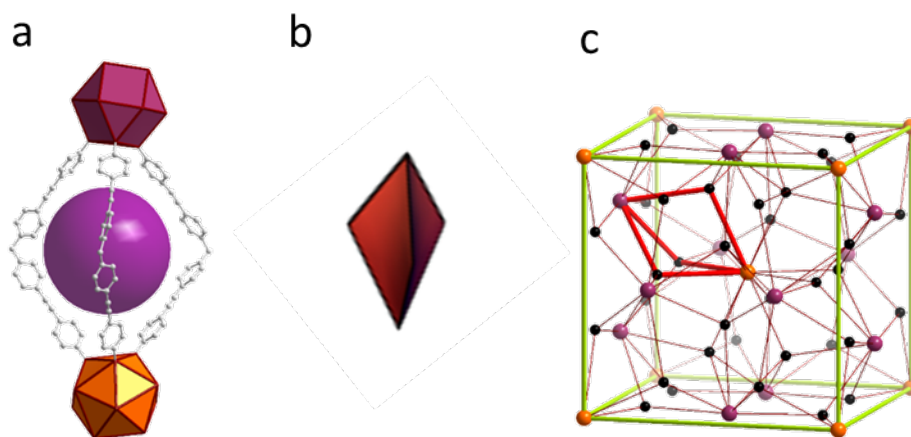


Figure S18. Cage 4 with trigonal bipyramidal shape. a) A sphere of diameter 12 Å can be fit in; b) Natural tiling of cage 4; c) Position of cage 4 in unit cell;

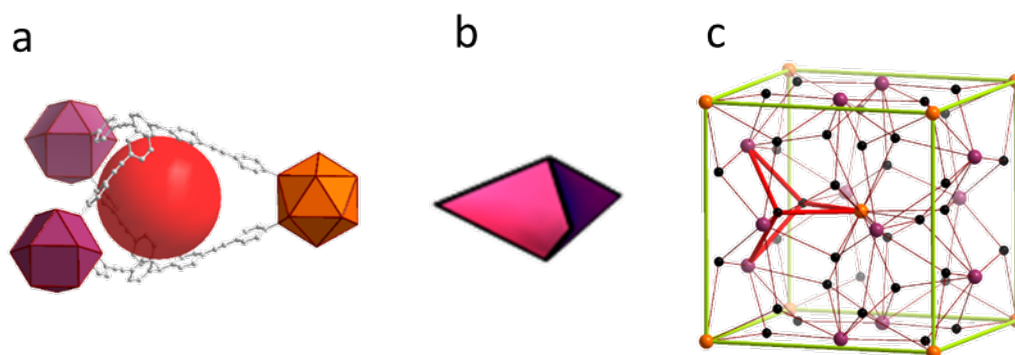


Figure S19. Cage 5 with trigonal bipyramidal shape. a) A sphere of diameter 12 Å can be fit in; b) Natural tiling of cage 5; c) Position of cage 5 in unit cell;

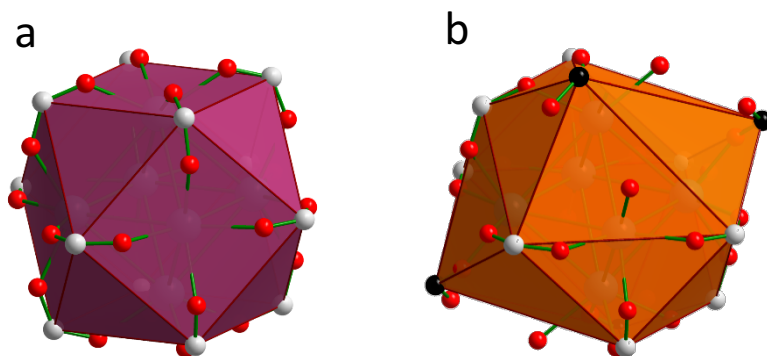


Figure S20. Zr_6 cluster: a) Cuboctahedron SBU in Uio series structures. b) Icosahedron SBU in MOF-812.

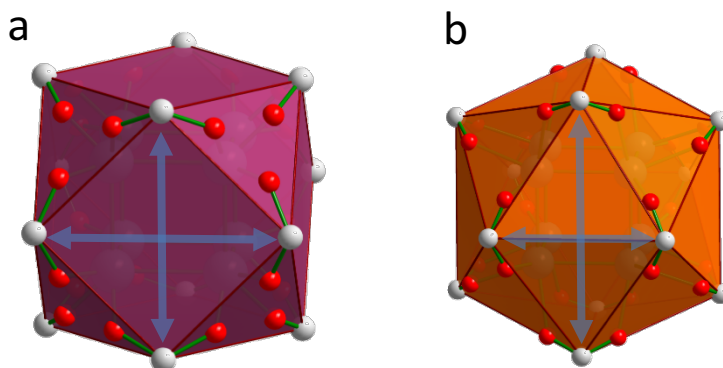


Figure S21. Zr_8 cluster: a) Cuboctahedron SBU in PCN-221. b) Icosahedron SBU in NPF-200 and NPF-201. In cuboctahedron SBU, the four carboxylic groups on each face of the Zr_8 cluster have a C_4 proper rotation axis, which is lost in icosahedron SBU due to different distance between the two carboxylic groups.

S-8 Dye uptake and ion Exchange Study of MOFs

Dye uptake of NPF-200

To confirm the electro-neutral properties of NPF-200, we performed dye uptake experiment. NPF-200 samples were immersed in DMF solution of anionic acid orange 7 and cationic methylene blue for 24 hours. After the removal of excessive dye solution, the samples were washed once by DMF, MOFs in anionic and cationic dye solutions changed color to orange (b) and blue (d) respectively, indicating both anionic and cationic dyes can be absorbed by NPF-200. Then the samples (b and d) were washed with fresh DMF for four times during 24 hours, and the resulting samples (c and e) become colorless indicating absorbed dyes were removed completely.

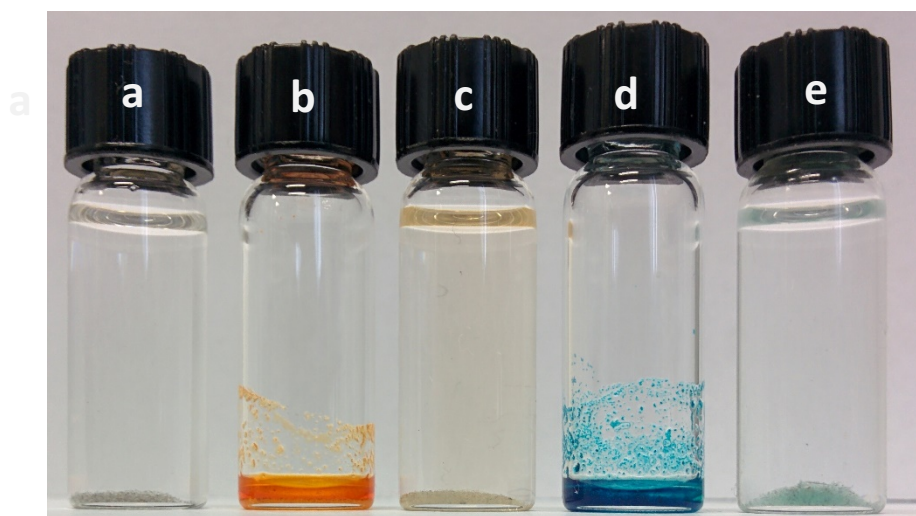


Figure S22. NPF-200 dye uptake: As prepared (a). After soaking in acid orange 7 for 24h (b) and subsequent washing with DMF (c), after soaking in methylene blue for 24h (d) and subsequent washing with DMF (e).

Dye uptake of NPF-201

Similar dye uptake experiment as NPF-200 was performed on NPF-201. Anionic acid orange 7 can be washed out by fresh DMF. However, DMF is not able to wash out cationic methylene blue from the sample due to strong electrostatic interaction between methylene blue and the anionic framework. After addition of 0.5 M NH_4Cl to sample, methylene blue was exchanged out indicated by a dark blue color in solution. After exchange with NH_4Cl solution several times, the sample became colorless.

S-9 Photo-oxidation of Thioanisole

Thioanisole (42 mg, 0.34 mmol) and Ru@NPF-201 were added in 5 mL methanol. The resulting suspension was bubbled by O₂ for 5 mins, and then stirred under O₂ with irradiation (light source: a 26 W household fluorescence lamp, distance app.10 cm). After 2.5 hours reaction, the crude reaction mixture was centrifuged to separate the catalyst. The recycled catalyst was used for next reaction to test the recyclability of Ru@NPF-201. The solution phase was dried under vacuum, and ¹H NMR was taken of the crude product, and ratios between the integrated peaks of the substrate and product were used to calculate conversions. Comparison of different catalysts is summarized in the Table S2. After 5 times recycle, PXRD of Ru@NPF-201 still remains intact, which demonstrates the catalyst is stable under catalytic condition, as shown in Figure S23.

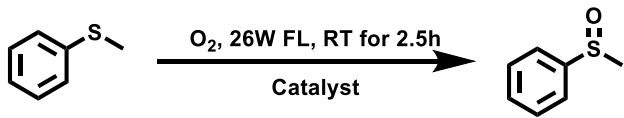
			
Entry	Photocatalyst	Catalyst Loading	Conversion
1	Ru(bpy) ₃ Cl ₂	1%	>99%
2	Ru@NPF-201	1%	>99%
3	NPF-201	1%	NR
4	Ru@NPF-201*	1%	>99%

Table S2. Comparison of different catalysts in thioanisole oxidation. Entry 4 is catalyst recycled 5 times.

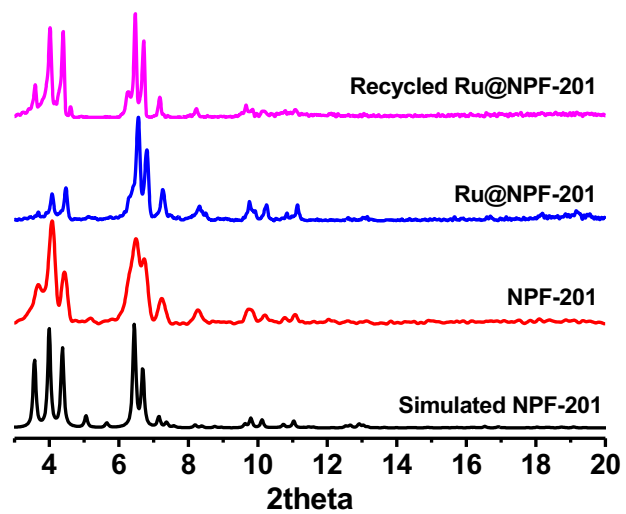


Figure S23. PXRD of Ru@NPF-201 before and after catalysis.

S-10 Thermal Gravimetric Analysis.

About 10 mg samples were brief washed by fresh DMF prior TGA analysis. Thermogravimetric Analysis (TGA) was performed on a Perkin Elmer STA 6000 Thermogravimetric Analyzer, heated from 30°C to 700°C at a rate of 3°C/minute under N₂ atmosphere.

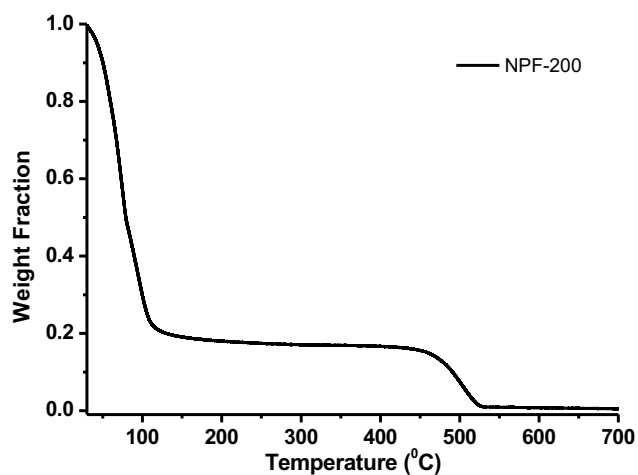


Figure S24. TGA of NPF-200

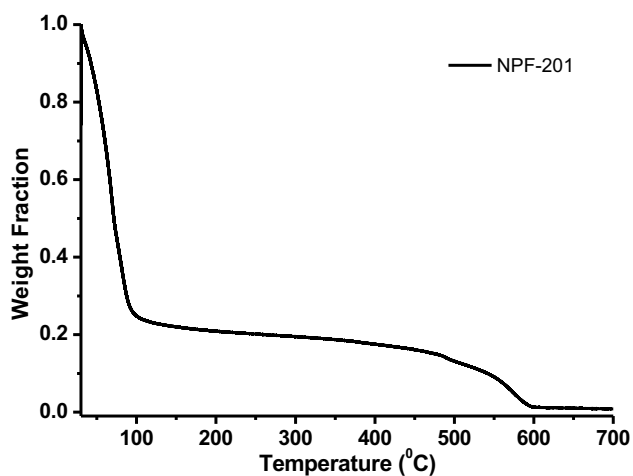


Figure S25. TGA of NPF-201

S-11 A list of Volumetric and Gravimetric BET Surface Areas of Some Highly Porous MOFs

Table S3 contains some MOFs with high BET surface area, and their volumetric surface area is calculated by gravimetric surface area \times density.

Table S3. Volumetric and Gravimetric BET Surface Areas of Some Highly Porous MOFs.

MOF	Gravimetric Surface Area (m ² /g)	Density (g/cm ³)	Volumetric Surface Area (m ² /cm ³)	Reference
NU-110E	7140	0.237	1692	14
NU-1103	6550	0.298	1952	15
MOF-210	6240	0.25	1560	16
NU-1104	6230	0.291	1813	15
NU-100 (PCN-610)	6143	0.303	1861	17,18
NPF-200	5463	0.389	2125	This work
UMCM-2	5200	0.4	2080	19
NU-111	4930	0.409	2016	20
NU-1102	4830	0.403	1946	15
PCN-229	4619	0.32	1478	21
MOF-200	4530	0.222	1006	16
PCN-228	4510	0.42	1894	21
MOF-205	4460	0.382	1704	16
PCN-230	4455	0.189	842	21
NU-1101	4340	0.458	1988	15
Cu-tbo-MOF-5	3971	0.595	2363	22
MOF-5	3800	0.59	2242	23

S-12 References

- (1) Liu, D.; Xie, Z.; Ma, L.; Lin, W. *Inorg. Chem.* **2010**, *49*, 9107.
- (2) Lu, W.; Yuan, D.; Zhao, D.; Schilling, C. I.; Plietzsch, O.; Muller, T.; Bräse, S.; Guenther, J.; Blümel, J.; Krishna, R.; Li, Z.; Zhou, H.-C. *Chem. Mater.* **2010**, *22*, 5964.
- (3) Pandey, P.; Farha, O. K.; Spokoyny, A. M.; Mirkin, C. A.; Kanatzidis, M. G.; Hupp, J. T.; Nguyen, S. T. *J. Mater. Chem.* **2011**, *21*, 1700.
- (4) Lu, J.; Zhang, J. *J. Mater. Chem. A*, **2014**, *2*, 13831.
- (5) Turp, D.; Wagner, M.; Enkelmann, V.; Mullen, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 4962.
- (6) Malek, N.; Maris, T.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **2005**, *127*, 5910.
- (7) Bruker; Bruker AXS Inc.: Madison, Wisconsin, USA, 2010.
- (8) Bruker; Data Reduction Software. Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
- (9) Sheldrick, G. M.; Program for empirical absorption correction: University of Göttingen, Göttingen, Germany, 2008.
- (10) Sheldrick, G. M. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **1990**, *46*, 467.
- (11) Sheldrick, G. M.; Program for structure refinement: University of Göttingen, Göttingen, Germany, 1997.
- (12) Sheldrick, G. M. *Acta Crystallogr. Sect. A: Found. Crystallogr.* **2008**, *A64*, 112.
- (13) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.
- (14) Farha, O. K.; Eryazici, I.; Jeong, N. C.; Hauser, B. G.; Wilmer, C. E.; Sarjeant, A. A.; Snurr, R. Q.; Nguyen, S. T.; Yazaydin, A. O.; Hupp, J. T. *J. Am. Chem. Soc.* **2012**, *134*, 15016.
- (15) Wang, T. C.; Bury, W.; Gomez-Gualdrón, D. A.; Vermeulen, N. A.; Mondloch, J. E.; Deria, P.; Zhang, K.; Moghadam, P. Z.; Sarjeant, A. A.; Snurr, R. Q.; Stoddart, J. F.; Hupp, J. T.; Farha, O. K. *J. Am. Chem. Soc.* **2015**, *137*, 3585.
- (16) Furukawa, H.; Ko, N.; Go, Y. B.; Aratani, N.; Choi, S. B.; Choi, E.; Yazaydin, A. O.; Snurr, R. Q.; O'Keeffe, M.; Kim, J.; Yaghi, O. M. *Science* **2010**, *329*, 424.
- (17) Farha, O. K.; Yazaydin, A. O.; Eryazici, I.; Malliakas, C. D.; Hauser, B. G.; Kanatzidis, M. G.; Nguyen, S. T.; Snurr, R. Q.; Hupp, J. T. *Nat. Chem.* **2010**, *2*, 944.
- (18) Yuan, D.; Zhao, D.; Sun, D.; Zhou, H. C. *Angew. Chem. Int. Ed.* **2010**, *49*, 5357.
- (19) Koh, K.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 4184.
- (20) Mason, J. A.; Veenstra, M.; Long, J. R. *Chem. Sci.* **2014**, *5*, 32.
- (21) Liu, T. F.; Feng, D.; Chen, Y. P.; Zou, L.; Bosch, M.; Yuan, S.; Wei, Z.; Fordham, S.; Wang, K.; Zhou, H. C. *J. Am. Chem. Soc.* **2015**, *137*, 413.
- (22) Spanopoulos, I.; Tsangarakis, C.; Klontzas, E.; Tylanakis, E.; Froudakis, G.; Adil, K.; Belmabkhout, Y.; Eddaoudi, M.; Trikalitis, P. N. *J. Am. Chem. Soc.* **2016**, *138*, 1568.
- (23) Kaye, S. S.; Dailly, A.; Yaghi, O. M.; Long, J. R. *J. Am. Chem. Soc.* **2007**, *129*, 14176.