Electronic Supplementary Material (ESI) for Chemical Science
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Supporting Information for:

Systematic Modulation and Enhancement of CO_2:N_2 Selectivity and Water Stability in an Isoreticular Series of Bio-MOF-11 Analogues

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1. Single crystal structures of bio-MOFs 12-14

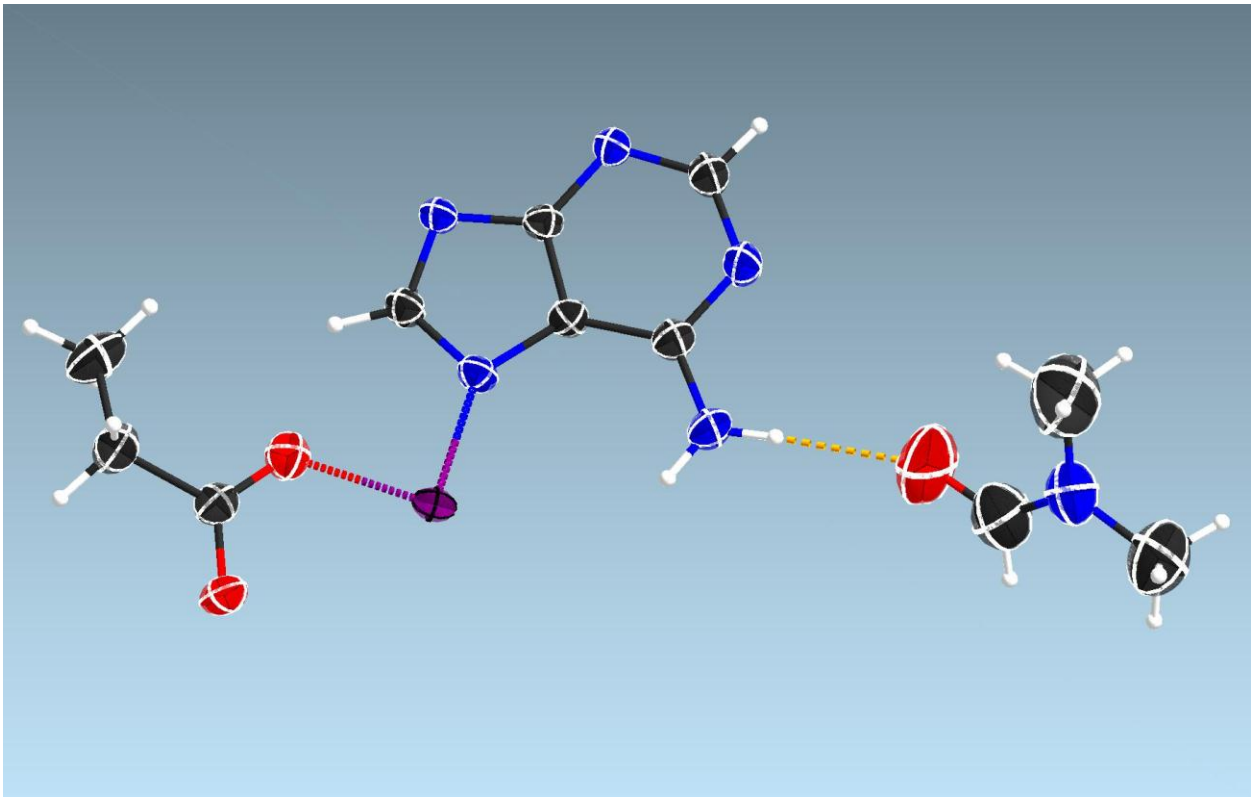

Figure S1. The asymmetric unit present in **bio-MOF-12** with all atoms represented by thermal ellipsoids drawn at the 50% probability level. The image was generated using Shelxle program.[1]

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Table S1. Crystal data and structure refinement for **Bio-MOF-12**.

Identification code	bio-MOF-12	
Empirical formula	C11 H16 Co N6 O3	
Formula weight	339.23	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I 4_1/a	
Unit cell dimensions	a = 17.243(3) Å	α= 90 °.
	b = 17.243(3) Å	β= 90 °.
	c = 20.157(6) Å	γ = 90 °.
Volume	5993(2) $Å^3$	
Z	16	
Density (calculated)	1.504 Mg/m^3	
Absorption coefficient	1.164 mm^{-1}	
F(000)	2800	
Crystal size	0.20 × 0.20 × 0.20 mm^3	
Theta range for data collection	2.36 to 28.39 °.	
Index ranges	-22<=h<=22, -23<=k<=22, -26<=l<=26	
Reflections collected	30135	
Independent reflections	3750 [R(int) = 0.0962]	
Completeness to theta = 28.39 °	99.7 %	
Absorption correction	multi-scan (Bruker SADABS)	
Max. and min. transmission	0.8005 and 0.8005	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3750 / 0 / 190	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0474, wR2 = 0.0855	
R indices (all data)	R1 = 0.0899, wR2 = 0.0985	
Largest diff. peak and hole	0.360 and -0.237 $e.Å^{-3}$	

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Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **bio-MOF-12**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	376(1)	4692(1)	604(1)	28(1)
C(1)	1162(2)	3444(2)	1344(1)	32(1)
C(2)	1268(2)	4415(2)	1988(1)	29(1)
C(3)	1274(2)	5117(2)	2340(2)	36(1)
C(4)	550(2)	3866(2)	-701(2)	36(1)
C(5)	895(2)	3222(2)	-1103(2)	53(1)
C(6)	1182(2)	2534(2)	-712(2)	71(1)
C(7)	1698(2)	3806(2)	2242(1)	27(1)
C(8)	2100(2)	4529(2)	3091(2)	43(1)
N(1)	920(1)	4176(1)	1399(1)	29(1)
N(2)	883(2)	5754(1)	2159(1)	50(1)
N(3)	1708(2)	5151(1)	2900(1)	44(1)
N(4)	1628(1)	3182(1)	1832(1)	30(1)
N(5)	2128(1)	3834(1)	2806(1)	32(1)
O(1)	727(1)	3910(1)	-101(1)	43(1)
O(2)	110(1)	4338(1)	-997(1)	44(1)
O(3)	1056(2)	7295(2)	2787(2)	109(1)
N(6)	1342(2)	8549(2)	2990(2)	71(1)
C(11)	876(3)	7957(3)	2914(2)	84(1)
C(10)	2160(3)	8433(3)	2936(3)	129(2)
C(9)	1078(4)	9314(3)	3149(3)	131(2)

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Table S3. Bond lengths [Å] and angles [°] for **Bio-MOF-12**.

Co(1)-O(2)#1	2.031(2)
Co(1)-O(1)	2.051(2)
Co(1)-N(1)	2.058(2)
Co(1)-N(4)#2	2.072(2)
Co(1)-N(5)#3	2.112(2)
Co(1)-Co(1)#1	2.9560(9)
C(1)-N(1)	1.334(3)
C(1)-N(4)	1.348(3)
C(1)-H(1)	0.9300
C(2)-C(7)	1.383(4)
C(2)-N(1)	1.393(3)
C(2)-C(3)	1.404(4)
C(3)-N(2)	1.338(4)
C(3)-N(3)	1.356(4)
C(4)-O(1)	1.249(3)
C(4)-O(2)	1.263(3)
C(4)-C(5)	1.497(4)
C(5)-C(6)	1.508(5)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(3)	0.9600
C(6)-H(4)	0.9600
C(6)-H(5)	0.9600
C(7)-N(5)	1.360(3)
C(7)-N(4)	1.361(3)
C(8)-N(3)	1.325(4)
C(8)-N(5)	1.329(4)
C(8)-H(6)	0.9300
N(2)-H(7)	0.8600
N(2)-H(8)	0.8600
N(4)-Co(1)#4	2.072(2)
N(5)-Co(1)#5	2.112(2)
O(2)-Co(1)#1	2.031(2)
O(3)-C(11)	1.210(5)

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N(6)-C(11)	1.307(5)
N(6)-C(10)	1.429(6)
N(6)-C(9)	1.432(5)
C(11)-H(11A)	0.9300
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600

O(2)#1-Co(1)-O(1)	159.01(9)
O(2)#1-Co(1)-N(1)	103.93(9)
O(1)-Co(1)-N(1)	96.87(9)
O(2)#1-Co(1)-N(4)#2	89.98(9)
O(1)-Co(1)-N(4)#2	89.63(9)
N(1)-Co(1)-N(4)#2	98.59(9)
O(2)#1-Co(1)-N(5)#3	88.65(9)
O(1)-Co(1)-N(5)#3	86.42(9)
N(1)-Co(1)-N(5)#3	96.04(9)
N(4)#2-Co(1)-N(5)#3	165.20(9)
O(2)#1-Co(1)-Co(1)#1	81.07(6)
O(1)-Co(1)-Co(1)#1	78.17(6)
N(1)-Co(1)-Co(1)#1	174.92(7)
N(4)#2-Co(1)-Co(1)#1	80.40(6)
N(5)#3-Co(1)-Co(1)#1	84.83(6)
N(1)-C(1)-N(4)	116.3(3)
N(1)-C(1)-H(1)	121.8
N(4)-C(1)-H(1)	121.8
C(7)-C(2)-N(1)	108.7(2)
C(7)-C(2)-C(3)	117.6(3)
N(1)-C(2)-C(3)	133.6(3)
N(2)-C(3)-N(3)	118.1(3)
N(2)-C(3)-C(2)	124.4(3)
N(3)-C(3)-C(2)	117.5(3)
O(1)-C(4)-O(2)	124.5(3)

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O(1)-C(4)-C(5)	118.1(3)
O(2)-C(4)-C(5)	117.4(3)
C(4)-C(5)-C(6)	115.5(3)
C(4)-C(5)-H(5A)	108.4
C(6)-C(5)-H(5A)	108.4
C(4)-C(5)-H(5B)	108.4
C(6)-C(5)-H(5B)	108.4
H(5A)-C(5)-H(5B)	107.5
C(5)-C(6)-H(3)	109.5
C(5)-C(6)-H(4)	109.5
H(3)-C(6)-H(4)	109.5
C(5)-C(6)-H(5)	109.5
H(3)-C(6)-H(5)	109.5
H(4)-C(6)-H(5)	109.5
N(5)-C(7)-N(4)	125.7(2)
N(5)-C(7)-C(2)	125.1(3)
N(4)-C(7)-C(2)	109.2(2)
N(3)-C(8)-N(5)	128.5(3)
N(3)-C(8)-H(6)	115.7
N(5)-C(8)-H(6)	115.7
C(1)-N(1)-C(2)	102.4(2)
C(1)-N(1)-Co(1)	119.22(19)
C(2)-N(1)-Co(1)	136.98(18)
C(3)-N(2)-H(7)	120.0
C(3)-N(2)-H(8)	120.0
H(7)-N(2)-H(8)	120.0
C(8)-N(3)-C(3)	119.3(3)
C(1)-N(4)-C(7)	103.3(2)
C(1)-N(4)-Co(1)#4	128.33(19)
C(7)-N(4)-Co(1)#4	128.12(18)
C(8)-N(5)-C(7)	111.9(2)
C(8)-N(5)-Co(1)#5	127.0(2)
C(7)-N(5)-Co(1)#5	120.87(18)
C(4)-O(1)-Co(1)	129.6(2)
C(4)-O(2)-Co(1)#1	126.4(2)
C(11)-N(6)-C(10)	119.2(4)

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C(11)-N(6)-C(9)	123.4(5)
C(10)-N(6)-C(9)	117.4(4)
O(3)-C(11)-N(6)	127.1(5)
O(3)-C(11)-H(11A)	116.4
N(6)-C(11)-H(11A)	116.4
N(6)-C(10)-H(10A)	109.5
N(6)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
N(6)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
N(6)-C(9)-H(9A)	109.5
N(6)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
N(6)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z #2 -y+1/4,x+1/4,-z+1/4 #3 y-1/4,-x+3/4,z-1/4

#4 y-1/4,-x+1/4,-z+1/4 #5 -y+3/4,x+1/4,z+1/4

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Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **Bio-MOF-12**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	25(1)	29(1)	29(1)	8(1)	-3(1)	-1(1)
C(1)	37(2)	30(2)	30(2)	2(1)	-8(1)	1(1)
C(2)	31(2)	27(1)	29(2)	3(1)	-1(1)	-1(1)
C(3)	39(2)	31(2)	36(2)	0(1)	-3(1)	3(1)
C(4)	31(2)	32(2)	44(2)	0(1)	4(1)	-1(1)
C(5)	63(2)	49(2)	46(2)	-8(2)	1(2)	17(2)
C(6)	80(3)	47(2)	86(3)	-3(2)	-7(2)	27(2)
C(7)	27(1)	25(1)	30(2)	4(1)	-2(1)	1(1)
C(8)	55(2)	36(2)	38(2)	-7(1)	-14(2)	8(2)
N(1)	31(1)	29(1)	28(1)	4(1)	-6(1)	0(1)
N(2)	66(2)	30(1)	53(2)	-5(1)	-21(2)	19(1)
N(3)	61(2)	32(1)	41(2)	-8(1)	-17(1)	11(1)
N(4)	34(1)	27(1)	30(1)	0(1)	-9(1)	4(1)
N(5)	36(1)	27(1)	34(1)	-3(1)	-8(1)	3(1)
O(1)	45(1)	44(1)	39(1)	-4(1)	1(1)	4(1)
O(2)	40(1)	33(1)	57(2)	1(1)	-7(1)	11(1)
O(3)	123(3)	57(2)	146(3)	-27(2)	-7(2)	-2(2)
N(6)	73(2)	61(2)	77(2)	-11(2)	-9(2)	-8(2)
C(11)	78(3)	77(3)	97(4)	-11(3)	-7(3)	-11(3)
C(10)	79(4)	123(5)	186(7)	-57(5)	11(4)	-24(3)
C(9)	168(6)	63(3)	162(6)	-30(4)	-58(5)	23(4)

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Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **Bio-MOF-12**.

	x	y	z	U(eq)
H(1)	1017	3131	989	39
H(5A)	1325	3430	-1357	63
H(5B)	508	3043	-1417	63
H(3)	1393	2155	-1010	107
H(4)	758	2309	-470	107
H(5)	1576	2699	-407	107
H(6)	2395	4586	3474	51
H(7)	911	6167	2396	60
H(8)	603	5749	1806	60
H(11A)	349	8056	2964	101
H(10A)	2262	7903	2819	194
H(10B)	2402	8550	3352	194
H(10C)	2364	8768	2598	194
H(9A)	522	9319	3167	196
H(9B)	1252	9671	2815	196
H(9C)	1284	9466	3572	196

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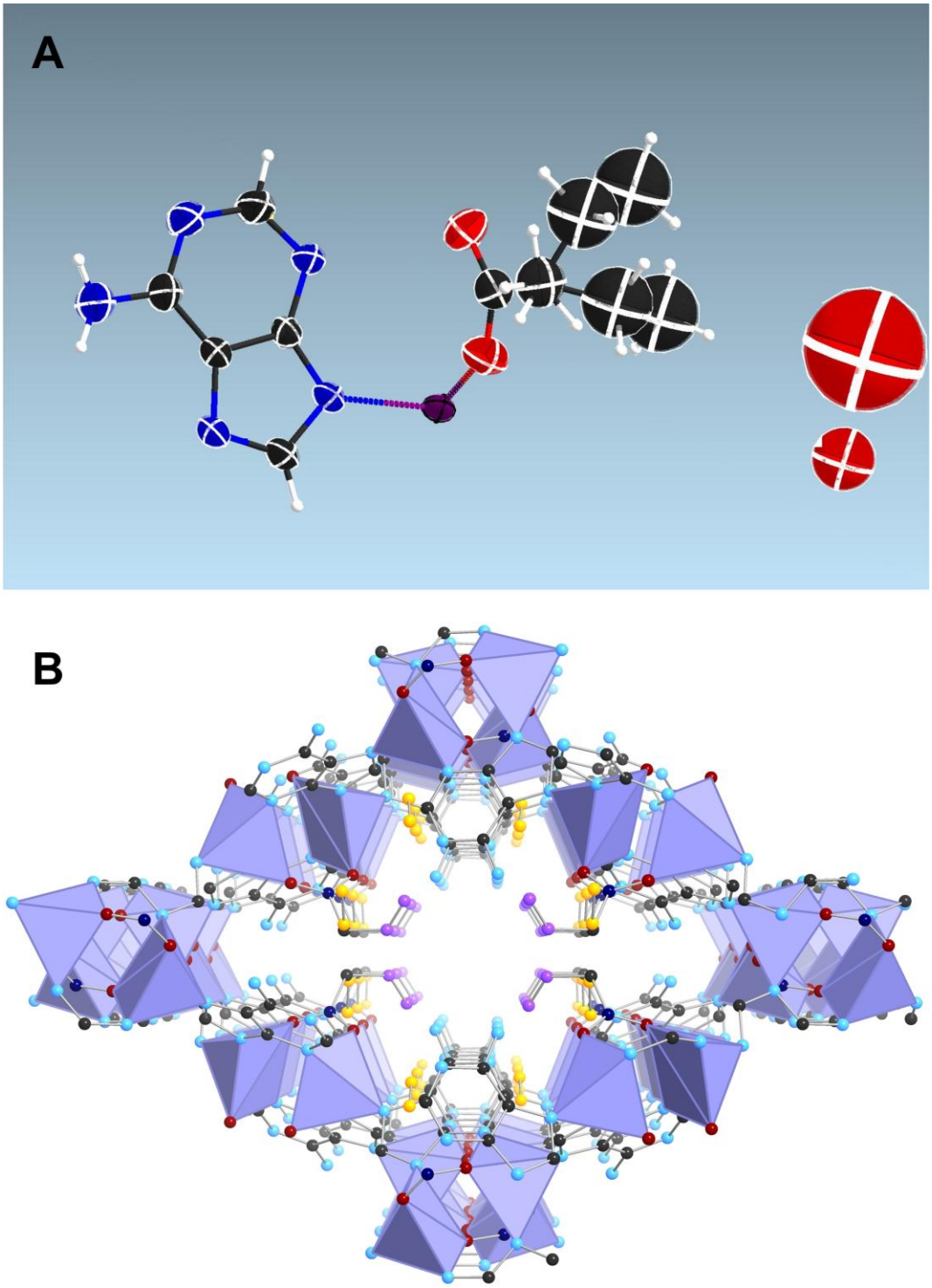

Figure S2. (A) The asymmetric unit present in **bio-MOF-13** with all atoms represented by thermal ellipsoids drawn at the 50% probability level. The image was generated using Shelxle program;[1] (B) Perspective view of the crystal structure of **bio-MOF-13**. (Co^{2+}, light purple tetrahedra; C, dark gray spheres; O, dark red spheres; N, light blue spheres. H atoms have been omitted for clarity. Disordered butyrate chains were illustrate as orange (configuration I), and purple (configuration II))

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Table S6. Crystal data and structure refinement for **bio-MOF-13**.

Identification code	bio-MOF-13	
Empirical formula	C9 H15 Co N5 O3	
Formula weight	300.19	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I 4_1/a	
Unit cell dimensions	a = 15.7869(10) Å	α= 90 °.
	b = 15.7869(10) Å	β= 90 °.
	c = 22.328(3) Å	γ = 90 °.
Volume	5564.7(8) $Å^3$	
Z	16	
Density (calculated)	1.433 Mg/m^3	
Absorption coefficient	1.242 mm^{-1}	
F(000)	2480	
Crystal size	0.25 × 0.25 × 0.25 mm^3	
Theta range for data collection	2.58 to 28.25 °.	
Index ranges	-20<=h<=20, -21<=k<=20, -29<=l<=29	
Reflections collected	28249	
Independent reflections	3450 [R(int) = 0.0320]	
Completeness to theta = 28.25 °	100.0 %	
Absorption correction	Multi scan (Bruker SADABS)	
Max. and min. transmission	0.7466 and 0.7466	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3450 / 5 / 165	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0541, wR2 = 0.1677	
R indices (all data)	R1 = 0.0687, wR2 = 0.1836	
Largest diff. peak and hole	0.760 and -0.395 e.$Å^{-3}$	

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Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **bio-MOF-13**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	5765(2)	6094(2)	9997(1)	65(1)
Co(1)	5407(1)	5170(1)	10590(1)	39(1)
O(2)	5149(2)	5924(2)	9122(1)	60(1)
N(1)	1556(3)	6911(4)	10443(2)	95(2)
N(2)	2201(2)	6181(3)	9676(2)	90(2)
N(3)	3581(2)	5559(2)	9747(1)	49(1)
N(4)	4250(2)	5783(2)	10706(1)	41(1)
N(5)	3188(2)	6506(2)	11166(1)	41(1)
C(1)	3964(2)	6177(2)	11203(1)	46(1)
C(2)	2950(2)	6309(2)	10587(1)	41(1)
C(3)	2227(2)	6482(3)	10243(2)	67(1)
C(4)	2867(3)	5745(4)	9465(2)	78(2)
C(5)	3602(2)	5868(2)	10315(1)	38(1)
C(6)	5651(2)	6299(2)	9467(2)	49(1)
C(7)	6147(3)	7046(3)	9235(3)	79(1)
C(8B)	6364(12)	7028(11)	8627(8)	167(4)
C(9B)	6773(14)	6457(12)	8368(10)	200(5)
C(8A)	7003(12)	6922(15)	9219(12)	167(4)
C(9A)	7462(14)	6275(16)	9261(15)	200(5)
O(1W)	9886(9)	7084(7)	9838(6)	133(6)
O(2W)	9740(30)	6740(20)	9010(20)	500(30)

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Table S8. Bond lengths [Å] and angles [°] for **bio-MOF-13**.

O(1)-C(6)	1.239(4)
O(1)-Co(1)	2.050(3)
Co(1)-O(2)#1	2.041(3)
Co(1)-N(5)#2	2.071(2)
Co(1)-N(4)	2.083(3)
Co(1)-N(3)#1	2.107(3)
Co(1)-Co(1)#1	2.9798(8)
O(2)-C(6)	1.254(4)
O(2)-Co(1)#1	2.041(3)
N(1)-C(3)	1.334(5)
N(1)-H(1N1)	0.85(2)
N(1)-H(2N1)	0.87(2)
N(2)-C(4)	1.341(5)
N(2)-C(3)	1.354(5)
N(3)-C(4)	1.326(5)
N(3)-C(5)	1.359(4)
N(3)-Co(1)#1	2.107(3)
N(4)-C(1)	1.350(4)
N(4)-C(5)	1.352(4)
N(5)-C(1)	1.333(4)
N(5)-C(2)	1.381(4)
N(5)-Co(1)#3	2.071(2)
C(1)-H(1A)	0.9300
C(2)-C(5)	1.382(4)
C(2)-C(3)	1.403(5)
C(4)-H(4A)	0.9300
C(6)-C(7)	1.508(5)
C(7)-C(8A)	1.366(18)
C(7)-C(8B)	1.400(17)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(7)-H(7C)	0.9700
C(7)-H(7D)	0.9701
C(8B)-C(9B)	1.25(2)

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C(8B)-H(7C)	0.9207
C(8B)-H(8B1)	0.9700
C(8B)-H(8B2)	0.9700
C(9B)-H(9B1)	0.9600
C(9B)-H(9B2)	0.9600
C(9B)-H(9B3)	0.9600
C(8A)-C(9A)	1.26(2)
C(8A)-H(8A1)	0.9700
C(8A)-H(8A2)	0.9700
C(9A)-H(9A1)	0.9600
C(9A)-H(9A2)	0.9600
C(9A)-H(9A3)	0.9600
O(1W)-O(1W)#4	1.36(2)

C(6)-O(1)-Co(1)	139.7(3)
O(2)#1-Co(1)-O(1)	157.56(11)
O(2)#1-Co(1)-N(5)#2	105.85(11)
O(1)-Co(1)-N(5)#2	96.58(11)
O(2)#1-Co(1)-N(4)	88.71(11)
O(1)-Co(1)-N(4)	89.50(12)
N(5)#2-Co(1)-N(4)	96.29(10)
O(2)#1-Co(1)-N(3)#1	88.63(12)
O(1)-Co(1)-N(3)#1	87.07(13)
N(5)#2-Co(1)-N(3)#1	99.36(10)
N(4)-Co(1)-N(3)#1	164.26(10)
O(2)#1-Co(1)-Co(1)#1	86.61(8)
O(1)-Co(1)-Co(1)#1	71.08(8)
N(5)#2-Co(1)-Co(1)#1	166.81(8)
N(4)-Co(1)-Co(1)#1	79.38(7)
N(3)#1-Co(1)-Co(1)#1	84.98(7)
C(6)-O(2)-Co(1)#1	118.5(2)
C(3)-N(1)-H(1N1)	121(4)
C(3)-N(1)-H(2N1)	111(4)
H(1N1)-N(1)-H(2N1)	123(6)
C(4)-N(2)-C(3)	119.0(3)
C(4)-N(3)-C(5)	112.5(3)

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C(4)-N(3)-Co(1)#1	126.7(2)
C(5)-N(3)-Co(1)#1	120.8(2)
C(1)-N(4)-C(5)	103.4(2)
C(1)-N(4)-Co(1)	127.6(2)
C(5)-N(4)-Co(1)	129.03(19)
C(1)-N(5)-C(2)	102.7(2)
C(1)-N(5)-Co(1)#3	119.2(2)
C(2)-N(5)-Co(1)#3	138.1(2)
N(5)-C(1)-N(4)	115.9(3)
N(5)-C(1)-H(1A)	122.1
N(4)-C(1)-H(1A)	122.1
N(5)-C(2)-C(5)	108.8(3)
N(5)-C(2)-C(3)	133.6(3)
C(5)-C(2)-C(3)	117.6(3)
N(1)-C(3)-N(2)	117.8(4)
N(1)-C(3)-C(2)	124.2(4)
N(2)-C(3)-C(2)	118.0(3)
N(3)-C(4)-N(2)	127.9(3)
N(3)-C(4)-H(4A)	116.0
N(2)-C(4)-H(4A)	116.0
N(4)-C(5)-N(3)	125.7(3)
N(4)-C(5)-C(2)	109.2(2)
N(3)-C(5)-C(2)	125.0(3)
O(1)-C(6)-O(2)	123.7(3)
O(1)-C(6)-C(7)	117.2(4)
O(2)-C(6)-C(7)	119.1(4)
C(8A)-C(7)-C(8B)	74.3(13)
C(8A)-C(7)-C(6)	114.2(11)
C(8B)-C(7)-C(6)	116.4(8)
C(8A)-C(7)-H(7A)	130.7
C(8B)-C(7)-H(7A)	108.2
C(6)-C(7)-H(7A)	108.2
C(8A)-C(7)-H(7B)	36.0
C(8B)-C(7)-H(7B)	108.2
C(6)-C(7)-H(7B)	108.2
H(7A)-C(7)-H(7B)	107.4

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C(8A)-C(7)-H(7C)	113.2
C(8B)-C(7)-H(7C)	40.9
C(6)-C(7)-H(7C)	108.6
H(7A)-C(7)-H(7C)	73.6
H(7B)-C(7)-H(7C)	140.6
C(8A)-C(7)-H(7D)	104.4
C(8B)-C(7)-H(7D)	131.2
C(6)-C(7)-H(7D)	108.5
H(7A)-C(7)-H(7D)	36.3
H(7B)-C(7)-H(7D)	73.1
H(7C)-C(7)-H(7D)	107.5
C(9B)-C(8B)-C(7)	126.2(18)
C(9B)-C(8B)-H(7C)	152.0
C(7)-C(8B)-H(7C)	43.6
C(9B)-C(8B)-H(8B1)	105.8
C(7)-C(8B)-H(8B1)	105.8
H(7C)-C(8B)-H(8B1)	65.0
C(9B)-C(8B)-H(8B2)	105.8
C(7)-C(8B)-H(8B2)	105.8
H(7C)-C(8B)-H(8B2)	102.2
H(8B1)-C(8B)-H(8B2)	106.2
C(8B)-C(9B)-H(9B1)	109.5
C(8B)-C(9B)-H(9B2)	109.5
H(9B1)-C(9B)-H(9B2)	109.5
C(8B)-C(9B)-H(9B3)	109.5
H(9B1)-C(9B)-H(9B3)	109.5
H(9B2)-C(9B)-H(9B3)	109.5
C(9A)-C(8A)-C(7)	133(2)
C(9A)-C(8A)-H(8A1)	103.9
C(7)-C(8A)-H(8A1)	103.9
C(9A)-C(8A)-H(8A2)	103.9
C(7)-C(8A)-H(8A2)	103.9
H(8A1)-C(8A)-H(8A2)	105.4
C(8A)-C(9A)-H(9A1)	109.5
C(8A)-C(9A)-H(9A2)	109.5
H(9A1)-C(9A)-H(9A2)	109.5

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C(8A)-C(9A)-H(9A3)	109.5
H(9A1)-C(9A)-H(9A3)	109.5
H(9A2)-C(9A)-H(9A3)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2 #2 -y+5/4,x+1/4,-z+9/4 #3 y-1/4,-x+5/4,-z+9/4

#4 -x+2,-y+3/2,z+0

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Table S9. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **Bio-MOF-13**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	78(2)	68(2)	48(1)	1(1)	6(1)	-8(1)
Co(1)	37(1)	47(1)	34(1)	-14(1)	-3(1)	1(1)
O(2)	57(1)	52(1)	71(2)	-6(1)	-12(1)	-8(1)
N(1)	58(2)	161(4)	64(2)	-39(3)	-11(2)	50(3)
N(2)	53(2)	156(4)	60(2)	-43(2)	-18(2)	41(2)
N(3)	39(1)	70(2)	39(1)	-19(1)	-4(1)	8(1)
N(4)	41(1)	47(1)	34(1)	-12(1)	1(1)	6(1)
N(5)	43(1)	48(1)	34(1)	-7(1)	7(1)	2(1)
C(1)	48(2)	55(2)	35(2)	-12(1)	3(1)	8(1)
C(2)	39(2)	50(2)	36(1)	-8(1)	4(1)	3(1)
C(3)	46(2)	101(3)	54(2)	-20(2)	-4(2)	20(2)
C(4)	55(2)	126(4)	51(2)	-38(2)	-12(2)	26(2)
C(5)	36(1)	42(1)	37(1)	-9(1)	5(1)	-1(1)
C(6)	52(2)	41(2)	54(2)	-1(1)	4(1)	-3(1)
C(7)	83(3)	69(3)	84(3)	12(2)	1(3)	-27(2)

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Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **Bio-MOF-13**.

	x	y	z	U(eq)
H(1N1)	1560(40)	7150(40)	10784(16)	113
H(2N1)	1250(30)	7090(40)	10140(20)	113
H(1A)	4288	6217	11549	55
H(4A)	2821	5551	9073	93
H(7A)	5818	7555	9308	94
H(7B)	6664	7093	9467	94
H(7C)	5912	7215	8851	94
H(7D)	6071	7516	9510	94
H(8B1)	5835	7077	8410	200
H(8B2)	6673	7549	8553	200
H(9B1)	6818	6588	7950	300
H(9B2)	6486	5926	8417	300
H(9B3)	7330	6419	8539	300
H(8A1)	7175	7177	8843	200
H(8A2)	7218	7296	9528	200
H(9A1)	8045	6444	9293	300
H(9A2)	7390	5930	8911	300
H(9A3)	7303	5958	9610	300

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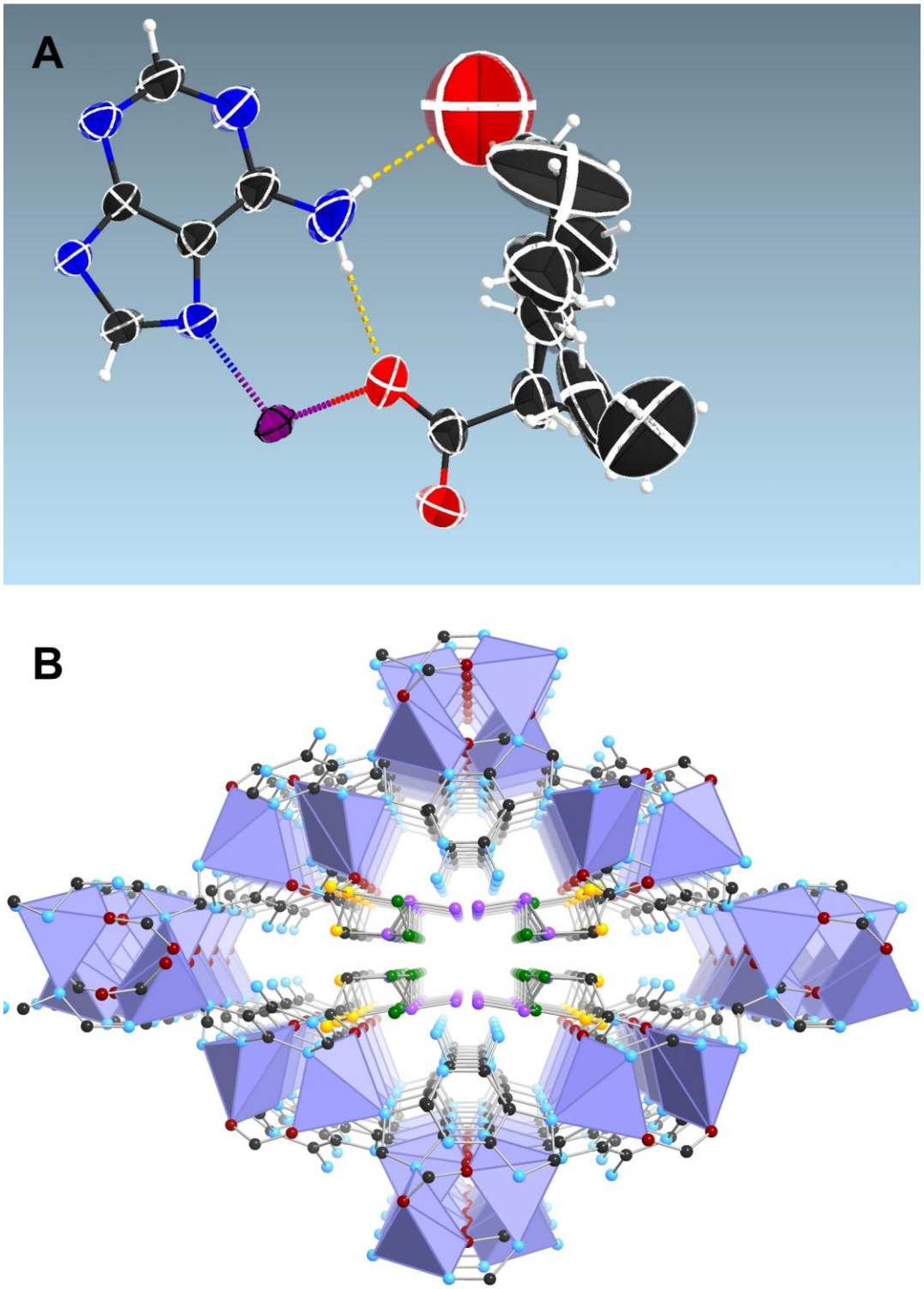

Figure S3. (A) The asymmetric unit present in **bio-MOF-14** with all atoms represented by thermal ellipsoids drawn at the 50% probability level. The image was generated using Shelxle program.[1] (B) Perspective view of the crystal structure of **bio-MOF-14**. (Co^{2+}, light purple tetrahedra; C, dark gray spheres; O, dark red spheres; N, light blue spheres. H atoms have been omitted for clarity. Disordered valerate chains were illustrate as orange (configuration I), purple (configuration II), and green (configuration III))

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Table S11. Crystal data and structure refinement for **bio-MOF-14**.

Identification code	bio-MOF-14	
Empirical formula	C10 H14 Co N5 O2.50	
Formula weight	303.19	
Temperature	273(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I 4_1/a	
Unit cell dimensions	a = 15.852(3) Å	α= 90 °.
	b = 15.852(3) Å	β= 90 °.
	c = 22.346(8) Å	γ = 90 °.
Volume	5616(2) $Å^3$	
Z	16	
Density (calculated)	1.434 Mg/m^3	
Absorption coefficient	1.229 mm^{-1}	
F(000)	2496	
Crystal size	0.08 × 0.08 × 0.08 mm^3	
Theta range for data collection	2.57 to 28.30 °.	
Index ranges	-21<=h<=21, -21<=k<=16, -29<=l<=29	
Reflections collected	21045	
Independent reflections	3426 [R(int) = 0.1036]	
Completeness to theta = 28.30 °	98.1 %	
Absorption correction	Multi scan (Bruker SADABS)	
Max. and min. transmission	0.9081 and 0.9081	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3426 / 145 / 222	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0658, wR2 = 0.1834	
R indices (all data)	R1 = 0.1442, wR2 = 0.2298	
Largest diff. peak and hole	0.660 and -0.514 e.$Å^{-3}$	

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Table S12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **bio-MOF-14**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(4)	1328(5)	9725(4)	2827(3)	92(2)
Co(1)	400(1)	10164(1)	595(1)	45(1)
N(1)	1729(3)	11749(3)	1782(2)	46(1)
O(1)	-142(3)	9071(3)	888(2)	66(1)
N(2)	996(3)	10688(3)	1329(2)	47(1)
C(2)	1197(4)	10466(3)	1909(2)	47(1)
C(1)	1331(4)	11453(4)	1296(2)	53(2)
O(2)	-743(3)	8925(3)	4(2)	69(1)
N(5)	1940(3)	11096(3)	2749(2)	54(1)
C(3)	1637(3)	11107(3)	2176(2)	43(1)
C(6)	-636(4)	8697(4)	531(3)	56(2)
C(4)	1026(5)	9735(4)	2257(3)	69(2)
C(5)	1748(5)	10388(4)	3030(3)	77(2)
N(3)	601(5)	9075(4)	2062(3)	97(2)
C(7)	-1128(6)	7958(5)	761(4)	92(2)
C(8)	-2038(10)	8022(14)	660(17)	146(10)
C(9)	-2530(13)	8789(14)	807(17)	166(12)
C(10)	-3430(20)	8870(20)	610(20)	220(20)
C(8A)	-1360(20)	7947(13)	1396(8)	124(7)
C(9A)	-1840(20)	8631(17)	1693(11)	194(10)
C(10A)	-1990(30)	8580(30)	2354(12)	370(30)
C(8B)	-1470(50)	8230(40)	1348(14)	144(10)
C(9B)	-1540(40)	7690(40)	1878(13)	169(12)
C(10B)	-1010(50)	7800(30)	2420(20)	161(17)
O(1S)	0	7500	2814(14)	363(13)

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Table S13. Bond lengths [Å] and angles [°] for **bio-MOF-14**.

N(4)-C(5)	1.324(8)
N(4)-C(4)	1.363(8)
Co(1)-O(2)#1	2.041(4)
Co(1)-O(1)	2.042(5)
Co(1)-N(2)	2.069(4)
Co(1)-N(1)#2	2.081(4)
Co(1)-N(5)#3	2.109(5)
Co(1)-Co(1)#1	2.9903(16)
N(1)-C(1)	1.341(7)
N(1)-C(3)	1.354(7)
N(1)-Co(1)#4	2.081(4)
O(1)-C(6)	1.265(7)
N(2)-C(1)	1.325(7)
N(2)-C(2)	1.379(7)
C(2)-C(3)	1.369(7)
C(2)-C(4)	1.421(8)
C(1)-H(1A)	0.9300
O(2)-C(6)	1.245(7)
O(2)-Co(1)#1	2.041(4)
N(5)-C(5)	1.321(8)
N(5)-C(3)	1.368(7)
N(5)-Co(1)#5	2.109(5)
C(6)-C(7)	1.498(9)
C(4)-N(3)	1.318(8)
C(5)-H(5A)	0.9300
N(3)-H(3A)	0.8600
N(3)-H(3B)	0.8600
C(7)-C(8)	1.464(15)
C(7)-C(8A)	1.465(14)
C(7)-C(8B)	1.485(18)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(7)-H(7C)	0.9700
C(7)-H(7D)	0.9700

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C(7)-H(7E)	0.9700
C(7)-H(7F)	0.9700
C(8)-C(9)	1.481(17)
C(8)-H(7C)	0.6663
C(8)-H(7E)	0.6301
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(10)	1.495(18)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600
C(8A)-C(9A)	1.483(17)
C(8A)-H(8A1)	0.9700
C(8A)-H(8A2)	0.9700
C(9A)-C(10A)	1.500(18)
C(9A)-H(9A1)	0.9700
C(9A)-H(9A2)	0.9700
C(10A)-H(10D)	0.9600
C(10A)-H(10E)	0.9600
C(10A)-H(10F)	0.9600
C(8B)-C(9B)	1.468(18)
C(8B)-H(8B1)	0.9700
C(8B)-H(8B2)	0.9700
C(9B)-C(10B)	1.497(19)
C(9B)-H(9B1)	0.9700
C(9B)-H(9B2)	0.9700
C(10B)-O(1S)	1.88(6)
C(10B)-H(10G)	0.9600
C(10B)-H(10H)	0.9600
C(10B)-H(10I)	0.9600
O(1S)-C(10B)#6	1.88(6)

C(5)-N(4)-C(4)	119.1(6)
O(2)#1-Co(1)-O(1)	157.28(18)

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O(2)#1-Co(1)-N(2)	96.56(19)
O(1)-Co(1)-N(2)	106.14(18)
O(2)#1-Co(1)-N(1)#2	89.67(19)
O(1)-Co(1)-N(1)#2	88.84(18)
N(2)-Co(1)-N(1)#2	96.28(18)
O(2)#1-Co(1)-N(5)#3	86.80(19)
O(1)-Co(1)-N(5)#3	88.48(19)
N(2)-Co(1)-N(5)#3	99.48(18)
N(1)#2-Co(1)-N(5)#3	164.14(17)
O(2)#1-Co(1)-Co(1)#1	69.77(13)
O(1)-Co(1)-Co(1)#1	87.66(13)
N(2)-Co(1)-Co(1)#1	165.72(14)
N(1)#2-Co(1)-Co(1)#1	80.02(12)
N(5)#3-Co(1)-Co(1)#1	84.26(12)
C(1)-N(1)-C(3)	102.3(5)
C(1)-N(1)-Co(1)#4	129.2(4)
C(3)-N(1)-Co(1)#4	128.5(3)
C(6)-O(1)-Co(1)	117.1(4)
C(1)-N(2)-C(2)	101.2(4)
C(1)-N(2)-Co(1)	120.3(4)
C(2)-N(2)-Co(1)	138.4(4)
C(3)-C(2)-N(2)	109.7(5)
C(3)-C(2)-C(4)	117.6(5)
N(2)-C(2)-C(4)	132.7(5)
N(2)-C(1)-N(1)	117.5(5)
N(2)-C(1)-H(1A)	121.2
N(1)-C(1)-H(1A)	121.2
C(6)-O(2)-Co(1)#1	142.1(4)
C(5)-N(5)-C(3)	112.0(5)
C(5)-N(5)-Co(1)#5	126.3(4)
C(3)-N(5)-Co(1)#5	121.6(4)
N(1)-C(3)-N(5)	125.5(5)
N(1)-C(3)-C(2)	109.2(5)
N(5)-C(3)-C(2)	125.3(5)
O(2)-C(6)-O(1)	123.0(6)
O(2)-C(6)-C(7)	118.7(6)

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O(1)-C(6)-C(7)	118.2(6)
N(3)-C(4)-N(4)	118.5(6)
N(3)-C(4)-C(2)	124.4(6)
N(4)-C(4)-C(2)	117.1(6)
N(5)-C(5)-N(4)	128.9(6)
N(5)-C(5)-H(5A)	115.6
N(4)-C(5)-H(5A)	115.6
C(4)-N(3)-H(3A)	120.0
C(4)-N(3)-H(3B)	120.0
H(3A)-N(3)-H(3B)	120.0
C(8)-C(7)-C(8A)	85(2)
C(8)-C(7)-C(8B)	76(4)
C(8A)-C(7)-C(8B)	19(2)
C(8)-C(7)-C(6)	114.0(12)
C(8A)-C(7)-C(6)	118.0(13)
C(8B)-C(7)-C(6)	106(3)
C(8)-C(7)-H(7A)	108.8
C(8A)-C(7)-H(7A)	120.3
C(8B)-C(7)-H(7A)	139.3
C(6)-C(7)-H(7A)	108.8
C(8)-C(7)-H(7B)	108.8
C(8A)-C(7)-H(7B)	24.4
C(8B)-C(7)-H(7B)	38.9
C(6)-C(7)-H(7B)	108.8
H(7A)-C(7)-H(7B)	107.7
C(8)-C(7)-H(7C)	21.6
C(8A)-C(7)-H(7C)	105.4
C(8B)-C(7)-H(7C)	97.2
C(6)-C(7)-H(7C)	107.4
H(7A)-C(7)-H(7C)	93.0
H(7B)-C(7)-H(7C)	129.1
C(8)-C(7)-H(7D)	120.9
C(8A)-C(7)-H(7D)	110.6
C(8B)-C(7)-H(7D)	129.9
C(6)-C(7)-H(7D)	107.8
H(7A)-C(7)-H(7D)	14.8

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H(7B)-C(7)-H(7D)	94.6
H(7C)-C(7)-H(7D)	107.0
C(8)-C(7)-H(7E)	18.9
C(8A)-C(7)-H(7E)	102.6
C(8B)-C(7)-H(7E)	94.5
C(6)-C(7)-H(7E)	109.1
H(7A)-C(7)-H(7E)	94.6
H(7B)-C(7)-H(7E)	126.3
H(7C)-C(7)-H(7E)	2.8
H(7D)-C(7)-H(7E)	108.4
C(8)-C(7)-H(7F)	120.0
C(8A)-C(7)-H(7F)	109.3
C(8B)-C(7)-H(7F)	128.6
C(6)-C(7)-H(7F)	109.4
H(7A)-C(7)-H(7F)	15.1
H(7B)-C(7)-H(7F)	93.7
H(7C)-C(7)-H(7F)	106.6
H(7D)-C(7)-H(7F)	1.7
H(7E)-C(7)-H(7F)	107.9
C(7)-C(8)-C(9)	123(2)
C(7)-C(8)-H(7C)	32.4
C(9)-C(8)-H(7C)	135.5
C(7)-C(8)-H(7E)	29.8
C(9)-C(8)-H(7E)	136.1
H(7C)-C(8)-H(7E)	2.8
C(7)-C(8)-H(8A)	106.6
C(9)-C(8)-H(8A)	106.6
H(7C)-C(8)-H(8A)	115.8
H(7E)-C(8)-H(8A)	114.2
C(7)-C(8)-H(8B)	106.6
C(9)-C(8)-H(8B)	106.6
H(7C)-C(8)-H(8B)	74.2
H(7E)-C(8)-H(8B)	76.9
H(8A)-C(8)-H(8B)	106.6
C(8)-C(9)-C(10)	121(2)
C(8)-C(9)-H(9A)	107.2

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C(10)-C(9)-H(9A)	107.2
C(8)-C(9)-H(9B)	107.2
C(10)-C(9)-H(9B)	107.2
H(9A)-C(9)-H(9B)	106.8
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(7)-C(8A)-C(9A)	123.5(18)
C(7)-C(8A)-H(8A1)	106.4
C(9A)-C(8A)-H(8A1)	106.4
C(7)-C(8A)-H(8A2)	106.4
C(9A)-C(8A)-H(8A2)	106.4
H(8A1)-C(8A)-H(8A2)	106.5
C(8A)-C(9A)-C(10A)	119(2)
C(8A)-C(9A)-H(9A1)	107.5
C(10A)-C(9A)-H(9A1)	107.5
C(8A)-C(9A)-H(9A2)	107.5
C(10A)-C(9A)-H(9A2)	107.5
H(9A1)-C(9A)-H(9A2)	107.0
C(9A)-C(10A)-H(10D)	109.5
C(9A)-C(10A)-H(10E)	109.5
H(10D)-C(10A)-H(10E)	109.5
C(9A)-C(10A)-H(10F)	109.5
H(10D)-C(10A)-H(10F)	109.5
H(10E)-C(10A)-H(10F)	109.5
C(9B)-C(8B)-C(7)	125(3)
C(9B)-C(8B)-H(8B1)	106.1
C(7)-C(8B)-H(8B1)	106.1
C(9B)-C(8B)-H(8B2)	106.1
C(7)-C(8B)-H(8B2)	106.1
H(8B1)-C(8B)-H(8B2)	106.3
C(8B)-C(9B)-C(10B)	123(2)
C(8B)-C(9B)-H(9B1)	106.6

C(10B)-C(9B)-H(9B1)	106.6
C(8B)-C(9B)-H(9B2)	106.6
C(10B)-C(9B)-H(9B2)	106.6
H(9B1)-C(9B)-H(9B2)	106.5
C(9B)-C(10B)-O(1S)	146(6)
C(9B)-C(10B)-H(10G)	109.5
O(1S)-C(10B)-H(10G)	38.4
C(9B)-C(10B)-H(10H)	109.5
O(1S)-C(10B)-H(10H)	80.9
H(10G)-C(10B)-H(10H)	109.5
C(9B)-C(10B)-H(10I)	109.5
O(1S)-C(10B)-H(10I)	96.7
H(10G)-C(10B)-H(10I)	109.5
H(10H)-C(10B)-H(10I)	109.5
C(10B)-O(1S)-C(10B)#6	125(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z #2 y-5/4,-x+5/4,-z+1/4 #3 -y+5/4,x+3/4,z-1/4

#4 -y+5/4,x+5/4,-z+1/4 #5 y-3/4,-x+5/4,z+1/4

#6 -x+0,-y+3/2,z+0

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Table S14. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **Bio-MOF-14**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(4)	146(6)	63(4)	67(4)	24(3)	-44(4)	-42(4)
Co(1)	44(1)	52(1)	38(1)	-14(1)	-3(1)	1(1)
N(1)	55(3)	42(3)	41(2)	0(2)	-11(2)	-5(2)
O(1)	62(3)	58(3)	79(3)	-6(2)	-11(2)	-9(2)
N(2)	55(3)	47(3)	40(2)	-7(2)	-5(2)	-1(2)
C(2)	53(3)	41(3)	46(3)	-3(2)	-7(2)	0(3)
C(1)	67(4)	56(4)	37(3)	-5(2)	-10(3)	-7(3)
O(2)	81(3)	74(3)	53(2)	3(2)	13(2)	-2(2)
N(5)	68(3)	47(3)	45(2)	7(2)	-18(2)	-6(2)
C(3)	43(3)	41(3)	45(3)	-5(2)	-5(2)	1(2)
C(6)	59(4)	44(3)	65(4)	-4(3)	9(3)	-6(3)
C(4)	95(5)	51(4)	62(4)	3(3)	-22(4)	-18(4)
C(5)	115(6)	62(4)	55(4)	9(3)	-31(4)	-23(4)
N(3)	149(6)	55(4)	87(4)	11(3)	-47(4)	-42(4)
C(7)	93(6)	77(5)	106(6)	23(5)	-1(5)	-27(4)
C(8)	78(9)	119(18)	240(30)	9(19)	58(16)	-29(11)
C(9)	115(15)	111(19)	270(30)	10(20)	120(20)	-15(12)
C(10)	210(30)	160(40)	290(50)	-80(30)	-20(40)	90(30)
C(8A)	158(16)	101(15)	114(10)	35(10)	41(11)	-53(12)
C(9A)	220(20)	190(20)	172(17)	-16(16)	76(17)	-18(18)
C(10A)	400(50)	520(60)	200(20)	10(30)	170(40)	120(50)
C(8B)	170(20)	120(20)	143(15)	7(15)	72(17)	-70(20)
C(9B)	230(30)	150(20)	132(14)	11(19)	60(20)	-40(20)
C(10B)	260(40)	90(30)	120(20)	-20(30)	70(30)	-70(30)

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Table S15. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **Bio-MOF-14**.

	x	y	z	U(eq)
H(1A)	1290	11773	948	64
H(5A)	1933	10351	3424	93
H(3A)	520	8650	2295	116
H(3B)	405	9069	1704	116
H(7A)	-921	7450	568	110
H(7B)	-1025	7901	1187	110
H(7C)	-1658	7944	545	110
H(7D)	-821	7450	655	110
H(7E)	-1673	7944	564	110
H(7F)	-832	7440	662	110
H(8A)	-2296	7560	878	175
H(8B)	-2131	7909	239	175
H(9A)	-2225	9267	643	199
H(9B)	-2521	8851	1239	199
H(10A)	-3664	9379	779	329
H(10B)	-3744	8395	750	329
H(10C)	-3453	8900	184	329
H(8A1)	-835	7886	1617	149
H(8A2)	-1675	7432	1460	149
H(9A1)	-2382	8670	1497	233
H(9A2)	-1544	9157	1615	233
H(10D)	-2342	9047	2476	562
H(10E)	-1466	8605	2563	562
H(10F)	-2275	8061	2446	562
H(8B1)	-1143	8715	1469	173
H(8B2)	-2039	8436	1269	173
H(9B1)	-1446	7113	1742	203
H(9B2)	-2123	7716	2009	203
H(10G)	-444	7613	2344	241
H(10H)	-1240	7483	2749	241
H(10I)	-996	8390	2532	241

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2. Simulation data tables

Table S16. Lennard-Jones parameters for the bio-MOF atoms and the CO_2 molecule. ε is the well depth and σ is the diameter of the molecule. The charges on the CO_2 atoms are 0.6512 for C and -0.3256 for each O.

	ε (K)	σ (Å)
C	52.84	3.431
Co	7.045	2.557
H	22.14	2.571
N	34.72	3.261
O	30.19	3.118
C (CO_2)	29.933	2.745
O (CO_2)	85.671	3.017

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Table S17. Atomic charges in the frameworks of **bio-MOF-12**, **bio-MOF-13**, and **bio-MOF-14**. The labels of each atomic type are given in Figure S6.

Atom type	**bio-MOF-12**	**bio-MOF-13**	**bio-MOF-14**
Co	0.620	0.456	0.581
O1	-0.737	-0.505	-0.650
O2	-0.573	-0.614	-0.613
N1	-0.070	0.089	-0.074
N2	-0.263	-0.193	-0.237
N3	-0.446	-0.464	-0.412
N4	-0.697	-0.691	-0.535
N5	-0.871	-0.820	-0.882
C1	-0.299	-0.498	-0.242
C2	0.488	0.563	0.494
C3	0.782	0.831	0.650
C4	-0.082	-0.143	-0.170
C5	0.368	0.406	0.281
C6	0.817	0.720	0.817
C7	-0.200	-0.231	-0.520
C8	-0.124	-0.064	0.033
H1	0.135	0.149	0.205
H2	0.068	0.048	0.074
H3	0.365	0.335	0.371
H4	0.424	0.360	0.434
H5	0.069	0.095	0.161
H6	0.072	0.067	0.135
H7	0.037	0.058	0.078
H8	0.053	0.061	0.026
H9	0.063	0.038	0.019
H10		0.035	-0.011
H11		0.060	0.095
C9		-0.147	0.132
C10			-0.400
H12			0.083
H13			0.076

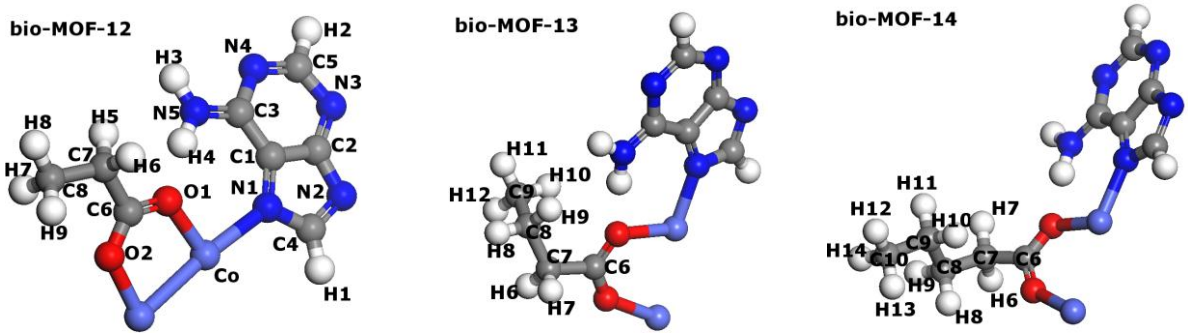

Figure S6. Labels for atom types in **bio-MOF-12**, **bio-MOF-13**, and **bio-MOF-14**. Note that the unlabeled atoms in **bio-MOF-13** and **bio-MOF-14** are the same to those in **bio-MOF-12** at the same sites.

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3. Elemental analysis (EA) and thermogravimetric analysis (TGA)

Table S18. Correlation of EA and TGA data

	EA of as-synthesized MOF	wt % of solvent in as-synthesized MOF	Weight loss in TGA at 200 ℃
Bio-MOF-11	$Co_2(ad)_2(CH_3CO_2)_2$ • 2.25 DMF, 0.6 H_2O	25.8	22.4
Bio-MOF-12	$Co_2(ad)_2(C_2H_5CO_2)_2$ • 2.25 DMF, 0.3 H_2O	24.2	21.7
Bio-MOF-13	$Co_2(ad)_2(C_3H_7CO_2)_2$ • 1.1 DMF, 0.6 H_2O	14.0	12.0
Bio-MOF-14	$Co_2(ad)_2(C_4H_9CO_2)_2$ • 0.6 DMF, 0.6 H_2O	8.5	8.7

We note that there exist small discrepancies between the calculated solvent content from EA and the observed solvent content from TGA. Such discrepancies are not uncommon for MOF samples, and they could be caused by several factors that may influence the amount of surface solvent, including drying time and crystallite size.

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4. BET surface area and total pore volume

Table S19. BET surface area and total pore volume of **bio-MOFs 11-14** based on N_2 adsorption isotherms at 77K (pressure range from 0.001 to 0.009 bar was selected for BET calculation; Pore volume was calculated based on amount of N_2 adsorbed at 0.995 bar).

	BET surface area (m^2/g)	**Total pore volume (cc/g)**
Bio-MOF-11	1148	0.45
Bio-MOF-12	1008	0.42
Bio-MOF-13	412	0.20
Bio-MOF-14	17	0.035

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5. CO_2 adsorption data tables

Table S20. CO_2 adsorption data of **bio-MOF-11** at various temperatures.

CO_2 adsorption of **bio-MOF-11** at various temperature									
273K		298K		303K		308K		313K	
Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)
2.07E-03	2.150316	2.05E-03	0.572088	2.09E-03	0.432483	2.13E-03	0.28638	2.14E-03	0.210191
3.12E-03	3.241832	3.10E-03	0.900596	3.13E-03	0.686371	3.19E-03	0.481782	3.08E-03	0.357191
4.11E-03	4.266571	4.18E-03	1.235827	4.21E-03	0.946757	4.12E-03	0.661274	4.13E-03	0.52391
5.19E-03	5.343746	5.35E-03	1.482992	5.19E-03	1.071349	5.33E-03	0.680097	5.38E-03	0.50307
6.26E-03	6.384843	6.17E-03	1.727468	6.23E-03	1.222382	6.39E-03	0.701385	6.45E-03	0.478421
7.15E-03	7.24981	7.16E-03	2.029983	7.22E-03	1.460808	7.44E-03	0.735222	7.50E-03	0.46632
8.19E-03	8.256398	8.20E-03	2.34527	8.33E-03	1.643212	8.48E-03	0.783176	8.55E-03	0.478645
9.27E-03	9.272845	9.28E-03	2.664142	9.32E-03	1.877157	9.53E-03	0.851746	9.60E-03	0.501501
1.04E-02	10.26151	1.04E-02	2.923632	1.05E-02	2.064716	1.06E-02	0.934209	1.07E-02	0.531305
2.05E-02	18.89414	2.03E-02	5.952584	2.08E-02	4.606283	2.12E-02	3.148837	2.15E-02	2.455295
3.10E-02	26.60355	3.05E-02	8.989154	3.10E-02	7.085107	3.14E-02	5.257697	3.17E-02	4.205396
4.14E-02	33.34424	4.07E-02	11.91861	4.12E-02	9.461749	4.16E-02	7.299332	4.18E-02	5.914713
5.18E-02	39.29705	5.10E-02	14.70219	5.15E-02	11.75369	5.18E-02	9.27038	5.20E-02	7.578766
6.23E-02	44.67732	6.11E-02	17.36118	6.17E-02	13.95599	6.19E-02	11.18899	6.22E-02	9.201587
7.26E-02	49.45413	7.14E-02	19.93591	7.19E-02	16.07247	7.21E-02	13.04643	7.24E-02	10.78945
8.29E-02	53.82602	8.16E-02	22.36118	8.21E-02	18.13181	8.23E-02	14.86107	8.24E-02	12.3614
9.08E-02	56.93026	9.19E-02	24.69076	9.23E-02	20.12302	9.25E-02	16.60377	9.27E-02	13.86322
1.03E-01	61.37028	1.02E-01	26.93385	1.02E-01	22.04589	1.03E-01	18.32698	1.03E-01	15.30005
1.54E-01	76.04648	1.53E-01	36.84377	1.54E-01	30.68682	1.54E-01	26.08681	1.54E-01	22.15032
2.02E-01	86.53498	2.04E-01	45.06498	2.04E-01	38.00161	2.05E-01	32.77977	2.05E-01	28.16139
2.54E-01	95.31193	2.55E-01	52.20679	2.55E-01	44.39564	2.55E-01	38.78636	2.55E-01	33.62838
3.05E-01	102.4136	3.06E-01	58.39399	3.06E-01	50.06498	3.06E-01	44.10232	3.06E-01	38.54636
3.56E-01	108.4247	3.57E-01	63.8789	3.57E-01	55.13087	3.57E-01	48.97549	3.57E-01	43.07601
4.07E-01	113.5681	4.07E-01	68.78143	4.08E-01	59.74701	4.08E-01	53.34312	4.08E-01	47.20544
4.58E-01	118.0563	4.58E-01	73.23601	4.58E-01	63.93582	4.58E-01	57.38112	4.58E-01	51.08031
5.09E-01	121.9935	5.09E-01	77.28858	5.09E-01	67.69753	5.09E-01	61.08815	5.09E-01	54.66634
5.60E-01	125.5472	5.60E-01	80.97096	5.57E-01	70.94586	5.57E-01	64.27665	5.57E-01	57.73114
6.07E-01	128.5515	6.10E-01	84.4362	6.07E-01	74.20069	6.10E-01	67.74033	6.07E-01	60.81007
6.61E-01	131.6932	6.58E-01	87.4302	6.58E-01	77.24376	6.58E-01	70.57254	6.58E-01	63.74109
7.09E-01	134.2502	7.09E-01	90.37825	7.09E-01	80.02958	7.09E-01	73.30614	7.09E-01	66.4505
7.60E-01	136.7438	7.60E-01	93.12038	7.60E-01	82.68498	7.60E-01	75.87595	7.60E-01	69.06109
8.11E-01	139.0703	8.11E-01	95.72715	8.11E-01	85.11787	8.11E-01	78.35925	8.11E-01	71.48165
8.61E-01	141.2172	8.61E-01	98.19634	8.61E-01	87.49899	8.62E-01	80.64783	8.61E-01	73.82064
9.12E-01	143.279	9.12E-01	100.5481	9.12E-01	89.69838	9.12E-01	82.80912	9.12E-01	75.94721
9.63E-01	145.1799	9.63E-01	102.8179	9.63E-01	91.818	9.63E-01	84.90857	9.63E-01	78.03792
1.01E+00	146.8563	1.01E+00	104.7811	1.01E+00	93.57482	1.01E+00	86.71626	1.01E+00	79.85121

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Table S21. CO_2 adsorption data of **bio-MOF-12** at various temperatures.

CO_2 adsorption of **bio-MOF-12** at various temperature									
273K		298K		303K		308K		313K	
Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)
2.04E-03	2.959261	2.06E-03	0.770179	2.11E-03	0.458477	2.13E-03	0.240891	2.05E-03	0.265764
3.10E-03	4.400574	3.12E-03	1.164792	3.17E-03	0.734773	3.18E-03	0.451306	3.05E-03	0.447721
4.07E-03	5.641106	4.20E-03	1.56299	4.08E-03	0.984852	4.09E-03	0.648277	4.13E-03	0.643795
5.14E-03	6.952673	5.10E-03	1.870658	5.29E-03	1.04894	5.33E-03	0.663066	5.28E-03	0.717071
6.24E-03	8.21046	6.13E-03	2.231435	6.34E-03	1.100255	6.41E-03	0.664411	6.35E-03	0.776677
7.15E-03	9.195984	7.20E-03	2.602071	7.40E-03	1.172411	7.46E-03	0.685027	7.41E-03	0.845023
8.18E-03	10.27652	8.26E-03	2.968449	8.45E-03	1.264509	8.51E-03	0.722225	8.51E-03	0.905302
9.26E-03	11.35325	9.29E-03	3.298526	9.50E-03	1.371174	9.56E-03	0.762112	9.53E-03	0.984628
1.04E-02	12.38829	1.03E-02	3.63891	1.06E-02	1.484336	1.06E-02	0.828441	1.06E-02	1.050509
2.16E-02	20.67315	2.10E-02	6.820912	2.13E-02	4.288531	2.15E-02	3.188948	2.18E-02	3.040604
3.00E-02	25.28795	3.14E-02	9.809752	3.16E-02	6.771613	3.19E-02	5.306324	3.21E-02	4.790481
4.02E-02	29.76516	4.18E-02	12.42303	4.19E-02	9.016717	4.22E-02	7.256532	4.23E-02	6.451172
5.08E-02	33.64518	5.21E-02	14.79631	5.22E-02	11.08323	5.24E-02	9.060413	5.25E-02	8.007664
6.15E-02	36.84892	6.24E-02	16.95828	6.24E-02	12.98234	6.26E-02	10.73858	6.27E-02	9.487967
7.19E-02	39.63766	7.26E-02	18.92439	7.27E-02	14.7134	7.28E-02	12.31883	7.29E-02	10.89522
8.23E-02	42.08197	8.29E-02	20.70631	8.29E-02	16.29095	8.30E-02	13.81078	8.30E-02	12.26527
9.26E-02	44.28853	9.32E-02	22.37216	9.32E-02	17.80733	9.32E-02	15.20257	9.32E-02	13.52754
1.03E-01	46.29902	1.03E-01	23.93761	1.03E-01	19.20316	1.03E-01	16.52646	1.03E-01	14.74275
1.54E-01	54.35128	1.55E-01	30.31887	1.55E-01	25.0661	1.55E-01	22.17967	1.51E-01	19.59553
2.05E-01	60.3312	2.02E-01	34.96258	2.02E-01	29.3199	2.02E-01	26.37633	2.02E-01	23.81526
2.56E-01	65.30476	2.53E-01	39.16909	2.53E-01	33.13338	2.53E-01	30.2335	2.53E-01	27.45328
3.04E-01	69.17671	3.04E-01	42.7242	3.05E-01	36.37767	3.04E-01	33.47376	3.04E-01	30.57724
3.55E-01	72.83893	3.55E-01	45.93645	3.55E-01	39.23139	3.55E-01	36.41868	3.55E-01	33.39936
4.06E-01	76.03818	4.06E-01	48.76933	4.06E-01	41.80993	4.06E-01	39.0035	4.06E-01	35.85511
4.57E-01	78.92708	4.57E-01	51.3649	4.57E-01	44.17851	4.57E-01	41.42899	4.57E-01	38.14592
5.07E-01	81.55739	5.08E-01	53.67902	5.08E-01	46.28288	5.08E-01	43.61561	5.08E-01	40.29265
5.58E-01	83.97324	5.58E-01	55.92502	5.59E-01	48.208	5.59E-01	45.66195	5.59E-01	42.31143
6.09E-01	86.20356	6.09E-01	57.8759	6.09E-01	50.08605	6.09E-01	47.59871	6.09E-01	44.16484
6.60E-01	88.27903	6.60E-01	59.73334	6.60E-01	51.80791	6.60E-01	49.42679	6.60E-01	45.89746
7.11E-01	90.22095	7.11E-01	61.55963	7.11E-01	53.41572	7.11E-01	51.1128	7.11E-01	47.50751
7.61E-01	92.05575	7.62E-01	63.208	7.62E-01	54.92157	7.62E-01	52.68588	7.62E-01	48.89683
8.12E-01	93.86143	8.12E-01	64.83418	8.12E-01	56.39112	8.12E-01	54.23161	8.13E-01	50.16627
8.63E-01	95.5201	8.63E-01	66.40165	8.63E-01	57.76229	8.63E-01	55.56761	8.63E-01	51.40389
9.13E-01	97.08914	9.14E-01	67.91713	9.14E-01	59.06624	9.14E-01	56.86013	9.14E-01	52.8145
9.64E-01	98.56182	9.64E-01	69.33559	9.65E-01	60.34643	9.64E-01	58.208	9.64E-01	54.14176
1.01E+00	99.87451	1.01E+00	70.51853	1.01E+00	61.52714	1.01E+00	59.44517	1.01E+00	55.22364

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Table S22. CO_2 adsorption data of **bio-MOF-13** at various temperatures.

CO_2 adsorption of **bio-MOF-13** at various temperature									
273K		298K		303K		308K		313K	
Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)
2.05E-03	3.045982	2.03E-03	0.758526	2.07E-03	0.407386	2.09E-03	0.403576	2.12E-03	0.299601
3.06E-03	4.356429	3.08E-03	1.126249	3.13E-03	0.670013	3.16E-03	0.612647	3.18E-03	0.468785
4.16E-03	5.66329	4.15E-03	1.478286	4.21E-03	0.938915	4.06E-03	0.807377	4.12E-03	0.60951
5.14E-03	6.737552	5.24E-03	1.826962	5.24E-03	1.01824	5.19E-03	0.953928	5.24E-03	0.699368
6.22E-03	7.827724	6.10E-03	2.099449	6.31E-03	1.124233	6.20E-03	1.152243	6.28E-03	0.793484
7.15E-03	8.688881	7.38E-03	2.500336	7.37E-03	1.237171	7.28E-03	1.358625	7.31E-03	0.951463
8.20E-03	9.597544	8.24E-03	2.758706	8.29E-03	1.443553	8.31E-03	1.562318	8.43E-03	1.050733
9.28E-03	10.47708	9.26E-03	3.065926	9.42E-03	1.585175	9.45E-03	1.725003	9.44E-03	1.210729
1.04E-02	11.29319	1.03E-02	3.386143	1.05E-02	1.719177	1.05E-02	1.921077	1.05E-02	1.369381
2.15E-02	17.26057	2.03E-02	6.095102	2.08E-02	3.979743	2.11E-02	3.954421	2.15E-02	3.060324
3.01E-02	20.32672	3.07E-02	8.579079	3.12E-02	6.02698	3.15E-02	5.716623	3.19E-02	4.51284
4.06E-02	23.07892	4.14E-02	10.61982	4.16E-02	7.832878	4.18E-02	7.301349	4.21E-02	5.858692
5.13E-02	25.24044	5.17E-02	12.40846	5.19E-02	9.420069	5.21E-02	8.71734	5.24E-02	7.093847
6.19E-02	27.0004	6.22E-02	13.94568	6.23E-02	10.85466	6.24E-02	10.00381	6.26E-02	8.234437
7.24E-02	28.47645	7.25E-02	15.3182	7.25E-02	12.13441	7.26E-02	11.19684	7.28E-02	9.290772
8.27E-02	29.7851	8.27E-02	16.5305	8.28E-02	13.27724	8.29E-02	12.26662	8.30E-02	10.28795
9.30E-02	30.93398	9.30E-02	17.62829	9.31E-02	14.33178	9.31E-02	13.26446	9.32E-02	11.20065
1.03E-01	31.97172	1.03E-01	18.63645	1.03E-01	15.29646	1.03E-01	14.18344	1.03E-01	12.03671
1.55E-01	36.02586	1.55E-01	22.59109	1.55E-01	19.19733	1.55E-01	17.95657	1.55E-01	15.61332
2.02E-01	38.84148	2.03E-01	25.26778	2.03E-01	21.872	2.03E-01	20.55976	2.03E-01	18.20934
2.53E-01	41.37073	2.54E-01	27.60655	2.54E-01	24.23139	2.54E-01	22.88374	2.54E-01	20.50352
3.05E-01	43.49012	3.05E-01	29.53861	3.05E-01	26.15628	3.05E-01	24.77502	3.05E-01	22.40398
3.55E-01	45.37019	3.56E-01	31.25241	3.56E-01	27.86559	3.56E-01	26.46193	3.56E-01	24.08932
4.06E-01	47.02035	4.07E-01	32.74526	4.06E-01	29.34769	4.07E-01	27.90571	4.07E-01	25.55259
4.57E-01	48.55129	4.57E-01	34.14646	4.57E-01	30.71304	4.57E-01	29.23632	4.57E-01	26.91122
5.08E-01	49.90006	5.08E-01	35.38498	5.08E-01	31.96208	5.08E-01	30.41993	5.08E-01	28.09842
5.59E-01	51.14149	5.59E-01	36.56546	5.59E-01	33.1094	5.59E-01	31.54215	5.59E-01	29.18859
6.09E-01	52.35603	6.10E-01	37.66728	6.09E-01	34.21996	6.10E-01	32.61305	6.10E-01	30.28817
6.60E-01	53.46569	6.60E-01	38.72025	6.60E-01	35.23731	6.60E-01	33.59477	6.60E-01	31.30776
7.11E-01	54.49783	7.11E-01	39.68942	7.11E-01	36.18048	7.11E-01	34.54197	7.11E-01	32.21777
7.62E-01	55.46206	7.62E-01	40.65612	7.62E-01	37.10057	7.62E-01	35.39058	7.62E-01	33.09573
8.12E-01	56.40008	8.12E-01	41.56366	8.12E-01	37.93887	8.12E-01	36.1937	8.13E-01	33.88316
8.63E-01	57.29754	8.63E-01	42.45193	8.63E-01	38.74445	8.63E-01	36.94304	8.63E-01	34.7069
9.14E-01	58.13091	9.14E-01	43.28217	9.14E-01	39.5543	9.14E-01	37.74168	9.14E-01	35.43338
9.64E-01	58.89997	9.65E-01	44.10187	9.65E-01	40.27137	9.65E-01	38.47466	9.65E-01	36.15941
1.01E+00	59.61816	1.01E+00	44.83082	1.01E+00	40.94519	1.01E+00	38.74289	1.01E+00	36.74853

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Table S23. CO_2 adsorption data of **bio-MOF-14** at various temperatures.

CO_2 adsorption of **bio-MOF-14** at various temperature									
273K		298K		303K		308K		313K	
Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)	Pressure (bar)	CO_2 adsorbed (cc/g)
2.03E-03	0.323802	2.28E-02	0.385874	3.31E-02	0.262851	3.31E-02	0.044369	4.34E-02	0.097701
3.04E-03	0.488056	3.30E-02	0.817237	4.33E-02	0.605925	4.33E-02	0.351589	5.36E-02	0.358087
4.10E-03	0.65119	4.32E-02	1.218348	5.34E-02	0.945637	5.34E-02	0.645588	6.36E-02	0.621163
5.17E-03	0.803343	5.33E-02	1.607583	6.36E-02	1.284677	6.36E-02	0.93152	7.38E-02	0.863622
6.25E-03	0.953032	6.35E-02	1.966791	7.37E-02	1.610944	7.37E-02	1.21409	8.40E-02	1.089723
7.32E-03	1.098015	7.36E-02	2.328463	8.38E-02	1.91189	8.38E-02	1.482096	9.41E-02	1.336217
8.38E-03	1.233362	8.38E-02	2.653386	9.40E-02	2.21799	9.40E-02	1.740017	1.04E-01	1.580245
9.46E-03	1.371846	9.39E-02	2.984807	1.04E-01	2.517142	1.04E-01	2.009815	1.54E-01	2.576525
1.05E-02	1.500695	1.04E-01	3.295612	1.54E-01	3.80406	1.54E-01	3.139874	2.05E-01	3.452696
2.21E-02	2.792767	1.54E-01	4.686282	2.04E-01	4.973334	2.05E-01	4.167526	2.55E-01	4.364944
3.25E-02	3.830951	2.04E-01	5.991574	2.55E-01	6.156277	2.55E-01	5.23753	3.06E-01	5.152602
4.27E-02	4.742975	2.55E-01	7.338323	3.06E-01	7.272666	3.06E-01	6.199525	3.57E-01	6.066195
5.29E-02	5.60458	3.06E-01	8.636445	3.56E-01	8.418635	3.57E-01	7.173845	4.07E-01	6.940797
6.31E-02	6.391565	3.56E-01	9.99507	4.07E-01	9.576256	4.07E-01	8.133599	4.58E-01	7.868955
7.32E-02	7.189755	4.07E-01	11.40008	4.58E-01	10.77869	4.58E-01	9.133465	5.09E-01	8.778515
8.34E-02	7.944696	4.57E-01	12.89965	5.08E-01	12.00242	5.09E-01	10.11137	5.59E-01	9.692556
9.35E-02	8.687985	5.08E-01	14.54466	5.59E-01	13.30592	5.59E-01	11.14597	6.10E-01	10.55752
1.04E-01	9.436427	5.58E-01	16.36423	6.09E-01	14.65312	6.10E-01	12.19917	6.61E-01	11.46619
1.51E-01	13.09685	6.09E-01	18.396	6.60E-01	16.1137	6.60E-01	13.31063	7.11E-01	12.3688
2.03E-01	20.85219	6.59E-01	20.60032	7.11E-01	17.61776	7.11E-01	14.41021	7.62E-01	13.262
2.55E-01	29.45435	7.10E-01	22.72285	7.61E-01	19.26993	7.62E-01	15.57007	8.12E-01	14.20741
3.05E-01	31.8487	7.61E-01	24.55609	8.12E-01	20.936	8.12E-01	16.78349	8.63E-01	15.15955
3.56E-01	33.64317	8.12E-01	26.04804	8.63E-01	22.47434	8.63E-01	18.0303	9.14E-01	16.13902
4.07E-01	35.08672	8.63E-01	27.35625	9.13E-01	23.93806	9.13E-01	19.28584	9.64E-01	17.09362
4.58E-01	36.31246	9.14E-01	28.57908	9.64E-01	25.22431	9.64E-01	20.54027	1.01E+00	18.15713
5.08E-01	37.39255	9.65E-01	29.69524	1.01E+00	26.23605	1.01E+00	21.66585		
5.59E-01	38.38121	1.01E+00	30.6727						
6.10E-01	39.29324								
6.61E-01	40.1526								
7.11E-01	40.93174								
7.62E-01	41.67615								
8.13E-01	42.39658								
8.63E-01	43.05427								
9.14E-01	43.66289								
9.65E-01	44.26612								
1.01E+00	44.79474								

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6. Additional CO_2 and N_2 adsorption isotherms

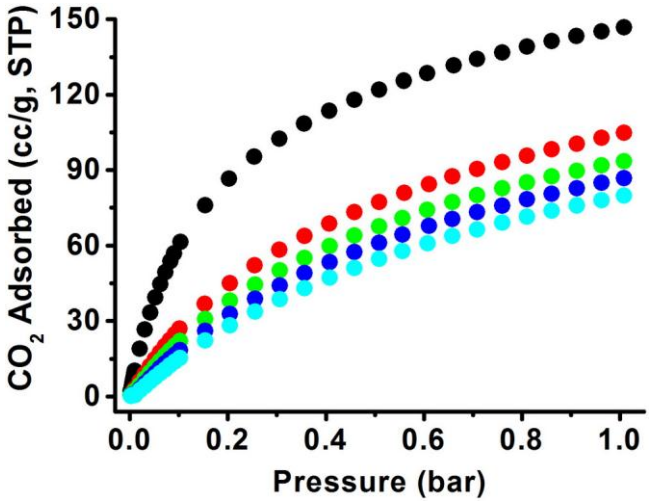

Figure S7. CO_2 adsorption isotherms of **bio-MOF-11** at 273 K (black), 298 K (red), 303 K (green), 308 K (blue), and 313 K (cyan).

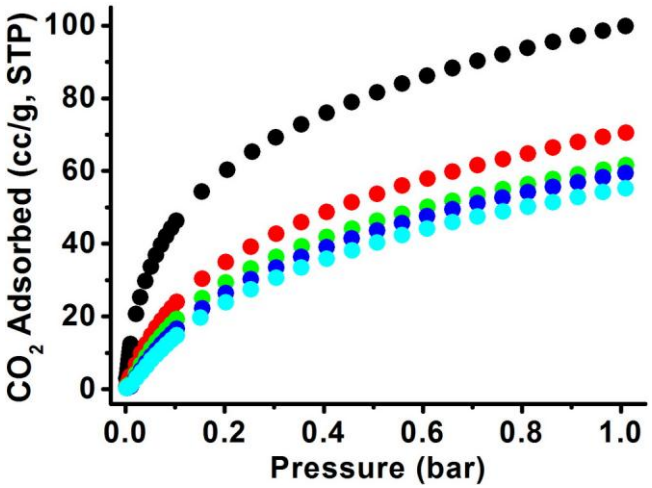

Figure S8. CO_2 adsorption isotherms of **bio-MOF-12** at 273 K (black), 298 K (red), 303 K (green), 308 K (blue), and 313 K (cyan).

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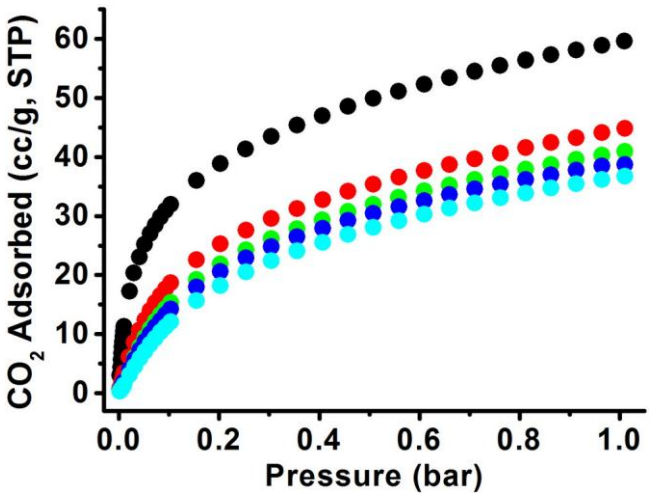

Figure S9. CO_2 adsorption isotherms of **bio-MOF-13** at 273 K (black), 298 K (red), 303 K (green), 308 K (blue), and 313 K (cyan).

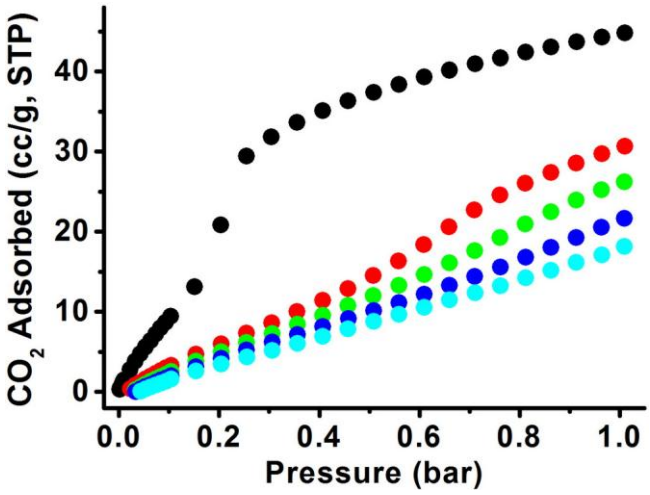

Figure S10. CO_2 adsorption isotherms of **bio-MOF-14** at 273 K (black), 298 K (red), 303 K (green), 308 K (blue), and 313 K (cyan).

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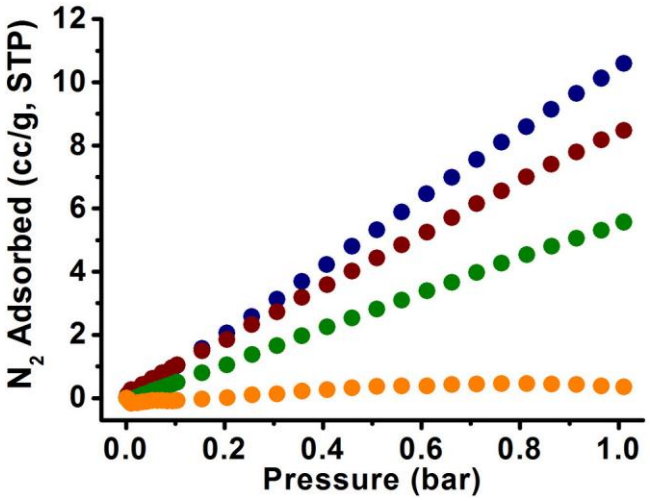

Figure S11. N_2 adsorption isotherms of **bio-MOF-11** (navy), **bio-MOF-12** (dark red), **bio-MOF-13** (green), and **bio-MOF-14** (orange) at 273 K. The isotherm data for **bio-MOF-14** reflects the instrument noise, because no measurable amount of N_2 was adsorbed.

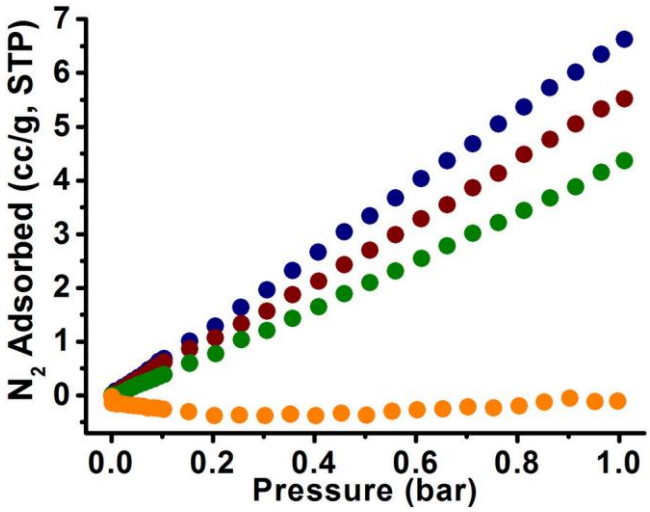

Figure S12. N_2 adsorption isotherms of **bio-MOF-11** (navy), **bio-MOF-12** (dark red), **bio-MOF-13** (green), and **bio-MOF-14** (orange) at 298 K. The isotherm data for **bio-MOF-14** reflects the instrument noise, because no measurable amount of N_2 was adsorbed.

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7. CO_2 isotherms fitting details

Table S24. Fitting equations, constants and estimated error of CO_2 isotherms for isosteric heats of adsorption calculations.

Bio- MOF	Temp. K	Constants			
		a	*b*	*c*	*d*
11	273	4.31907	1.05872	4.93959	0.113029
	298	4.8926	0.371175	4.77658	3.40143
	303	2.92966	1.53268	4.39239	0.465668
	308	2.37393	0.67473	4.36922	0.795414
	313	4.03048	0.90846	2.76736	0.923252
12	273	2.06284	0.033473	4.30731	0.769994
	298	4.7187	2.39924	1.97776	0.131818
	303	6.05072	6.40008	2.33383	0.22117
	308	2.66924	0.31853	23.8319	37.9556
	313	2.57505	0.352666	10.0766	17.4637
13	273	2.32496	0.797528	1.37895	0.019962
	298	1.36656	0.087907	3.83663	4.2019
	303	1.48023	0.146465	5.75071	9.86365
	308	1.41326	0.153541	4.15856	7.16274
	313	4.38588	8.48581	1.40738	0.200442

CO_2 adsorption isotherms of **bio-MOF-11** to **13** at different temperatures (273 K, 298 K, 303 K, 308 K, and 313 K) were fit to the dual site Langmuir model.

$$C = \frac{a \times P}{b + P} + \frac{c \times P}{d + P}$$

(*C*, moles adsorbed; *P*, pressure; *a*, *b*, *c*, and *d*, constants.)

Due to the unusual behavior of **bio-MOF-14**, we cannot fit the isotherms to the dual site Langmuir model.

Isosteric heats were computed by first plotting adsorption isosteres, plots of *ln(P)* versus *1/T* at constant loading of CO_2, by interpolating data within the experimental range from the dual site Langmuir model. Points on the adsorption isosteres were computed at 273, 298, 303, 308, and 313 K. The isostere data were then fitted to a line, with the slope of the line being proportional to the isosteric heat at that loading. The error bars for the isosteric heats were estimated by taking the difference between isosteric heats

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computed from using all five temperature data points with those computed from using only the first three temperatures. These two approaches give slightly different values because the points on the isosteres do not lie perfectly on straight lines. The absolute average errors in Q_{st} are 0.3, 1.7 and 1.7 kJ/mol for **bio-MOF-11**, **bio-MOF-12**, and **bio-MOF-13**, respectively.

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8. Fitting of CO_2 isotherms

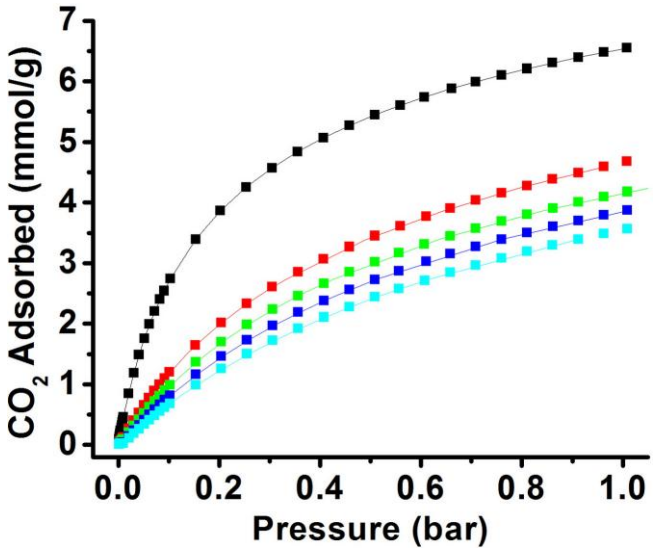

Figure S13. Dual site Langmuir fits of **bio-MOF-11** CO_2 adsorption isotherms at 273 K (black), 298 K (red), 303 K (green), 308 K (blue), and 313 K (cyan). (Square: experimental data; line: Langmuir fits)

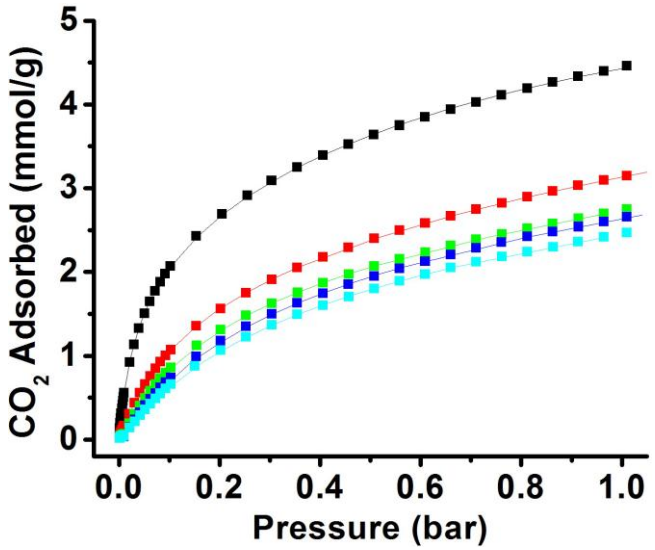

Figure S14. Dual site Langmuir fits of **bio-MOF-12** CO_2 adsorption isotherms at 273 K (black), 298 K (red), 303 K (green), 308 K (blue), and 313 K (cyan). (Squares: experimental data; lines: Langmuir fits)

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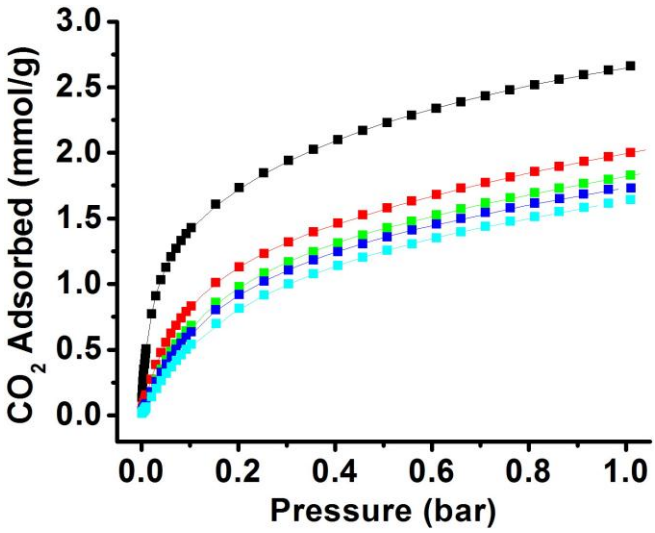

Figure S15. Dual site Langmuir fits of **bio-MOF-13** CO_2 adsorption isotherms at 273 K (black), 298 K (red), 303 K (green), 308 K (blue), and 313 K (cyan). (Squares: experimental data; lines: Langmuir fits)

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9. CO_2:N_2 selectivity

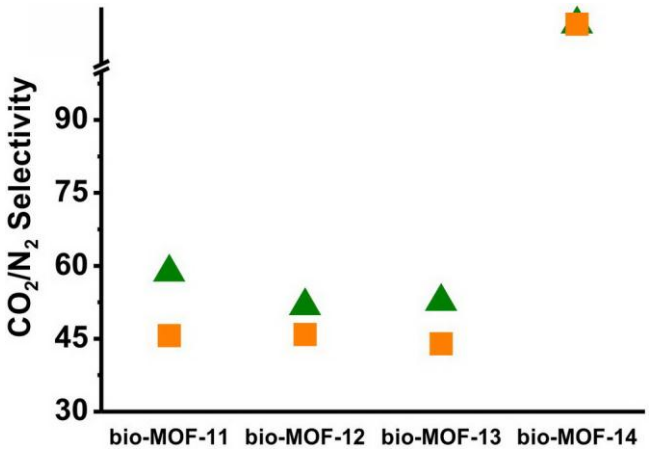

Figure S16. CO_2:N_2 selectivity of **bio-MOF 11-14** at 273 K (green) and 298 K (orange) calculated from single component isotherms. Note that the selectivity for **bio-MOF-14** is inferred to be extremely high.

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10. Connolly Surface Diagrams

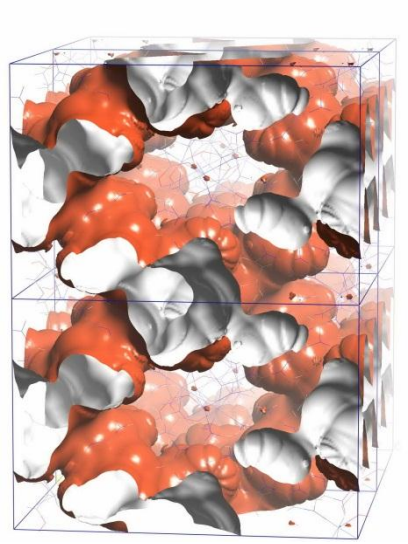

Figure S17. Connolly surface diagram of **bio-MOF-11** using N_2 as a probe molecule (probe radius 1.86 Å). The inner surfaces of the cavities have been shown in white, while the outer surfaces are represented in orange.

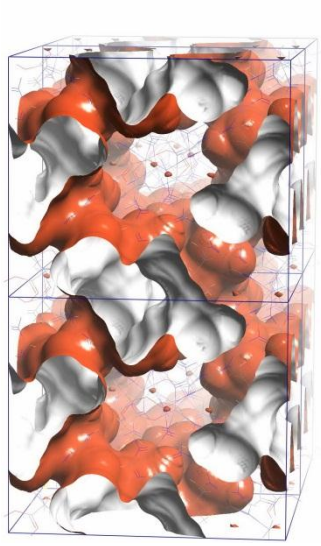

Figure S18. Connolly surface diagram of **bio-MOF-12** using N_2 as a probe molecule (probe radius 1.86 Å). The inner surfaces of the cavities have been shown in white, while the outer surfaces are represented in orange.

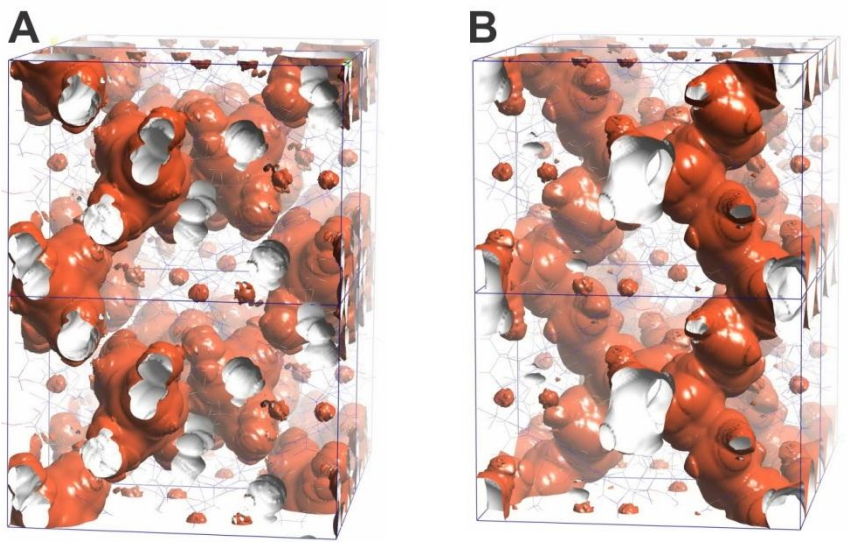

Figure S19. Connolly surface diagram of **bio-MOF-13** using N_2 as a probe molecule (probe radius 1.86 Å). The inner surfaces of the cavities have been shown in white, while the outer surfaces are represented in orange. A and B represent configuration I and II respectively.

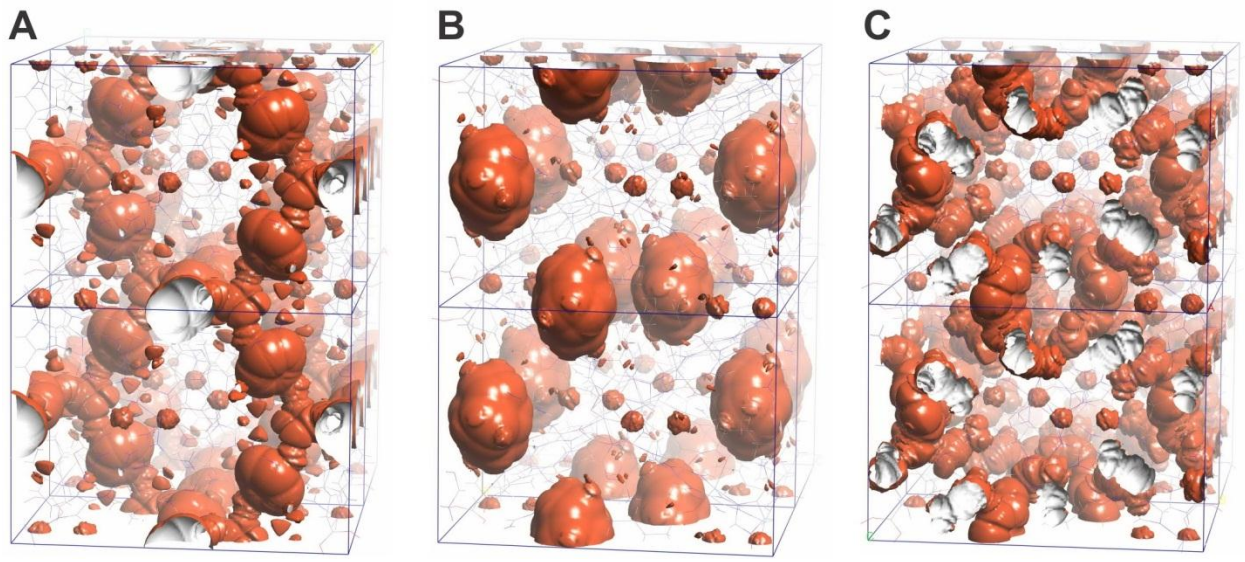

Figure S20. Connolly surface diagram of **bio-MOF-14** using N_2 as a probe molecule (probe radius 1.86 Å). The inner surfaces of the cavities have been shown in white, while the outer surfaces are represented in orange. A, B, and C represent configuration I, II, and III respectively.

11. Additional SEM images

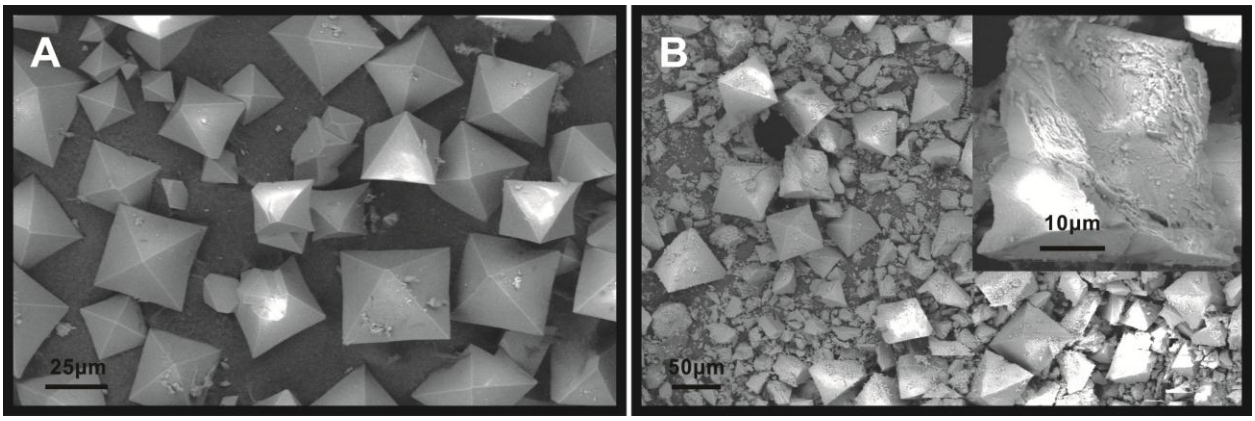

Figure S21. SEM images of **bio-MOF-12** before (A) and after (B) 1 hour soaking in water.

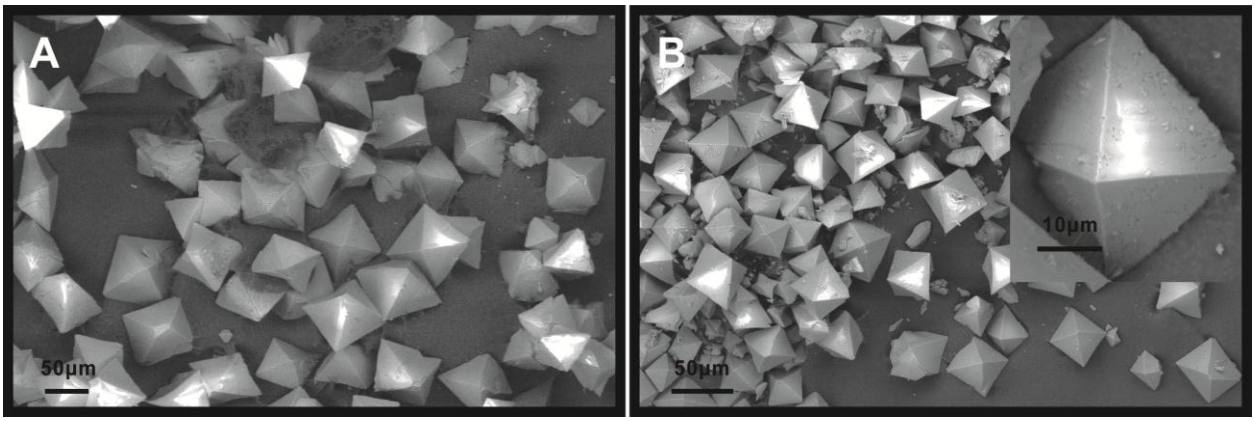

Figure S22. SEM images of **bio-MOF-13** before (A) and after (B) 1 hour soaking in water.

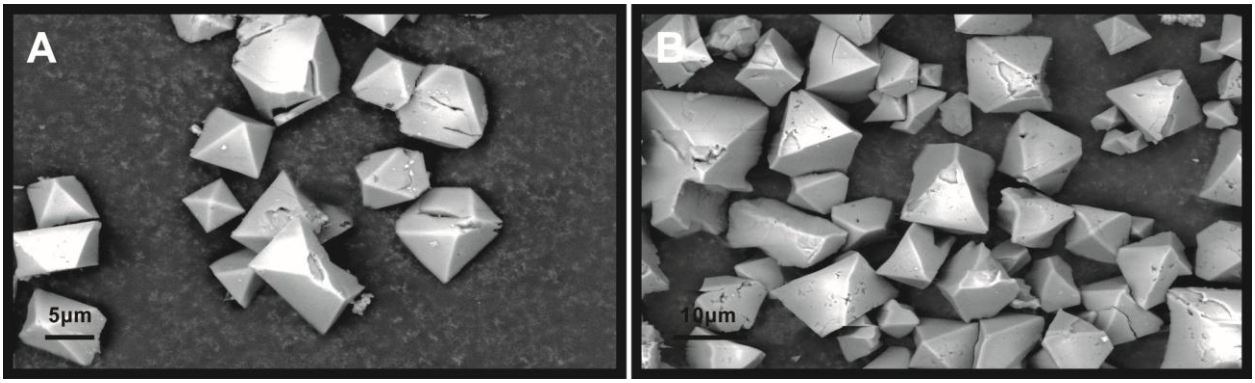

Figure S23. SEM images of **bio-MOF-14** after soaking in water for 7 days (A) and 30 days (B).

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12. Additional PXRD patterns

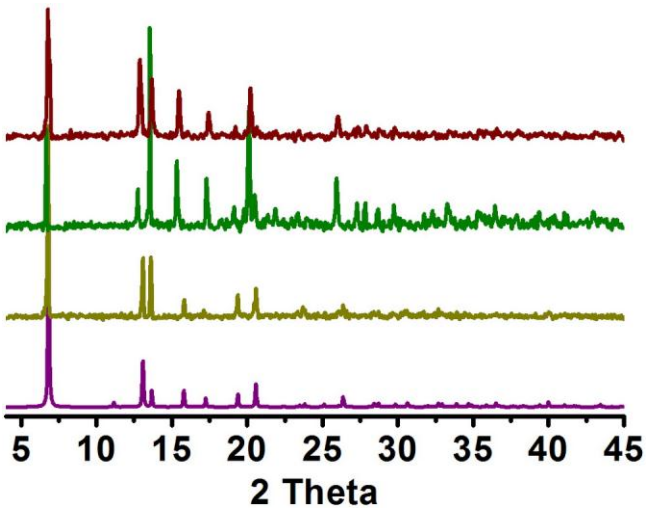

Figure S24. PXRD pattern of **bio-MOF-14** simulated from crystal structure (purple); PXRD patterns of **bio-MOF-14** before (dark yellow) and after soaking in water for 7 (green) or 30 (dark red) days.

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13. References:

(1) Hubschle, C. B.; Sheldrick, G. M.; Dittrich, B. *J. Appl. Crystallogr.* **2011**, *44*, 1281.