Electronic Supplementary Material (ESI) for Chemical Communications

Functional Group Effects on Metal-Organic Framework Topology

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Supplementary Information

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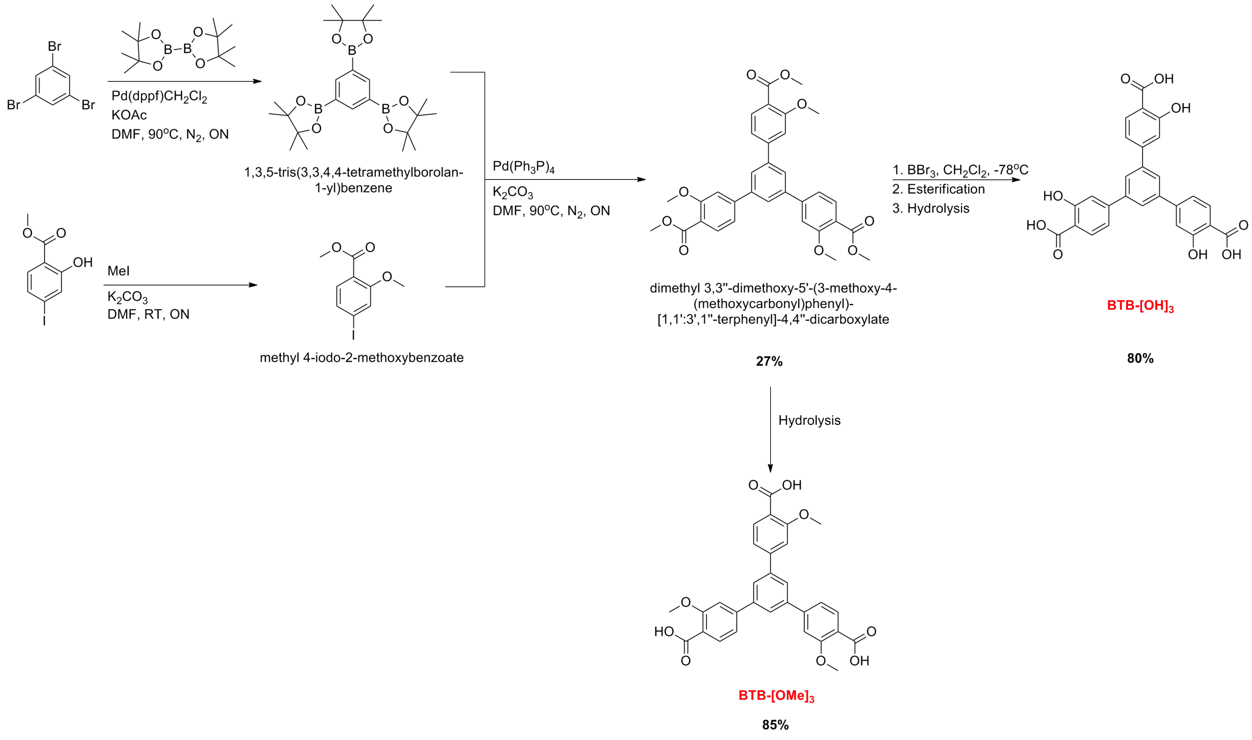
General Methods for Metal-Organic Frameworks Experiments

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded by a Varian FT-NMR spectrometer (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, *J*, were reported in Hertz unit (Hz). Column chromatography was performed using a CombiFlask automated chromatography system.

Ligand Synthesis



Scheme S1. Synthesis of BTB-[OMe]$_3$ and BTB-[OH]$_3$ via Pd-coupling reaction.

Synthesis of 1, 3, 5-tris(3, 3, 4, 4-tetramethylborolan-1-yl)benzene. 1,3,5-Tribromobenzene (2.0 g, 6.4 mmol), bis(pinacolato)diboron (5.1 g, 20.1 mmol), 1,1'-bis(diphenylphosphino)ferrocene-palladium(II) dichloride dichloromethane (0.16 g, 0.2 mmol), and KOAc (3.8 g, 38.2 mmol) were dissolved in *N,N*-dimethylformamide (DMF, 20 mL). The mixture was heated to 90 °C under N_2 overnight. H_2O (200 mL) was added to the cooled mixture resulting in a dark black precipitate. Upon filtration, the product was obtained as a black solid (2.2 g), which was used for the next step without any additional purification. ^{1}H NMR ($CDCl_3$): δ 8.36 (s, 3H), δ 1.32 (s, 36H). ESI-MS(+): *m/z* 474.09 $[M+NH_4]^+$.

Synthesis of methyl 4-iodo-2-methoxybenzoate. Methyl 2-hydroxy-4-iodobenzoate (4.8 g, 17.3 mmol), and K_2CO_3 (4.8 g, 34.6 mmol) were added into DMF (20 mL). Iodomethane (2.1 mL, 34.5 mmol) was added and the mixture was stirred at room temperature overnight. K_2CO_3 was filtered off and the filtrate was used without additional purification. ^{1}H NMR ($CDCl_3$): δ 7.45 (d, 1H, J = 8.4 Hz), δ 7.34 (d, 1H, J = 8.4 Hz), δ 7.30 (s, 1H), δ 3.84 (s, 3H), δ 3.82 (s, 3H). ESI-MS(+): *m/z* 292.82 $[M+H]^+$.

Synthesis of dimethyl 3,3''-dimethoxy-5'-(3-methoxy-4-(methoxycarbonyl)phenyl)-[1,1':3',1''-terphenyl]-4,4''-dicarboxylate. 1,3,5-Tris(3, 3, 4, 4-tetramethylborolan-1-yl)benzene (2.2 g, 4.8 mmol), $Pd(PPh_3)_4$ (1.0 g, 0.9 mmol), and K_2CO_3 (10.4 g, 75 mmol) were dissolved in DMF (20 mL). This mixture was added to the methyl 4-iodo-2-methoxybenzoate solution synthesized above. This was heated to 90 °C under N_2 overnight. H_2O (500 mL) was added to the solution and the mixture was filtered to yield a black solid. The solid was taken up in dichloromethane

(CH_2Cl_2, 60 mL), and insoluble by-products were removed by filtration. The organic solution was dried with anhydrous $MgSO_4$ and removed under vacuum to yield a red brownish solid-gel. The product was purified by using column chromatography (CH_2Cl_2/ hexane) to obtain a white solid (750 mg, 1.32 mmol, 27%). ^{1}H NMR ($CDCl_3$): δ 7.94 (d, 3H, $J = 8$ Hz), 7.78 (s, 3H), 7.28 (dd, 3H, J = 8 Hz), 7.22 (s, 3H), 4.00 (s, 9H), 3.93 (s, 9H).

Synthesis of BTB-[OMe]$_3$. Dimethyl 3,3’’-dimethoxy-5’-(3-methoxy-4-(methoxycarbonyl)phenyl)-[1,1’:3’,1’’-terphenyl]-4,4’’-dicarboxylate (400 mg, 0.7 mmol) was dissolved in tetrahydrofuran (THF, 35 mL) and 4% KOH (35 mL). The mixture was stirred at room temperature overnight. The aqueous layer was collected and then acidified with concentrated HCl to yield a white solid as product (314 mg, 0.6 mmol, 85%). ^{1}H NMR (DMSO-*d$_6$*): δ 8.06 (s, 3H), 7.79 (d, 3H, J = 8 Hz), 7.51 (m, 6H, J = 8Hz), 3.96 (s, 9H).

Synthesis of BTB-[OH]$_3$. Dimethyl 3,3’’-dimethoxy-5’-(3-methoxy-4-(methoxycarbonyl)phenyl)-[1,1’:3’,1’’-terphenyl]-4,4’’-dicarboxylate (400 mg, 0.7 mmol) was dissolved in anhydrous CH_2Cl_2 (20 mL). The solution was cooled to -78 °C by an isopropanol/ dry ice bath under N_2. BBr_3 (1.0 M in CH_2Cl_2, 15 mL, excess) was added slowly and stirred overnight under N_2. MeOH was added dropwise to quench the excess BBr_3. The solvent was removed under vacuum to yield an orange solid-gel. The solid-gel was dissolved in MeOH (100 mL) and several drops of concentrated H_2SO_4 were added. The mixture was heated to reflux overnight. The solvent was removed under vacuum and saturated sodium bicarbonate solution was added. The aqueous solution was extracted with ethyl acetate (EtOAc, 3×100 mL). The organic layer was dried with anhydrous $MgSO_4$ and the solvent was removed under vacuum to yield a white solid. The white solid was dissolved in THF (40 mL) and 4% KOH (40 mL). The mixture was stirred at room temperature overnight. The aqueous solution was then separated and acidified with concentrated HCl to yield a white solid as the final product (272 mg, 0.56 mmol, 80%). ^{1}H NMR (DMSO-d_6): δ 8.04 (s, 3H), 7.89 (d, 3H, J = 8 Hz), 7.54 (s, 3H), 7.49 (d, 3H, J = 8 Hz).

MOF Synthesis

Synthesis of MOF-177-OMe. BTB-[OMe]$_3$ (26 mg, 0.05 mmol) and $Zn(NO_3)_2{\bullet}6H_2O$ (47 mg, 0.15 mmol) were dissolved in DMF (10 mL) in a scintillation vial. The vial was then kept in an isothermal oven at 85 °C for 48 h. Clear colorless hexagonal crystals of MOF-177-OMe were obtained and rinsed with DMF (3×10 mL). The solvent was then exchanged with $CHCl_3$ (3×10 mL) for 3 d, with fresh $CHCl_3$ provided every 24 h. The crystals were stored in $CHCl_3$ prior to analysis.

Synthesis of Zn(II)-MOF-BTB[OH]$_3$. BTB-[OH]$_3$ (25 mg, 0.05 mmol) and $Zn(NO_3)_2{\bullet}6H_2O$ (47 mg, 0.15 mmol) were dissolved in DMF (2 mL) and H_2O (0.1 mL) in a scintillation vial. The vial was kept in an isotherm oven at 100 °C for 24 h. Clear colorless block crystals were obtained and rinsed with DMF (3×10 mL). The solvent was then exchanged with $CHCl_3$ (3×10 mL) for 3 d, with fresh $CHCl_3$ provided every 24 h. The crystals were stored in $CHCl_3$ prior to analysis.

MOF Characterization

Powder X-ray Diffraction (PXRD). Approximately 20-30 mg of MOF materials were air dried for ~1 min prior to the PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer using a LynxEye detector at 40 kV, 40 mA for Cu Kα (λ= 1.5418 Å), with a scan speed of 1 sec/step, a step size of 0.02°, 2θ range of 2-45°.

Single Crystal X-ray Diffraction. Single crystals of MOF-177-OMe taken from $CHCl_3$ were mounted on nylon loops with paratone oil and placed under a nitrogen cold stream (100 K). Data was collected on a Bruker Apex diffractometer using either Cu Kα (λ= 1.5418 Å) or Mo Kα (λ= 0.71073 Å) radiation controlled using the APEX 2010 software package. In both cases, the diffraction was weak and the resolution is only at ~1.7 Å, even though the exposure time has been set up to 120 second per image. The data was collected up to 1.12 Å. A solution for the structure of MOF-177-OMe was unattainable due to low resolution of the data. Unit cell and space group information are summarized in Table S1 below.

A single crystal of Zn(II)-MOF-BTB-OH taken from $CHCl_3$ was mounted on nylon loops with paratone oil and placed under a nitrogen cold stream (200 K). Data was collected on a Bruker Apex diffractometer using Mo Kα (λ= 0.71073 Å) radiation controlled using the APEX 2010 software package. The diffraction was weak and the resolution was low at ~1 Å. The data was collected up to 0.83 Å. A multi-scan method utilizing equivalents was employed to correct for absorption. All data collections were solved and refined using the SHELXTL software suite.[1] Structures Zn(II)-MOF-BTB-OH was treated with the "SQUEEZE" protocol in PLATON[2] to account for partially occupied or disordered solvent (e.g. $CHCl_3$ or DMF) within the porous frameworks.

Digestion and Analysis by ^{1}H NMR. MOF materials (~10 mg) were dried under vacuum at room temperature overnight. MOF materials were then digested with DMSO-d_6 (500 uL) and DCl (50 uL).

BET Surface Area Analysis. 10-30 mg of MOF was evacuated under vacuum for 2 min at room temperature. Samples were then transferred to a pre-weighed sample tube and degassed at 105 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 hours or until the outgas rate was <5 μmHg/min. The sample tube was re-weighed to obtain a consistent mass for the degassed MOF. Brunauer-Emmett-Teller (BET) surface area (m^2/g) measurements were collected at 77 K with N_2 on a Micromeritics ASAP 2020.

Thermal Analysis. Approximately 10-15 mg of MOF was used for thermogravimetric analysis (TGA) measurements, which were obtained immediately after collection of gas sorption data (i.e. activated samples). Samples were analyzed under a stream of N_2 (10 mL/min) using a TA Instrument Q600 SDT running from room temperature to 600 °C with a ramping rate of 5 °C/min.

Estimation of the volume of the octahedral cage of Zn(II)-MOF-BTB[OH]$_3$. The octahedral cages are assumed to have a regular octahedral shape. Thus, the volume of the octahedral cage can be calculated using the formula $V = \frac{1}{3} \times \sqrt{2} \times s^3$, where *s* is the side of the octahedral cage (Fig. S3). The side of the pseudo-octahedral cage is estimated by first calculating the centroids of two adjacent SBUs. The distance between these two centroids is the side of the octahedral cage. The volume of the octahedral cage is estimated to be ~2763 Å^3.

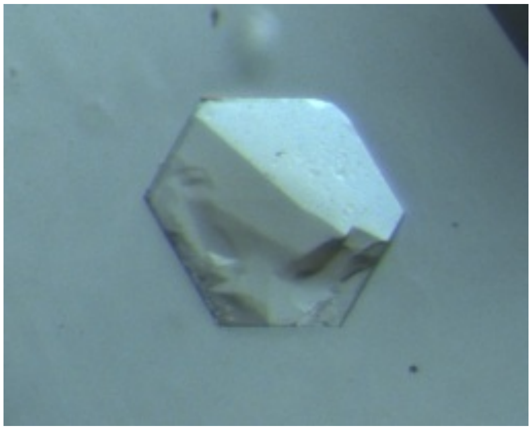


Figure S1. Picture of hexagonal crystal of MOF-177-OMe.

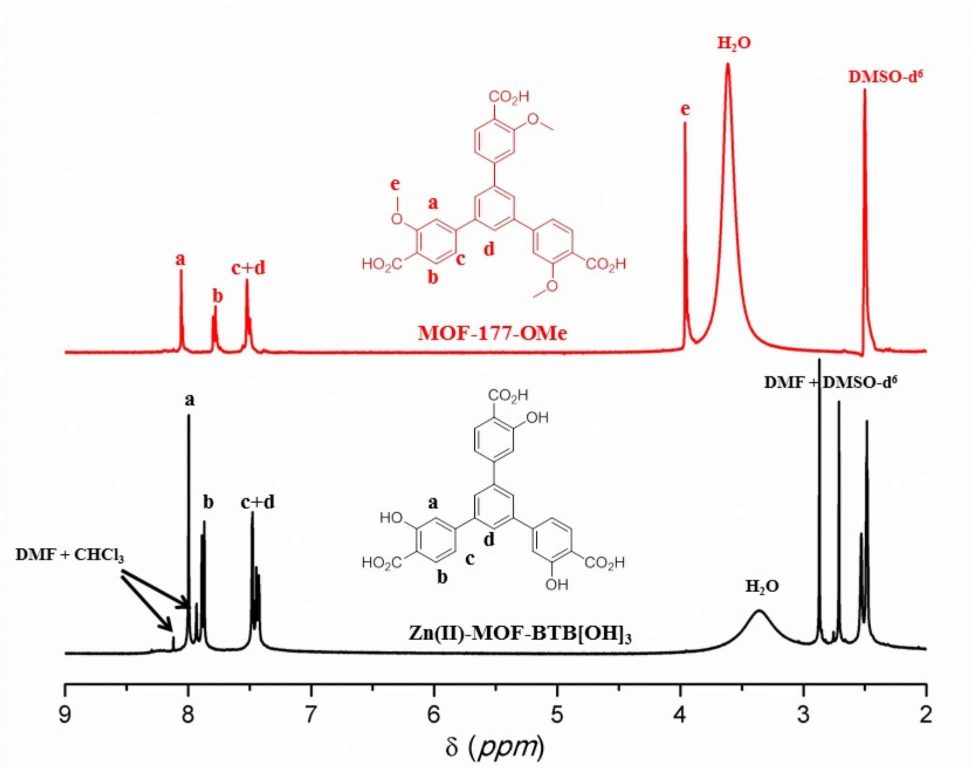


Figure S2. ^{1}H NMR analysis of digested Zn(II)-MOF-BTB[OH]$_3$ and MOF-177-OMe.

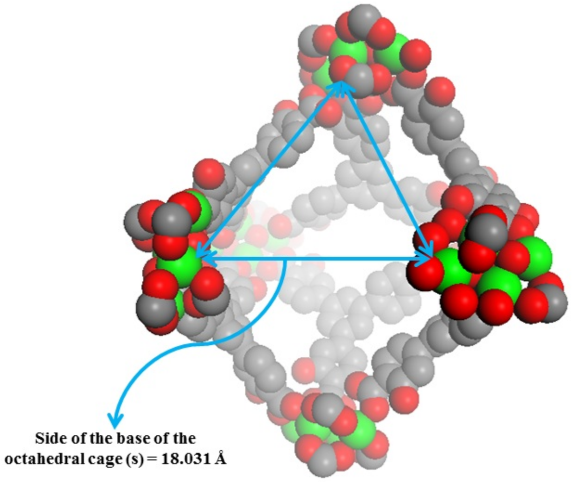


Figure S3. Dimension of the space-filling model octahedral cage of Zn(II)-MOF-BTB[OH]$_3$. Color scheme: Carbon (grey), oxygen (red), and zinc (green).

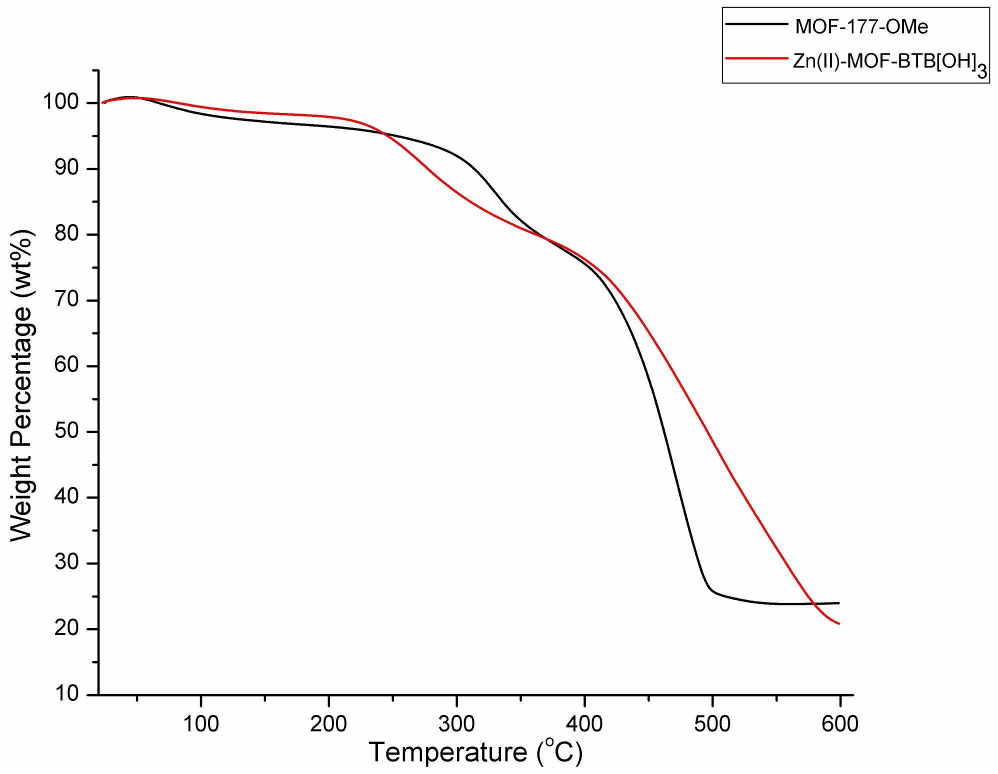


Figure S4. Thermogravimetric analysis (TGA) of MOF-177-OMe and Zn(II)-MOF-BTB[OH]$_3$.

Table S1. Summary of unit cell and space group information of isomers of Zn(II) and H_3BTB MOFs.

MOFs	**MOF-39**[3]	**Zn/BTB ant**[4]	**Zn/BTB tsx**[4]	**Zn/BTB dia**[4]	**MOF-177**[5]	**MOF-177-OMe**
Unit cell	Orthorhombic a = 17.158 Å b =21.591 Å c = 25.308 Å α = β = γ = 90 °	Monoclinic a = 26.385 Å b = 28.385 Å c = 31.613 Å α = γ = 90 ° β = 113.567 °	Tetragonal a = b = 13.957 Å c = 28.7133 Å α = β = γ = 90	Cubic a = b =c = 25.976 Å α = β = γ = 90	Trigonal a = b = 37.072 Å c = 30.033 Å α = β = 90 ° γ = 120 °	Trigonal a = b = 36.629 Å c = 29.660 Å α = β = 90 ° γ = 120 °
Space group	*Pnma* (#62)	*C*2/*c* (#15)	*I*-42*d* (#122)	*F*-*d*3 (#203)	*P*-31*c* (#163)	*P*-31*c* (#163)

Table S2. Crystal data and structure refinement for Zn(II)-MOF-BTB[OH]$_3$.

Identification code	Zn(II)-MOF-BTB[OH]$_3$
Empirical formula	$C_{41} H_{27} Cl_6 N O_{14} Zn_2$
Formula weight	1101.08
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Rhombohedral
Space group	R-3
Unit cell dimensions	a = b = 36.061(3) Å c = 24.163(3) Å $\alpha = \beta = 90^{\circ}$ $\gamma = 120^{\circ}$
Volume	27212(5) Å^3
Z	18
Density (calculated)	1.209 Mg/m^3
Absorption coefficient	1.108 mm^{-1}
F(000)	9972
Crystal size	0.04 x 0.05 x 0.10 mm^3
Theta range for data collection	1.55 to 25.44°.
Index ranges	-43<=h<=21, 0<=k<=43, 0<=l<=29
Reflections collected	10180
Independent reflections	10180 [R(int) = 0.0000]
Completeness to theta = 25.44°	91.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10180 / 3 / 542
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R1 = 0.1084, wR2 = 0.2983
R indices (all data)	R1 = 0.1539, wR2 = 0.3195
Largest diff. peak and hole	2.156 and -1.173 e.Å^{-3}

References

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