Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Detection of Adsorbates on Emissive MOF Surfaces with X-ray Photoelectron Spectroscopy

Jingjing Yan,[†] *Alexander D. Carl,* [†] *John C. MacDonald,* [†]*Peter Müller,*[‡] *Ronald L. Grimm,* [†] *and Shawn C. Burdette*[†]*

[†]Department of Chemistry and Biochemistry, Worcester Polytechnic Institute, 100 Institute Road, Worcester, MA 01609-2280 (USA). E-mail: scburdette@wpi.edu

[‡]Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139 (USA).

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{Zn_2(BDC)$_2$(AzoAE*p*P)}$_n$ (ABMOF-2). AzoAE*p*P (21.1 mg, 50.0 µmol), $Zn(NO_3)_2 \cdot 4H_2O$ (26.1 mg, 0.100 mmol) and terephthalic acid (BDC, 16.6 mg, 0.100 mmol) were combined in a sealed microwave vial in DMF/H_2O (6.8 mL/0.2 mL). After the reaction mixture was sonicated for 2 min, the clear solution was subjected to a programmed reaction cycle that involved steady gradual heating to 100 °C over 1 h, followed by maintaining a constant temperature for 48 h and gradual cooling to room temperature over 6 h. The resulting orange needles were harvested by filtration, washed and stored in DMF. NMR analysis of the MOF after digestion with D_2SO_4 in DMSO-d_6 is consistent with a 2:1 ratio of BDC:AzoAE*p*P. Elemental analysis calcd. for activated ABMOF-2 $C_{42}H_{34}N_6O_8Zn_2$: C 57.22%, H 3.86%, N 9.54%; Found: C 56.95%, H 3.80%, N 9.36%. FT-R (diamond-ATR, cm^{-1}) 3235.4, 3055.0, 1681.1, 1635.7, 1598.0, 1576.6, 1501.7, 1472.2, 1431.8, 1383.8, 1316.8, 1292.5, 1244.3, 1220.3, 1161.2, 1078.1, 1032.7, 823.5, 746.0. TGA shows no mass loss in either freshly prepared or ABMOF-2 dried at 80 °C. Decomposition occurs at 207 °C.

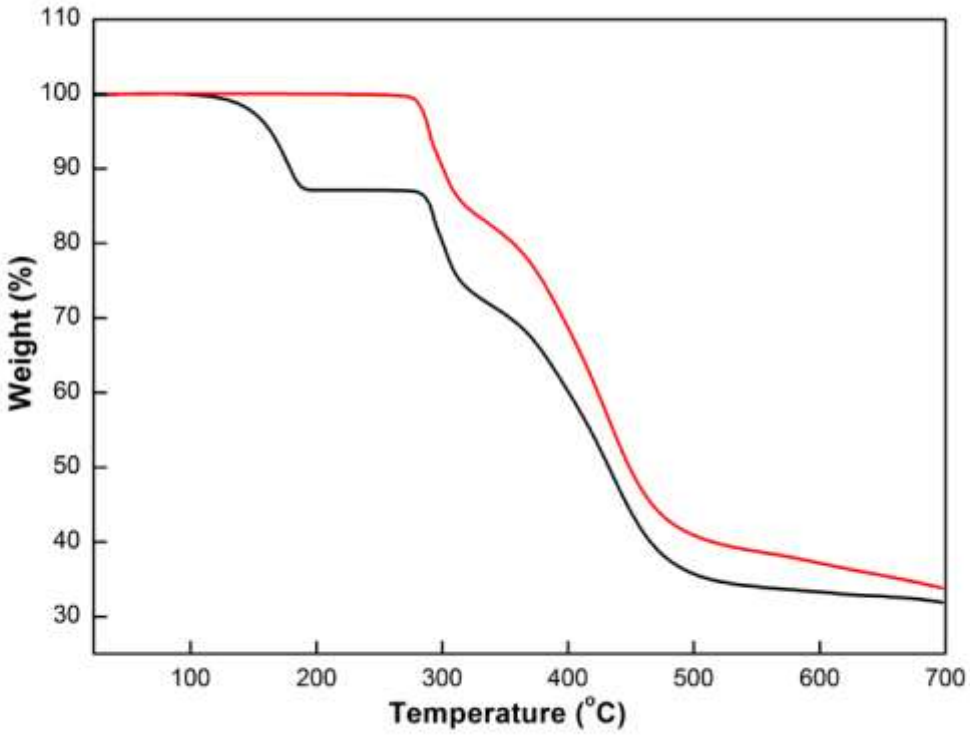

Figure S1. The thermogravimetric analysis (TGA) diagrams of fresh prepared (black) and activated (red) ABMOF-1.

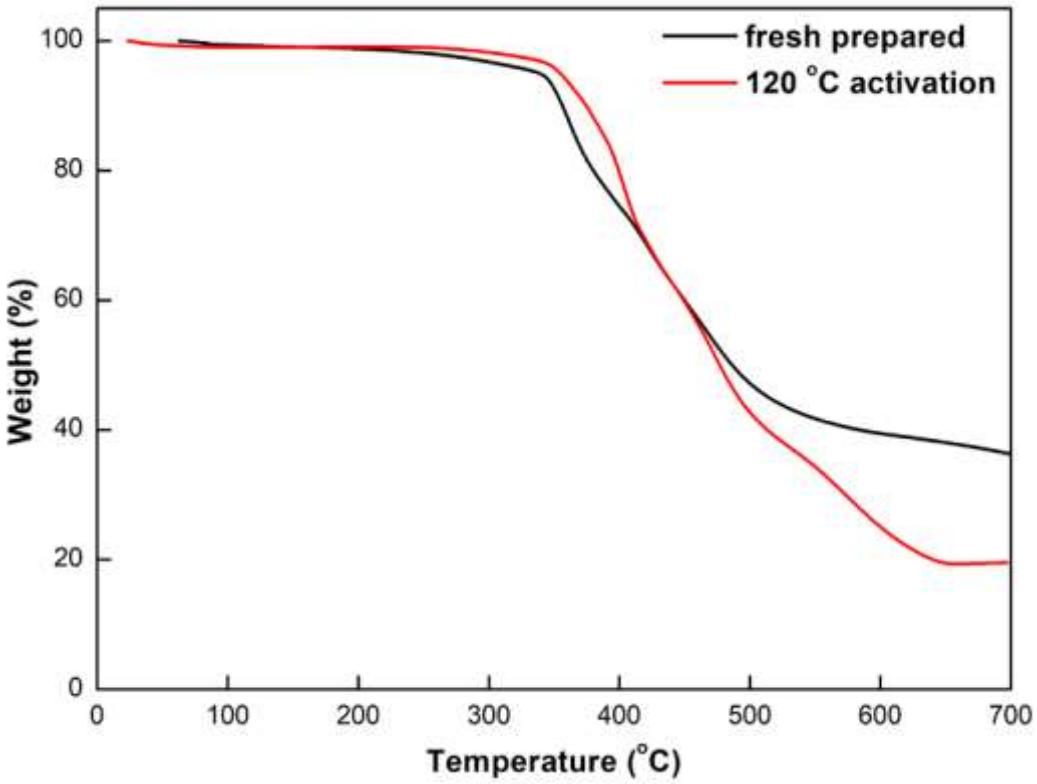

Figure S2. The thermogravimetric analysis (TGA) diagrams of fresh prepared (black) and activated (red) ABMOF-2.

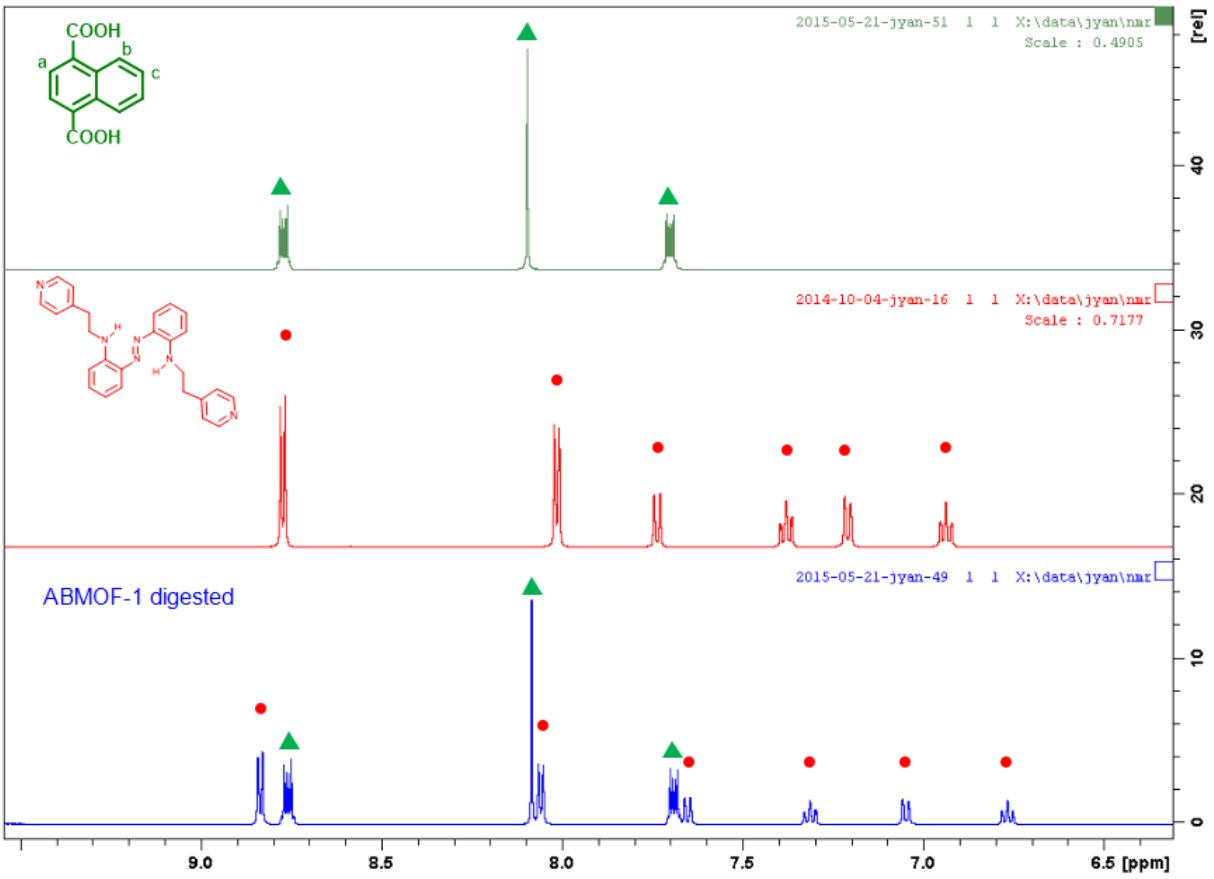

Figure S3. Digested NMR of ABMOF-1, comparing with original ligands NDC and AzoAE*p*P.

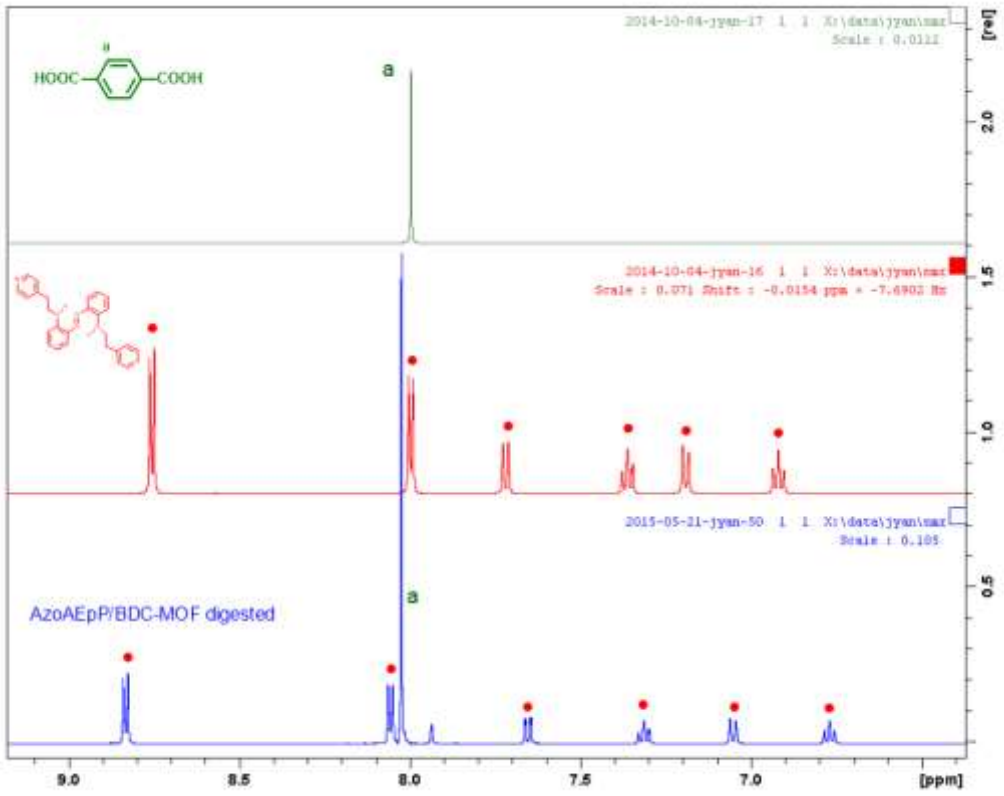

Figure S4. Digested NMR of ABMOF-2, comparing with original ligands BDC and AzoAE*p*P.

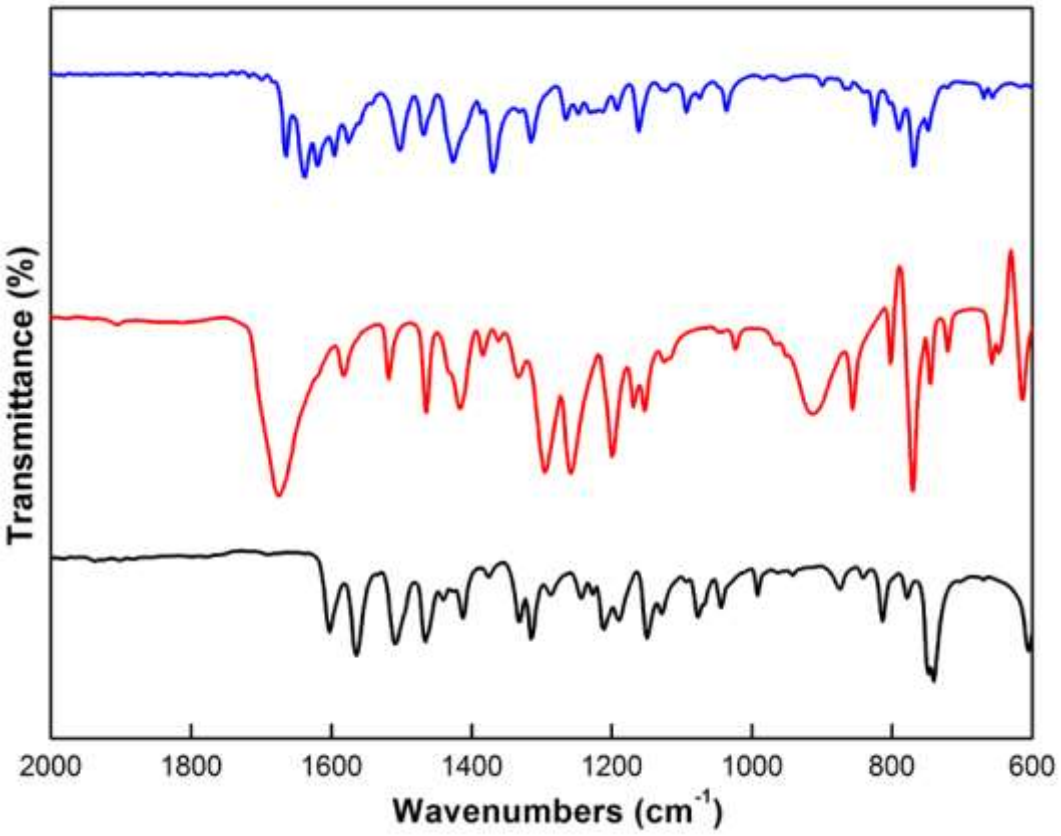

Figure S5. FTIR spectra of ABMOF-1 (blue), comparing with ligands NDC (red) and AzoAE*p*P (black). The peaks of ABMOF-1 match well with the peaks from two ligands.

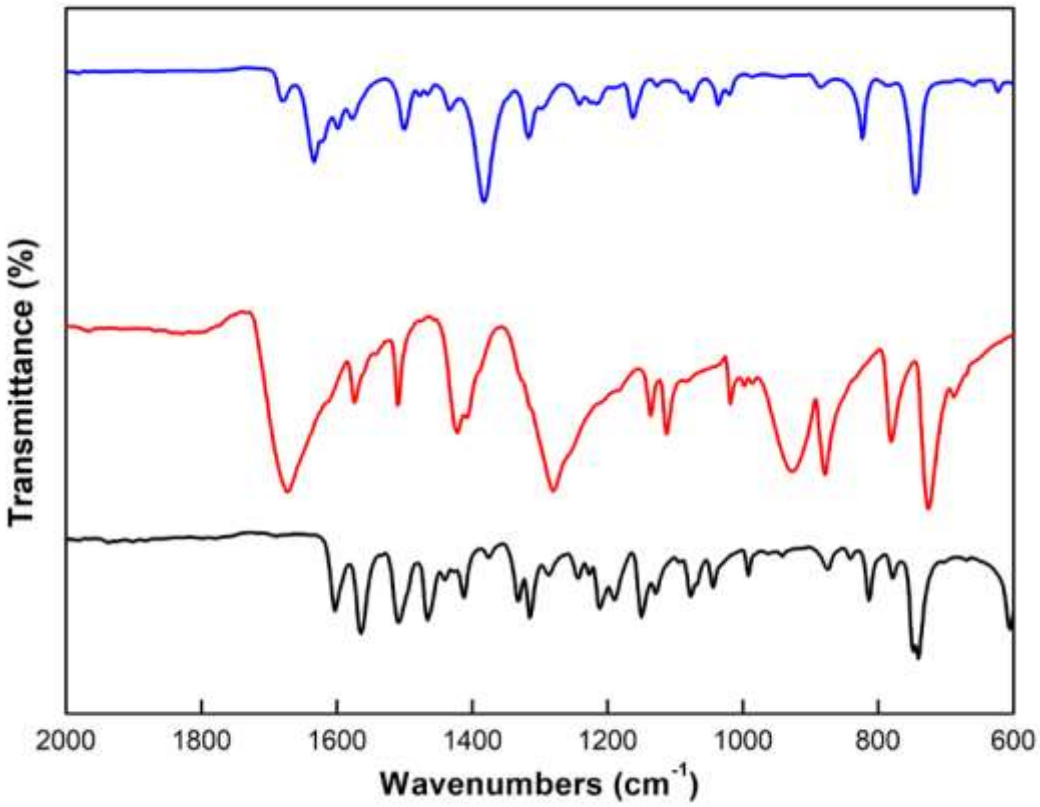

Figure S6. FTIR spectra of ABMOF-2 (blue), comparing with ligands BDC (red) and AzoAE*p*P (black). The peaks of ABMOF-2 match well with the peaks from two ligands.

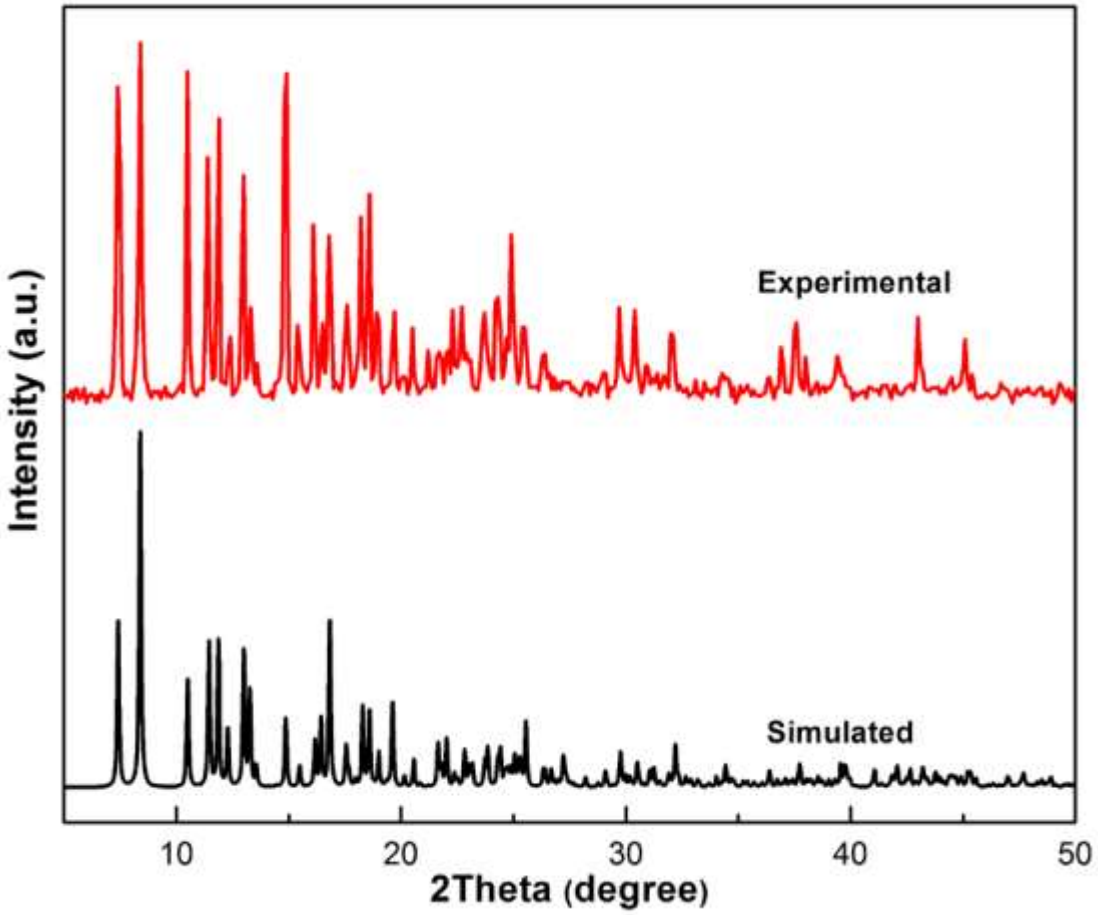

Figure S7: Powder X-ray diffraction patterns of ABMOF-1. Both experimental and simulated patterns from single crystal structures are shown to confirm the phase purity.

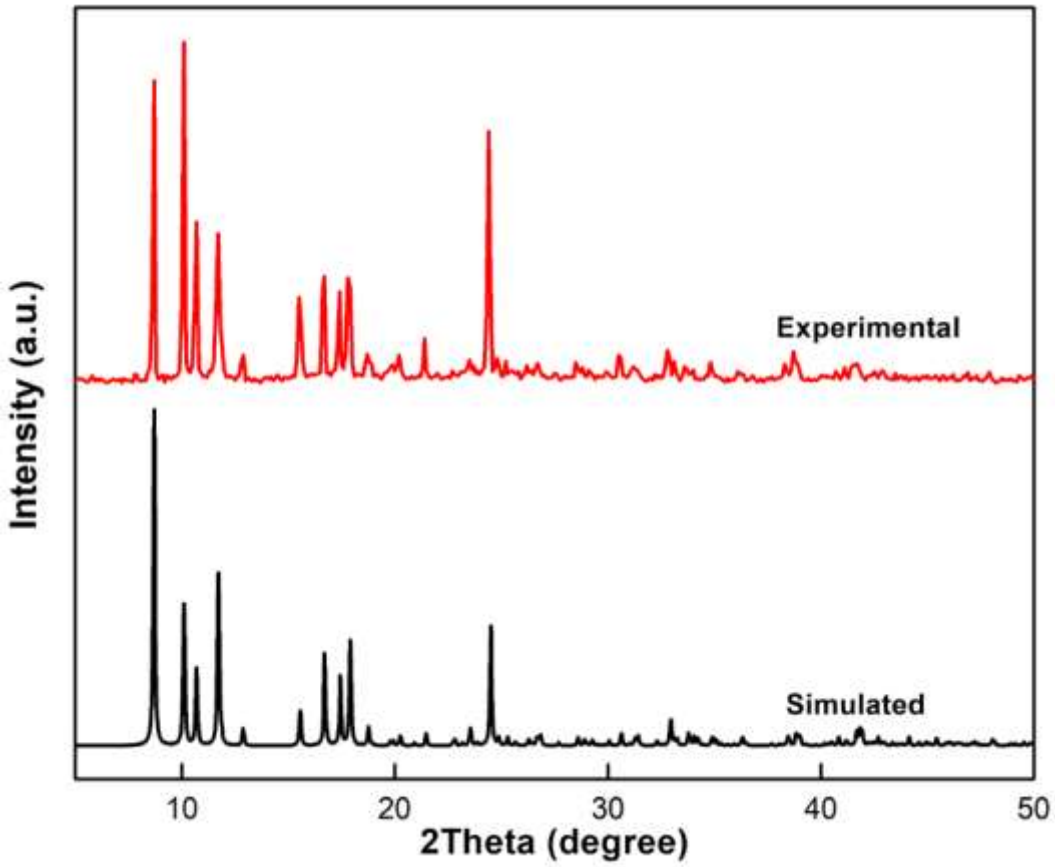

Figure S8: Powder X-ray diffraction patterns of ABMOF-2. Both experimental and simulated patterns from single crystal structures are shown to confirm the phase purity.

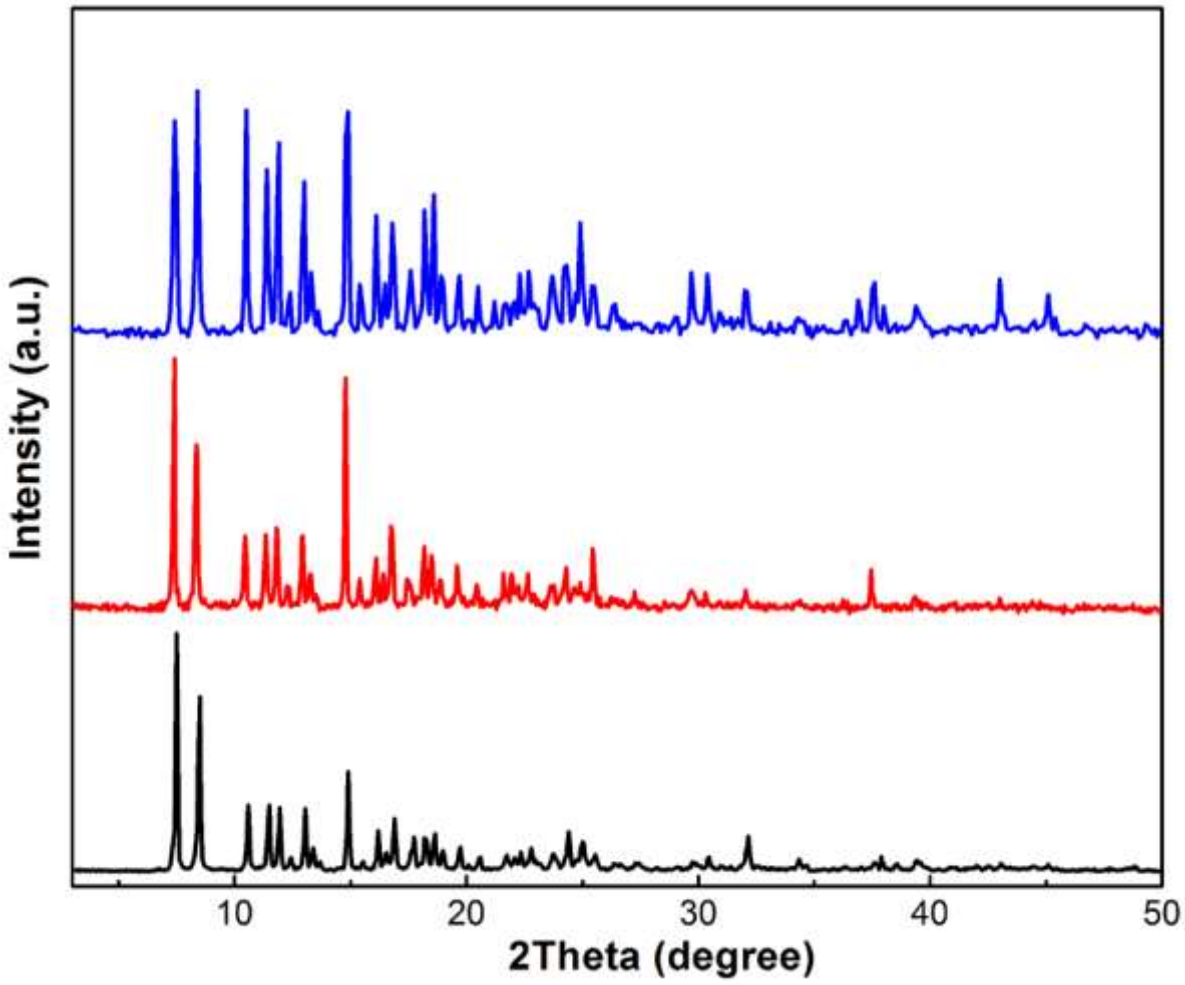

Figure S9. PXRD diffraction patterns of ABMOF-1 (black) and after quenching with 2,4-DNP (red) and 2,6-DNP-4-CF_3 (blue). The nearly identical patterns confirm no significant change of MOF structure after quenching.

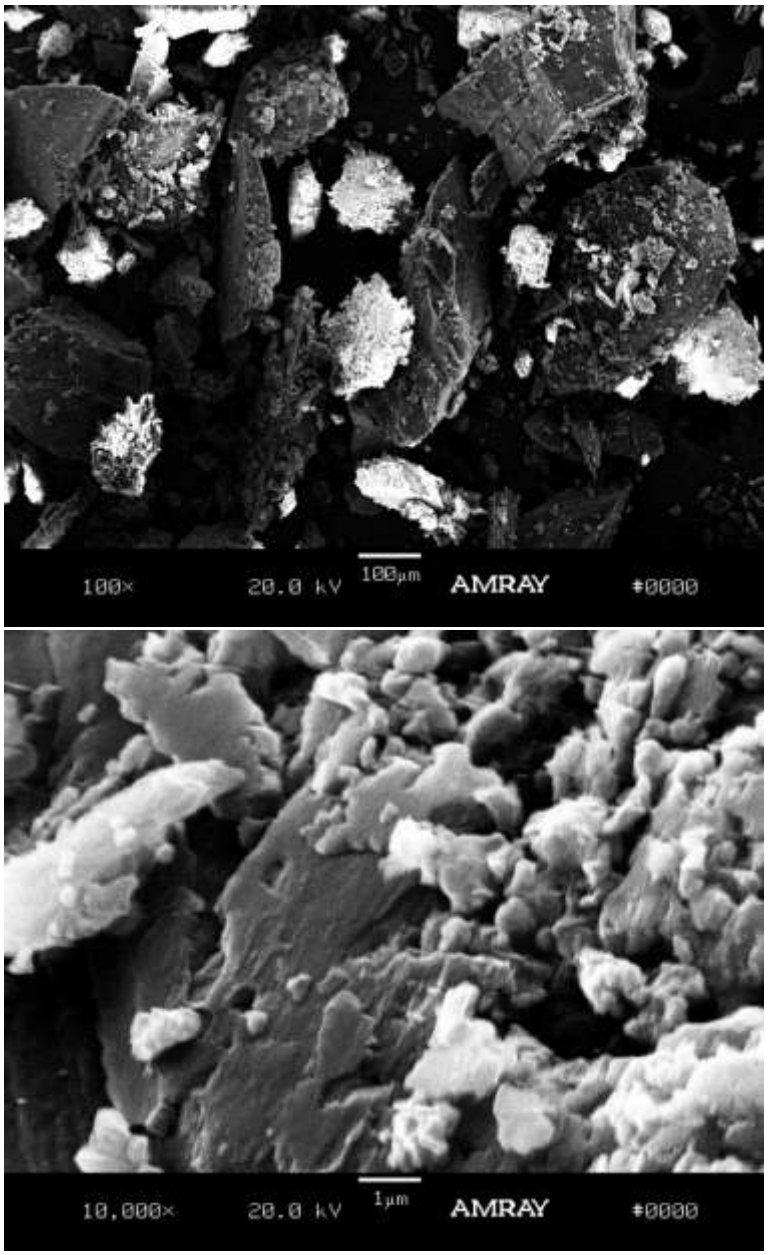

Figure S10. SEM images of ABMOF-1 crystals at 100× and 10,000× magnification

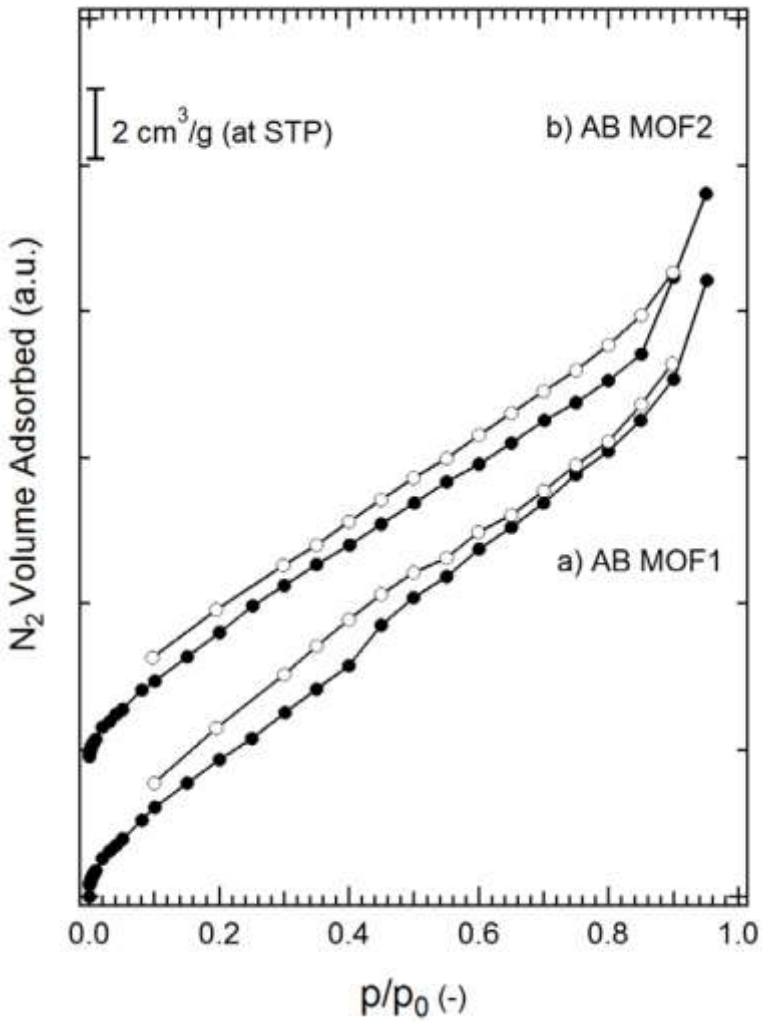

Figure S11. N_2 adsorption (filled circles) and desorption (empty circles) isotherms of thermally activated AzoMOF-1(left) and AzoMOF-2. Using the Brunauer-Emmett-Teller (BET) method, the surface area for AzoMOF-1 and AzoMOF-2 is 19.7 and 19.8 m^2/g, respectively.

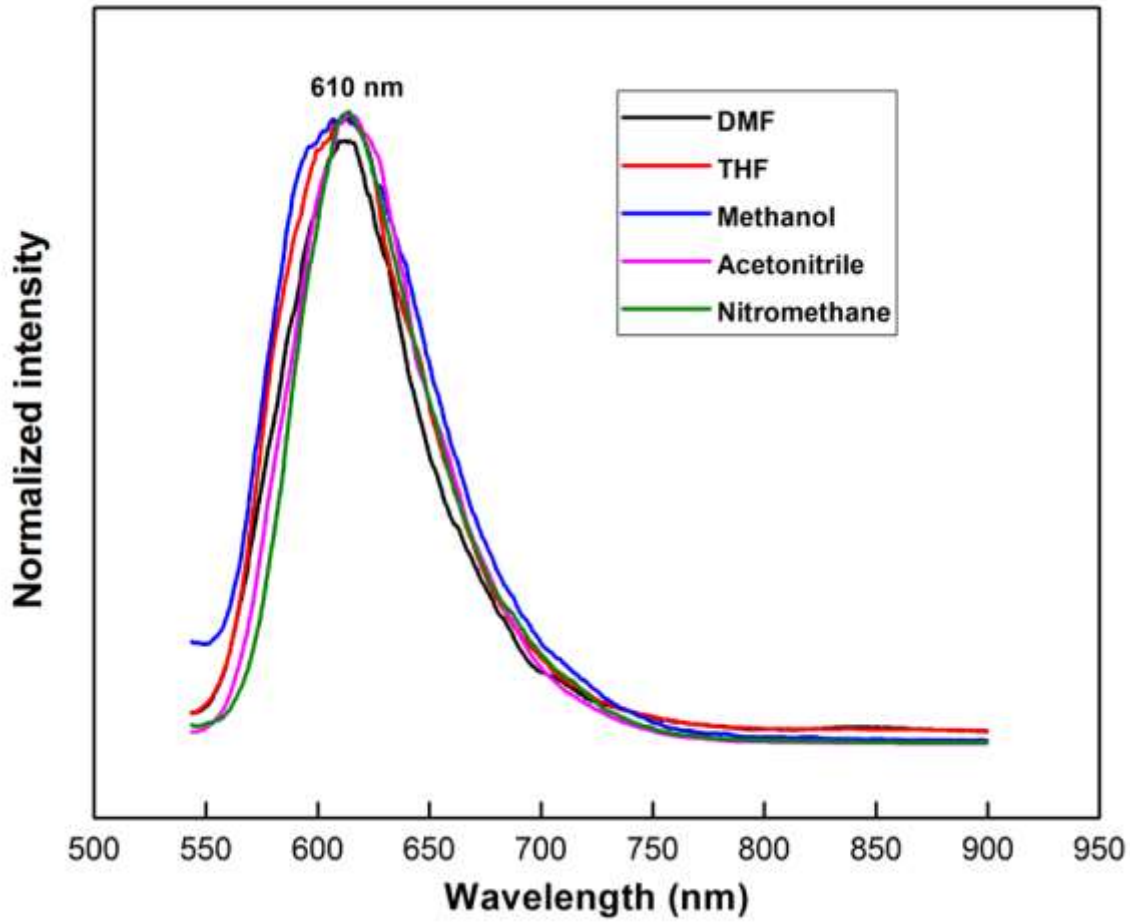

Figure S12. Normalized fluorescence spectra of ABMOF-1 in different solvents (40 μM), the excitation wavelength is 523 nm.

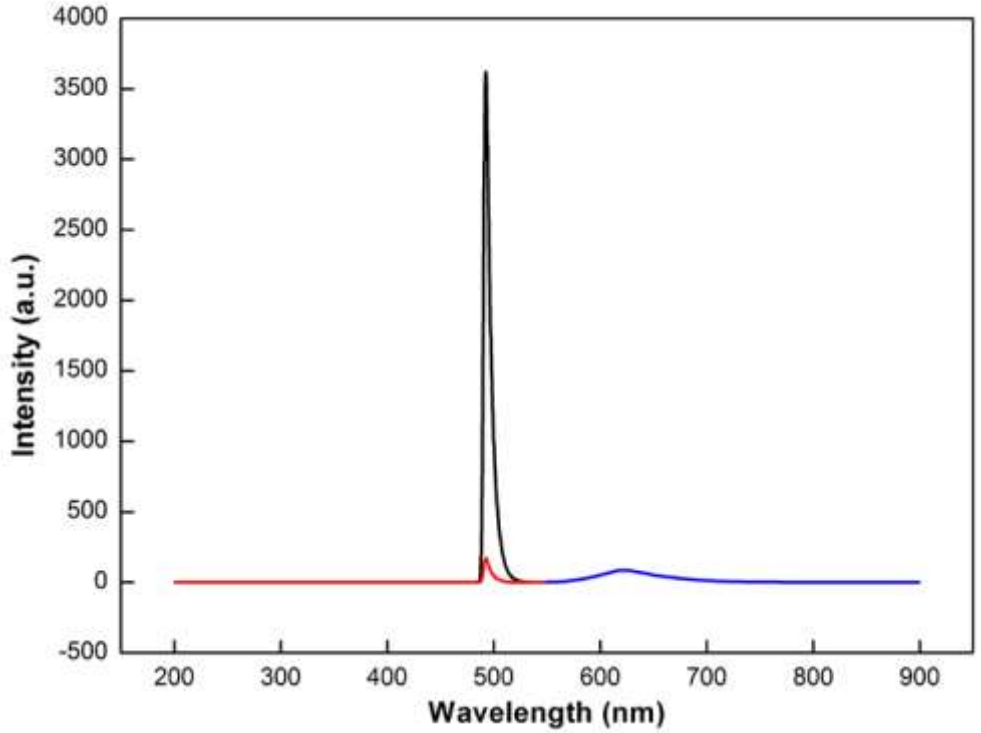

Figure S13. Steady-state emission and quantum yield determination of ABMOF-1. Reflectance from the sample and sodium sulfate are shown by red and black lines, respectively. Emission from the sample (enlarged by 50 times) is shown by blue trace. The excitation wavelength is 500 nm.

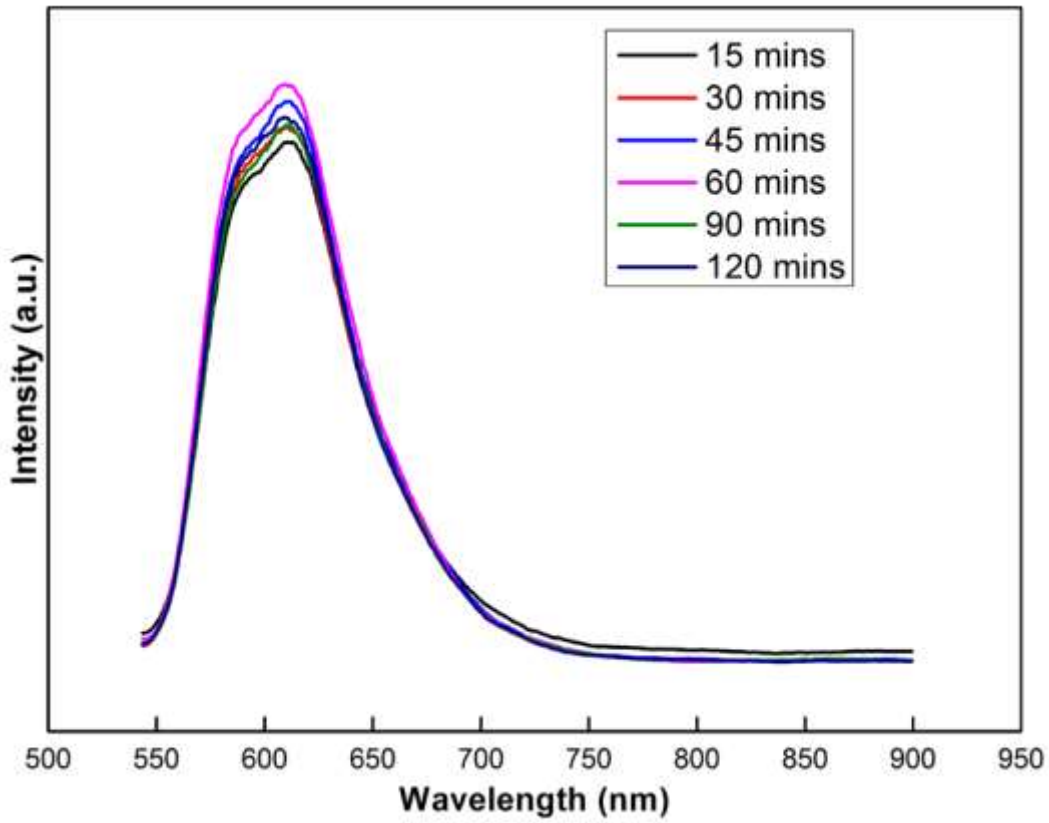

Figure S14. Fluorescence spectra of ABMOF-1 (40 μM in 2 mL DMF) after sonication for different time.

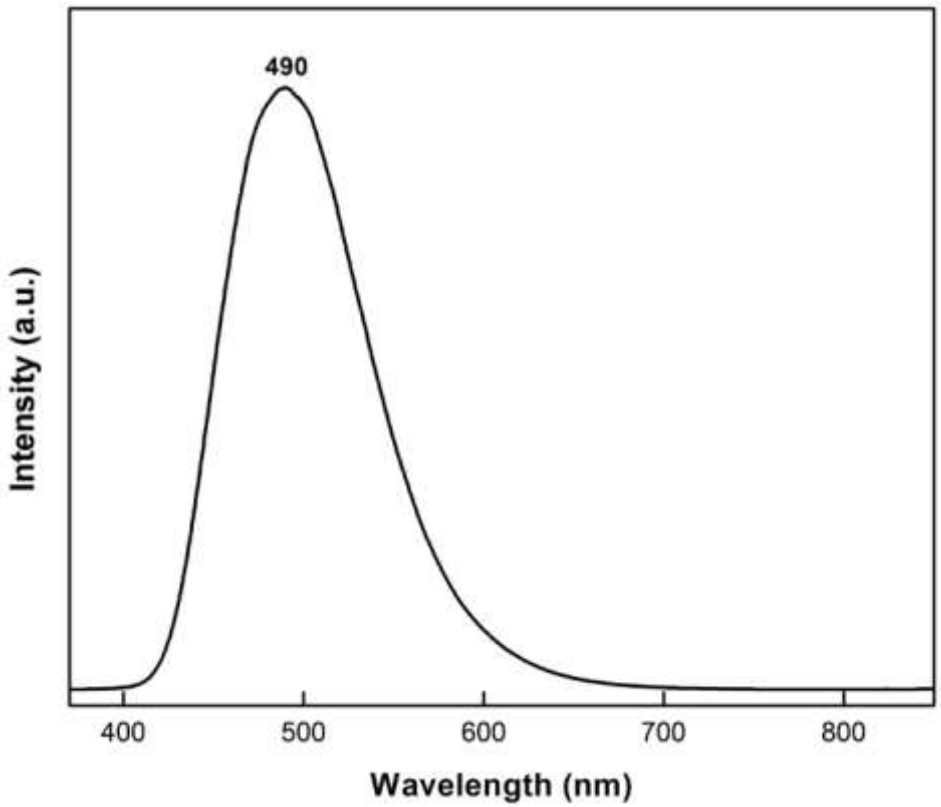

Figure S15. Solid state fluorescence spectra of NDC powder. The excitation wavelength is 350 nm.

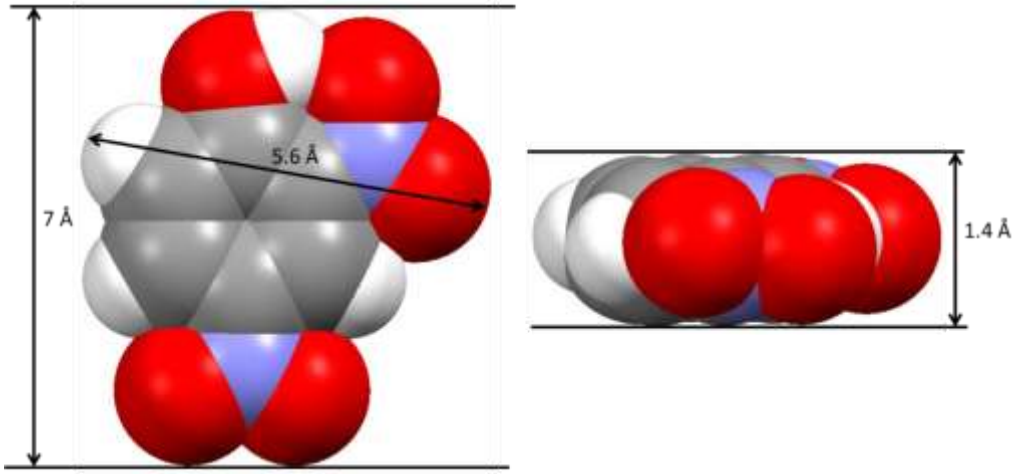

Figure S16. Measurement of the 2,4-dinitrophenol (2,4-DNP) analyte. The ABMOF-1 pores are smaller than 2,4-DNP precluding encapsulation

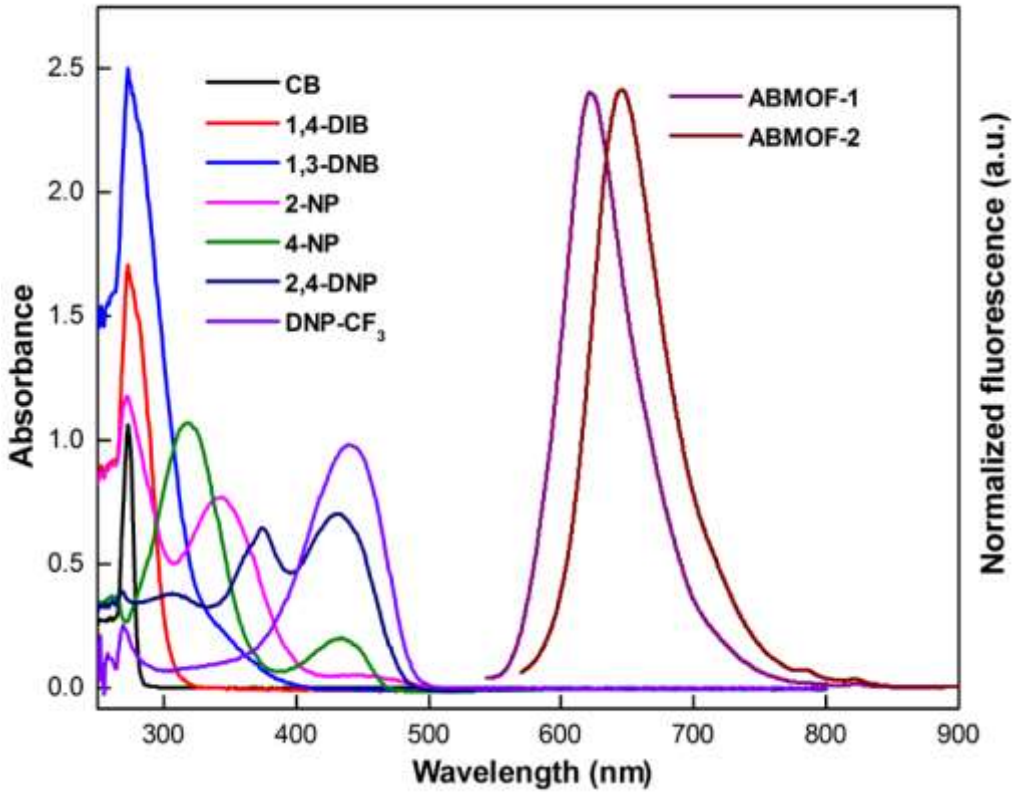

Figure S17. Absorbance spectra of 0.1 mM DMF solutions of CB, 1,4-DIB, 1,3-DNB, 2-NP, 4-NP, 2,4-DNP and 2,6-DNP-4-CF_3, showing no obvious overlap with the emission spectra of ABMOF-1 and ABMOF-2 suspended in DMF (40 μM).

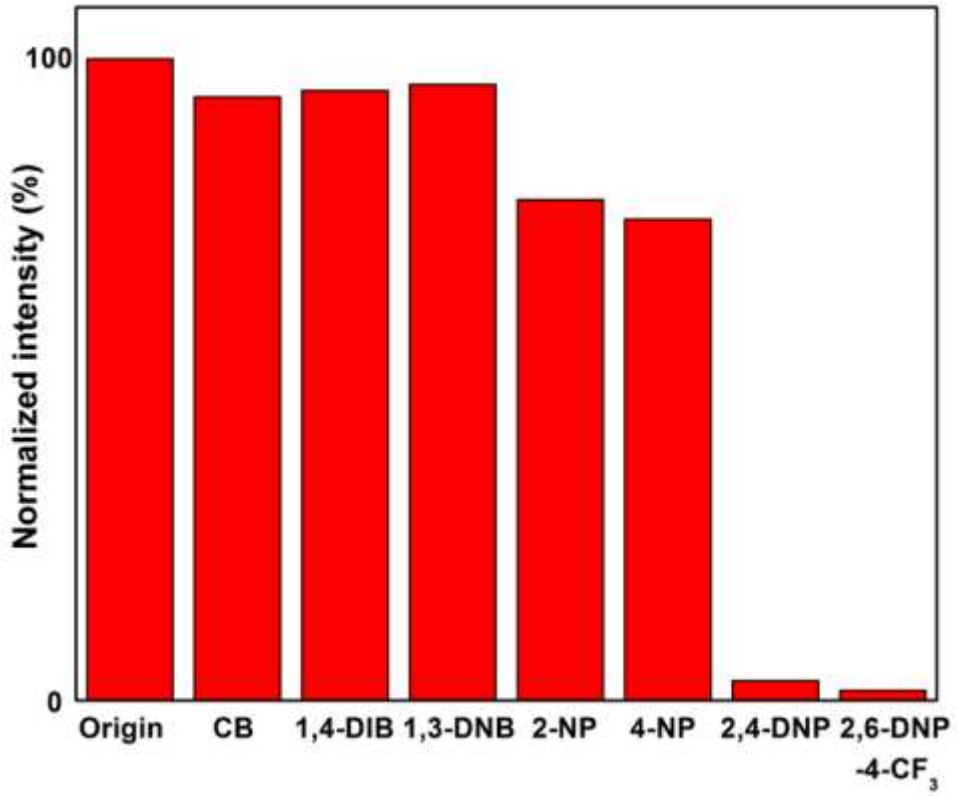

Figure S18. Normalized fluorescence intensity of 40 μM ABMOF-1 suspension in 2 mL DMF (original), and after adding 10 eq of different analytes, after each adding the suspension was stirring for 30 min before measuring. The excitation wavelength is 500 nm and the area under the emission spectra was integrated over a wavelength range of 540-800 nm.

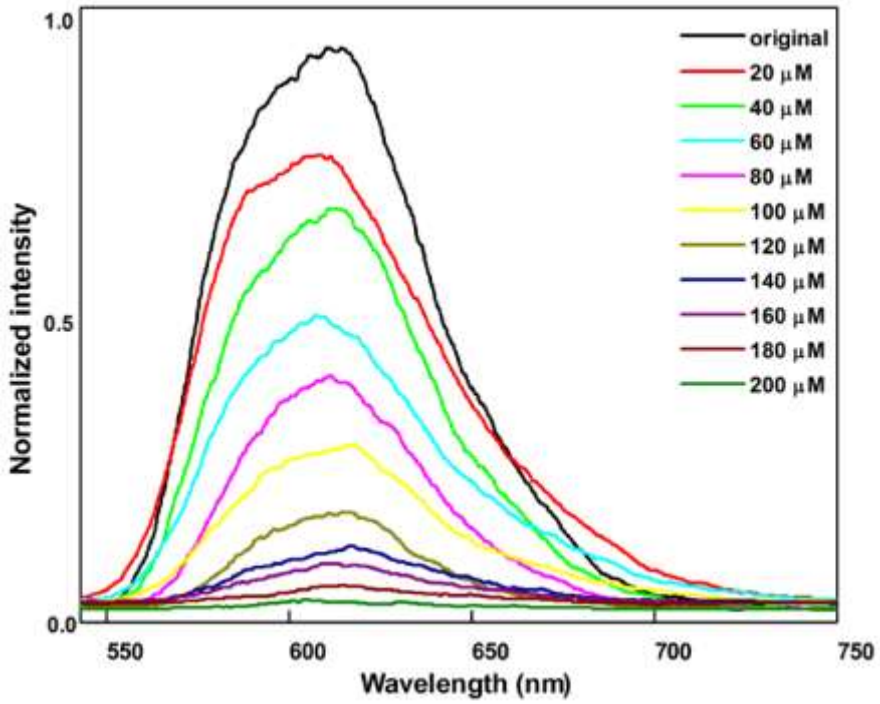

Figure S19. Normalized emission response of ABMOF-1 to 2,6-DNP-4-CF_3 (λex = 523 nm). ABMOF-1 (40 μM) was suspended in DMF (black) and treated with 2,6-DNP-4-CF_3 in DMF to obtain final concentration of 20 μM, 40 μM, 60 μM, 80 μM, until 200 μM. Solutions were equilibrated for 30 min before each measurement.

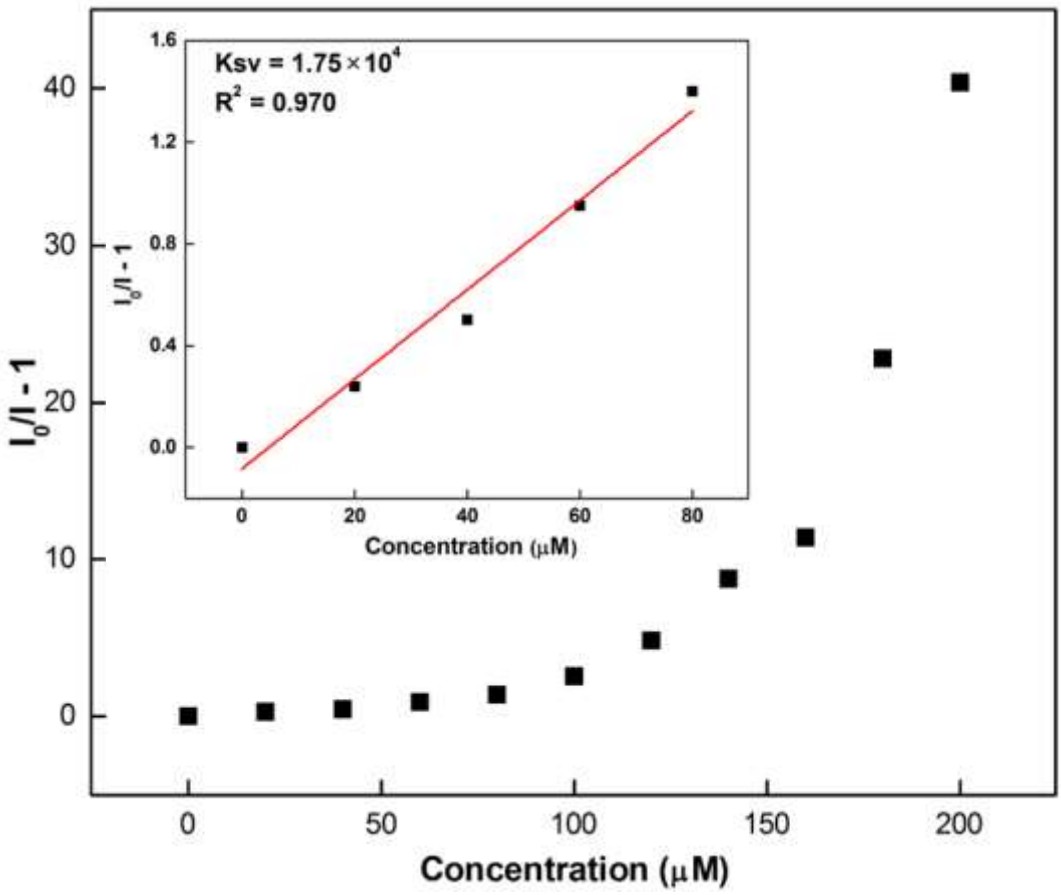

Figure S20. Stern-Volmer plot for ABMOF-1 with the addition of 2,6-DNP-4-CF_3 (insert: enlarged view of a selected area) using the SV equation $I_0/I = 1 + K_{sv}[A]$, where I_0 is the initial fluorescence intensity at 610 nm, I is the fluorescence intensity after adding 2,6-DNP-4-CF_3, [A] is the molar concentration of analyte, and K_{sv} is the quenching constant (M^{-1}).

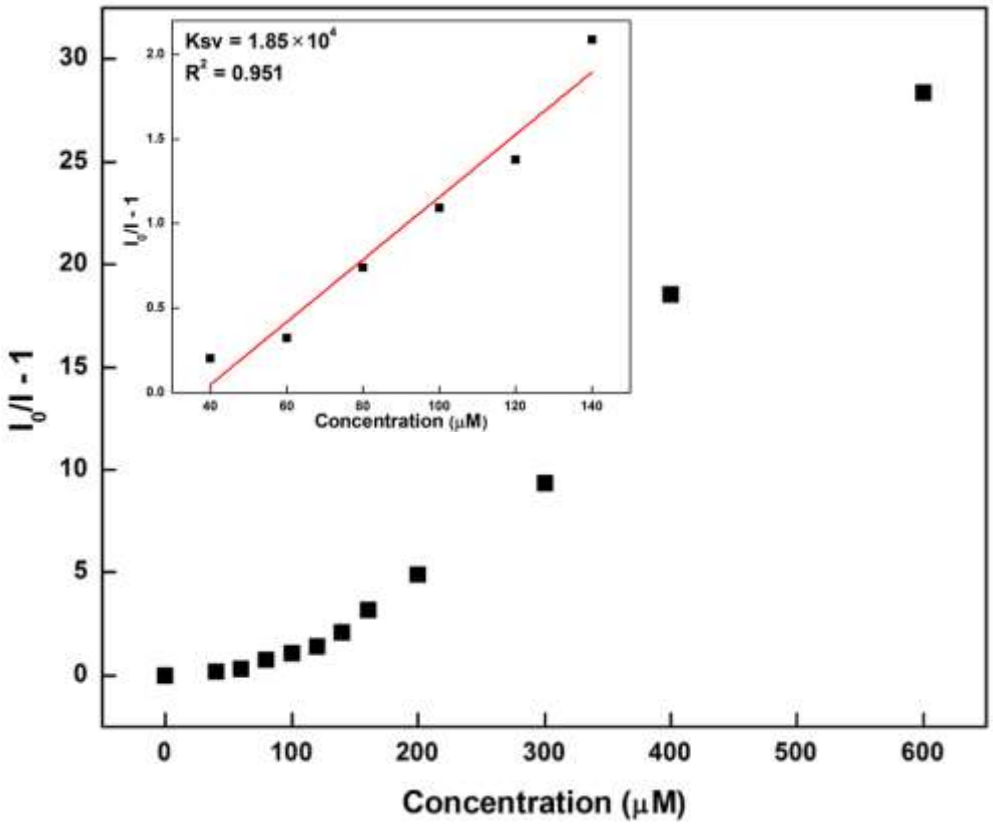

Figure S21. Stern-Volmer plot for ABMOF-1 with the addition of 2,4-DNP (insert: enlarged view of a selected area) using the SV equation $I_0/I = 1 + K_{sv}[A]$, where I_0 is the initial fluorescence intensity at 610 nm, I is the fluorescence intensity after adding 2,4-DNP, [A] is the molar concentration of analyte, and K_{sv} is the quenching constant (M^{-1}).

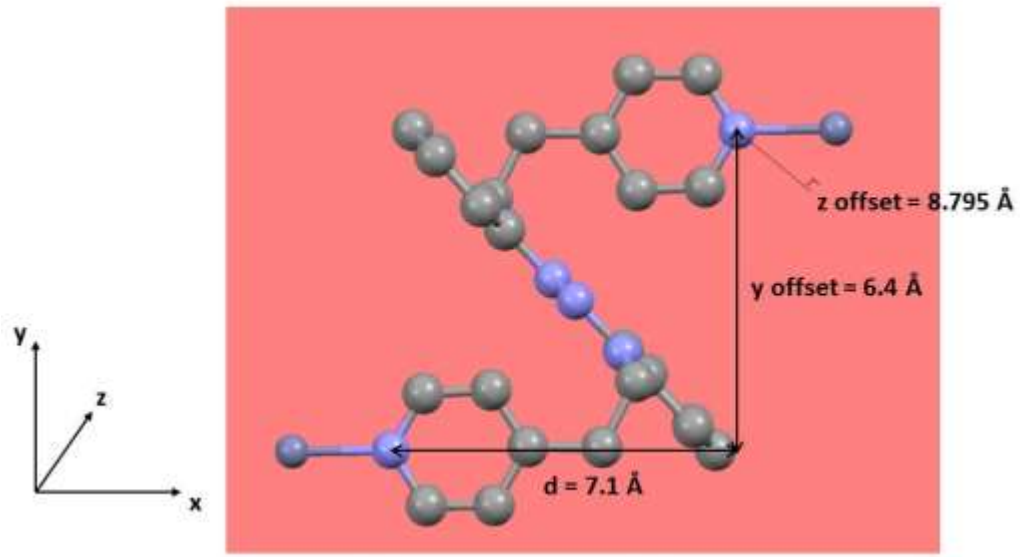

Figure S22. The effective distance between the two pyridine nitrogen atoms in AzoAE*p*P ligand in ABMOF-1 and the y and z offsets. The x-axis is a line going through pyridine nitrogen and its para carbon, y-axis is the axis perpendicular to x-axis in the plane containing the pyridine ring, and z-axis is defined as an axis perpendicular to the xy plane.

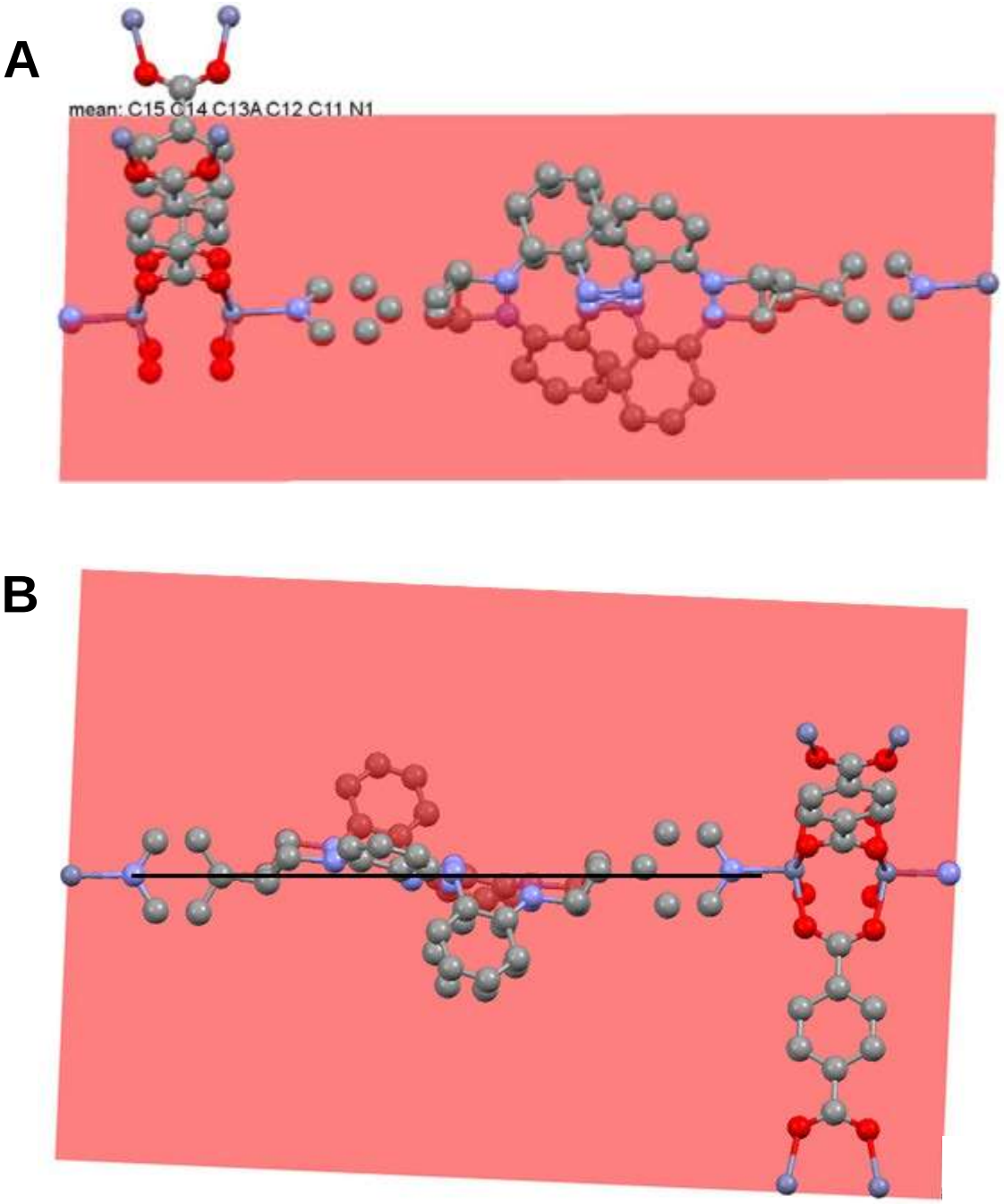

Figure S23A. A 60° tilted view along plane, showing two pyridine rings are in the same plane in AzoAE*p*P ligand in ABMOF-2. **S23B.** View along the plane, showing the effective distance between the two pyridine nitrogen atoms is almost equal to the point to point distance.

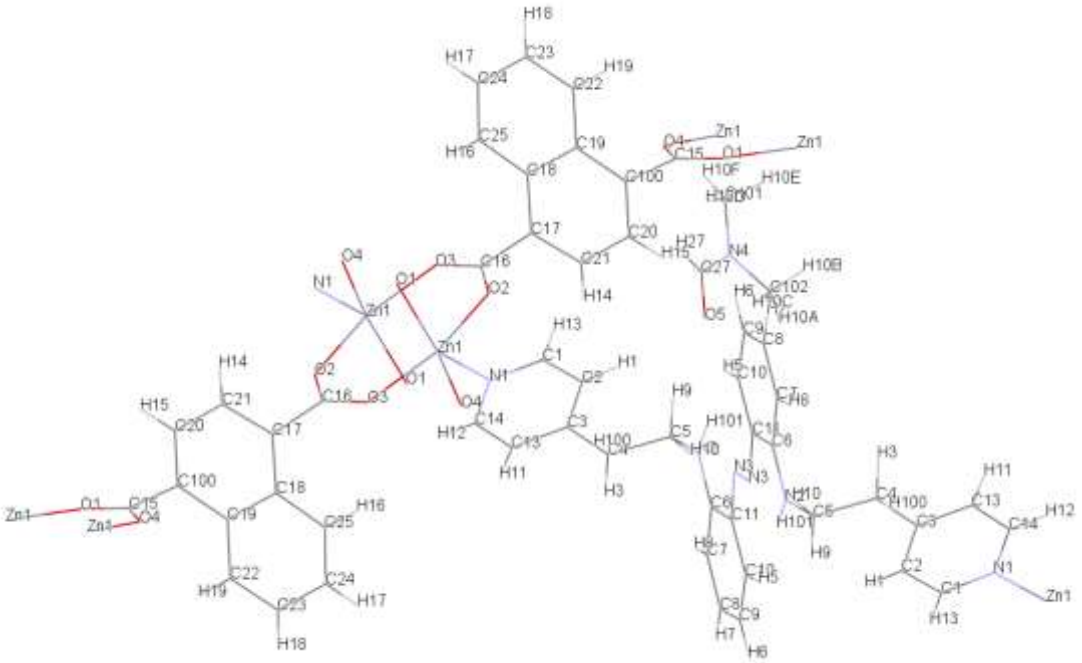

Figure S24. Completely labeled wireframe diagram of ABMOF-1.

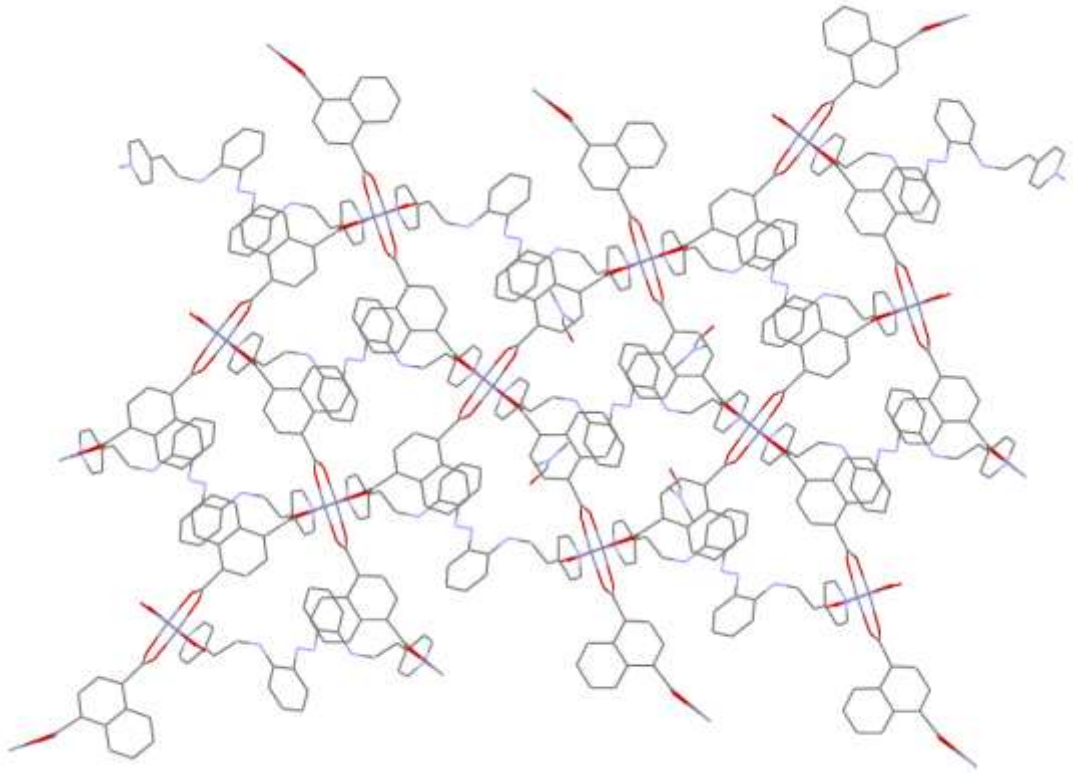

Figure S25. Packing diagrams of ABMOF-1 viewing from a axis. Hydrogen atoms are omitted for clarity.

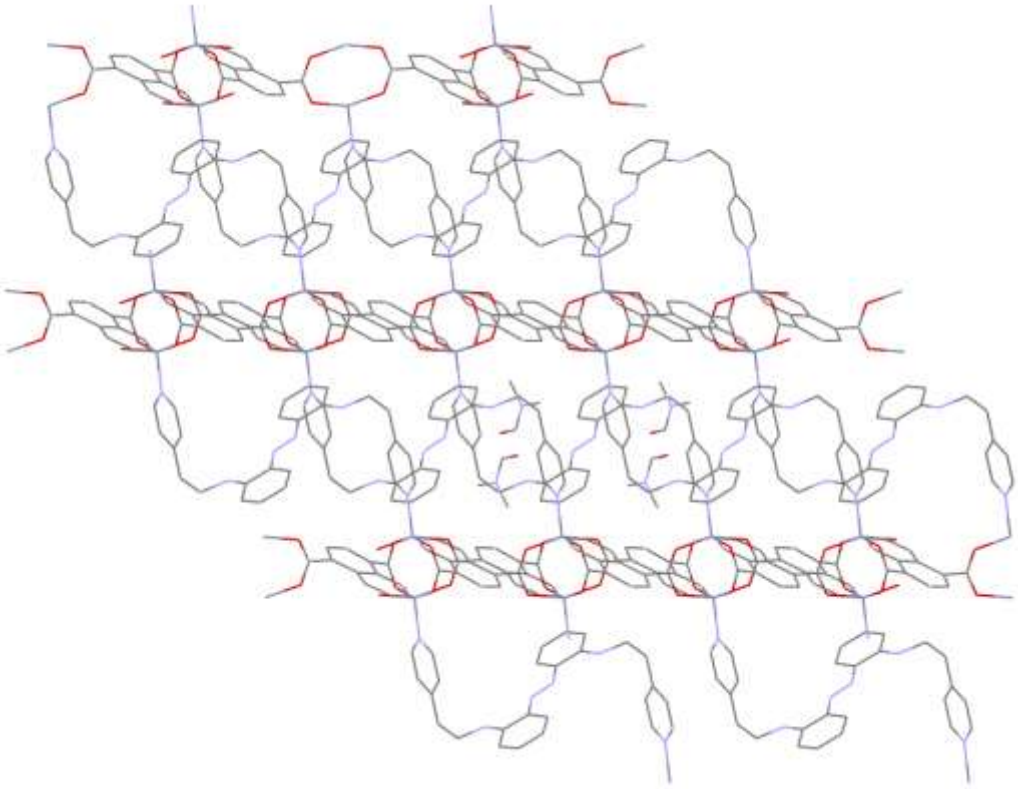

Figure S26. Packing diagrams of ABMOF-1 viewing from b axis. Hydrogen atoms are omitted for clarity.

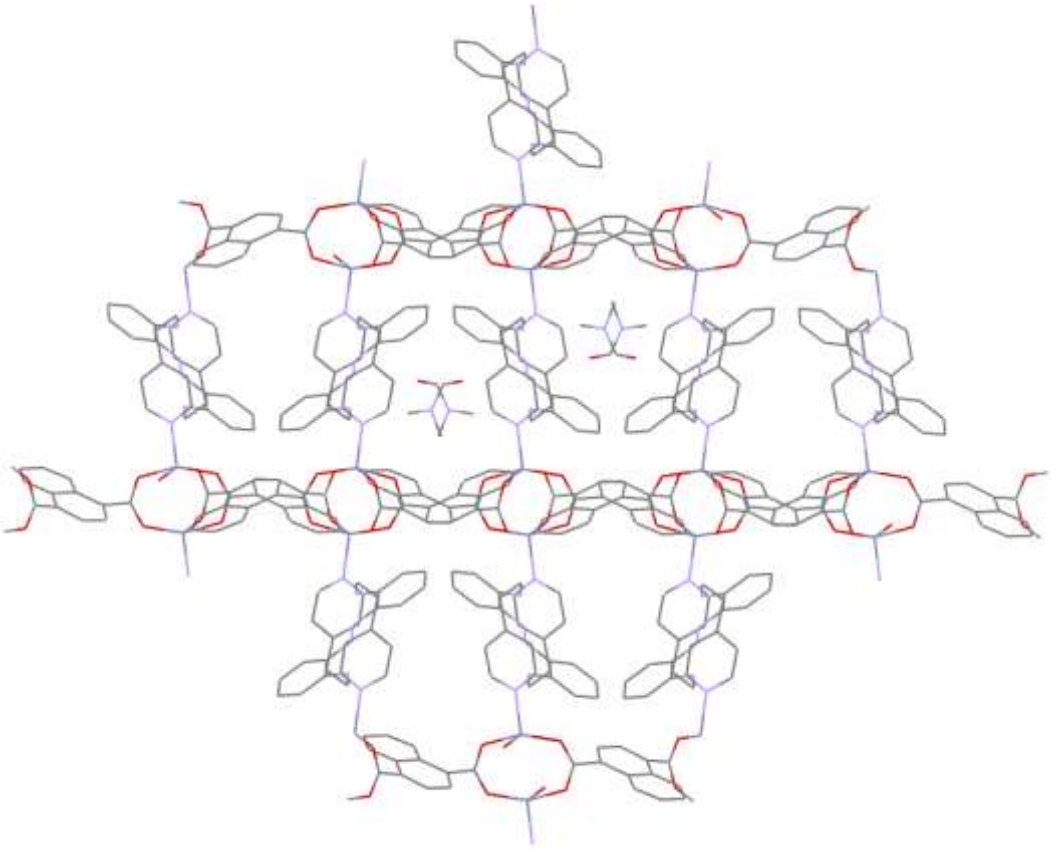

Figure S27. Packing diagrams of ABMOF-1 viewing from c axis. Hydrogen atoms are omitted for clarity.

Table S1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for ABMOF-1.

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.35113(16)	0.53210(12)	0.61230(16)	0.0468(5)
C10	0.60856(18)	0.36142(16)	1.03354(17)	0.0551(6)
C100	0.03019(12)	0.85483(9)	0.77710(10)	0.0276(3)
C101	0.6686(3)	0.8466(4)	0.6684(4)	0.161(3)
C102	0.7572(3)	0.7457(3)	0.7825(3)	0.1069(13)
C11	0.59873(14)	0.42707(13)	0.96760(13)	0.0401(4)
C13	0.45301(16)	0.38512(14)	0.57667(16)	0.0509(5)
C14	0.34230(16)	0.40120(12)	0.54179(15)	0.0460(5)
C15	-0.02341(14)	0.41886(10)	0.64698(11)	0.0306(3)
C16	0.01210(14)	0.64366(9)	0.58655(11)	0.0318(3)
C17	0.02164(13)	0.72130(9)	0.64802(11)	0.0281(3)
C18	-0.02696(13)	0.80186(9)	0.61778(10)	0.0278(3)
C19	-0.02155(13)	0.87009(9)	0.68360(10)	0.0272(3)
C2	0.46309(18)	0.52022(14)	0.64914(19)	0.0518(6)
C20	0.08049(15)	0.77863(11)	0.80201(12)	0.0378(4)
C21	0.07706(16)	0.71118(11)	0.73712(12)	0.0378(4)
C22	-0.06658(18)	0.95122(11)	0.65300(13)	0.0426(4)
C23	-0.1133(2)	0.96459(13)	0.56302(16)	0.0571(6)
C24	-0.1182(2)	0.89742(16)	0.49803(15)	0.0599(7)
C25	-0.07674(18)	0.81851(12)	0.52466(12)	0.0438(4)
C27	0.5586(3)	0.7409(2)	0.7358(2)	0.0773(8)
C3	0.51593(14)	0.44515(12)	0.63212(12)	0.0369(3)
C4	0.63705(14)	0.42633(15)	0.67045(14)	0.0451(4)

C5	0.69525(17)	0.48786(14)	0.74414(16)	0.0444(4)
C6	0.65900(14)	0.42411(12)	0.89305(13)	0.0388(4)
C7	0.72888(16)	0.35252(14)	0.88790(15)	0.0473(5)
C8	0.73608(18)	0.28788(14)	0.95287(18)	0.0561(5)
C9	0.67623(19)	0.29152(16)	1.02589(19)	0.0637(7)
H1	0.5024	0.5629	0.6853	0.062
H10	0.7734	0.4721	0.7589	0.053
H100	0.6783	0.4258	0.6189	0.054
H101	0.6129	0.5346	0.8412	0.056
H10A	0.7403	0.712	0.8334	0.16
H10B	0.8022	0.7939	0.8061	0.16
H10C	0.7973	0.7112	0.7446	0.16
H10D	0.7045	0.8277	0.618	0.242
H10E	0.7135	0.8898	0.7035	0.242
H10F	0.5966	0.8699	0.644	0.242
H11	0.4854	0.3337	0.5628	0.061
H12	0.3018	0.3601	0.5042	0.055
H13	0.317	0.5832	0.6248	0.056
H14	0.1126	0.6596	0.755	0.045
H15	0.1176	0.7708	0.8625	0.045
H16	-0.0812	0.7748	0.4809	0.053
H17	-0.1499	0.907	0.4363	0.072
H18	-0.1423	1.0182	0.5443	0.069

H19	-0.0639	0.996	0.6955	0.051
H27	0.4953	0.764	0.6995	0.093
H3	0.6415	0.3691	0.6968	0.054
H5	0.5692	0.3648	1.083	0.066
H6	0.6816	0.2474	1.0693	0.076
H7	0.7819	0.241	0.9477	0.067
H8	0.7706	0.349	0.84	0.057
H9	0.6914	0.5452	0.7181	0.053
N1	0.29067(11)	0.47385(8)	0.55999(10)	0.0296(3)
N2	0.64903(17)	0.48951(11)	0.82959(13)	0.0470(4)
N3	0.52874(15)	0.49953(10)	0.96801(13)	0.0417(4)
N4	0.65564(19)	0.77531(16)	0.72768(18)	0.0729(7)
O1	0.11171(12)	0.55416(11)	0.39839(10)	0.0525(4)
O2	0.10024(11)	0.60581(8)	0.57999(12)	0.0502(4)
O3	0.08360(12)	0.37825(9)	0.45215(12)	0.0557(4)
O4	0.07208(12)	0.43708(11)	0.63338(10)	0.0559(4)
O5	0.5448(2)	0.68212(15)	0.78641(19)	0.1034(8)
Zn1	0.123969(13)	0.490245(10)	0.520527(11)	0.02144(6)

Table S2. Atomic displacement parameters (Å^2) for ABMOF-1.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0346(9)	0.0377(8)	0.0628(13)	-0.0115(8)	-0.0073(9)	0.0098(7)
C10	0.0417(11)	0.0666(14)	0.0603(13)	0.0148(10)	0.0182(10)	0.0143(9)
C100	0.0248(7)	0.0311(6)	0.0265(7)	-0.0102(5)	0.0030(5)	-0.0001(5)
C101	0.080(3)	0.196(5)	0.207(5)	0.137(4)	0.020(3)	0.011(3)
C102	0.0648(19)	0.108(3)	0.138(3)	0.042(2)	-0.012(2)	-0.0081(19)
C11	0.0271(8)	0.0502(10)	0.0426(10)	0.0005(8)	0.0051(7)	0.0080(7)
C13	0.0341(10)	0.0512(10)	0.0643(13)	-0.0173(9)	-0.0004(9)	0.0144(8)
C14	0.0325(9)	0.0447(9)	0.0572(12)	-0.0169(8)	-0.0033(8)	0.0087(7)
C15	0.0351(8)	0.0331(7)	0.0244(7)	0.0092(5)	0.0077(6)	0.0031(6)
C16	0.0395(9)	0.0228(6)	0.0329(8)	-0.0076(5)	0.0058(6)	-0.0014(5)
C17	0.0289(7)	0.0242(6)	0.0307(7)	-0.0094(5)	0.0035(6)	0.0008(5)
C18	0.0306(7)	0.0263(6)	0.0258(7)	-0.0059(5)	0.0026(6)	-0.0004(5)
C19	0.0285(7)	0.0252(6)	0.0278(7)	-0.0061(5)	0.0041(6)	0.0013(5)
C2	0.0324(10)	0.0475(10)	0.0696(15)	-0.0124(10)	-0.0090(10)	-0.0007(8)
C20	0.0401(9)	0.0415(8)	0.0281(8)	-0.0083(6)	-0.0050(7)	0.0098(7)
C21	0.0411(9)	0.0320(7)	0.0372(9)	-0.0066(6)	-0.0030(7)	0.0113(6)
C22	0.0569(11)	0.0285(7)	0.0410(9)	-0.0047(6)	0.0034(8)	0.0071(7)
C23	0.0816(17)	0.0355(9)	0.0493(12)	0.0051(8)	-0.0033(11)	0.0126(10)
C24	0.0885(19)	0.0516(12)	0.0334(10)	0.0045(8)	-0.0076(11)	0.0098(11)
C25	0.0606(12)	0.0402(8)	0.0271(8)	-0.0067(6)	-0.0027(8)	0.0013(8)
C27	0.0576(16)	0.0766(18)	0.099(2)	-0.0140(16)	0.0157(15)	-0.0080(14)
C3	0.0238(7)	0.0497(9)	0.0368(9)	0.0021(7)	0.0042(6)	0.0027(6)
C4	0.0243(8)	0.0684(12)	0.0423(10)	-0.0031(8)	0.0042(7)	0.0099(8)

C5	0.0273(9)	0.0651(12)	0.0408(10)	0.0006(8)	0.0061(8)	0.0006(8)
C6	0.0268(8)	0.0499(9)	0.0384(9)	-0.0038(7)	0.0018(7)	0.0058(7)
C7	0.0329(9)	0.0587(11)	0.0506(11)	-0.0047(9)	0.0076(8)	0.0139(8)
C8	0.0371(10)	0.0554(12)	0.0757(16)	0.0030(10)	0.0094(10)	0.0162(9)
C9	0.0458(12)	0.0636(14)	0.0835(18)	0.0283(12)	0.0163(12)	0.0164(10)
N1	0.0240(6)	0.0304(5)	0.0335(7)	0.0004(5)	0.0026(5)	0.0017(5)
N2	0.0463(10)	0.0569(10)	0.0396(9)	0.0018(7)	0.0125(8)	0.0145(7)
N3	0.0334(8)	0.0519(8)	0.0412(9)	-0.0011(6)	0.0102(7)	0.0078(6)
N4	0.0494(12)	0.0756(15)	0.0931(18)	0.0211(13)	0.0097(11)	0.0011(10)
O1	0.0400(7)	0.0781(10)	0.0416(7)	0.0353(7)	0.0136(6)	0.0199(7)
O2	0.0409(7)	0.0331(6)	0.0789(11)	-0.0263(6)	0.0164(7)	-0.0013(5)
O3	0.0429(8)	0.0394(6)	0.0776(11)	-0.0301(7)	-0.0105(7)	0.0022(6)
O4	0.0353(7)	0.0844(11)	0.0474(8)	0.0382(8)	0.0049(6)	-0.0101(7)
O5	0.1173(19)	0.0766(14)	0.126(2)	-0.0101(14)	0.0472(15)	-0.0410(14)
Zn1	0.02109(10)	0.02049(9)	0.02254(10)	0.00106(5)	0.00307(6)	0.00097(5)

Table S3. Geometric parameters – bond length (Å) for ABMOF-1.

C1	C2	1.389(3)	C25	H16	0.93
C1	H13	0.93	C27	O5	1.206(4)
C10	C11	1.396(3)	C27	H27	0.93
C10	H5	0.93	C3	C13	1.382(3)
C100	C20	1.358(2)	C3	C4	1.513(2)
C100	C19	1.423(2)	C4	C5	1.524(3)
C100	C15	1.5033(19)	C4	H100	0.97
C101	H10D	0.96	C4	H3	0.97
C101	H10E	0.96	C5	H10	0.97
C101	H10F	0.96	C5	H9	0.97
C102	H10A	0.96	C6	C11	1.408(3)
C102	H10B	0.96	C6	C7	1.412(2)
C102	H10C	0.96	C7	C8	1.376(3)
C11	N3	1.415(2)	C7	H8	0.93
C13	C14	1.379(3)	C8	C9	1.386(4)
C13	H11	0.93	C8	H7	0.93
C14	H12	0.93	C9	C10	1.381(3)
C15	O1	1.237(2)	C9	H6	0.93
C15	C100	1.5033(19)	N1	C1	1.327(2)
C16	O3	1.252(2)	N1	C14	1.343(2)
C16	C17	1.4998(19)	N2	C6	1.369(3)
C17	C21	1.369(2)	N2	C5	1.449(3)
C17	C18	1.427(2)	N2	H101	0.86
C18	C25	1.415(2)	N3	N3	1.255(4)

C18	C19	1.4274(19)	N4	C27	1.319(4)
C19	C22	1.421(2)	N4	C102	1.431(4)
C2	C3	1.378(3)	N4	C101	1.433(4)
C2	H1	0.93	O1	C15	1.237(2)
C20	C21	1.411(2)	O2	C16	1.240(2)
C20	H15	0.93	O3	C16	1.252(2)
C21	H14	0.93	O4	C15	1.242(2)
C22	C23	1.356(3)	Zn1	O1	2.0246(12)
C22	H19	0.93	Zn1	N1	2.0273(14)
C23	C24	1.408(3)	Zn1	O3	2.0309(12)
C23	H18	0.93	Zn1	O4	2.0339(13)
C24	C25	1.362(3)	Zn1	O2	2.0417(12)
C24	H17	0.93	Zn1	Zn1	2.9871(6)

Table S4. Geometric parameters – bond angles (º) for ABMOF-1.

C1	N1	C14	117.36(15)	C5	C4	H100	108.2
C1	N1	Zn1	120.53(11)	C5	C4	H3	108.2
C1	C2	H1	120	C6	N2	C5	124.34(17)
C10	C9	C8	119.3(2)	C6	N2	H101	117.8
C10	C9	H6	120.3	C6	C7	H8	119.6
C10	C11	C6	120.75(18)	C6	C11	N3	114.78(17)
C10	C11	N3	124.46(19)	C7	C8	C9	121.1(2)
C100	C19	C18	118.87(13)	C7	C8	H7	119.4
C100	C20	C21	120.78(15)	C8	C7	C6	120.9(2)
C100	C20	H15	119.6	C8	C7	H8	119.6
C102	N4	C101	114.6(3)	C8	C9	H6	120.3
C11	C6	C7	117.45(18)	C9	C8	H7	119.4
C11	C10	H5	119.8	C9	C10	C11	120.5(2)
C13	C3	C4	119.59(17)	C9	C10	H5	119.8
C13	C14	H12	118.7	H10	C5	H9	107.6
C14	N1	Zn1	121.85(12)	H100	C4	H3	107.3
C14	C13	C3	120.19(17)	H10A	C102	H10B	109.5
C14	C13	H11	119.9	H10A	C102	H10C	109.5
C15	O1	Zn1	124.64(11)	H10B	C102	H10C	109.5
C15	O4	Zn1	130.22(11)	H10D	C101	H10E	109.5
C16	O2	Zn1	129.63(11)	H10D	C101	H10F	109.5
C16	O3	Zn1	125.89(11)	H10E	C101	H10F	109.5
C17	C18	C19	118.61(13)	N1	Zn1	O3	100.31(6)
C17	C21	C20	120.33(15)	N1	Zn1	O4	98.52(6)

C17	C21	H14	119.8	N1	Zn1	O2	101.29(5)
C18	C17	C16	122.68(13)	N1	Zn1	Zn1	174.91(4)
C18	C25	H16	119.4	N1	C1	C2	122.93(17)
C19	C100	C15	121.63(13)	N1	C1	H13	118.5
C19	C22	H19	119.4	N1	C14	C13	122.64(17)
C2	C1	H13	118.5	N1	C14	H12	118.7
C2	C3	C13	116.92(16)	N2	C5	C4	114.61(18)
C2	C3	C4	123.49(18)	N2	C5	H10	108.6
C20	C100	C19	120.67(13)	N2	C5	H9	108.6
C20	C100	C15	117.52(14)	N2	C6	C11	119.87(17)
C20	C21	H14	119.8	N2	C6	C7	122.68(18)
C21	C17	C18	120.51(13)	N3	N3	C11	114.9(2)
C21	C17	C16	116.78(14)	N4	C27	H27	117.2
C21	C20	H15	119.6	N4	C102	H10A	109.5
C22	C19	C100	122.38(13)	N4	C102	H10B	109.5
C22	C19	C18	118.75(14)	N4	C102	H10C	109.5
C22	C23	C24	120.03(19)	N4	C101	H10D	109.5
C22	C23	H18	120	N4	C101	H10E	109.5
C23	C22	C19	121.21(16)	N4	C101	H10F	109.5
C23	C22	H19	119.4	O1	Zn1	N1	103.63(6)
C23	C24	H17	119.7	O1	Zn1	O3	90.90(7)
C24	C23	H18	120	O1	Zn1	O4	157.65(6)
C24	C25	C18	121.20(17)	O1	Zn1	O2	86.76(7)
C24	C25	H16	119.4	O1	Zn1	Zn1	81.33(4)
C25	C18	C17	123.15(14)	O1	C15	O4	125.94(15)
C25	C18	C19	118.20(14)	O1	C15	C100	118.11(15)

C25	C24	C23	120.61(19)	O2	Zn1	Zn1	77.66(4)
C25	C24	H17	119.7	O2	C16	O3	125.72(15)
C27	N4	C102	121.3(3)	O2	C16	C17	116.66(14)
C27	N4	C101	124.0(3)	O3	Zn1	O4	87.94(8)
C3	C2	C1	119.95(18)	O3	Zn1	O2	158.21(6)
C3	C2	H1	120	O3	Zn1	Zn1	80.57(4)
C3	C4	C5	116.53(17)	O3	C16	C17	117.60(15)
C3	C4	H100	108.2	O4	Zn1	O2	86.11(7)
C3	C4	H3	108.2	O4	Zn1	Zn1	76.46(4)
C3	C13	H11	119.9	O4	C15	C100	115.88(14)
C4	C5	H10	108.6	O5	C27	N4	125.6(3)
C4	C5	H9	108.6	O5	C27	H27	117.2
C5	N2	H101	117.8				

checkCIF (basic structural check) running

checkCIF/PLATON (basic structural check)

Datablock: shawn260_0m

Bond precision:	C-C = 0.0026 A		Wavelength=0.71073
Cell:	a=12.1475(19)	b=15.602(2)	c=14.578(2)
	alpha=90	beta=99.566(8)	gamma=90
Temperature:	296 K		

	Calculated	Reported
Volume	2724.5(7)	2724.5(7)
Space group	P 21/c	P2(1)/c
Hall group	-P 2ybc	?
Moiety formula	C25 H19 N3 O4 Zn, C3 H7 N O	C25 H19 N3 O4 Zn, C3 H7 N O
Sum formula	C28 H26 N4 O5 Zn	C28 H26 N4 O5 Zn
Mr	563.92	563.92
Dx,g cm-3	1.375	0.000
Z	4	4
Mu (mm-1)	0.945	0.937
F000	1168.0	1084.0
F000'	1169.58	
h,k,lmax	18,23,22	18,23,22

Nref 10392 10334

Tmin,Tmax 0.435,0.869 0.425,0.872

Tmin' 0.388

Correction method= # Reported T Limits: Tmin=0.425 Tmax=0.872 AbsCorr = MULTI-SCAN

Data completeness= 0.994 Theta(max)= 33.130

R(reflections)= 0.0403(8084) wR2(reflections)= 0.1439(10334)

S = 1.056 Npar= 345

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level C

ABSTY02_ALERT_1_C An _exptl_absorpt_correction_type has been given without

a literature citation. This should be contained in the

_exptl_absorpt_process_details field.

Absorption correction given as multi-scanPLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... Please CheckPLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of O2 Check PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of O4 Check PLAT242_ALERT_2_C Low 'MainMol' Ueq as Compared to Neighbors of Zn1 Check PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of N4 Check

---

Alert level G

PLAT004_ALERT_5_G Polymeric Structure Found with Maximum Dimension 3 Info PLAT005_ALERT_5_G No Embedded Refinement Details Found in the CIF Please Do ! PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..... 1 ReportPLAT063_ALERT_4_G Crystal Size Likely too Large for Beam Size .... 1.00 mm PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as mixed Check PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 25 Do !

ZN1 -ZN1 -N1 -C1 -76.90 0.50 3.566 1.555 1.555 1.555 PLAT710_ALERT_4_G Delete 1-2-3 or 2-3-4 Linear Torsion Angle ... # 30 Do !

ZN1 -ZN1 -N1 -C14 97.00 0.50 3.566 1.555 1.555 1.555 PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2016 Note

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0 **ALERT level A** = Most likely a serious problem - resolve or explain

0 **ALERT level B** = A potentially serious problem, consider carefully

6 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight

8 **ALERT level G** = General information/check it is not something unexpected

3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

3 ALERT type 2 Indicator that the structure model may be wrong or deficient

0 ALERT type 3 Indicator that the structure quality may be low

5 ALERT type 4 Improvement, methodology, query or suggestion

3 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

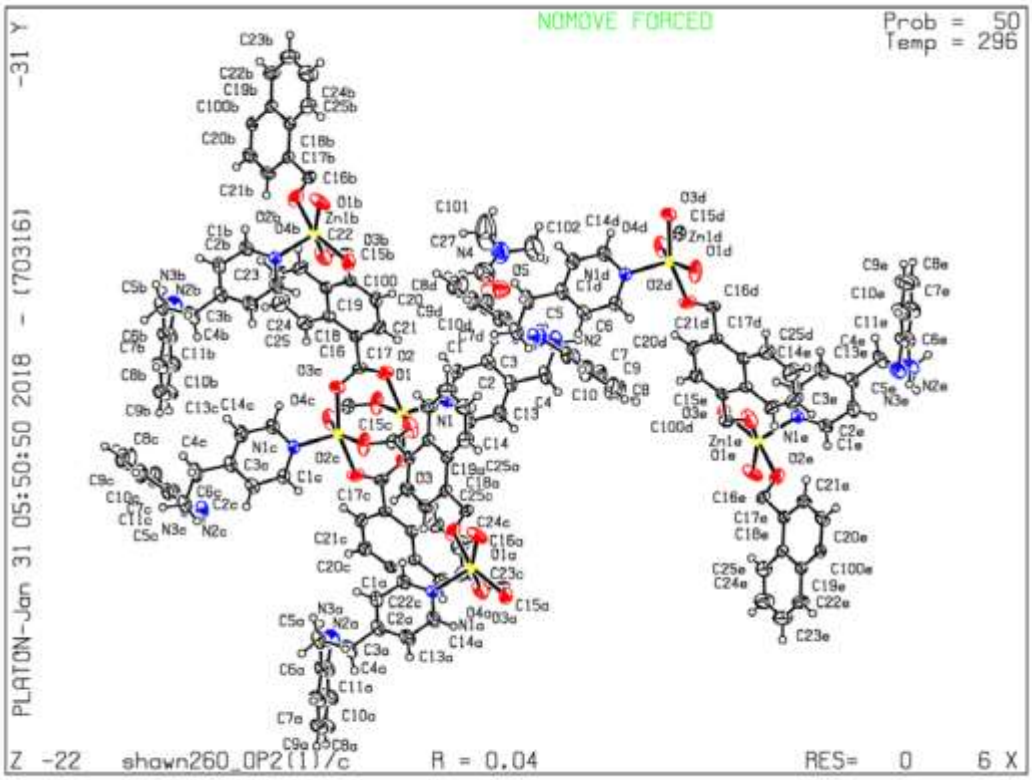
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 13/08/2017; check.def file version of 12/12/2017

Datablock shawn260_0m - ellipsoid plot



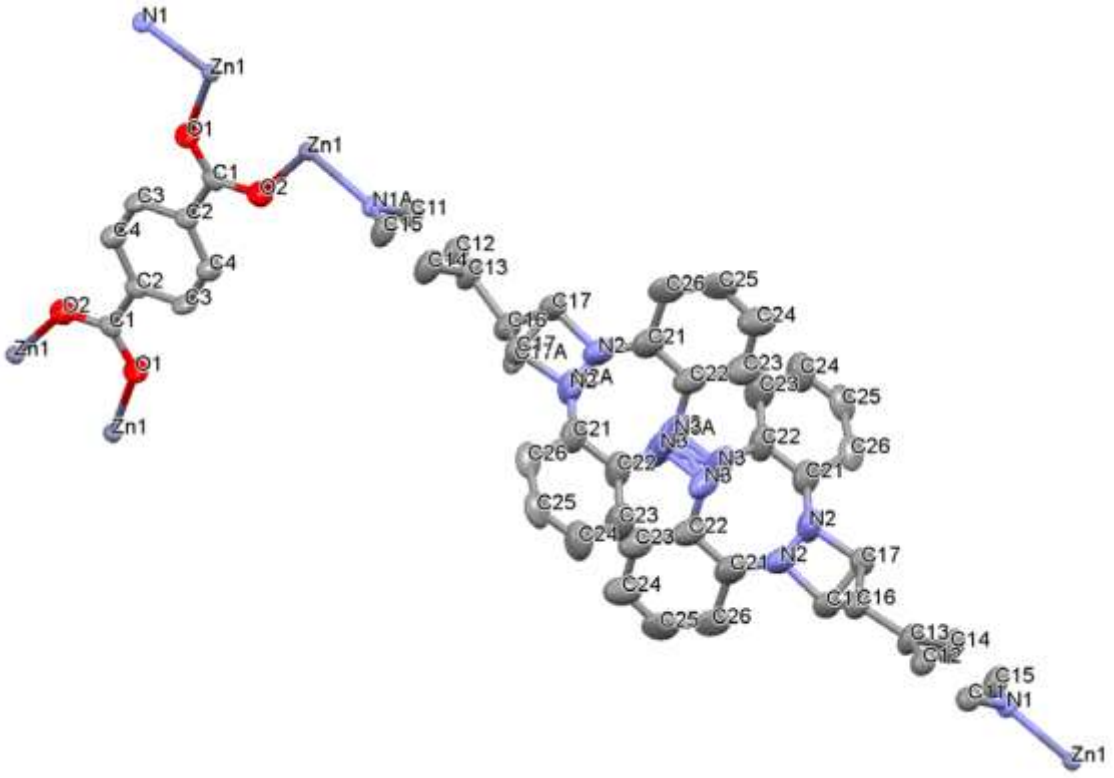


Figure S29. Completely labeled ORTEP plot of 50% thermal ellipsoids for ABMOF-2, showing highly disordered on the AzoAE*p*P ligand.

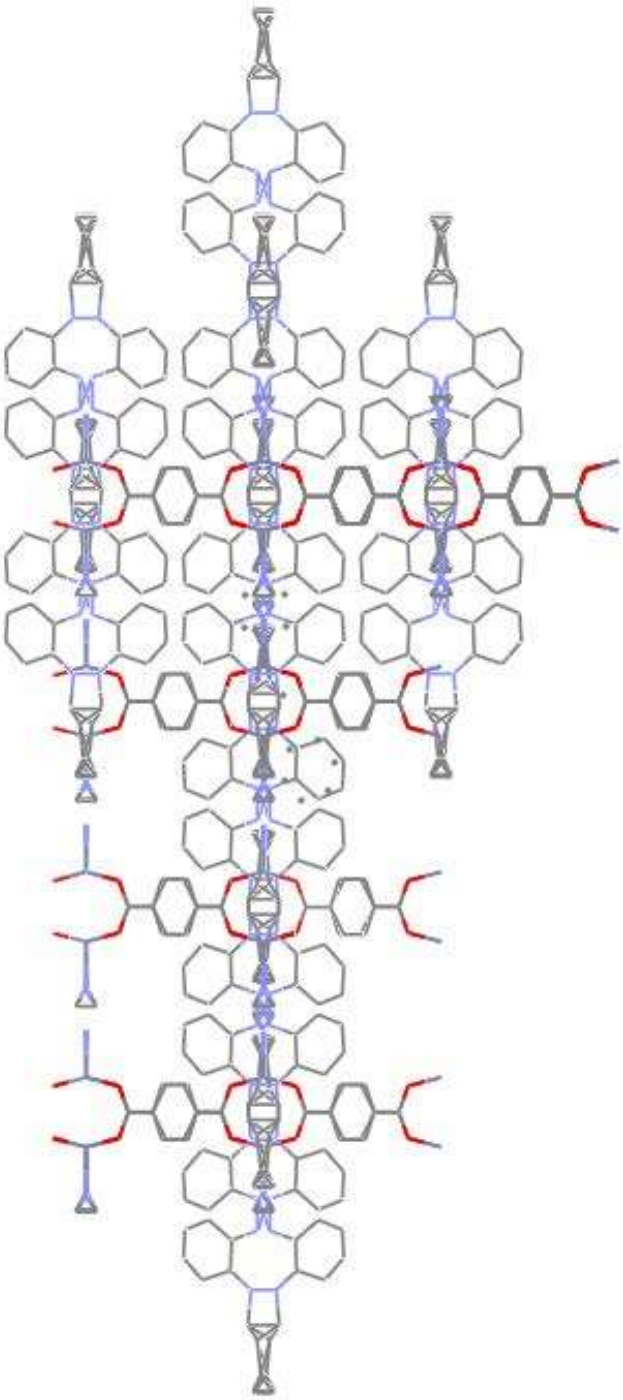


Figure S30. Packing diagrams of ABMOF-2 viewing from a axis. Hydrogen atoms are omitted for clarity.

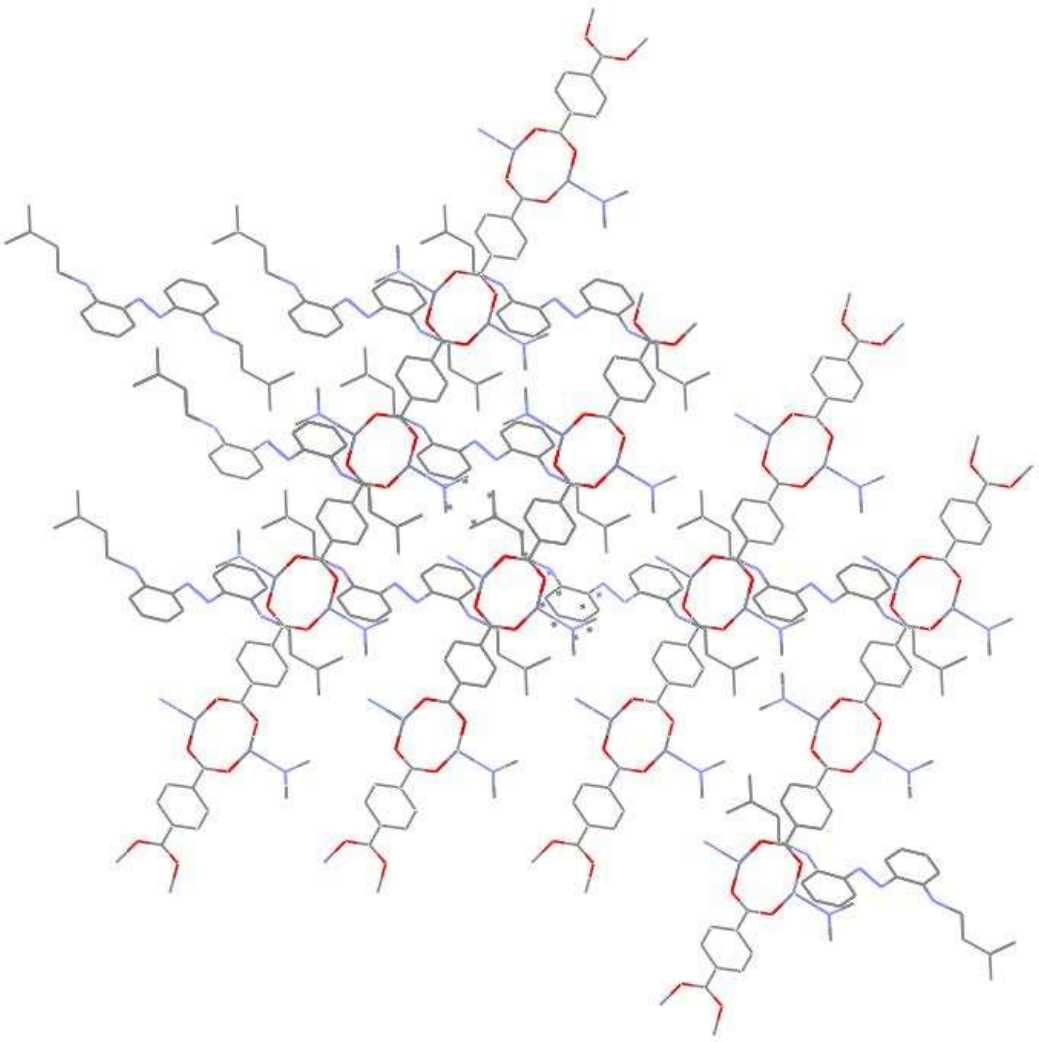


Figure S31. Packing diagrams of ABMOF-2 viewing from b axis. Hydrogen atoms are omitted for clarity.

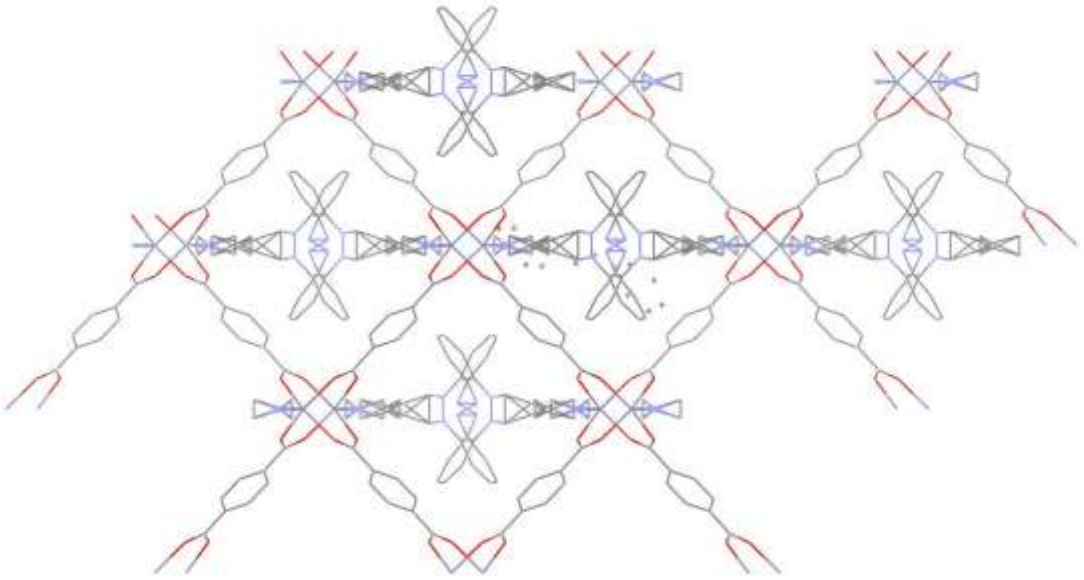


Figure S32. Packing diagrams of ABMOF-2 viewing from c axis. Hydrogen atoms are omitted for clarity.

Table S5. Crystal data and structure refinements for ABMOF-2.

Compound	$\{Zn_2(BDC)_2(AzoAE\textit{p}P)\}_n$
Formula	$C_{50}H_{40}N_6O_8Zn$
Formula weight (g mol^{-1})	918.25
Crystal size	0.25 × 0.18 × 0.01
Crystal system	Monoclinic
Color	Orange
Space group	C 1 2/m 1
a/Å	15.730(3)
b/Å	15.100(3)
c/Å	10.023(2)
α/°	90.00
β/°	119.21(3)
γ/°	90.00
Volume/$Å^3$	2078.0(9)
Z	2
Temp, K	100 (2)
ρ_{calcg}/cm^3	1.468
Radiation	Mo Kα (λ = 0.71073Å)
2θ range for data collection/°	4.92 to 46.36
Index ranges	-20≤h≤20, -16≤k≤19, -12≤l≤12
Reflections collected	11989
Independent reflections	2357
Observed reflections	1825
R	0.0521
wR2	0.1397
no. of parameters	344
Goodness-of-fit on F2	1.090

Table S6. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for ABMOF-2.

	x	*y*	*z*	U_{iso}*/U_{eq}
Zn1	0.05302(4)	0.5	0.16979(7)	0.0165(2)
C1	0.1153(3)	0.6193(2)	-0.0016(5)	0.0262(8)
C11	0.0909(12)	0.4707(11)	0.4854(15)	0.033(5)
C11A	0.1067(18)	0.448(2)	0.483(2)	0.034(6)
C12	0.1397(11)	0.4706(11)	0.6434(14)	0.037(5)
C12A	0.1574(19)	0.446(2)	0.641(2)	0.049(8)
C13	0.2321(18)	0.492(4)	0.7201(14)	0.046(5)
C13A	0.231(3)	0.498(5)	0.722(2)	0.046(7)
C14	0.2735(11)	0.5286(13)	0.6316(15)	0.054(6)
C14A	0.2520(14)	0.5631(16)	0.636(2)	0.029(5)
C15	0.2185(10)	0.5278(12)	0.4749(15)	0.045(6)
C15A	0.1985(14)	0.5594(16)	0.479(2)	0.027(5)
C16	0.285(2)	0.482(3)	0.8914(16)	0.047(6)
C16A	0.288(4)	0.483(4)	0.892(2)	0.041(7)
C17	0.373(2)	0.544(2)	0.9630(19)	0.043(6)
C17A	0.366(3)	0.555(3)	0.970(2)	0.036(6)
C2	0.1842(3)	0.6881(3)	-0.0022(5)	0.0269(9)
C21	0.4761(11)	0.5933(12)	1.2283(18)	0.056(5)
C21A	0.5002(15)	0.5735(16)	1.235(2)	0.043(5)
C22	0.5032(11)	0.5901(12)	1.3771(18)	0.055(4)
C22A	0.5478(17)	0.5589(17)	1.386(2)	0.055(6)
C23	0.5617(13)	0.6542(12)	1.475(2)	0.068(5)
C23A	0.6291(19)	0.6062(18)	1.482(3)	0.061(7)
C24	0.6003(13)	0.7214(13)	1.428(2)	0.066(5)
C24A	0.656(2)	0.6817(19)	1.435(3)	0.069(7)
C25	0.5791(12)	0.7261(12)	1.291(2)	0.055(4)
C25A	0.6112(17)	0.7003(18)	1.297(3)	0.048(5)
C26	0.5176(12)	0.6723(12)	1.183(2)	0.050(4)
C26A	0.5419(17)	0.6520(17)	1.188(3)	0.042(6)
C3	0.2647(3)	0.7129(3)	0.1338(5)	0.0377(11)
C4	0.3288(3)	0.7742(3)	0.1342(5)	0.0396(11)
H11	0.0266	0.4515	0.4359	0.04
H11A	0.0555	0.4085	0.4327	0.04
H12	0.1066	0.4552	0.6957	0.045
H12A	0.1384	0.4057	0.6917	0.059
H14	0.3361	0.5522	0.6796	0.064

H14A	0.2999	0.6059	0.6844	0.035
H15	0.2458	0.5509	0.4183	0.054
H15A	0.2138	0.5997	0.4233	0.033
H16A	0.3069	0.4209	0.9182	0.057
H16B	0.2415	0.4953	0.9312	0.057
H16C	0.3198	0.4251	0.9111	0.05
H16D	0.2446	0.4825	0.9338	0.05
H17A	0.4198	0.5279	0.9303	0.052
H17B	0.3525	0.6047	0.9317	0.052
H17C	0.4056	0.5597	0.9208	0.043
H17D	0.335	0.6112	0.9629	0.043
H2	0.4053	0.4894	1.171	0.073
H23	0.576	0.6524	1.5763	0.082
H23A	0.6671	0.587	1.5824	0.073
H24	0.6419	0.7629	1.4976	0.08
H24A	0.707	0.7173	1.5038	0.083
H25	0.6085	0.7704	1.2636	0.066
H25A	0.6274	0.7532	1.2669	0.057
H26	0.4999	0.6823	1.0808	0.06
H26A	0.5191	0.6651	1.085	0.051
H2A	0.4148	0.4799	1.1654	0.047
H3	0.2752	0.6878	0.2254	0.045
H4	0.3824	0.7904	0.2264	0.048
N1	0.1285(12)	0.496(2)	0.4001(7)	0.0232(14)
N1A	0.1265(19)	0.503(3)	0.4003(9)	0.0232(14)
N2	0.4187(15)	0.5356(14)	1.1346(19)	0.061(6)
N2A	0.429(2)	0.529(2)	1.136(2)	0.040(5)
N3	0.4670(16)	0.5173(17)	1.423(2)	0.084(9)
N3A	0.507(2)	0.490(3)	1.434(4)	0.079(14)
O1	0.1284(2)	0.5928(2)	0.1243(3)	0.0387(7)
O2	0.0501(2)	0.5927(2)	-0.1293(3)	0.0396(7)

Table S7. Atomic displacement parameters (Å^2) for ABMOF-2.

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0123(3)	0.0189(3)	0.0227(4)	0	0.0121(2)	0
C1	0.0222(17)	0.0219(19)	0.039(2)	-0.0020(17)	0.0187(16)	-0.0041(15)
C11	0.027(5)	0.042(12)	0.036(5)	-0.001(4)	0.019(4)	-0.001(6)
C11A	0.027(9)	0.042(11)	0.034(6)	0.006(6)	0.016(5)	0.000(9)
C12	0.030(5)	0.050(12)	0.035(5)	0.000(4)	0.018(4)	-0.001(6)
C12A	0.044(11)	0.065(13)	0.035(6)	0.007(6)	0.017(6)	-0.007(11)
C13	0.032(5)	0.071(13)	0.030(5)	0.005(6)	0.010(4)	-0.008(7)
C13A	0.040(9)	0.064(12)	0.030(6)	0.006(6)	0.014(5)	-0.005(10)
C14	0.036(6)	0.082(16)	0.038(5)	0.005(6)	0.014(4)	-0.012(7)
C14A	0.025(8)	0.038(10)	0.031(6)	-0.002(6)	0.019(5)	0.012(7)
C15	0.030(5)	0.070(15)	0.035(5)	0.007(5)	0.016(4)	-0.014(7)
C15A	0.023(7)	0.035(9)	0.031(6)	-0.001(5)	0.018(5)	0.003(7)
C16	0.040(8)	0.060(12)	0.036(5)	0.003(5)	0.015(5)	0.000(8)
C16A	0.032(10)	0.063(13)	0.034(6)	0.007(6)	0.019(6)	0.002(10)
C17	0.032(8)	0.047(9)	0.039(6)	0.005(5)	0.009(5)	0.007(7)
C17A	0.027(9)	0.063(12)	0.029(7)	0.006(7)	0.022(6)	0.001(9)
C2	0.0207(17)	0.028(2)	0.035(2)	0.0021(17)	0.0153(16)	-0.0060(15)
C21	0.038(8)	0.071(9)	0.047(5)	0.012(5)	0.013(5)	0.010(7)
C21A	0.032(8)	0.062(10)	0.039(6)	0.012(6)	0.019(5)	0.019(8)
C22	0.038(8)	0.072(9)	0.048(6)	0.017(5)	0.015(5)	-0.005(6)
C22A	0.056(10)	0.066(11)	0.037(7)	0.014(6)	0.019(6)	-0.005(9)
C23	0.055(9)	0.081(9)	0.057(7)	0.009(6)	0.018(6)	-0.020(7)
C23A	0.056(11)	0.073(12)	0.045(8)	0.005(8)	0.017(7)	-0.006(10)

C24	0.048(9)	0.075(9)	0.069(7)	0.022(6)	0.023(7)	-0.001(7)
C24A	0.062(12)	0.078(12)	0.059(9)	0.014(8)	0.023(8)	-0.001(10)
C25	0.034(8)	0.058(8)	0.068(7)	0.024(6)	0.021(6)	0.027(6)
C25A	0.027(9)	0.068(11)	0.058(8)	0.013(8)	0.028(7)	0.018(8)
C26	0.032(8)	0.065(9)	0.059(7)	0.024(6)	0.026(6)	0.033(6)
C26A	0.026(10)	0.055(10)	0.053(8)	0.023(7)	0.024(7)	0.032(8)
C3	0.035(2)	0.046(3)	0.028(2)	0.008(2)	0.0119(18)	-0.018(2)
C4	0.032(2)	0.045(3)	0.034(2)	0.003(2)	0.0096(19)	-0.017(2)
N1	0.0177(19)	0.031(4)	0.026(2)	0.001(4)	0.0150(17)	0.005(5)
N1A	0.0177(19)	0.031(4)	0.026(2)	0.001(4)	0.0150(17)	0.005(5)
N2	0.058(9)	0.065(9)	0.041(6)	0.012(5)	0.010(5)	-0.006(8)
N2A	0.037(7)	0.059(11)	0.032(7)	0.010(6)	0.024(5)	0.010(7)
N3	0.087(16)	0.103(15)	0.038(9)	-0.001(8)	0.013(10)	-0.055(12)
N3A	0.073(19)	0.11(2)	0.020(10)	0.018(13)	-0.004(11)	-0.045(19)
O1	0.0431(16)	0.0411(18)	0.0387(17)	-0.0020(14)	0.0253(14)	-0.0217(14)
O2	0.0329(15)	0.0414(18)	0.0419(17)	-0.0004(14)	0.0164(13)	-0.0188(13)

Table S8. Geometric parameters – bond and H-bond length (Å) for ABMOF-2.

Zn1	Zn1	2.9708(16)	C22	N3	1.42(2)
Zn1	N1	2.016(6)	C21A	C22A	1.340(19)
Zn1	N1A	2.017(8)	C21A	C26A	1.538(18)
Zn1	O2	2.029(3)	C21	C22	1.337(18)
Zn1	O2	2.029(3)	C21	C26	1.534(17)
Zn1	O1	2.026(3)	C2	C1	1.503(5)
Zn1	O1	2.026(3)	C2	C4	1.361(6)
O2	Zn1	2.029(3)	C2	C3	1.385(5)
O2	C1	1.253(5)	C17A	H17C	0.97
O1	C1	1.242(5)	C17A	H17D	0.97
N2A	H2A	0.86	C17A	N2A	1.513(17)
N2A	C21A	1.275(15)	C17	H17A	0.97
N2	H2	0.86	C17	H17B	0.97
N2	C21	1.276(14)	C17	N2	1.512(16)
N1A	C11A	1.312(19)	C16A	H16C	0.97
N1A	C15A	1.33(2)	C16A	H16D	0.97
N1	C11	1.311(18)	C16A	C17A	1.532(12)
N1	C15	1.329(19)	C16	H16A	0.97
C4	C2	1.361(6)	C16	H16B	0.97
C4	H4	0.93	C16	C17	1.532(12)
C4	C3	1.367(6)	C15A	H15A	0.93
C3	H3	0.93	C15	H15	0.93
C26A	H26A	0.93	C14A	H14A	0.93
C26	H26	0.93	C14A	C15A	1.376(15)
C25A	H25A	0.93	C14	H14	0.93
C25A	C26A	1.324(18)	C14	C15	1.375(14)
C25	H25	0.93	C13A	C14A	1.44(3)
C25	C26	1.324(17)	C13A	C16A	1.507(13)
C24A	H24A	0.93	C13	C14	1.44(3)
C24A	C25A	1.24(2)	C13	C16	1.507(12)
C24	H24	0.93	C12A	H12A	0.93
C24	C25	1.240(19)	C12A	C13A	1.31(2)
C23A	H23A	0.93	C12	H12	0.93
C23A	C24A	1.38(2)	C12	C13	1.31(2)
C23	H23	0.93	C11A	H11A	0.93
C23	C24	1.38(2)	C11A	C12A	1.381(15)
C22A	C23A	1.37(2)	C11	H11	0.93
C22A	N3A	1.42(2)	C11	C12	1.382(13)
C22	C23	1.364(19)			

Table S8. Geometric parameters – bond angles (º) for ABMOF-2.

N1	Zn1	Zn1	177.6(9)	C23A	C22A	N3A	124.5(19)
C1	O2	Zn1	127.0(3)	C23A	C24A	H24A	121.1
C1	O1	Zn1	128.8(3)	C24	C23	H23	118.9
C11	N1	Zn1	123.7(12)	C24	C25	H25	117.7
C11	N1	C15	115.6(10)	C24	C25	C26	124.6(17)
C11	C12	H12	119.7	C24A	C23A	H23A	119
C11A	N1A	Zn1	122.2(16)	C24A	C25A	H25A	117
C11A	N1A	C15A	115.4(13)	C24A	C25A	C26A	126(2)
C11A	C12A	H12A	118.8	C25	C24	C23	119.5(18)
C12	C11	H11	117.5	C25	C24	H24	120.2
C12	C13	C14	115.9(11)	C25	C26	C21	118.6(14)
C12	C13	C16	119(2)	C25	C26	H26	120.7
C12A	C11A	H11A	118	C25A	C24A	C23A	118(2)
C12A	C13A	C14A	115.6(14)	C25A	C24A	H24A	121.1
C12A	C13A	C16A	118(2)	C25A	C26A	C21A	118.2(17)
C13	C12	C11	120.6(14)	C25A	C26A	H26A	120.9
C13	C12	H12	119.7	C26	C25	H25	117.7
C13	C14	H14	120.7	C26A	C25A	H25A	117
C13	C16	H16A	109.7	C3	C2	C1	119.8(4)
C13	C16	H16B	109.7	C3	C4	H4	119.3
C13	C16	C17	110.0(17)	C4	C2	C1	121.7(4)
C13A	C12A	C11A	122.3(18)	C4	C2	C3	118.4(4)
C13A	C12A	H12A	118.8	C4	C3	C2	120.3(4)
C13A	C14A	H14A	121.1	C4	C3	H3	119.9
C13A	C16A	H16C	109.5	H16A	C16	H16B	108.2
C13A	C16A	H16D	109.5	H16C	C16A	H16D	108.1
C13A	C16A	C17A	110.8(19)	H17A	C17	H17B	108.5
C14	C13	C16	125.1(18)	H17C	C17A	H17D	108.4
C14	C15	H15	118.3	N1	Zn1	O2	100.0(7)
C14A	C13A	C16A	127(2)	N1	Zn1	O2	102.6(8)
C14A	C15A	H15A	117.6	N1	Zn1	O1	98.8(8)
C15	N1	Zn1	120.3(12)	N1	Zn1	O1	101.4(7)
C15	C14	C13	118.6(13)	N1	C11	H11	117.5
C15	C14	H14	120.7	N1	C11	C12	124.9(12)
C15A	N1A	Zn1	122.5(15)	N1	C15	C14	123.4(12)
C15A	C14A	C13A	117.8(18)	N1	C15	H15	118.3
C15A	C14A	H14A	121.1	N1A	Zn1	Zn1	178.7(9)
C16	C17	H17A	110.2	N1A	Zn1	O2	101.5(7)

C16	C17	H17B	110.2	N1A	Zn1	O2	99.8(14)
C16A	C17A	H17C	110.1	N1A	Zn1	O1	99.9(7)
C16A	C17A	H17D	110.1	N1A	Zn1	O1	101.5(14)
C17	C16	H16A	109.7	N1A	C11A	H11A	118
C17	C16	H16B	109.7	N1A	C11A	C12A	123.9(18)
C17	N2	H2	118.2	N1A	C15A	C14A	124.8(17)
C17A	C16A	H16C	109.5	N1A	C15A	H15A	117.6
C17A	C16A	H16D	109.5	N2	C17	C16	107.4(14)
C17A	N2A	H2A	117.5	N2	C17	H17A	110.2
C2	C4	H4	119.3	N2	C17	H17B	110.2
C2	C4	C3	121.3(4)	N2	C21	C22	121.6(15)
C2	C3	H3	119.9	N2	C21	C26	124.2(14)
C21	N2	C17	123.5(14)	N2A	C17A	C16A	108.0(17)
C21	N2	H2	118.2	N2A	C17A	H17C	110.1
C21	C22	C23	120.8(15)	N2A	C17A	H17D	110.1
C21	C22	N3	115.6(15)	N2A	C21A	C22A	126.0(18)
C21	C26	H26	120.7	N2A	C21A	C26A	121.1(17)
C21A	N2A	C17A	125.0(18)	O1	Zn1	Zn1	78.78(9)
C21A	N2A	H2A	117.5	O1	Zn1	Zn1	78.78(9)
C21A	C22A	C23A	121.6(18)	O1	Zn1	O2	88.62(13)
C21A	C22A	N3A	113.8(18)	O1	Zn1	O2	88.62(13)
C21A	C26A	H26A	120.9	O1	Zn1	O2	158.61(13)
C22	C21	C26	114.2(13)	O1	Zn1	O2	158.62(13)
C22	C23	H23	118.9	O1	Zn1	O1	87.56(18)
C22	C23	C24	122.1(16)	O1	C1	O2	125.6(4)
C22A	C21A	C26A	112.9(16)	O1	C1	C2	117.7(3)
C22A	C23A	H23A	119	O2	Zn1	Zn1	79.84(9)
C22A	C23A	C24A	122(2)	O2	Zn1	Zn1	79.84(9)
C23	C22	N3	123.6(15)	O2	Zn1	O2	87.30(18)
C23	C24	H24	120.2	O2	C1	C2	116.7(4)

checkCIF (basic structural check) running

checkCIF/PLATON (basic structural check)

Datablock: pm

Bond precision: C-C = 0.0067 A Wavelength=0.71073

Cell: a=15.730(3) b=15.100(3) c=10.023(2)

alpha=90 beta=119.21(3) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	2078.0(9)	2078.0(9)
Space group	C 2/m	C 1 2/m 1
Hall group	-C 2y	-C 2y
Moiety formula	C42 H34 N6 O8 Zn2	C42 H34 N6 O8 Zn2
Sum formula	C42 H34 N6 O8 Zn2	C42 H34 N6 O8 Zn2
Mr	881.53	881.53
Dx,g cm-3	1.409	1.409
Z	2	2
Mu (mm-1)	1.213	1.213
F000	904.0	952.0

F000'	905.47	
h,k,lmax	20,19,12	20,19,12
Nref	2370	2357
Tmin,Tmax	0.785,0.941	
Tmin'	0.785	

Correction method= Not given

Data completeness= 0.995 Theta(max)= 27.058

R(reflections)= 0.0521(1825) wR2(reflections)= 0.1397(2357)

S = 1.090 Npar= 344

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

Alert level B

PLAT088_ALERT_3_B Poor Data / Parameter Ratio ..... 6.85 Note

PLAT213_ALERT_2_B Atom C26A has ADP max/min Ratio ..... 4.3 prolat

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Alert level C

PLAT057_ALERT_3_C Correction for Absorption Required RT(exp) ... 1.20 Do !

PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)... Please Check

PLAT213_ALERT_2_C Atom N3A has ADP max/min Ratio ..... 3.3 prolat

PLAT220_ALERT_2_C Non-Solvent Resd 1 N Ueq(max)/Ueq(min) Range 3.6 Ratio

PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of 01
Check

PLAT334_ALERT_2_C Small Aver. Benzene C-C Dist C21 -C26 1.36 Ang.

PLAT341_ALERT_3_C Low Bond Precision on C-C Bonds .....
0.00667 Ang.

PLAT411_ALERT_2_C Short Inter H...H Contact H4 ..H12A 2.02 Ang.

1/2-x,1/2+y,1-z = 4_556 Check

PLAT922_ALERT_1_C wR2 in the CIF and FCF Differ by 0.0013
Check

Alert level G

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 33
Note

PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ... 39
Report

PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms 2
Report

PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records 1
Report

PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records 1
Report

PLAT174_ALERT_4_G The CIF-Embedded .res File Contains FLAT Records 4
Report

PLAT175_ALERT_4_G The CIF-Embedded .res File Contains SAME Records 1
Report

PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records 1
Report

PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records 1
Report

PLAT301_ALERT_3_G Main Residue Disorder .....(Resd 1) 53% Note

PLAT335_ALERT_2_G Check Large C6 Ring C-C Range C21 -C26 0.28 Ang.

PLAT335_ALERT_2_G Check Large C6 Ring C-C Range C21A -C26A 0.30 Ang.

PLAT343_ALERT_2_G Unusual sp? Angle Range in Main Residue for C2 Check

PLAT343_ALERT_2_G Unusual sp? Angle Range in Main Residue for C4 Check

PLAT367_ALERT_2_G Long? C(sp?)-C(sp?) Bond C1 - C2 . 1.50 Ang.

PLAT432_ALERT_2_G Short Inter X...Y Contact C4 ..C26 3.16 Ang.

x,y,-1+z = 1_554 Check

PLAT607_ALERT_4_G ADDSYM Test Skipped Due to Severe Disorder ..... ! Info

PLAT721_ALERT_1_G Bond Calc 0.96000, Rep 0.97000 Dev... 0.01 Ang.

C16A -H16D 1.555 1.555 ..... # 50 Check

PLAT721_ALERT_1_G Bond Calc 0.96000, Rep 0.97000 Dev... 0.01 Ang.

C17A -H17D 1.555 1.555 ..... # 53 Check

PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) . 1.17 Ratio

PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group # 58 Check

PLAT802_ALERT_4_G CIF Input Record(s) with more than 80 Characters 2 Info

PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms .... ! Info

PLAT860_ALERT_3_G Number of Least-Squares Restraints ..... 865 Note

PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L= 0.600 13 Note

PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ... 1 Note

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PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density. 4 Info

0 ALERT level A = Most likely a serious problem - resolve or explain

S60

2 ALERT level B = A potentially serious problem, consider carefully

9 ALERT level C = Check. Ensure it is not caused by an omission or oversight

27 ALERT level G = General information/check it is not something unexpected

4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

16 ALERT type 2 Indicator that the structure model may be wrong or deficient

5 ALERT type 3 Indicator that the structure quality may be low

11 ALERT type 4 Improvement, methodology, query or suggestion

2 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta*

Crystallographica, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta*

Crystallographica Section C or *E* or *IUCrData*, you should make sure thatfull publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 14/07/2018; check.def file version of 05/06/2018

Datablock pm - ellipsoid plot

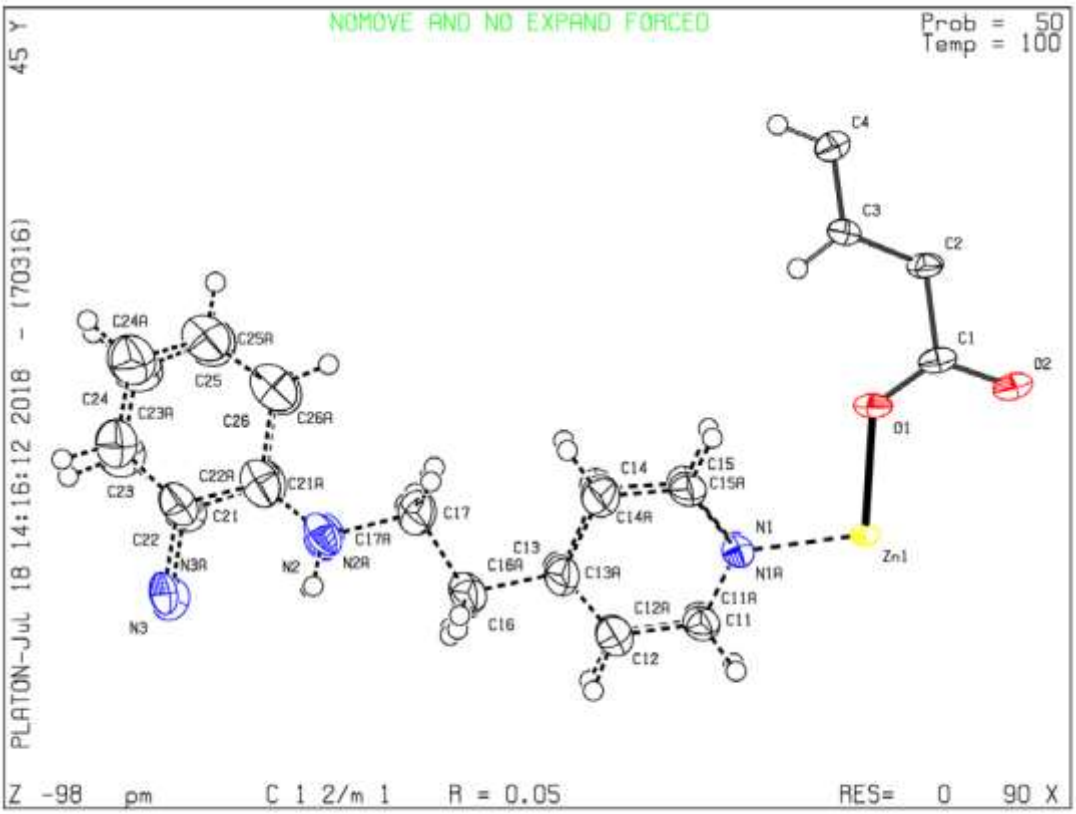

Figure S33. Ellipsoid plot.

Overlayer coverage interpretation of x-ray photoelectron spectroscopy

Interpreting photoelectron data in terms of coverages requires assumptions regarding the adsorbed species and the associated parameters in substrate over layer models. A substrate over layer model[S1–S3] converts photoelectron-determined peak area ratios to fractional monolayer coverage values for the 4-trifluoromethyl-2,6-dinitrophenol (4-CF_3-2,6-DNP) adsorbed to the ABMOF–1 surface similarly to previous reports from our group.[S4] Equation 1 models the ratio of the experimentally quantified intensity of an over layer species, I_{Ov}, to the intensity of a species in the substrate, I_{Sub}. Importantly, eq S1 models a fractional-monolayer coverage $0 < \Phi < 1$, of the chemical over layer, "Ov", of thickness d_{Ov} that is spaced from the substrate, "Sub", by a distance d_{space}.

$$\frac{I_{Ov}}{I_{Sub}} = \frac{I_{Ov}^{\infty}}{I_{Sub}^{\infty}} \frac{\Phi\left(1 - \exp\frac{d_{Ov}\ d_{space}}{\lambda_{Ov,self}\cos\theta}\right)}{1 - \Phi + \Phi\exp\frac{d_{Ov}\ d_{space}}{\lambda_{Sub,Ov}\cos\theta}} \tag{S1}$$

The signal intensity from an ideal, pure, infinitely thick over layer sample, I_{Ov}^{∞}, is attenuated due to only having fractional coverage, $0 < \Phi < 1$, and being a layer l_{Ov} thick, to yield the measured intensity from the overlayer, I_{Ov}. Electrons that are photogenerated in the over layer are attenuated in traveling through the over layer itself by $\lambda_{Ov,self} \cos\theta$, where θ represents the angle between the electron collection direction and the surface normal (45° in our coverage quantification). The signal intensity from an ideal, pure, infinitely thick substrate, I_{Sub}^{∞}, is attenuated due to being partially obscured by the fractional monolayer coverage represented by the Φ exp … term, while the non-obscured substrate fraction, $1 - \Phi$, is not attenuated to cumulatively yield the measured intensity from the substrate, I_{Sub}. The exponential term in the denominator relies on substrate-generated electrons that travel through the over layers of thickness l_{Ov} whilst being attenuated though the over layers by $\lambda_{Sub,Ov} \cos\theta$.

Each ideal pure intensity term I^{∞} may be disassembled and rearranged to better describe the specific systems under study. In each case the pure intensity term may be broken up into an instrument-specific relative sensitivity factor, "*SF*", and the density within each layer, ρ, to yield $I_{Ov}^{\infty} = SF_{Ov}\rho_{Ov}$ and $I_{Sub}^{\infty} = SF_{Sub}\rho_{Sub}$. We employ published sensitivity factors for the Phi 5600 instrument with an OmniFocus III lens.[S5] Considering that we utilize the F 1s peak for the fluorine species in the overlayer, $SF_{Ov} = SF_{F\,1s}$, and for the ABMOF–1 substrate, $SF_{Sub} = SF_{Zn\,2p_{3/2}}$.

The density term for the overlayer, ρ_{Ov}, represents that of the fluorine atoms in the 4-trifluoromethyl-2,6-dinitrophenol (2,6-DNP-4-CF_3) adsorbates. Representing this density for practical coverages requires a few initial assumptions regarding the ABMOF–1 surface structure, binding motifs of the adsorbate to that surface, and adsorbate orientation. We initially assume that the ABMOF–1 principally presents its (100) face in the crystals employed in the XPS analyses. Under the assumption of adsorption of one singular 2,6-DNP-4-CF_3 molecule per interfacial zinc cation., we further consider how many zinc atoms may be present on a (100) face. The structure data above reveals a surface density of two zinc atoms per unit cell. Thus the picture below in Fig. S30 represents our model of 100% packing in which one 2,6-DNP-4-CF_3 molecule adsorbs to each of the zinc sites highlighted by the red arrows. Lastly, we assume that the adsorbate molecules orient themselves perpendicularly with the surface, such that the C–O phenol bond and the C–C methyl-to-phenol bond in the adsorbate is parallel to the [100] direction or "*a*" vector in Fig. S30.

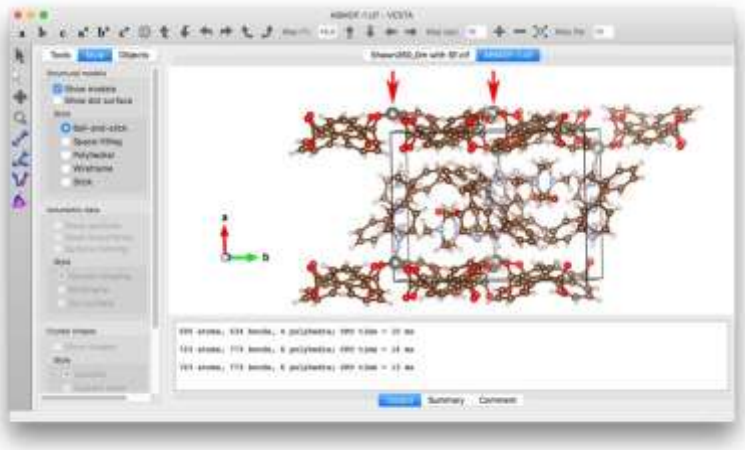

Figure S34. A (100) face of ABMOF–1 revealing two zinc atoms per unit cell to indicate a maximal adsorbate packing density.

The adsorbate binding motifs above enable a breakdown of the overlayer density term, ρ_{Ov}. For "complete" molecular coverages where there are three fluorine atoms per 2,6-DNP-4-CF_3 adsorbates that each bind to the two interfacial zinc atoms, $\rho_{Ov} = \rho_F = 3\,\sigma_{Zn}\,d_F^{-1}$, where σ_{Zn} is the surface density of zinc atoms on an idealized ABMOF–1(100) face, and d_F is a cubic-equivalent height of a fluorine atom. As the overlayer model only considers linear depth, we approximate a spherical size of

a fluorine atom as a cube of identical volume of that sphere, so $d_F^3 = \frac{4}{3}\pi r_F^3$, or $d_F = 2\sqrt[3]{\pi/6}\, r_F$, where r_F = 0.064 nm, a covalent radius of fluorine.[S6] Thus $d_{Ov} = d_F$ = 0.103 nm.

The density term for the substrate, ρ_{Sub}, is the volumetric density of zinc atoms in ABMOF–1, which is four zinc atoms per unit cell. We represent this volumetric density $\rho_{Sub} = \rho_{Zn} = 2\,\sigma_{Zn}\,a^{-1}$, where a is the length of the a-axis of the ABMOF–1 unit cell, or a = 1.21475 nm.

Importantly, the normal molecular orientation of the adsorbate to the ABMOF–1 surface introduces a separation between the zinc atoms producing the substrate signal, and the fluorine atoms producing the overlayer signal, and the zinc signal is attenuated by both the fluorine and the atoms comprising that spatial separation. We model that spatial distance, d_{space}, as two C–C covalent bond lengths and two aromatic C–C bond lengths, or d_{space} = 0.568 nm.

Photoelectron attenuation lengths $\lambda_{Sub,Ov}$ and $\lambda_{Ov,self}$ similarly bear important discussion. We assign an attenuation length value for photoelectrons generated in the fluorine atoms, $\lambda_{Ov,self} = \lambda_F$ = 2.05 nm from prior experimental investigations of F 1s photoelectrons travelling through poly(tetrafluoroethylene).[S7]

To consider the attenuation of Zn $2p_{3/2}$ photoelectrons we employ an empirical model[S8] previously utilized for photoelectrons of non-traditional energies traveling through materials in which they did not originate as would be relevant for photoelectrons from zinc travelling through the zinc-free organic overlayer. As described by eq S2, this model relies on: that relies on: E, the photoelectron kinetic energy; $\langle A \rangle$, the average atomic mass of species in the overlayer in g mol^{-1}; ρ, the overlayer density in kg m^{-3}; N, Avogadro's number; as well as $\langle Z \rangle$, the average atomic number of atoms in the overlayer.

$$\lambda = 0.316 \times 10^{12} \left(\frac{\langle A \rangle}{\rho N} \right)^{1/2} \left[\frac{\mathbf{E}}{\langle Z \rangle^{0.45} \left(3 + \ln \frac{\mathbf{E}}{27} \right)} + 4 \right] \qquad \text{(S2)}$$

To determine value of $\lambda_{Sub,Ov} = \lambda_{Zn}$ via eq S2, we employ $\langle A \rangle$ = 12.60 g mol^{-1} as the average atomic mass and $\langle Z \rangle$ = 6.3 for CF_3-2,6-DNP. We use a 1,3-dinitrobenzene bulk density of ρ = 1368 kg m^{-3} as the density of the CF_3-2,6-DNP. Lastly, a Zn 2p3/2 photoelectron kinetic energy **E** = 460 eV yields λ_{Zn} = 1.50 nm.

Together, the above representations of the parameters and their associated values may be inserted into a rearranged eq S1 to yield eq S2.

$$\frac{I_{\mathrm{F\ 1s}}}{I_{\mathrm{Zn\ 2p_{3/2}}}} = \frac{SF_{\mathrm{F\ 1s}}}{SF_{\mathrm{Zn\ 2p_{3/2}}}} \frac{3d_{\mathrm{U}}^{-1}\Phi}{2a^{-1}} \frac{1-\exp\frac{-d_{\mathrm{U}}-d_{\mathrm{spacer}}}{\lambda_{\mathrm{F}}\cos\theta}}{1-\Phi+\Phi\exp\frac{-d_{\mathrm{U}}-d_{\mathrm{spacer}}}{\lambda_{\mathrm{Zn}}\cos\theta}} \tag{S1}$$

With all parameters known, one may empirically employ experimental values of $I_{\mathrm{F\ 1s}}$ and $I_{\mathrm{Zn\ 2p_{3/2}}}$ to calculate a value of Φ, but it is also useful to understand what may be expected of the term $I_{\mathrm{F\ 1s}}$ / $I_{\mathrm{Zn\ 2p_{3/2}}}$ when Φ = 1 corresponding to "complete" singly capped Zn sites by CF_3-2,6-DNP. For the parameters discussed above, $I_{\mathrm{F\ 1s}}$ / $I_{\mathrm{Zn\ 2p_{3/2}}}$ = 0.687 for Φ = 1.

For three ABMOF–1 samples with surface-adsorbed 4-CF_3-2,6-DNP, $I_{\mathrm{F\ 1s}}$ / $I_{\mathrm{Zn\ 2p_{3/2}}}$ = 0.691, 0.663, and 0.691 for an average ratio of 0.68 ± 0.02. This average fluorine-to-zinc coverage corresponds to Φ = 100 ± 2%. We caution against overinterpretation of 100% coverage values as implying "perfect" coverage due to the real ABMOF–1 surfaces under study certainly contain step edges, pits, and other surface defects, as well as a lack of insight into the specific modes of adsorption. We do, however, interpret these coverage values as implying qualitatively high coverage and strong adsorption surface adsorption of this substituted nitrophenol molecule on the ABMOF–1 surface. Investigation of the precise binding modes and substrate-adsorbate interaction strength remains the subject of ongoing studies in our laboratories.

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