Supporting Information for

Distinct interpenetrated metal-organic frameworks constructed from crown ether-based strut analogue

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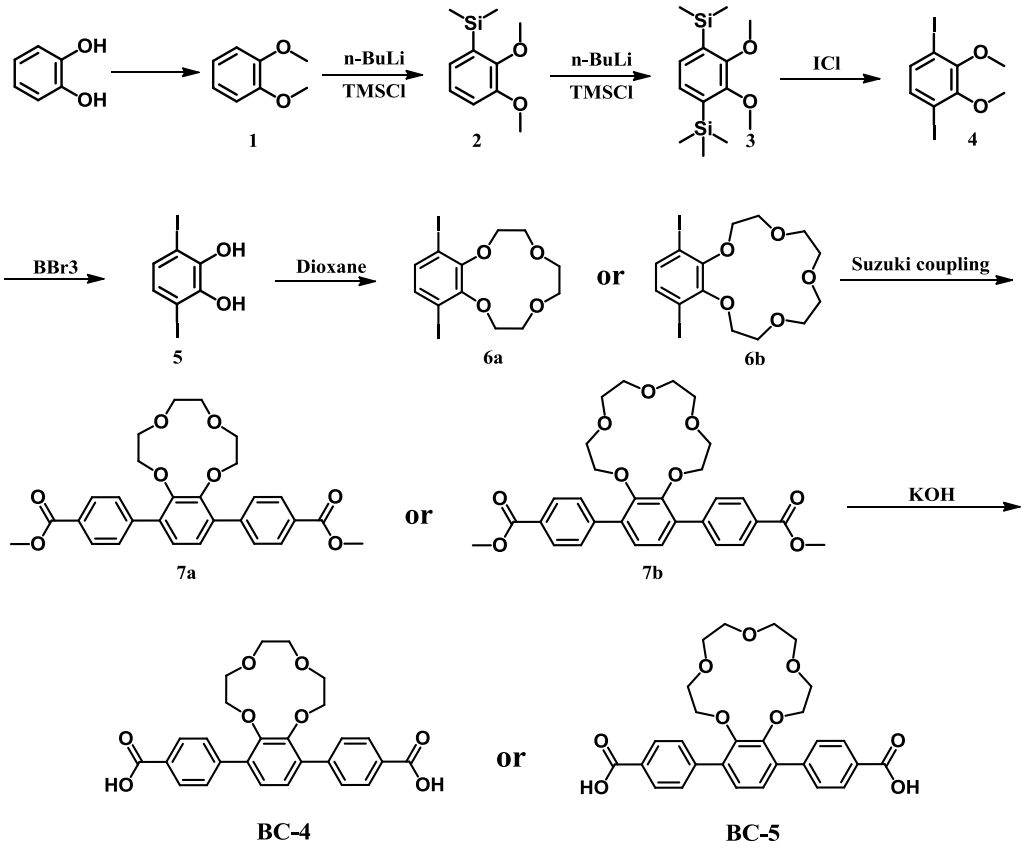
1. Materials and Measurements:

All chemical reagents were commercially available and used as received unless otherwise stated, and solvents were dried or purified according to standard procedures prior to use. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker BBFO-400 spectrometer. The electronic spray ionization (ESI) mass spectra were recorded on a ThermoFinnigan LCQ quadrupole ion trap mass spectrometer. HR-MS was performed on a Waters Q-tof Premier MS spectrometer. Absorption spectra were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. Gas sorption isotherms were obtained with Quantachrome Autosorb-iQ-MP. The samples were degassed overnight at 100 °C. Thermogravimetric analyses (TGA) were performed on a TGA 500 thermogravimetric analyzer by heating the samples at 5 °C min^{-1} to 600 °C in the atmosphere of nitrogen. Single crystal X-ray diffraction data were collected on a Bruker SMART APEXII three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo *Kα* radiation (λ = 0.71073 Å). Crystals were mounted on nylon CryoLoops in a liquid N_2 cooled stream of nitrogen. ICP-MS analysis was carried out on the Agilent 7700-Japan equipment.

2. Synthesis of BC-4 and BC-5:



Scheme S1. Synthetic routes of BC-4 and BC-5.

Synthesis of BC-4: A mixture of 6a[S1,S2] (1.24 g, 2.6 mmol), Cs_2CO_3 (2.0 g, 6.1 mmol) and H_2O (25 mL) in 1,4-dioxane (50 mL) was bubbled with Argon for 30 min. Then, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.07g, 0.1 mmol) and 4-(methoxycarbonyl) benzenebornic acid pinacol ester (1.71g, 6.5 mmol) were added to the solution and the reaction mixture was refluxed under Argon atmosphere for another 5 h. After cooling down to room temperature, the resulting mixture was filtrated and the solvents were evaporated in vacuum. The residue was dissolved in THF/H_2O (2:1, v/v, 50 mL), and KOH (0.58g, 10.4 mmol) was added to the solution. After stirring at room temperature for 48 h, the mixture solution was washed successively with ethyl acetate until there was no organic compound in eluate as indicated by TLC. Then, HCl (1 N) was added to the organic solution in order to adjust the solution pH to 1. The precipitate was collected and dried under vacuum to give BC-4 (0.57 g, 47.5%) as white solid. ^{1}H-NMR (400MHz, DMSO-d_6, ppm): δ 13.01 (br, 2H), 8.03 (d, J = 8.4 Hz, 4H), 7.72 (d, J = 8.4 Hz, 4H), 7.28 (s, 2H), 3.91 (m, 4H), 3.63 (m, 8H);

^{13}C-NMR (100MHz, DMSO-d_6, ppm): δ 167.6, 150.6, 142.3, 135.4, 130.1; 129.8, 129.6, 126.2, 77.4, 70.8, 70.0; ESI-MS m/z: 950.8 $[2M+Na-H]^+$; HRMS (TOF) m/z calcd. for $C_{26}H_{25}O_8$: 465.1549, found: 465.1562.

Synthesis of BC-5: A similar procedure was adopted to afford BC-5 (0.66 g, 50.1%) as white solid. ^{1}H-NMR (400MHz, DMSO-d_6, ppm): δ 12.83 (br, 2H), 8.02 (d, J = 8.4 Hz, 4H), 7.69 (d, J = 8.4 Hz, 4H), 7.26 (s, 2H), 3.89 (m, 4H), 3.63 (m, 4H), 3.33 (m, 8H); ^{13}C-NMR (100MHz, DMSO-d_6, ppm): δ 167.6, 150.6, 142.3, 135.2, 130.2; 129.8, 129.6, 126.0, 73.4, 70.7, 70.0, 69.9; ESI-MS m/z: 1054.6 $[2M+K-H]^+$; HRMS (TOF) m/z calcd. for $C_{28}H_{29}O_9$: 509.1812, found: 509.1824.

^{1}HNMR, ^{13}CNMR & Mass Spectra of BC-4 and BC-5:

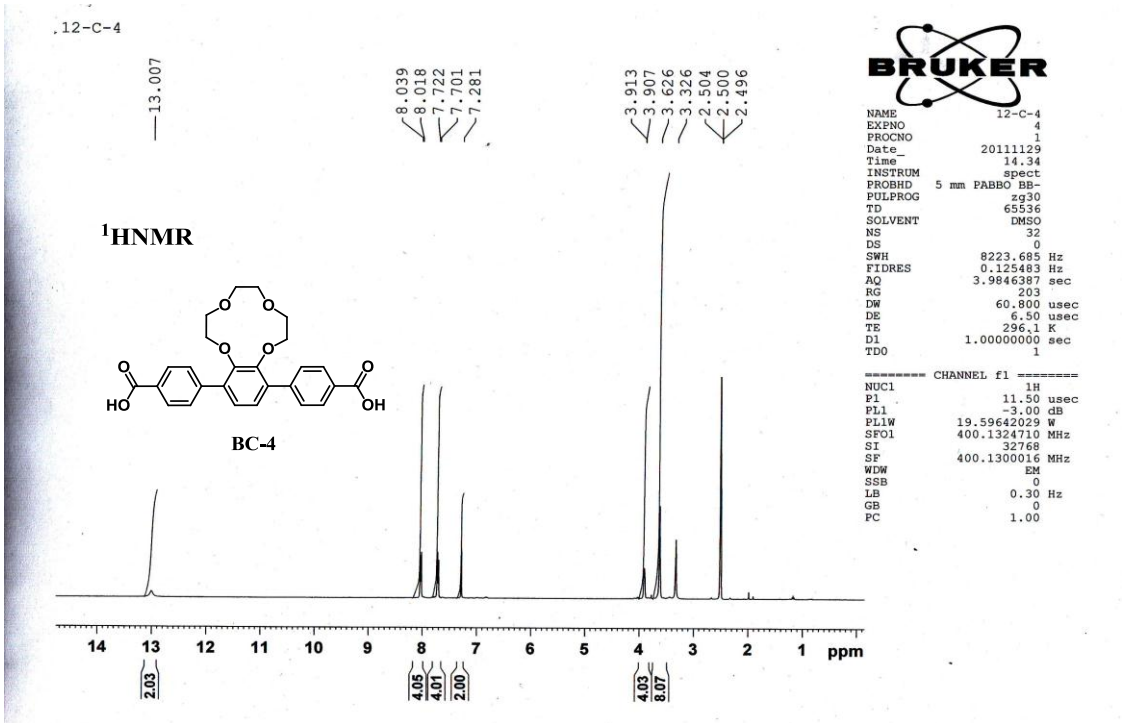


Figure S1. ^{1}H NMR spectrum of BC-4.

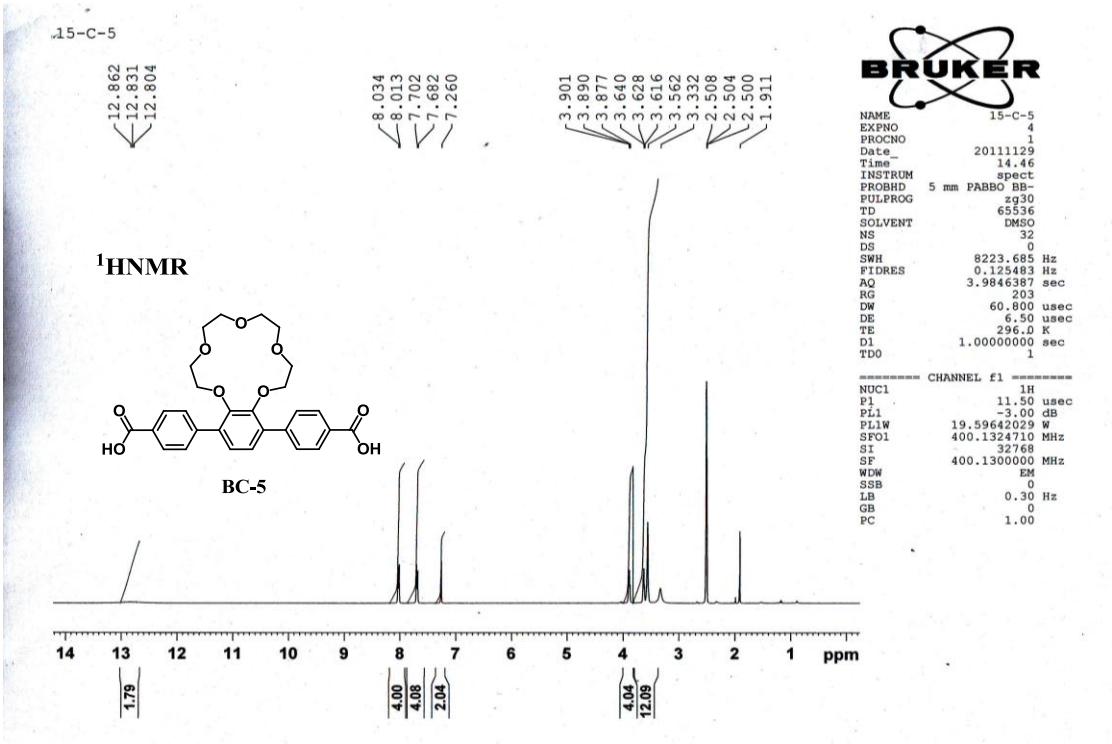


Figure S2. ^{1}H NMR spectrum of BC-5.

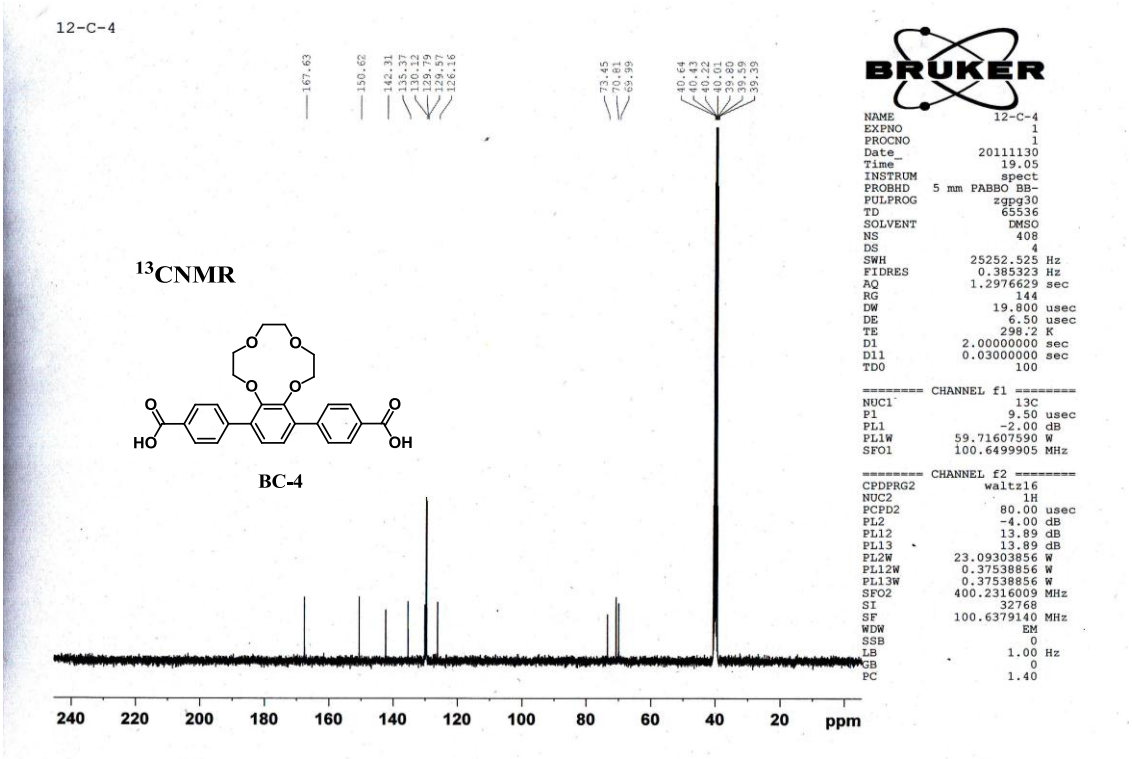


Figure S3. ^{13}C NMR spectrum of BC-4.

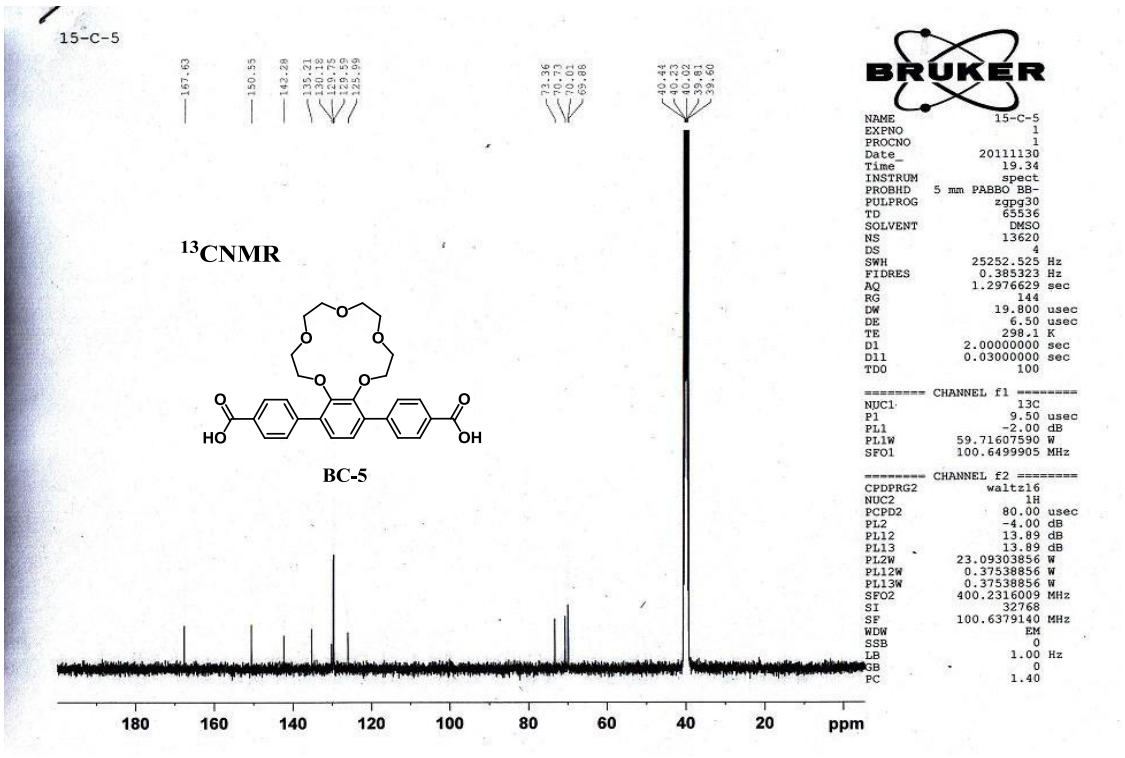


Figure S4. ^{13}C NMR spectrum of BC-5.

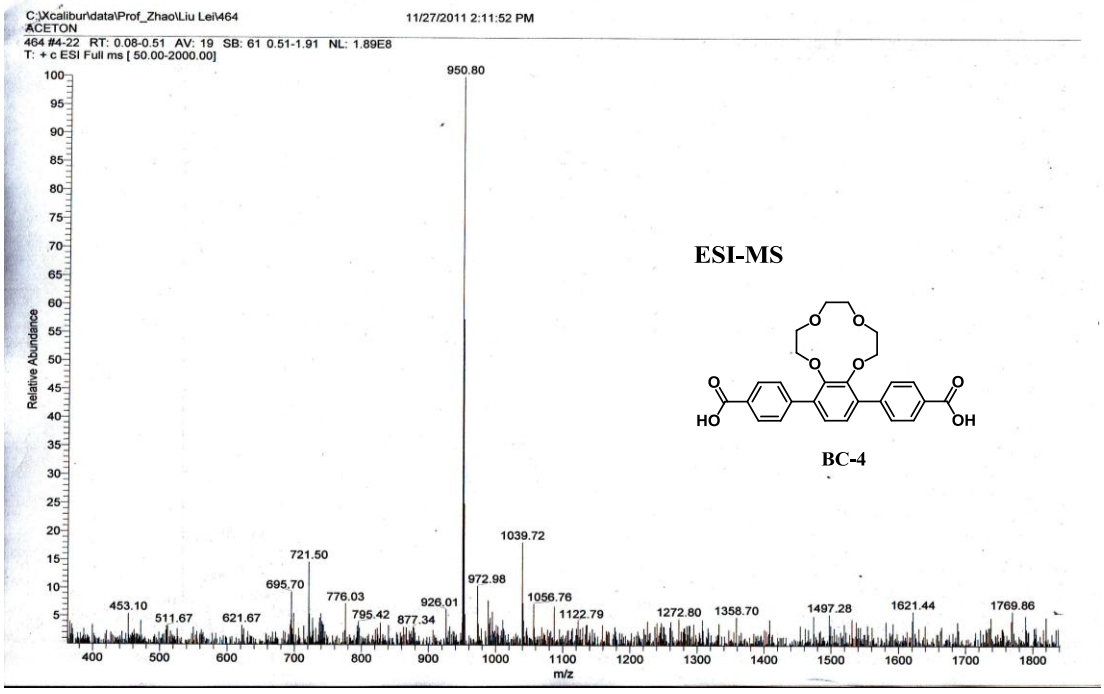


Figure S5. ESI-MS of BC-4.

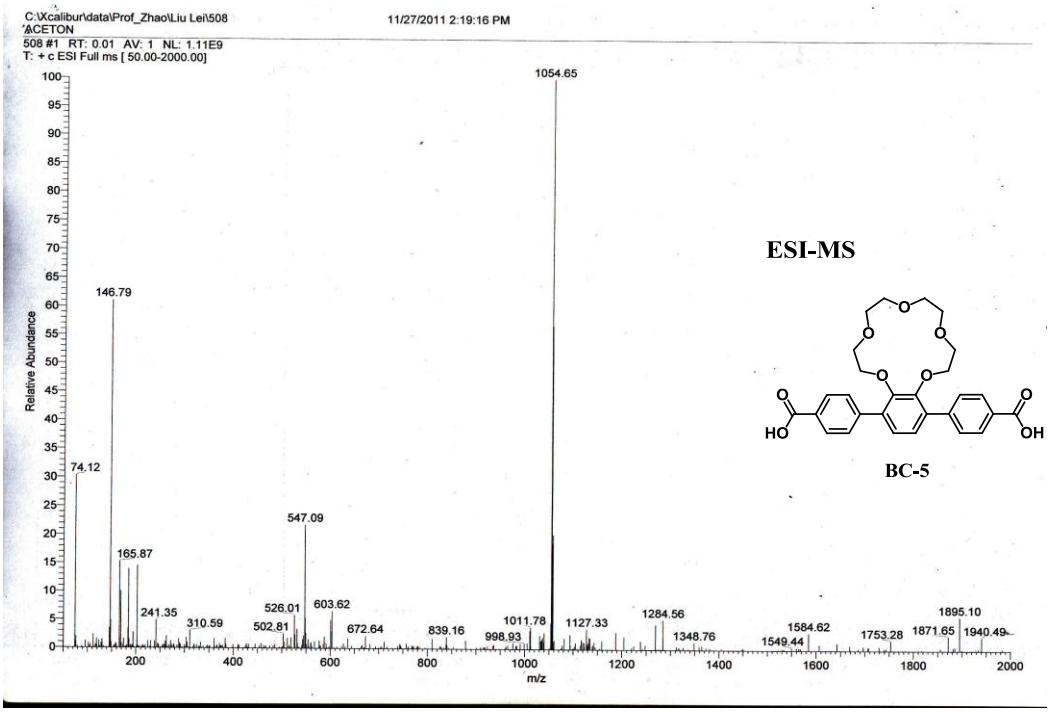


Figure S6. ESI-MS of BC-5.

3. Crystal Data and Structure Refinement Details for BC-4 and BC-5:

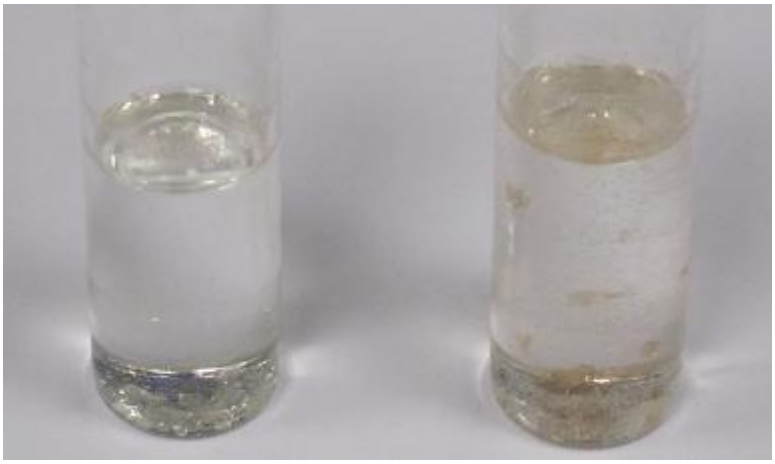


Figure S7. Photos of BC-5 (*left*) and BC-4 (*right*) crystals.

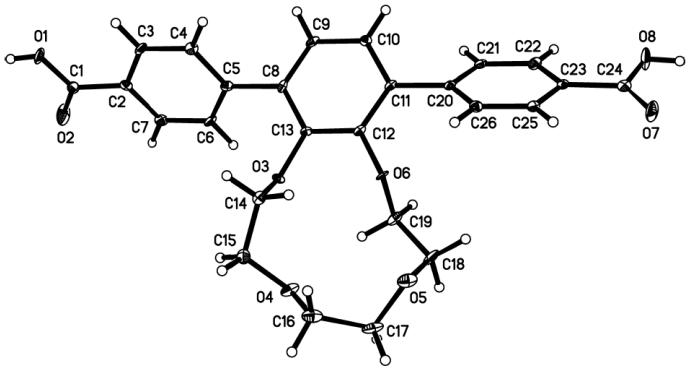


Figure S8. Single crystal X-ray structure of BC-4, with three DMF molecules omitted for clarity.

Table S1. Crystal data and structure refinement for BC-4.

Identification code	BC-4	
Empirical formula	C35 H45 N3 O11	
Formula weight	683.74	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2812(5) Å	α= 90.146(4)°.
	b = 10.8141(7) Å	β= 96.815(4)°.
	c = 17.5421(12) Å	γ = 99.763(3)°.
Volume	1722.44(19) $Å^3$	
Z	2	
Density (calculated)	1.318 Mg/m^3	
Absorption coefficient	0.098 mm^{-1}	
F(000)	728	
Crystal size	0.40 x 0.36 x 0.34 mm^3	
Theta range for data collection	1.17 to 26.00°.	
Index ranges	-11<=h<=11, -13<=k<=13, -21<=l<=21	
Reflections collected	28037	
Independent reflections	6776 [R(int) = 0.0766]	
Completeness to theta = 26.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9673 and 0.9617	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6776 / 6 / 442	
Goodness-of-fit on F^2	1.130	
Final R indices [I>2sigma(I)]	R1 = 0.0761, wR2 = 0.1692	
R indices (all data)	R1 = 0.0999, wR2 = 0.1942	
Largest diff. peak and hole	0.342 and -0.496 $e.Å^{-3}$	

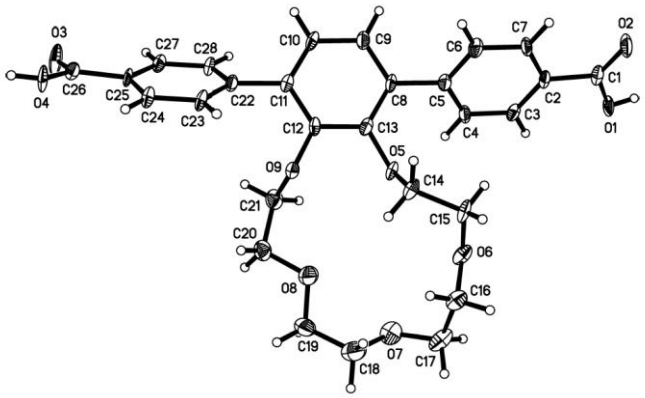


Figure S9. Single-crystal X-ray structure of BC-5, with two DMSO molecules omitted for clarity.

Table S2. Crystal data and structure refinement for BC-5.

Identification code	BC-5	
Empirical formula	C32 H40 O11 S2	
Formula weight	664.76	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.5432(16) Å	α= 105.358(8)°.
	b = 10.5250(19) Å	β= 93.281(9)°.
	c = 17.119(3) Å	γ = 96.235(9)°.
Volume	1641.6(5) $Å^3$	
Z	2	
Density (calculated)	1.345 Mg/m^3	
Absorption coefficient	0.221 mm^{-1}	
F(000)	704	
Crystal size	0.40 x 0.16 x 0.10 mm^3	
Theta range for data collection	2.02 to 25.37°.	
Index ranges	-10<=h<=11, -12<=k<=12, -20<=l<=20	
Reflections collected	23865	
Independent reflections	5704 [R(int) = 0.0998]	
Completeness to theta = 25.00°	96.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9782 and 0.9168	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5704 / 0 / 412	
Goodness-of-fit on F^2	1.006	
Final R indices [I>2sigma(I)]	R1 = 0.0587, wR2 = 0.1416	
R indices (all data)	R1 = 0.1250, wR2 = 0.1827	
Largest diff. peak and hole	0.378 and -0.473 $e.Å^{-3}$	

4. ^{1}H NMR Titration by Alkali Ions:

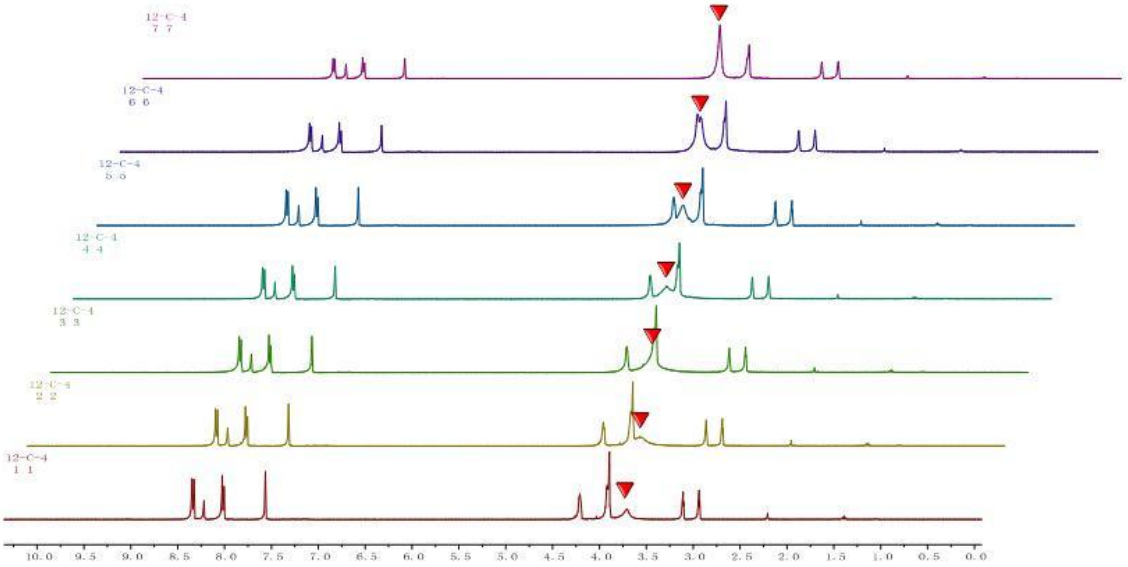


Figure S10. Partial ^{1}H NMR spectra (400 MHz) of BC-4 (1.3×10^{-3} M in DMF-d_7) at 25 ^{o}C in the presence of increasing amount of LiCl (from bottom to top: 0 to 1.02 equiv). Protons labeled with ▼ correspond to ones from the crown ether rings.

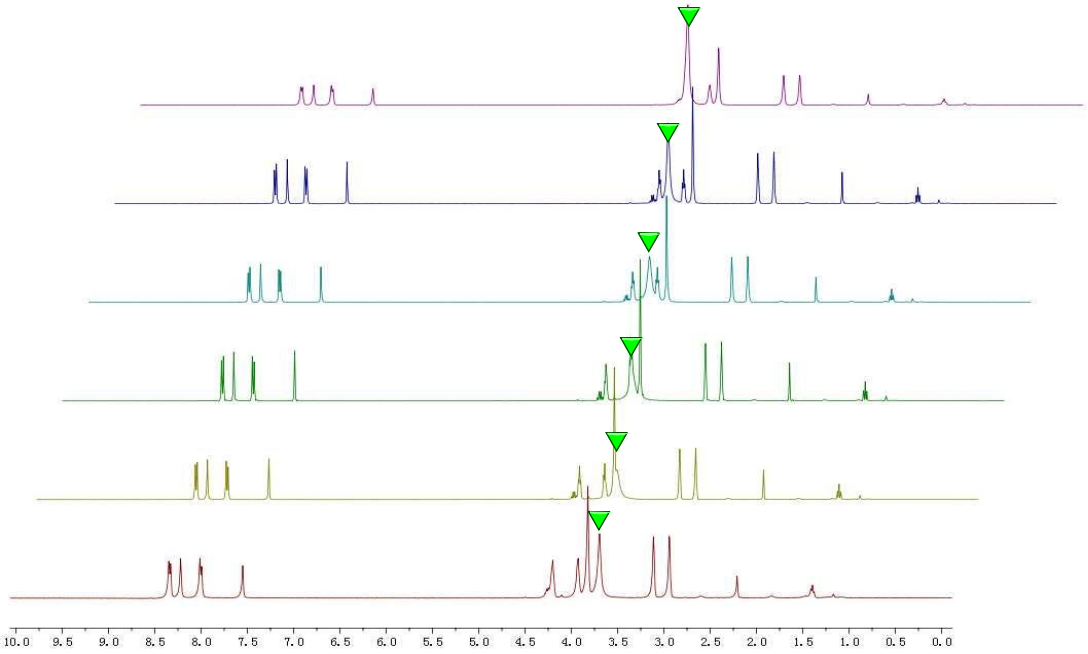
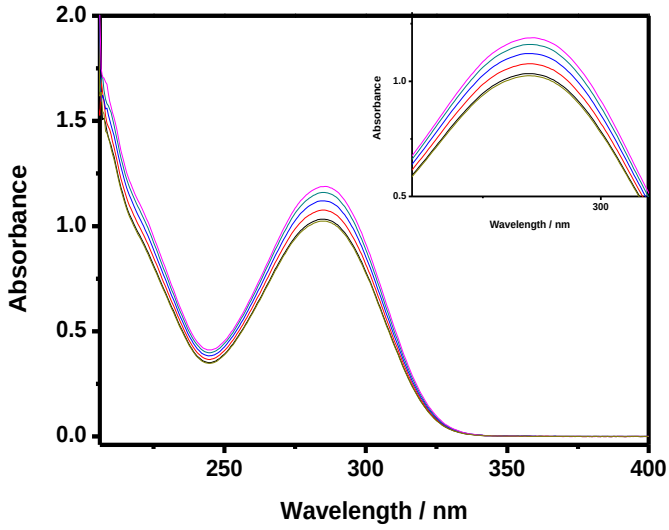
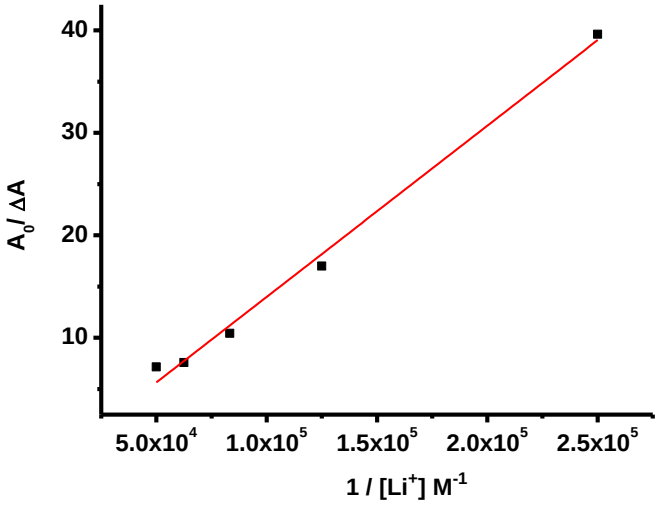


Figure S11. Partial ^{1}H NMR spectra (400 MHz) of BC-5 (1.4×10^{-3} M in DMF-d_7) at 25 ^{o}C in the presence of increasing amount of NaCl (from bottom to top: 0 to 1.0 equiv). Protons labeled with ▼ correspond to ones from the crown ether rings.

5. UV-Vis Titration by Alkali Ions

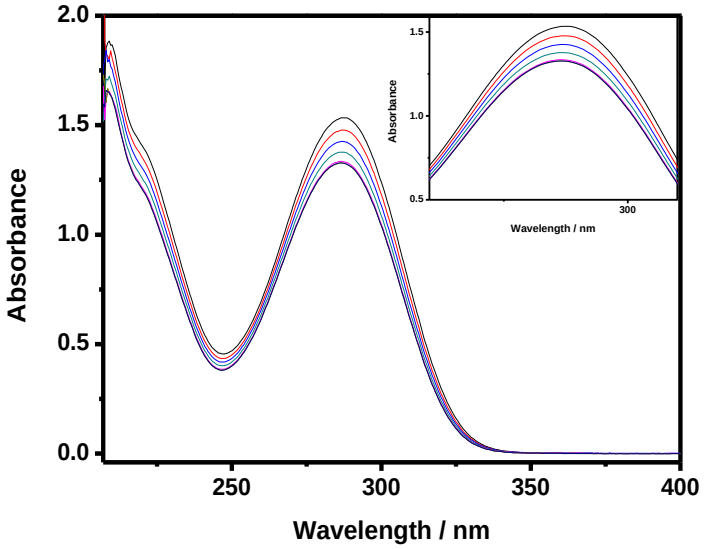


(a)

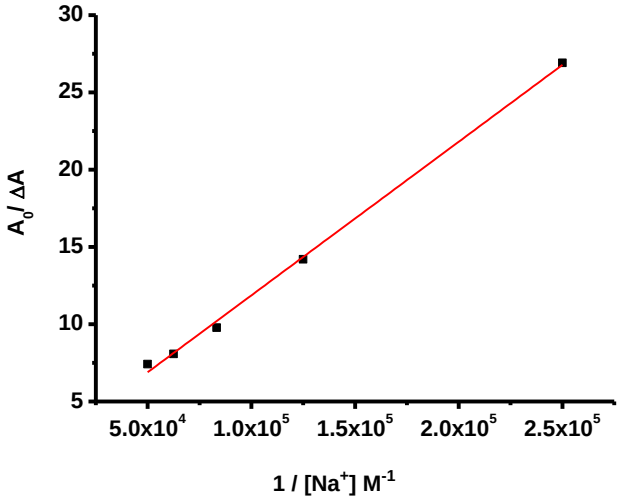


(b)

Figure S12. (a) The absorbance spectra of BC-4 (2.0×10^{-4} M in DMF) in the presence of increasing amount of LiCl (curves from top to bottom: 0, 4.0×10^{-6}, 8.0×10^{-6}, 8.0×10^{-5}, 1.0×10^{-4}, 2.0×10^{-4} M), and (b) plot fitting (R = 0.9854) for the calculation of binding constant using Benesi-Hildebrand equation, $1/\Delta A = 1/\alpha + 1/\alpha K[\text{Metal}]$.



(a)



(b)

Figure S13. (a) The absorbance spectra of BC-5 (2.1×10^{-4} M in DMF) in the presence of increasing amount of NaCl (curves from top to bottom: 0, 4.0×10^{-6}, 8.0×10^{-6}, 8.0×10^{-5}, 1.0×10^{-4}, 2.0×10^{-4} M), and (b) plot fitting (R = 0.9883) for the calculation of binding constant using the same equation indicated in Figure S12.

6. ESI-MS of Complexes

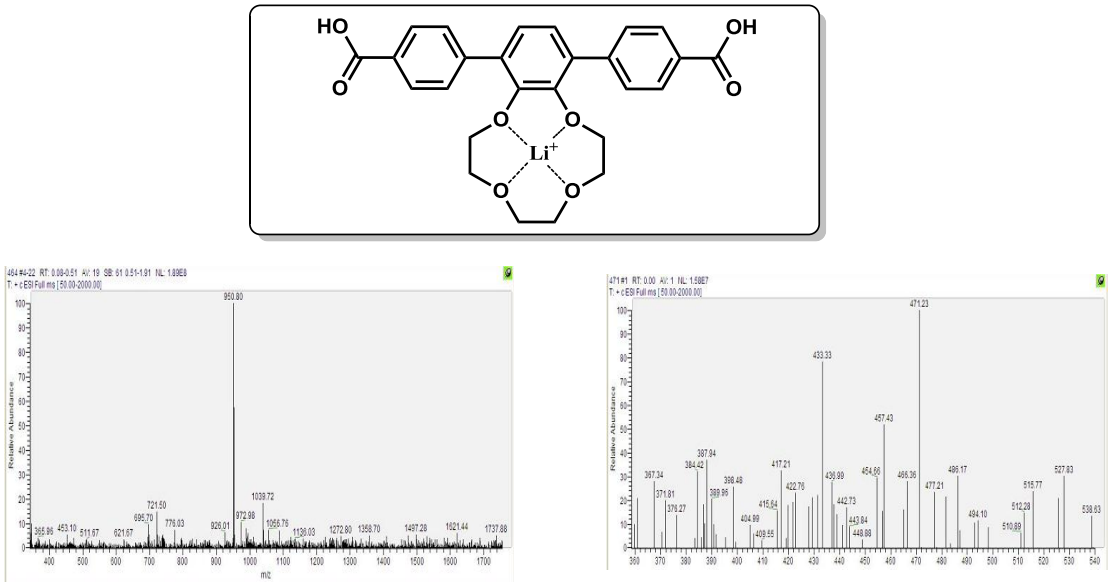


Figure S14. The ESI/MS spectra of BC-4 (2.0×10^{-5} M in DMF) before (*left*) and after (*right*) adding 1.0 equiv of LiCl. The signal at 950.8 (m/z) corresponds to the complex cation $[2M+\text{Na-H}]^+$ and the signal at 471.2 (m/z) corresponds to $[M+\text{Li-H}]^+$.

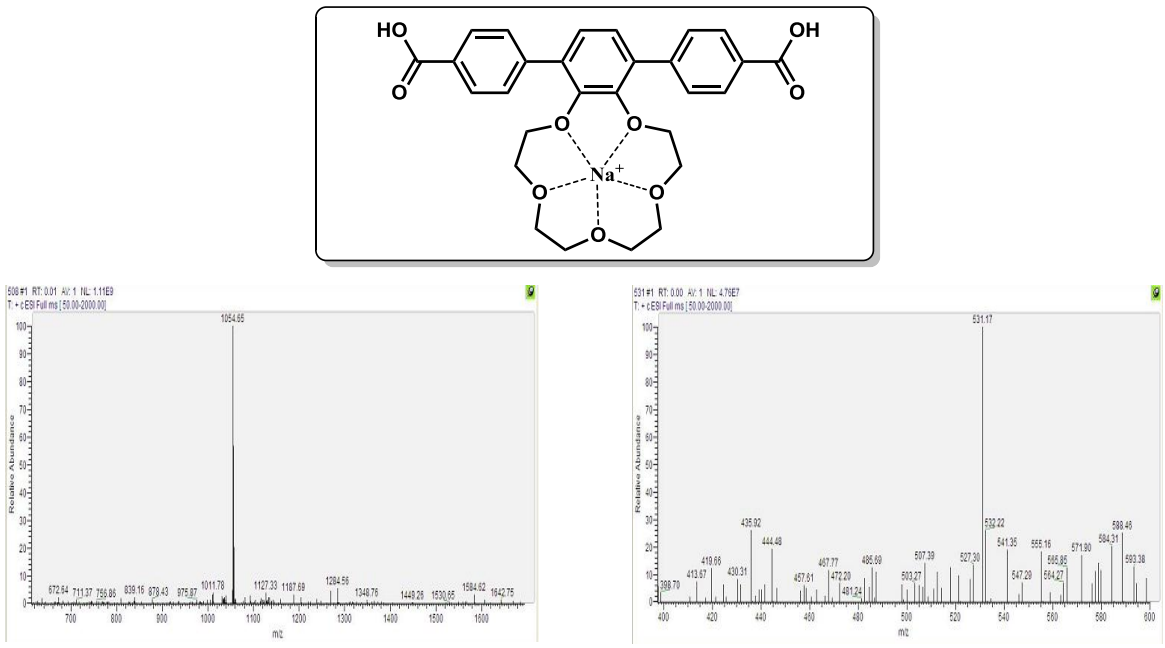
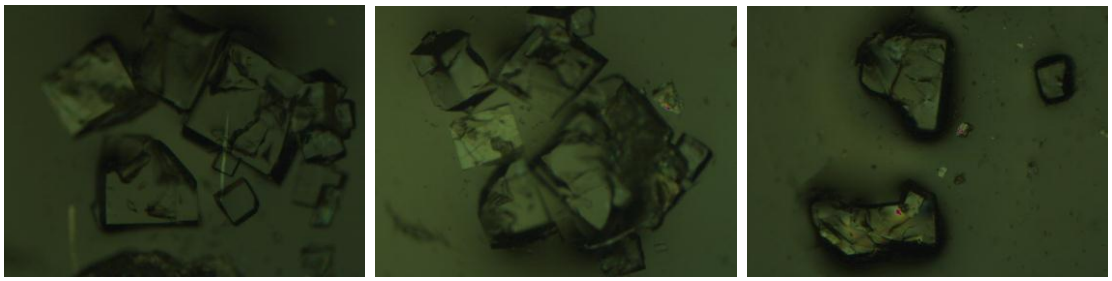


Figure S15. The ESI/MS spectra of BC-5 (1.9×10^{-5} M in DMF) before (*left*) and after (*right*) adding 1.0 equiv of NaCl. The signal at 1054.6 (m/z) corresponds to the complex cation $[2M+\text{K-H}]^+$ and the signal at 531.2 (m/z) corresponds to $[M+\text{Na-H}]^+$.

7. Crystal Data and Structure Refinement Details for MOF-BC-4, MOF-BC-5 and IRMOF-15



MOF-BC-4 **MOF-BC-5** **IRMOF-15**

Figure S16. Photos of MOF-BC-4, MOF-BC-5, and IRMOF-15 crystals.

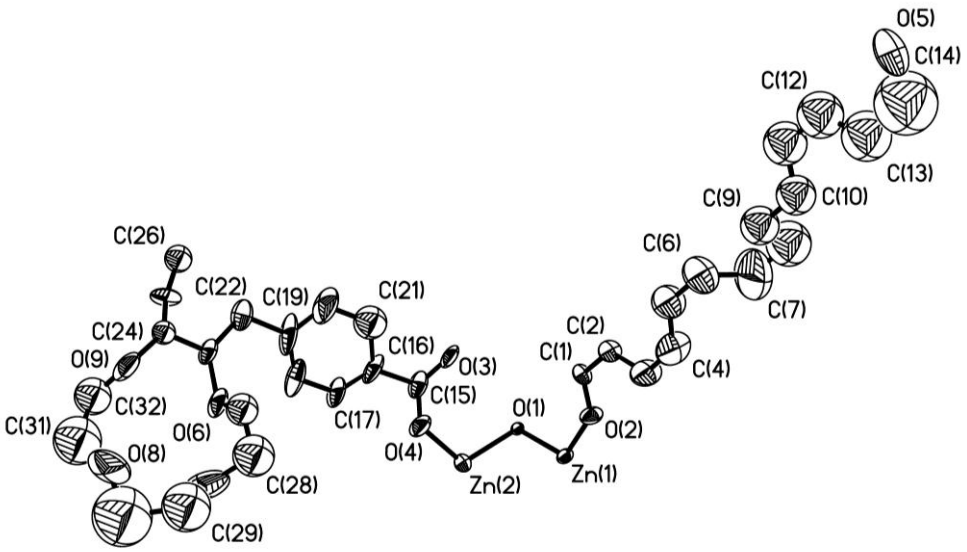


Figure S17. Asymmetrical unit of MOF-BC-4. Hydrogen atoms, and partial bismethylenedioxy units of BC-4 are not shown.

Table S3. Crystal data and structure refinement for MOF-BC-4.

Identification code	MOF-BC-4	
Empirical formula	C70 H48 O21 Zn4	
Formula weight	1486.64	
Temperature	143(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P42/ncm	
Unit cell dimensions	a = 21.4901(11) Å	α= 90.00°.
	b = 21.4901(11) Å	β= 90.00°.
	c = 42.883(4) Å	γ = 90.00°.
Volume	19805(2) $Å^3$	
Z	4	
Density (calculated)	0.499 Mg/m^3	
Absorption coefficient	0.504 mm^{-1}	
F(000)	3024	
Crystal size	0.60 x 0.60 x 0.60 mm^3	
Theta range for data collection	1.90 to 22.60°.	
Index ranges	-23<=h<=23, -22<=k<=23, -39<=l<=46	
Reflections collected	77217	
Independent reflections	6856 [R(int) = 0.1495]	
Completeness to theta = 22.60°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6856 / 47 / 255	
Goodness-of-fit on F^2	0.945	
Final R indices [I>2sigma(I)]	R1 = 0.0767, wR2 = 0.2138	
R indices (all data)	R1 = 0.1245, wR2 = 0.2301	
Largest diff. peak and hole	0.598 and -0.657 $e.Å^{-3}$	

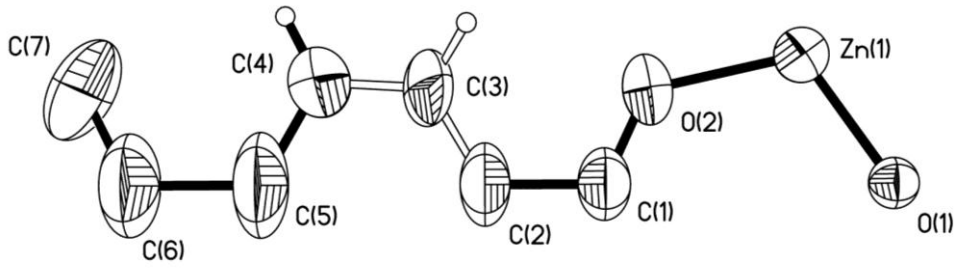
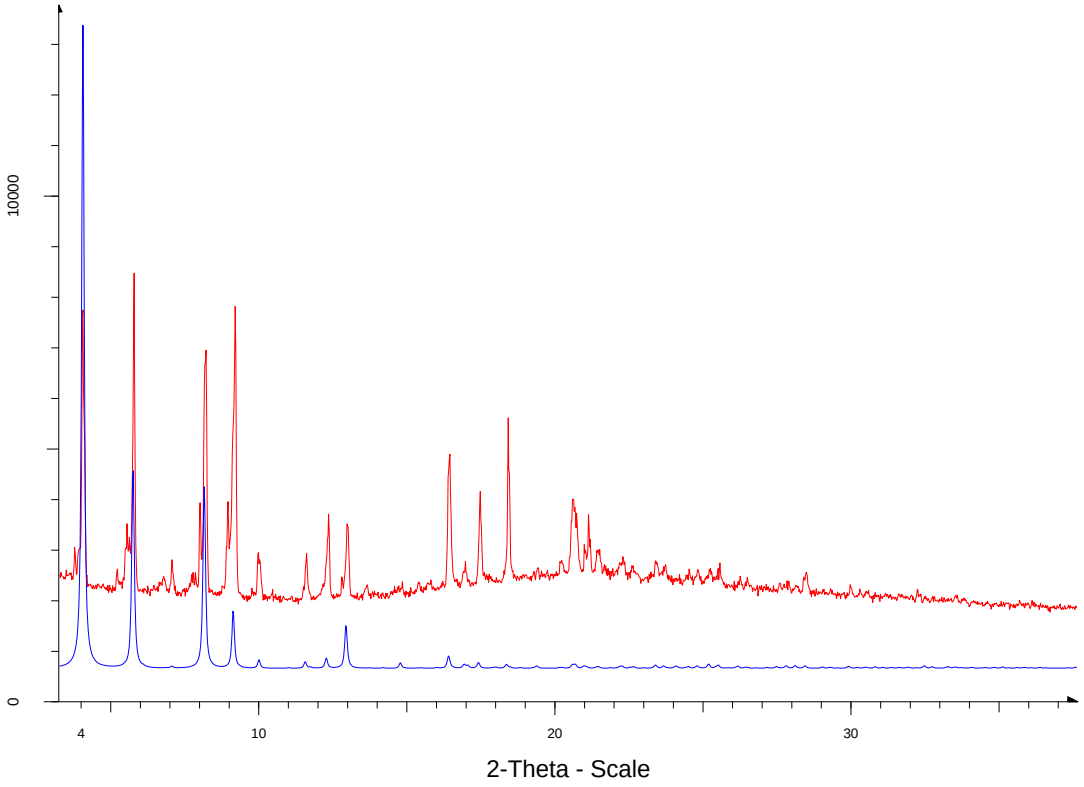


Figure S18. Asymmetrical unit of MOF-BC-5. Bismethylenedioxy units of BC-5 are not shown.

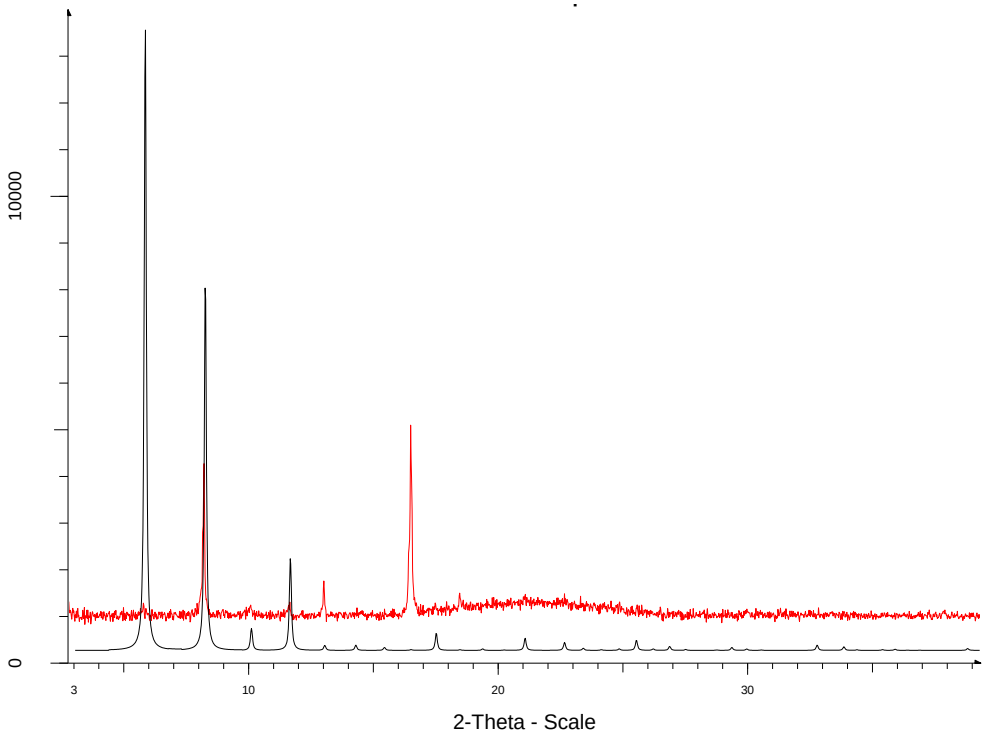
Table S4. Crystal data and structure refinement for MOF-BC-5.

Identification code	MOF-BC-5	
Empirical formula	C60 H24 O13 Zn4	
Formula weight	1214.27	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	Im-3m	
Unit cell dimensions	a = 21.4744(13) Å	α= 90.00°.
	b = 21.4744(13) Å	β= 90.00°.
	c = 21.4744(13) Å	γ = 90.00°.
Volume	9902.9(10) $Å^3$	
Z	2	
Density (calculated)	0.407 Mg/m^3	
Absorption coefficient	0.496 mm^{-1}	
F(000)	1216	
Crystal size	0.30 x 0.25 x 0.25 mm^3	
Theta range for data collection	1.90 to 25.16°.	
Index ranges	-25<=h<=25, -25<=k<=24, -19<=l<=25	
Reflections collected	25086	
Independent reflections	907 [R(int) = 0.1062]	
Completeness to theta = 25.16°	99.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	907 / 6 / 44	
Goodness-of-fit on F^2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0921, wR2 = 0.2759	
R indices (all data)	R1 = 0.1460, wR2 = 0.3150	
Largest diff. peak and hole	0.365 and -0.409 $e.Å^{-3}$	

8. Powder X-Ray Diffraction



(a)



(b)

Figure S19. Powder XRD patterns of (a) as-synthesized MOF-BC-4 (red curve) with simulated one from single crystal data (blue curve), and (b) as-synthesized MOF-BC-5 (red curve) with simulated one from single crystal data (black curve).

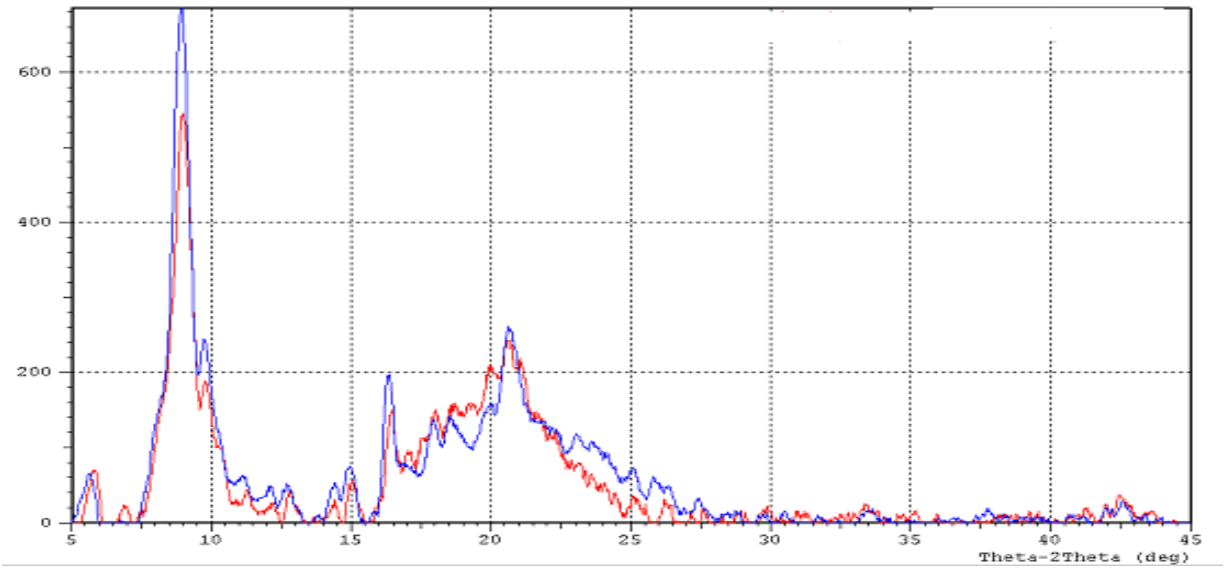


Figure S20. Powder XRD patterns of activated MOF-BC-4 before (red curve) and after (blue curve) immersing into Li^+ solution followed by drying.

9. TGA for BC-4, BC-5, MOF-BC-4 and MOF-BC-5

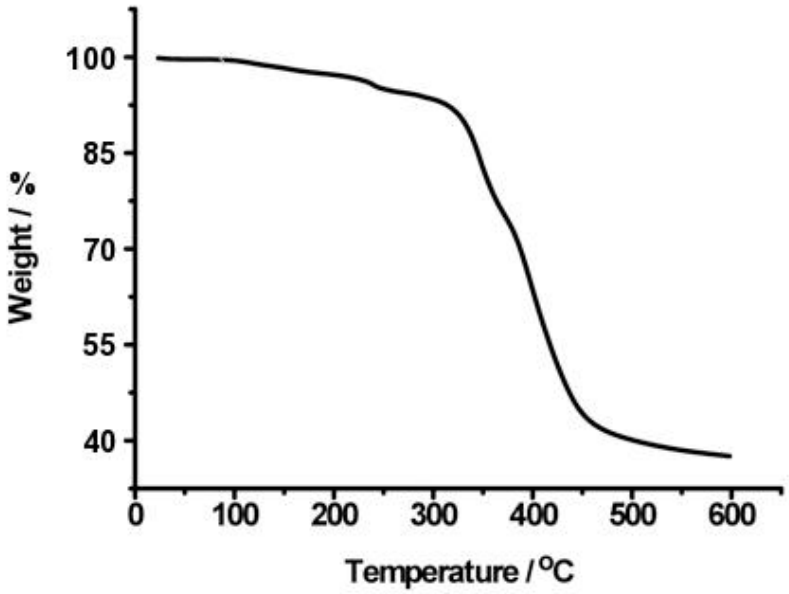


Figure S21. TGA trace for BC-4. Experimental conditions: nitrogen atmosphere, heating rate of 5 ^{o}C min^{-1} in the temperature range of 22-600 ^{o}C.

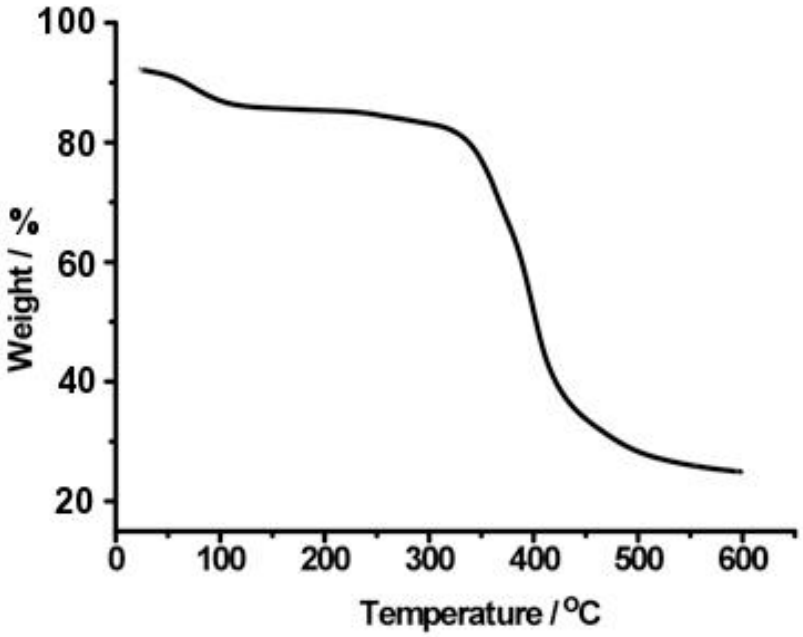


Figure S22. TGA trace for BC-5. Experimental conditions: nitrogen atmosphere, heating rate of 5 ^{o}C min^{-1} in the temperature range of 22-600 ^{o}C.

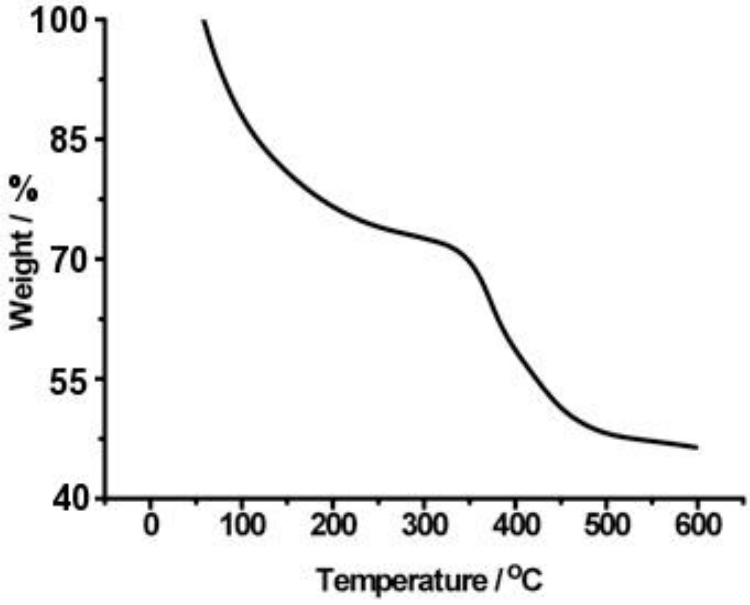


Figure S23. TGA trace for as-synthesized MOF-BC-4. Experimental conditions: nitrogen atmosphere, heating rate of 5 ^{o}C min^{-1} in the temperature range of 22-600 ^{o}C.

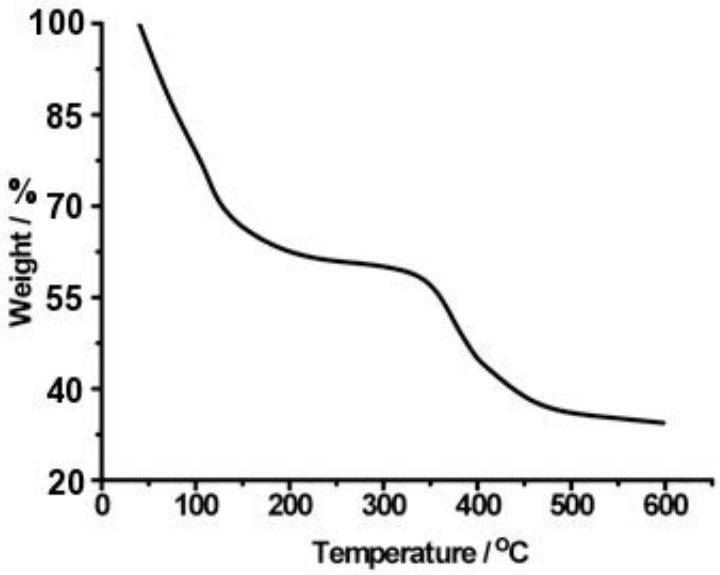


Figure S24. TGA trace for as-synthesized MOF-BC-5. Experimental conditions: nitrogen atmosphere, heating rate of 5 ^{o}C min^{-1} in the temperature range of 22-600 ^{o}C.

10. References

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