Supporting Information

Table S1. Selected Bond Length (Å) and Bond Angles (˚) of complex **1**

Co1-O1	2.0539(19)	Co1-O3	2.1463(9)
Co1-O4	2.2068(12)	Co1-O5	2.0201(8)
Co1-N6	2.148(2)	Co-N7 [a]	2.133(2)
Co2-O1	2.3019(19)	Co2-O2	2.1628(17)
Co2-O6	2.0428(11)	Co2-N1	2.178(2)
Co2-N5	2.176(2)	Co2-O8 [b]	2.000 (12)
O1-Co1-O3	100.01(6)	O2-Co2-N1	90.16(7)
O1-Co1-O4	160.10(6)	O2-Co2-N5	87.07(7)
O1-Co1-O5	102.71(6)	O2-Co2-O8 [b]	116.31(6)
O1-Co1-N6	88.16(8)	O6-Co2-N1	91.52(6)
O1-Co1-N7[a]	91.87(8)	O6-Co2-N5	91.38(6)
O3-Co1-O4	60.16(4)	O6-Co2-O8 [b]	92.78(4)
O3-Co1-O5	157.27(4)	N5-Co2-N1	177.05(8)
O3-Co1-N6	88.27(6)	O3-Co1-N7 [a]	90.66(7)
O8[b]-Co2-N1	87.93(7)	O4-Co1-O5	97.11(3)
O4-Co1-N6	89.44(6)	O8 [b]-Co2-N5	92.40(7)
O4-Co1-N7 [a]	90.17(7)	Co1-O1-Co2	118.68(8)
O5-Co1-N6	91.74(6)	O5-Co1-N7 [a]	89.31(6)
N6-Co1-N7 [a]	178.92(8)	O1-Co2-N1	86.31(7)
O1-Co2-O2	57.77(7)	O1-Co2-N5	93.05(7)
O2-Co2-O6	150.90(6)	O1-Co2-O8 [b]	171.69(6)
O1-Co2-O6	93.35(5)		

Symmetry Code: *a* = -x, 1-y, 1-z, *b* = 1-x, 2-y, 1-z.

Table S2. Hydrogen Bonding Interactions of Complex 2-4 (Å, °)

Complex	D-H…A	D-H	H….A	D….A	∠D-H…A
1	O1S-H1S...O7	0.8200	1.8800	2.666(2)	161.00
	O2S-H2S...O4	0.8200	2.0700	2.846(2)	158.00
	O1W-H1WA … $O3^{i}$	0.8500	2.2000	2.636(5)	112.00
	O1W-H1WB ... $O2^{ii}$	0.8500	2.0700	2.779(4)	140.00
	O1W-H1WB …$O1^{iii}$	0.8500	2.2800	2.958(5)	137.00
2	O2W-H2WA…$O4^{i}$	0.8600	1.8800	2.673(6)	153.00
	O2W-H2WB…$O3W^{iv}$	0.8600	2.2000	3.046(11)	166.00
	O3W-H3WB…$O5W^{v}$	0.8500	2.5300	2.930(2)	110.00
	O5W-H5WA…$O3W^{vi}$	0.8500	2.3300	2.930(2)	128.00
	O4W-H4WB... O3	0.8500	1.8900	2.666(12)	151.00
3	O1W-H1WA ... $O3^{vii}$	0.8500	1.9000	2.721(3)	162.00
	O1W-H1WA…$O4^{viii}$	0.8500	1.9000	2.720(3)	161.00
	O1W-H1WB…$O1^{ix}$	0.8500	1.9500	2.738(3)	154.00
4	O3W-H3WA...O3	0.8500	2.1600	2.815(6)	134.00
	O3W-H3WB…O2W	0.8500	2.1200	2.966(5)	172.00
	O2W-H2WB…$O3W^{x}$	0.8500	2.2100	3.055(5)	170.00
5	C6-H6...$O1S^{xi}$	0.9300	2.4300	3.324(5)	161.00

Symmetry Code : (i) = 1-x,2-y,-z ; (ii) = x,y,-1+z; (iii) = x,3/2-y,-1/2+z; (iv) = 1-x,2-y,1-z; (v) = -x,1/2+y,1/2-z; (vi) = -x,-1/2+y,1/2-z; (vii) = 2-x,1-y,2-z; (viii) = 1+x,-1+y,z; (ix) = 2-x,2-y,1-z; (x) = 1+x, y, z; (xi) = x, 1+y, z.

Table S3. Selected Bond Length (Å) and Bond Angles (˚) of Complex **2**

Co1-O1	2.055(3)	Co1-O1W	2.056(3)
Co1-O2W	2.158(3)	Co1-N1	2.150(4)
Co1-$O2^{a}$	2.118(3)	Co1-$N4^{b}$	2.166(5)
O1-Co1-O1W	178.28(14)	O1-Co1-O2W	95.82(13)
O1-Co1-N1	90.94(13)	O1-Co1-$O2^{a}$	80.70(12)
O1-Co1-$N4^{b}$	90.17(14)	O1W-Co1-O2W	85.90(13)
O1W-Co1-N1	89.14(13)	O1W-Co1-$O2^{a}$	97.59(12)
O1W-Co1-$N4^{b}$	89.75(14)	O2W-Co1-N1	91.21(13)
$O2^{a}$-Co1-O2W	176.32(12)	O2W-Co1-$N4^{b}$	89.17(13)
$O2^{a}$-Co1-N1	87.69(13)	N1-Co1-$N4^{b}$	178.79(15)
$O2^{a}$-Co1-$N4^{b}$	92.01(13)		

Symmetry Code: *a* = x, 3/2-y,-1/2+z, *b* = 1+x,3/2-y,1/2+z.

Table S4. Selected Bond Length (Å) and Bond Angles (˚) of Complex **3**

Zn1-O1	2.411(4)	Zn1-N1	2.057(3)
Zn1-O1W	2.032(2)	Zn1-O3 [a]	2.041(2)
Zn1-O2	2.021(3)	Zn1-O4 [a]	2.443(2)
O1-Zn1-O1W	104.75(11)	O1W-Zn1-O2	93.57(11)
O1-Zn1-O2	57.41(12)	O1W-Zn1-N1	101.41(10)
O1-Zn1-N1	87.42(11)	O1W-Zn1-O3 [a]	97.17(10)
O1-Zn1-O3 [a]	154.62(10)	O1W-Zn1-O4 [a]	153.84(9)
O1-Zn1-O4 [a]	98.67(10)	O2-Zn1-N1	144.39(13)
O2-Zn1-O3 [a]	109.22(11)	O4 [a] -Zn1-N1	91.01(10)
O2-Zn1-O4 [a]	89.26(10)	O3 [a] -Zn1-O4 [a]	57.59(9)
O3 [a] -Zn1-N1	100.78(11)		

Symmetry code: *a* = -1+x, y, z.

Table S5. π-π interactions in Complex **3**

Ring(i) → Ring(j)	Distance of centroid(i) from ring(j),(Å)	Dihedral angle (i,j) (deg)	Distance between the (i,j) ring centroids,(Å)
R(1)→ R(2)^{i}	3.953(2)	9.3 (2)	3.6277(18)
R(2)→ R(1)	3.953(2)	9.3 (2)	3.4986(16)

Symmetry code: (i) = -x,-y, 1-z ; R(i)/R(j) denotes the ith/jth rings: R(1) = N(1)/C(10) /C(11)/C(12)/ C(13)/C(14); R(2) = N(4)/C(24)/C(25)/C(27)/C(28)/C(33).

Table S6. Selected Bond Length (Å) and Bond Angles (˚) of Complex **4**

Zn1-O1	2.060(2)	Zn1-O1W	2.031(3)
Zn1-O2	2.349(3)	Zn1-N1	2.033(3)
Zn1-O4 [a]	1.958(2)	O4 [a] -Zn1-N1	124.26(10)
O1-Zn1-O1W	90.42(10)	O1-Zn1-O2	57.94(10)
O1-Zn1-N1	123.22(10)	O1-Zn1-O4 [a]	107.34(9)
O1W-Zn1-O2	147.52(10)	O1W-Zn1-N1	101.35(10)
O1W-Zn1-O4 [a]	100.06(10)	O2-Zn1-N1	91.67(10)
O2-Zn1-O4 [a]	96.73(10)		

Symmetry Code: *a* = x,-1+y, z.

Table S7. Selected Bond Length (Å) and Bond Angles (˚) of Complex **5**

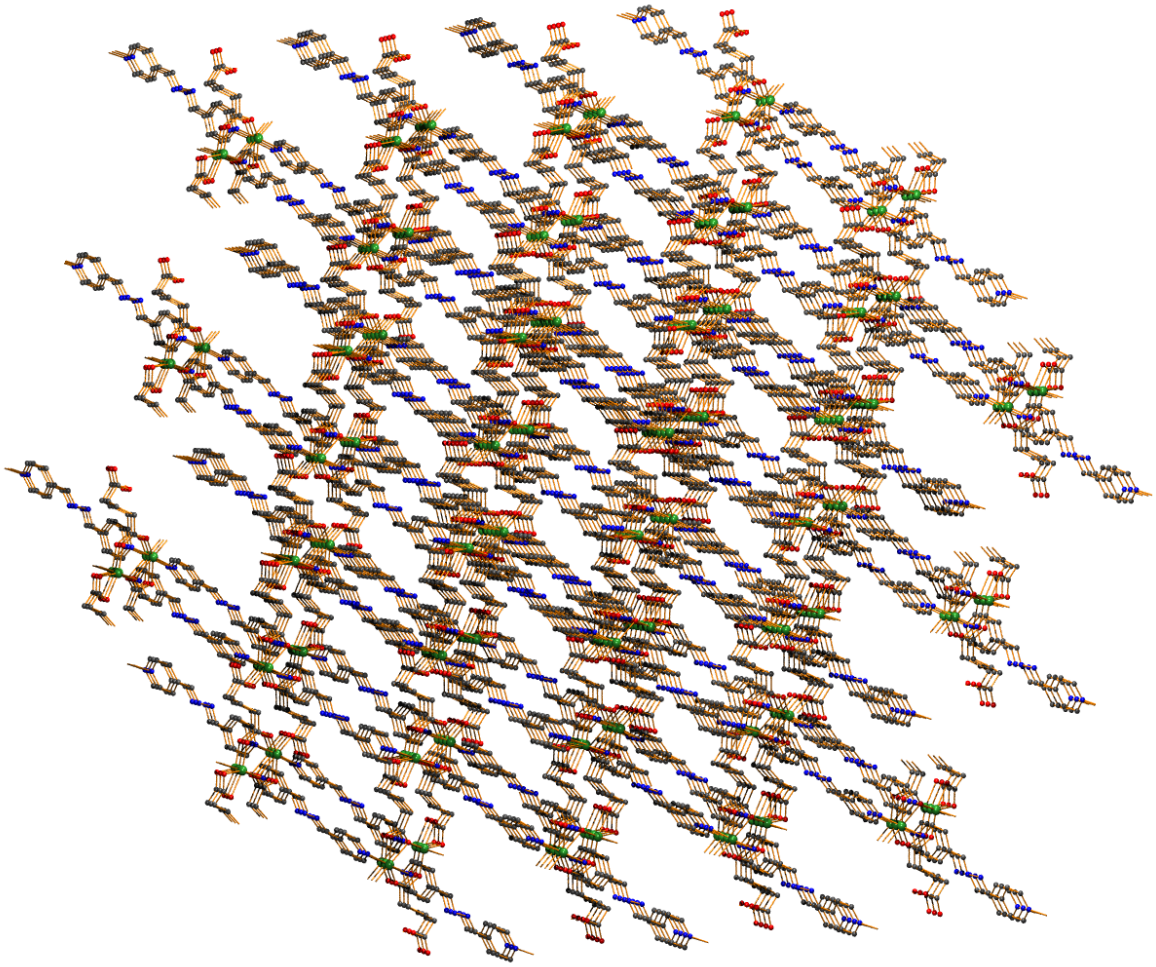
Cd1-O1	2.427(2)	Cd1-O2	2.357(3)
Cd1-N1	2.317(2)	Cd1-O3 ^{d}	2.371(2)
Cd1-O4^{d}	2.527(3)	Cd1-N2^{c}	2.325(2)
Cd1-O4^{b}	2.333(2)	O1-Cd1-O2	54.30(7)
O1-Cd1-N1	92.17(7)	O1-Cd1-N2 ^{c}	91.31(7)
O1-Cd1-O3 ^{d}	85.27(7)	O1-Cd1-O4 ^{b}	147.57(8)
O1-Cd1-O4 ^{d}	137.29(7)	O2-Cd1-N1	95.03(9)
O3 ^{d} -Cd1-O4^{b}	127.15(9)	O2-Cd1-O3 ^{d}	139.38(7)
O3 ^{d} -Cd1-N1	89.73(8)	O2-Cd1-O4 ^{d}	166.80(7)
O4 ^{d} -Cd1-N1	91.03(8)	O2-Cd1-N2 ^{c}	85.87(9)
N1-Cd1-N2 ^{c}	176.25(7)	O2-Cd1-O4 ^{b}	93.36(8)
O4 ^{b} -Cd1-N1	88.14(7)	O4 ^{d} -Cd1-N2 ^{c}	87.37(8)
O3 ^{d} -Cd1-O4 ^{d}	52.16(7)	O4 ^{d} -Cd1-O4 ^{b}	75.09(8)
O3 ^{d} -Cd1-N2^{c}	91.95(8)	O4 ^{b} -Cd1-N2 ^{c}	88.17(7)

Symmetry Code: *a* = 1+x, y, z, *b* = 2-x, 2-y, 1-z, *c* = x, -1+y, -1+z, *d*= -1+x, y, z.

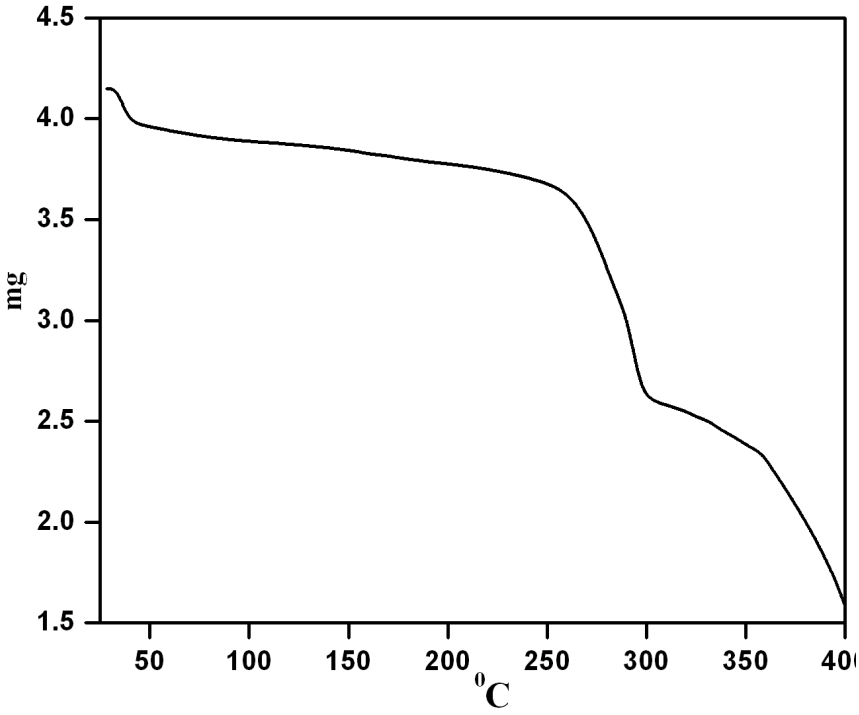
Table S8. Selected Bond Length (Å) and Bond Angles (˚) of Complex **6**

Cd1-O1	2.292(2)	Cd1-O3	2.397(2)
Cd1-O4	2.437(3)	Cd1-N1	2.333(2)
Cd1-N4 ^{b}	2.317(2)	Cd1-O1 ^{a}	2.563(2)
Cd1-O2 ^{b}	2.316(2)	O1-Cd1-O3	94.31(8)
O1-Cd1-N1	88.73(8)	O1-Cd1-N4 ^{b}	91.76(8)
O1-Cd1-O1 ^{a}	77.58(8)	O1-Cd1-O2 ^{a}	129.13(9)
O3-Cd1-O4	52.39(9)	O3-Cd1-N1	87.33(9)
O3-Cd1-N4 ^{b}	90.00(9)	O1 ^{a} -Cd1-O3	170.27(8)
O2 ^{a} -Cd1-O3	135.99(9)	O4-Cd1-N1	96.48(10)
O4-Cd1-N4 ^{b}	81.65(10)	O1 ^{a} -Cd1-O4	134.52(8)
O2 ^{a} -Cd1-O4	85.05(9)	N1-Cd1-N4 ^{b}	177.32(9)
O1 ^{a} -Cd1-N1	97.72(8)	O2 ^{a} -Cd1-N1	86.99(8)
O1 ^{a}-Cd1-N4 ^{b}	84.96(9)	O2^{b} -Cd1-N4 ^{b}	94.74(8)
O1 ^{a} -Cd1-O2 ^{a}	52.99(8)	Cd1-O1-Cd1 ^{a}	102.02(8)
O1-Cd1-O4	145.74(9)		

Symmetry Code: *a* = 1/2-x, y, 7/4-z, *b* = x, 1+y, z.



FigureS1. The packing diagram for the 2D grids in **1**



FigureS2. TGA of **1** under nitrogen atmosphere

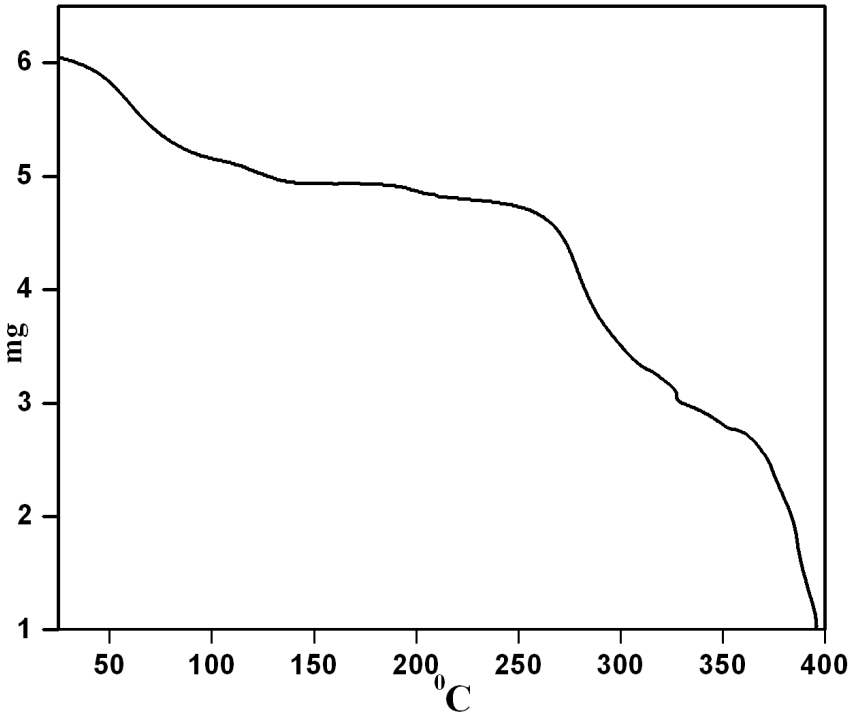


Figure S3. TGA of **2** under nitrogen atmosphere

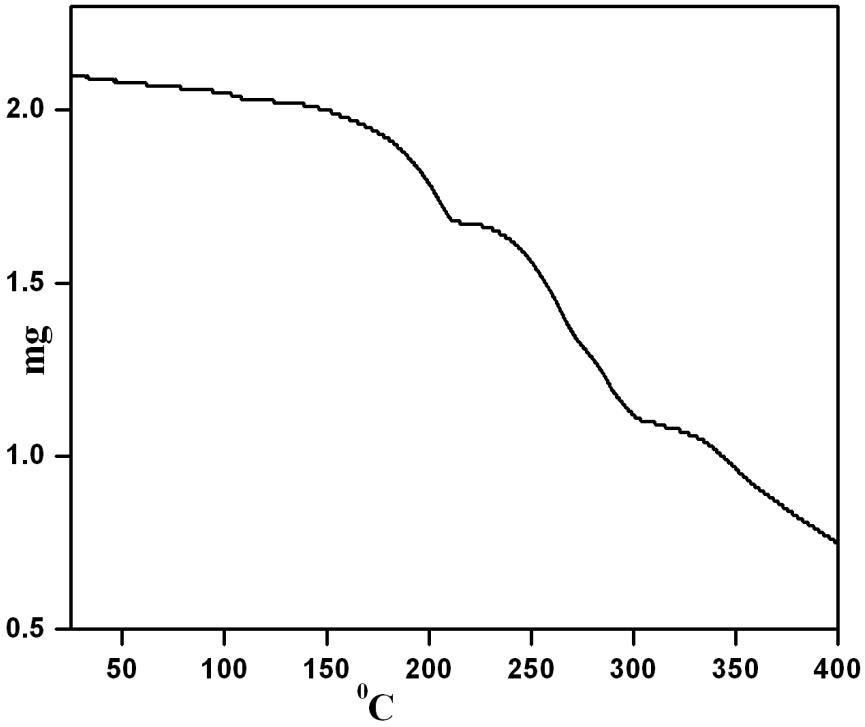


Figure S4. TGA of **3** under nitrogen atmosphere

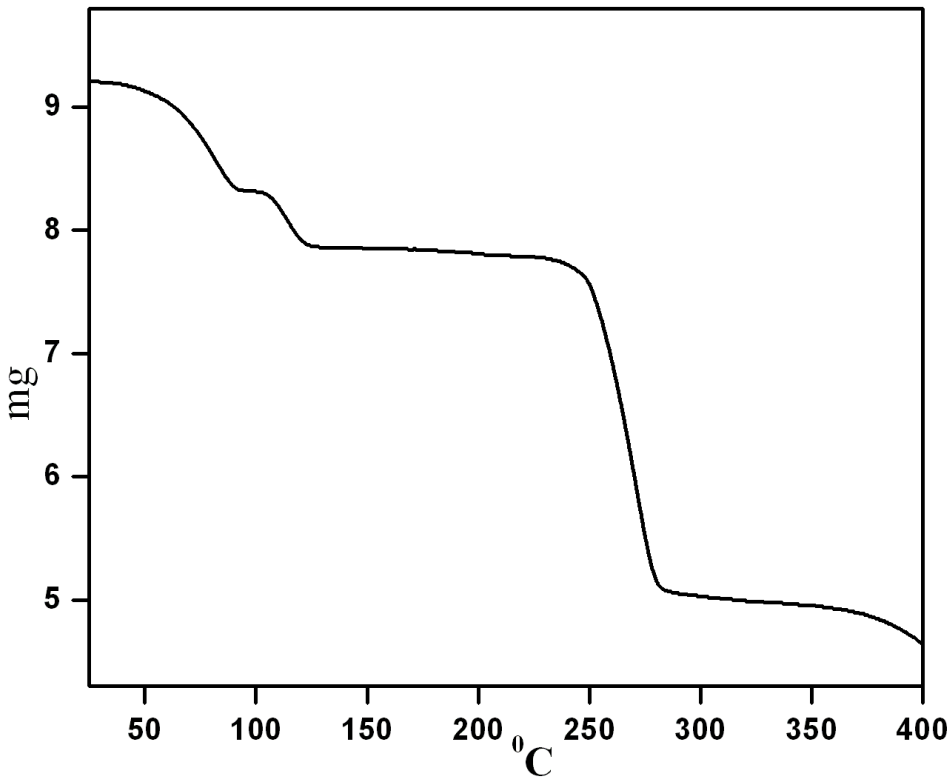


Figure S5. TGA of **4** under nitrogen atmosphere

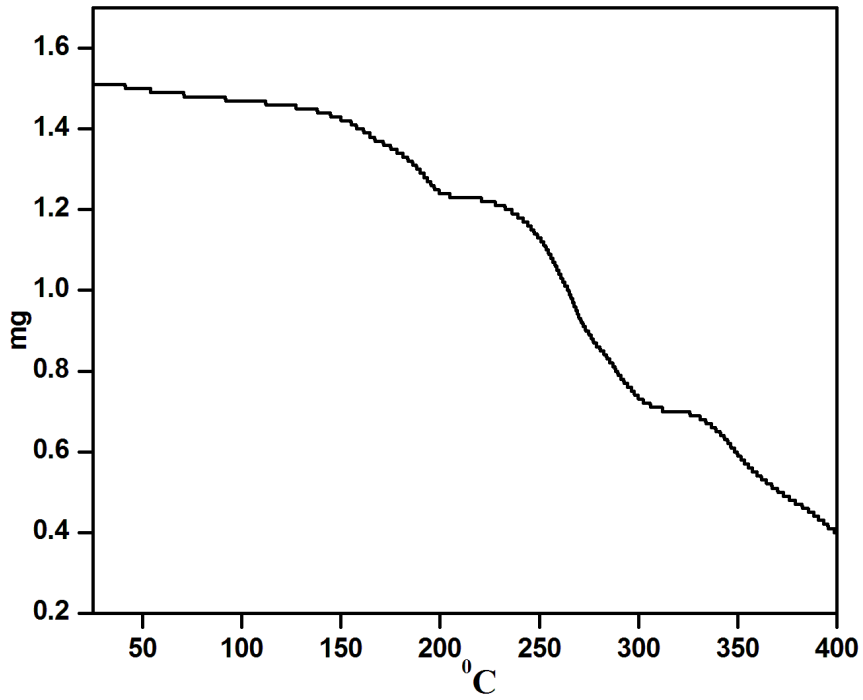


Figure S6. TGA of **5** under nitrogen atmosphere

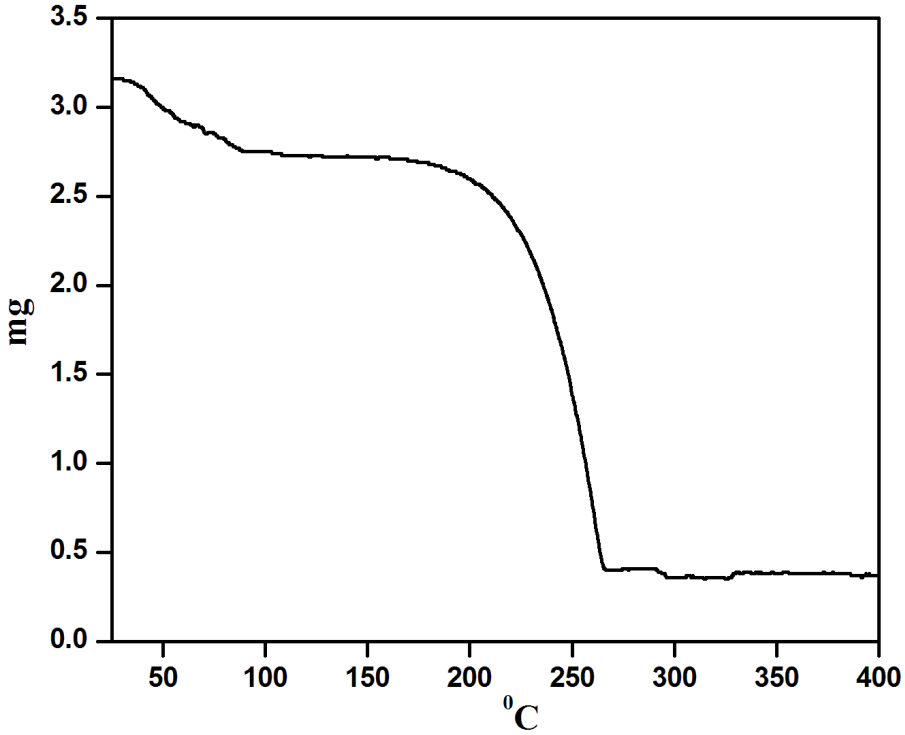


Figure S7. TGA of **6** under nitrogen atmosphere

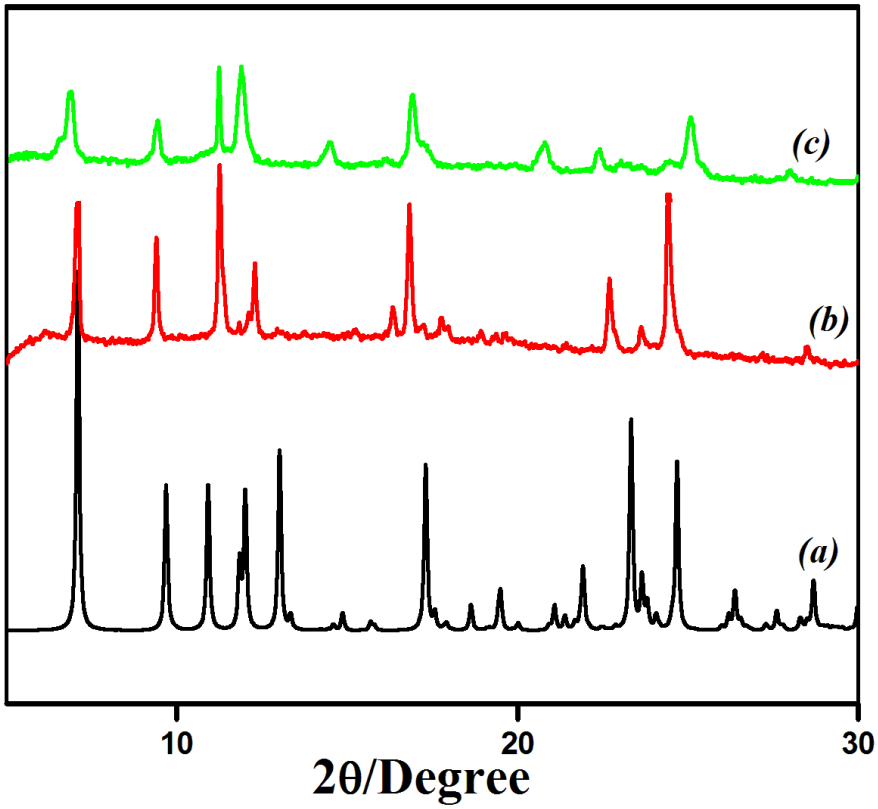


Figure S8. PXRD patterns of **1** in different states (*a*) Simulated from X-ray single crystal data; (*b*) bulk as-synthesized compound; (*c*) de-solvated

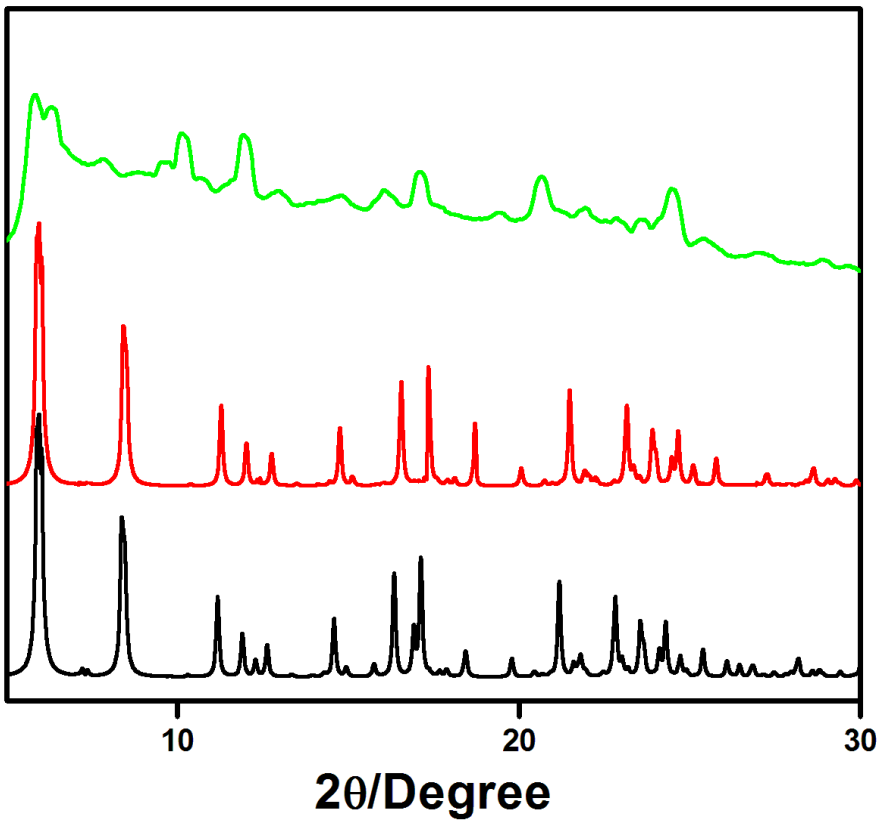


Figure S9. PXRD patterns of **2** in different states (*a*) Simulated from X-ray single crystal data; (*b*) bulk as-synthesized compound; (*c*) de-solvated

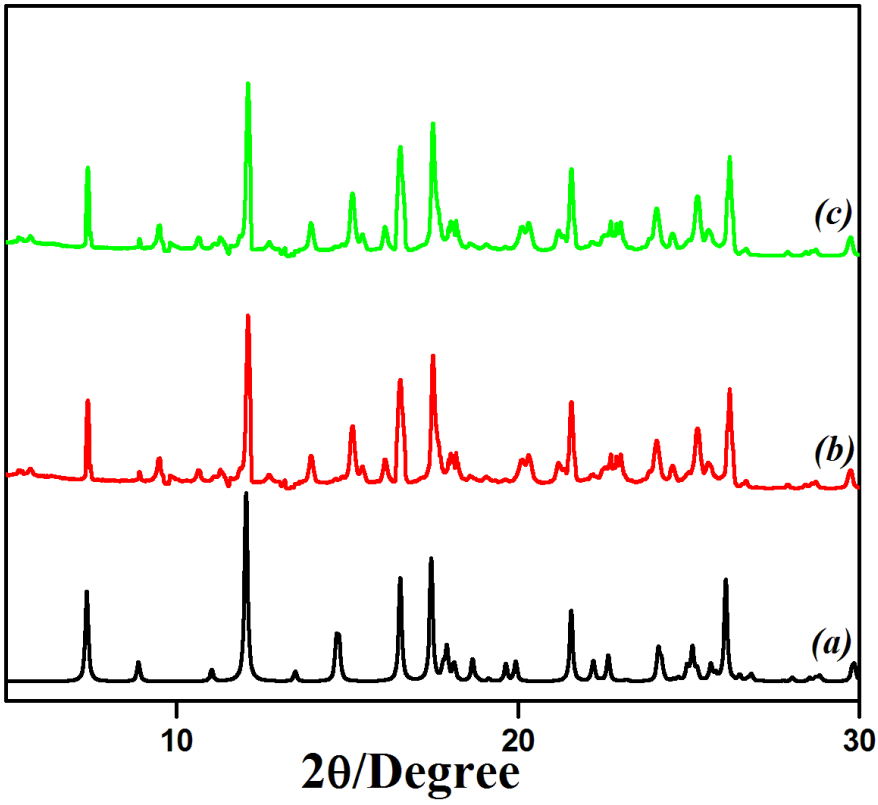


Figure S10. PXRD patterns of **3** in different states (*a*) Simulated from X-ray single crystal data; (*b*) bulk as-synthesized compound; (*c*) de-solvated

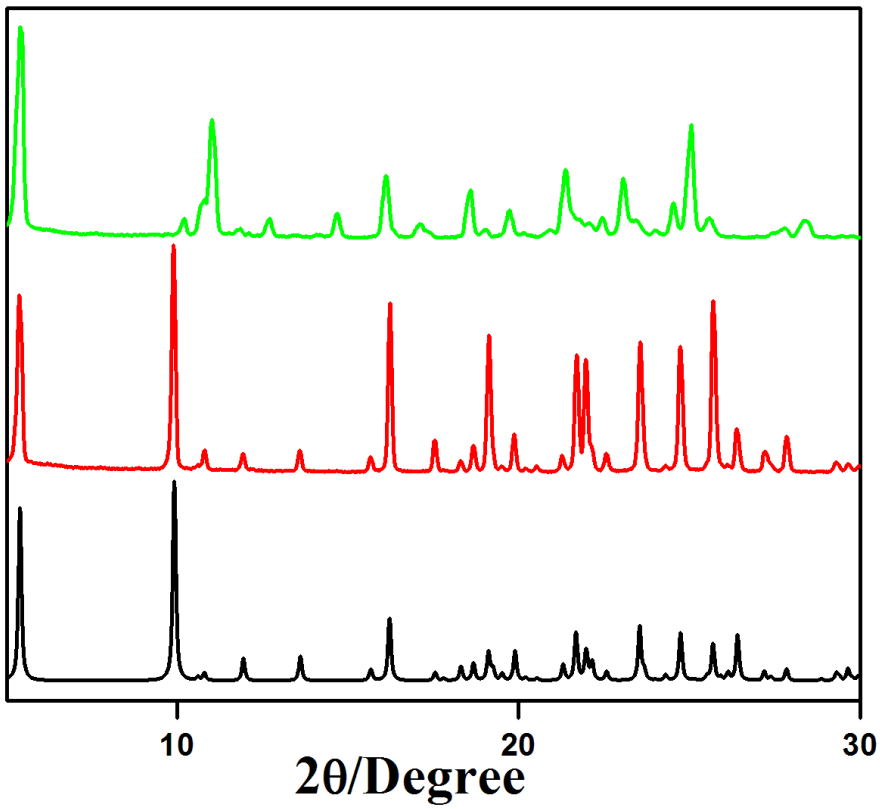


Figure S11. PXRD patterns of **4** in different states (*a*) Simulated from X-ray single crystal data; (*b*) bulk as-synthesized compound; (*c*) de-solvated

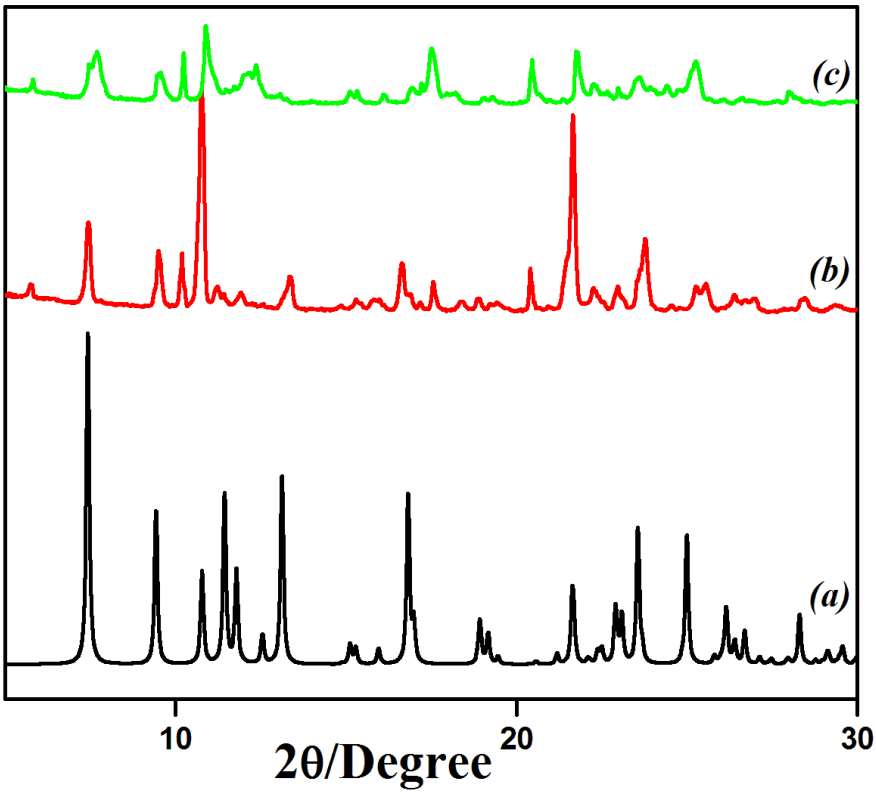


Figure S12. PXRD patterns of **5** in different states (*a*) Simulated from X-ray single crystal data; (*b*) bulk as-synthesized compound; (*c*) de-solvated

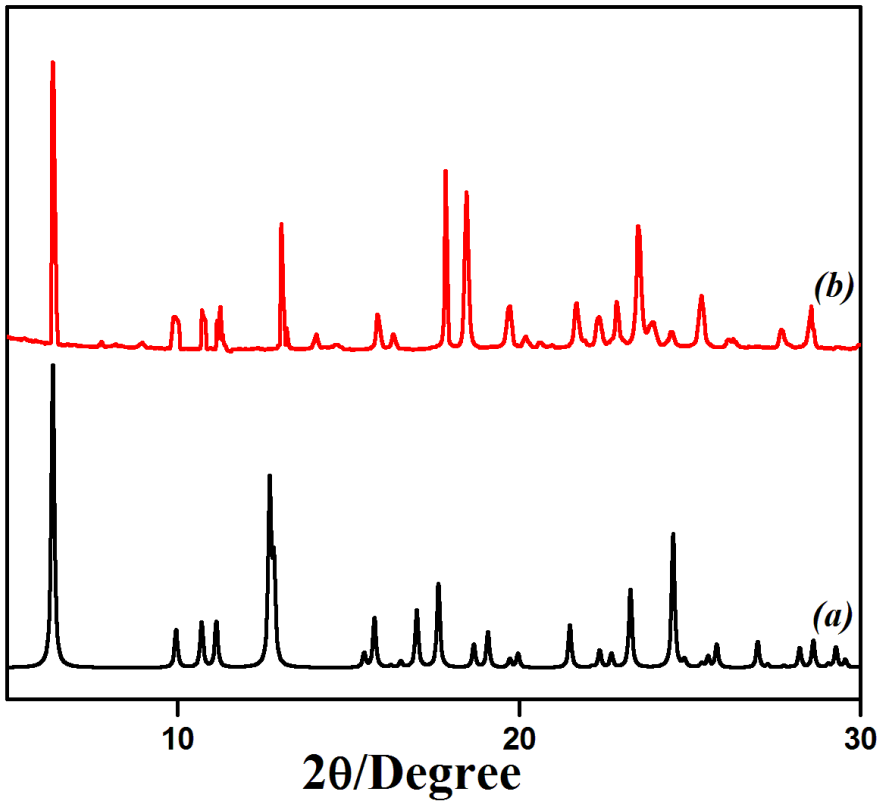


Figure S13. PXRD patterns of **6** in different states (*a*) Simulated from X-ray single crystal data; (*b*) bulk as-synthesized compound.

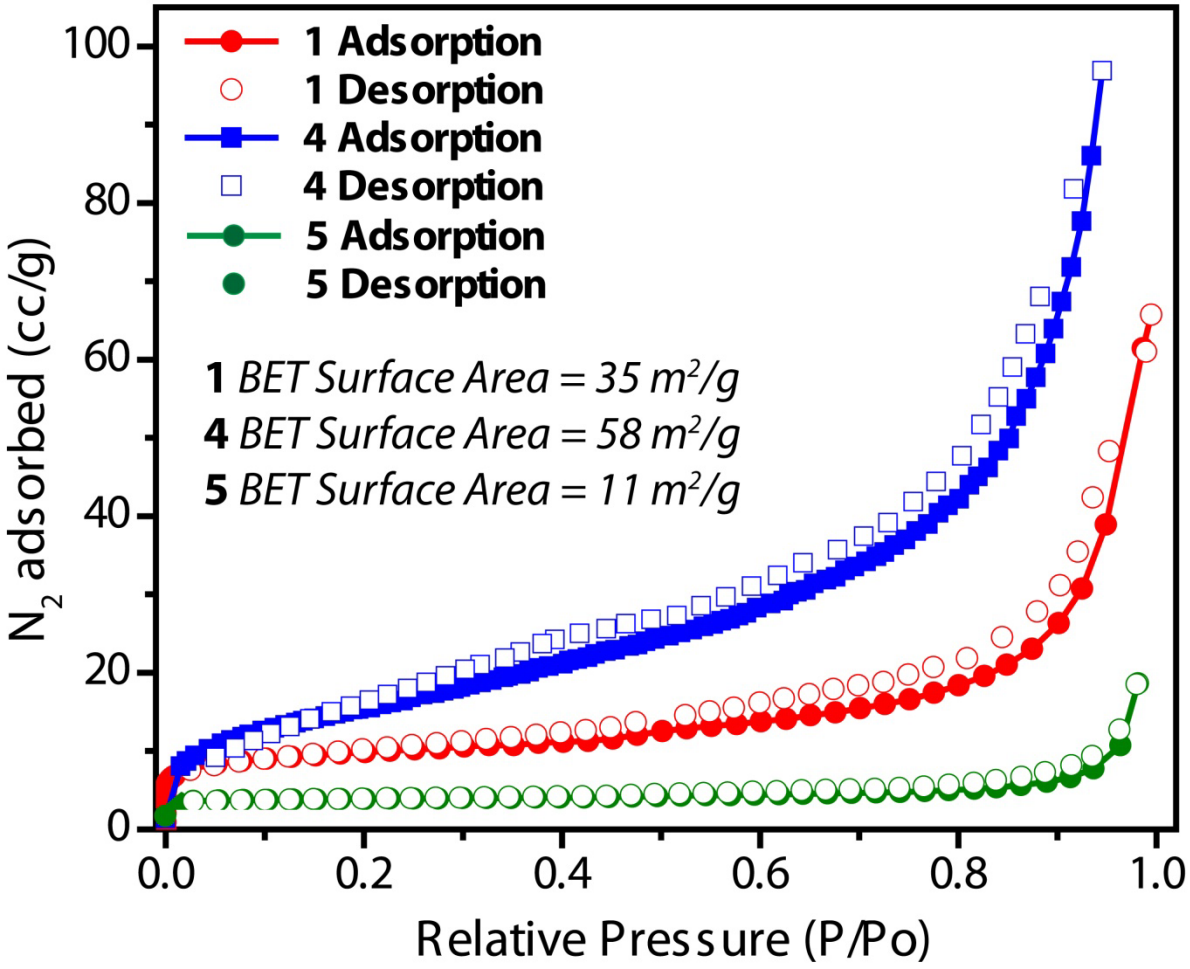


Figure S14. N_2 adsorption isotherms for compounds **1**, **4** and **5** collected at 77 K (The filled and open shapes in the figures represents the adsorption and desorption branches, respectively).