Supporting information

Regulation of pore size by shifting coordination sites of ligands in two MOFs: Enhancement of CO_2 uptake and selective sensing of nitrobenzene

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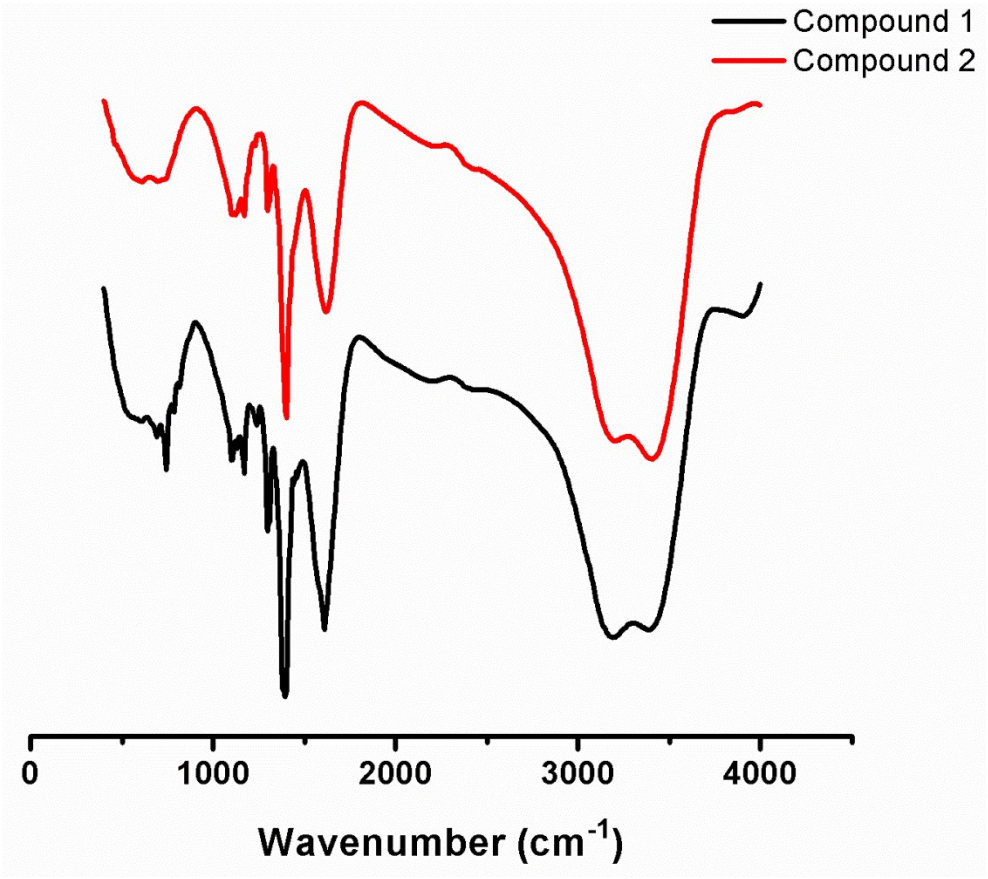

Figure S1. FT-IR spectra of compounds **1** and **2**.

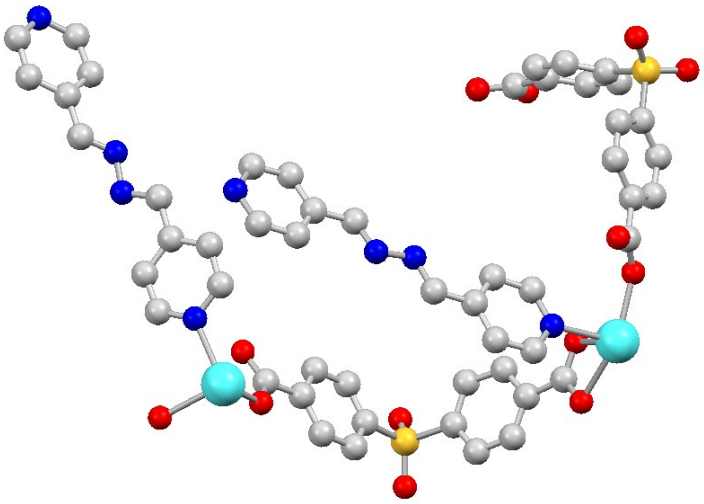

Figure S2. Asymetric unit of **1**. Color code: carbon (gray), nitrogen (blue), oxygen (red) and cadmium (cyan). (Hydrogens are omitted for clarity).

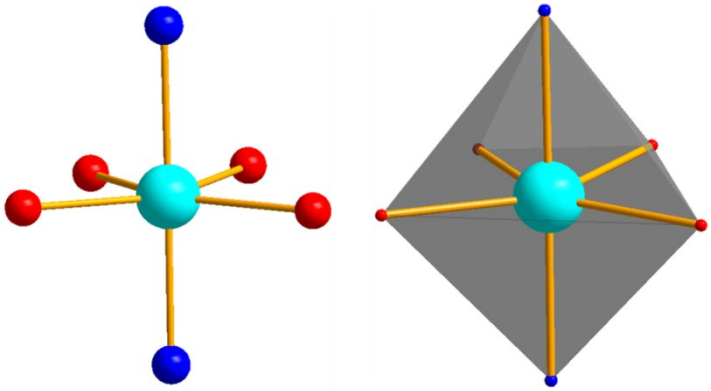

Figure S3. Octahedral arrangement of Cd(II) atom (left) and its polyhedral view (right) in **1**. Color code; same as in Figure S2.

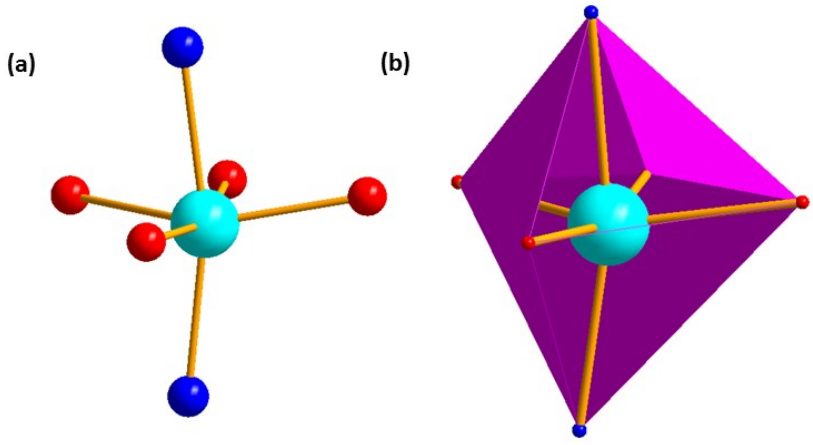

Figure S4. Octahedral arrangement of Cd(II) atom (left) and its polyhedral view (right) in **1**. Color code; same as in Figure S2.

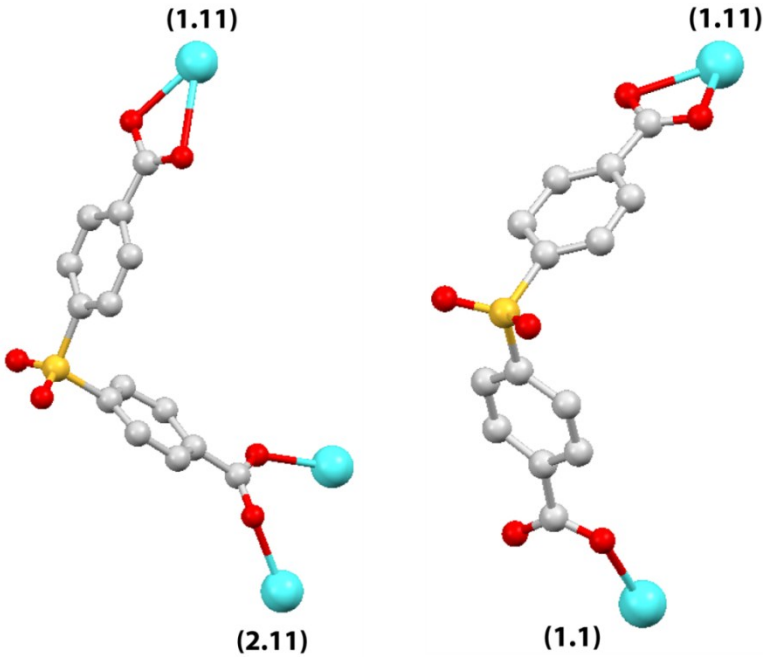

Figure S5. Various Bridging Modes of sdb found in compound **1** (Harris Notation). Color code; same as in Figure S2.

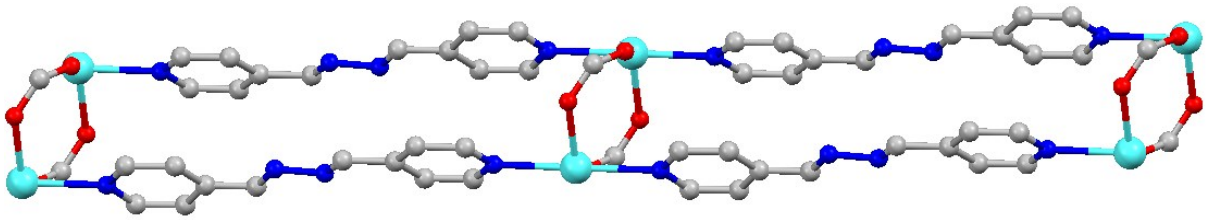

Figure S6. Illustration of 1D chain along the *b*-axis. Color code; same as in Figure S2.

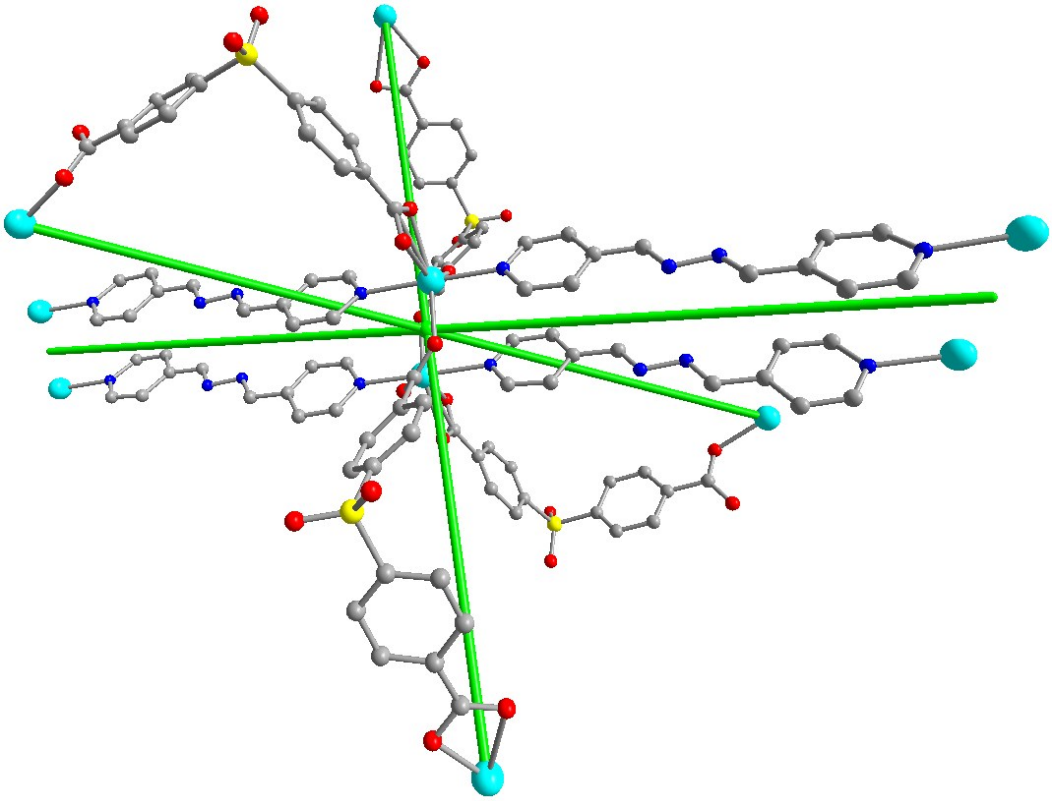

Figure S7. View of the 6-connected binodal net. Color code; same as in Figure S2.

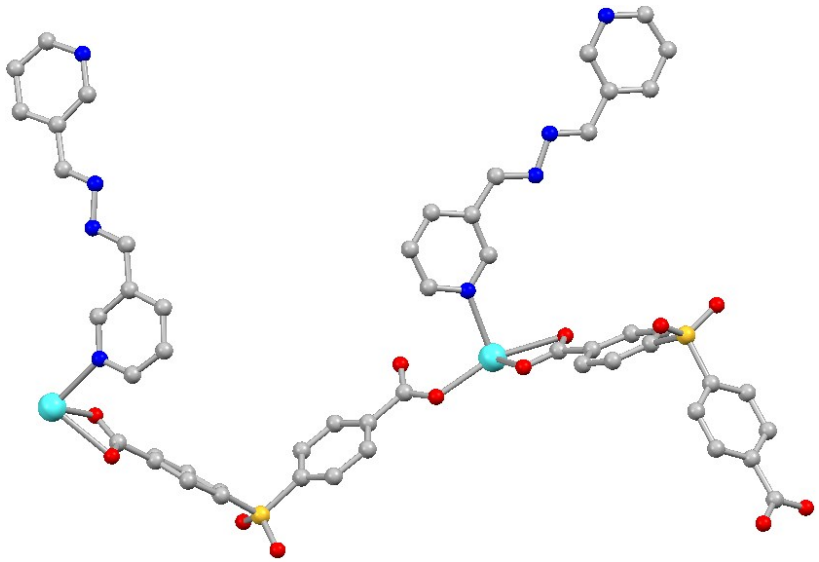

Figure S8. Asymetric unit of **2**. Color code; same as in Figure S2.

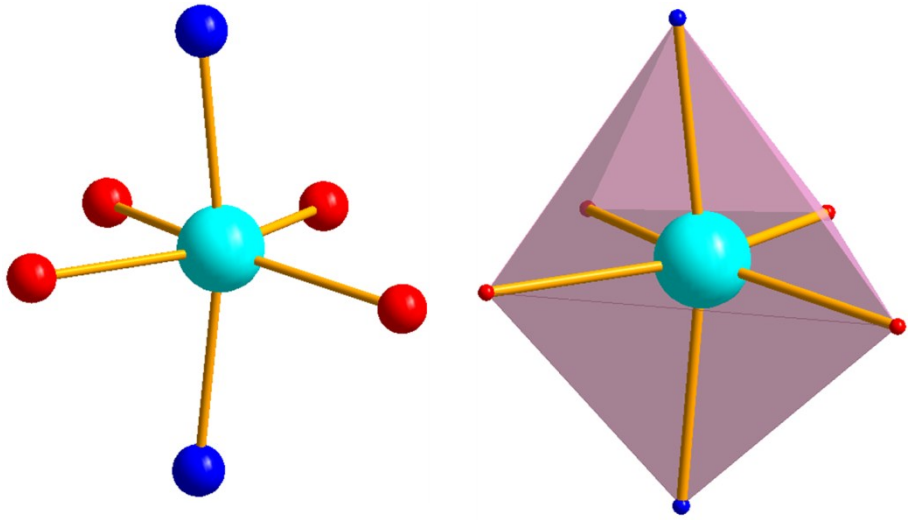

Figure S9. Distorted octahedral arrangement of Cd(II) atom (left) and its polyhedral view (right) in **2**. Color code; same as in Figure S2.

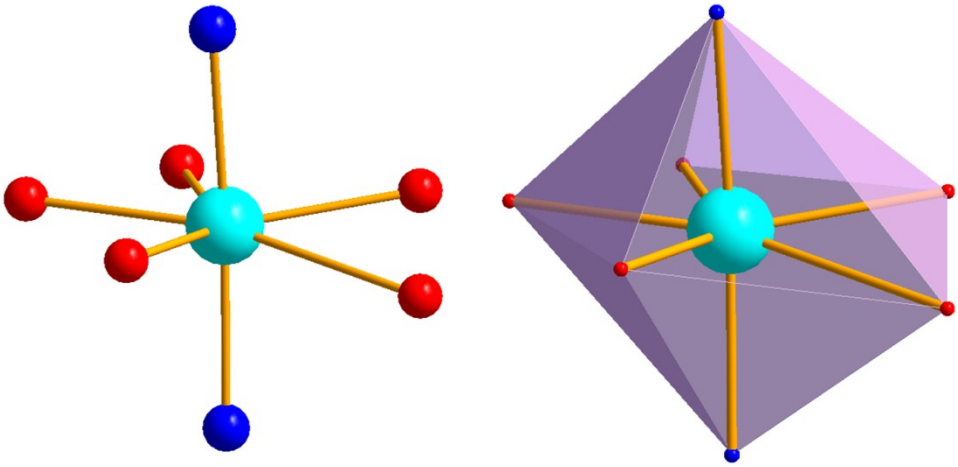

Figure S10. Pentagonal bipyramidal arrangement (left) of Cd(II) atom and its polyhedral view (right) in **2**. Color code; same as in Figure S2.

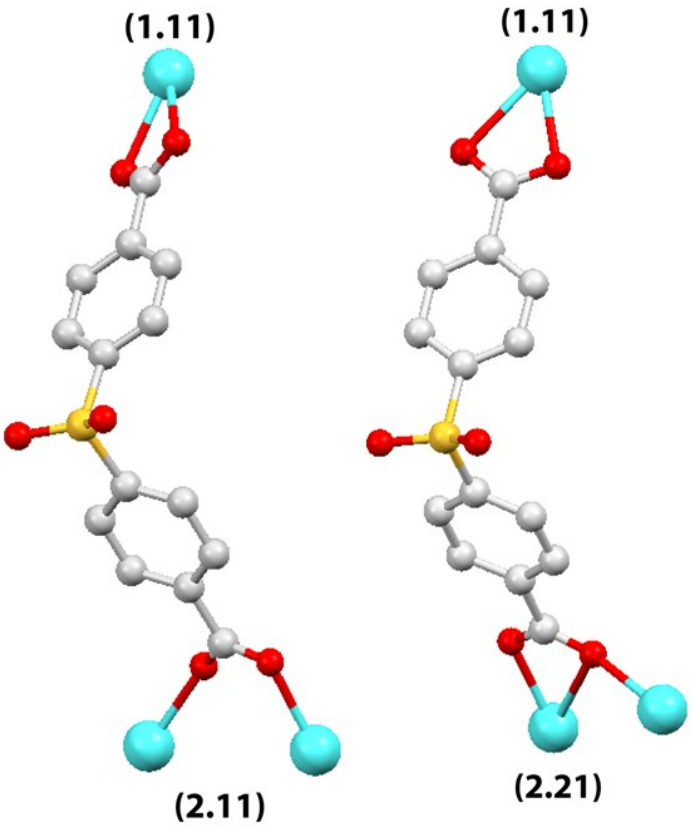

Figure S11. Various Bridging Modes of sdb found in compound **2** (Harris Notation). Color code; same as in Figure S2.

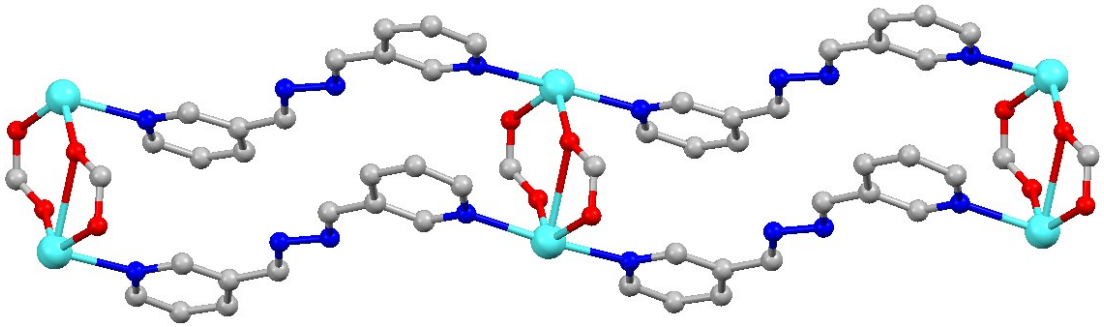

Figure S12. Illustration of 1D chain in compound **2**. Color code; same as in Figure S2.

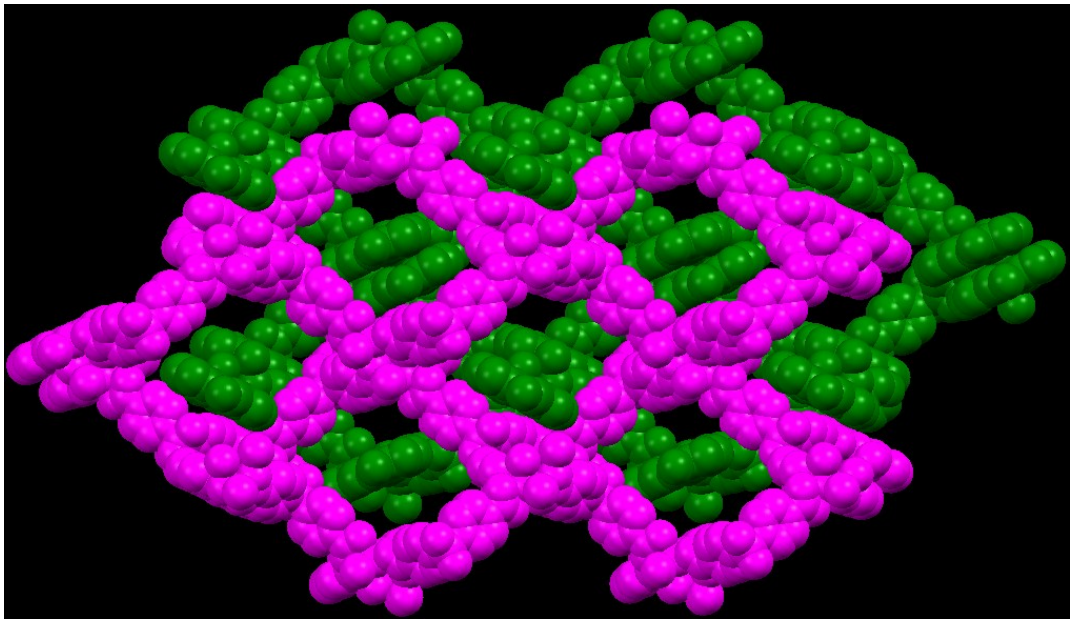

Figure S13.Interpenatration of one 2D net over another to generate a 2-fold interwoven 3D network found in compound **2**.

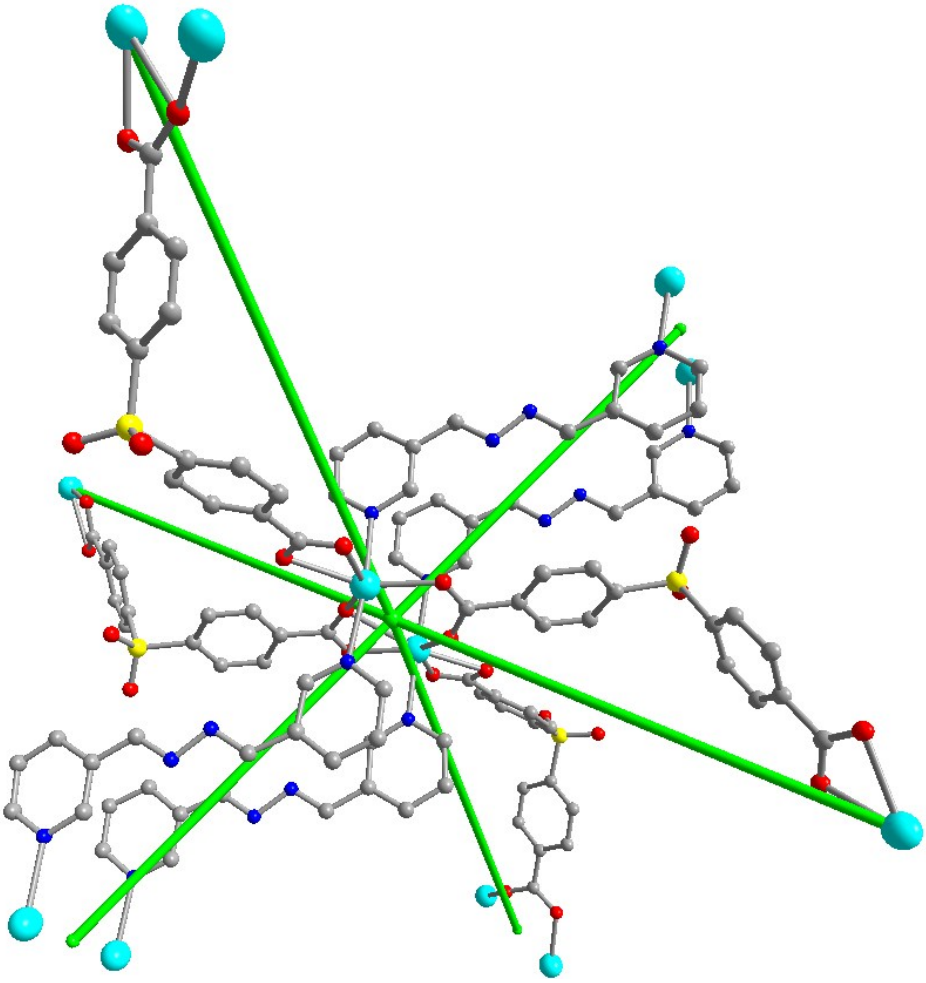

Figure S14. View of the 6-connected uninodal net in **2**. Color code; same as in Figure S2.\

Calculation of solvent accessible void volume for compound 1 by using van der Waals radii

van der Waals (or ion) Radii used in the Analysis

==========

C H Cd N O S

1.70 1.20 1.58 1.55 1.52 1.80

:: Note: VOID/SOLV/SQUEEZE is relatively compute intense and experimental

:: Nr of gridpoints at least 1.20 Å. from nearest van der Waals Surface= 7964

:: Total Potential Solvent Area Vol 319.0 $Å^3$

per Unit Cell Vol 2735.5 $Å^3$[11.7%]

Note: Expected volumes for solvent molecules are:

A hydrogen bonded H_2O-molecule 40 $Å^3$

Small molecules (e.g. Toluene) 100-300 $Å^3$

Calculation of solvent accessible void volume for compound 2 by using van der Waals radii

Van der Waals (or ion) Radii used in the Analysis

==========

C H Cd N O S

1.70 1.20 1.58 1.55 1.52 1.80

:: Note: VOID/SOLV/SQUEEZE is relatively compute intense and experimental

:: Nr of grid points at least 1.20 Å. from nearest Van der Waals Surface= 61360

:: Total Potential Solvent Area Vol 1713.1 $Å^3$

per Unit Cell Vol 6250.1 $Å^3$ [27.4%]

Note: Expected volumes for solvent molecules are:

A Hydrogen bonded H_2O-molecule 40 $Å^3$

Small molecules (e.g. Toluene) 100-300 $Å^3$.

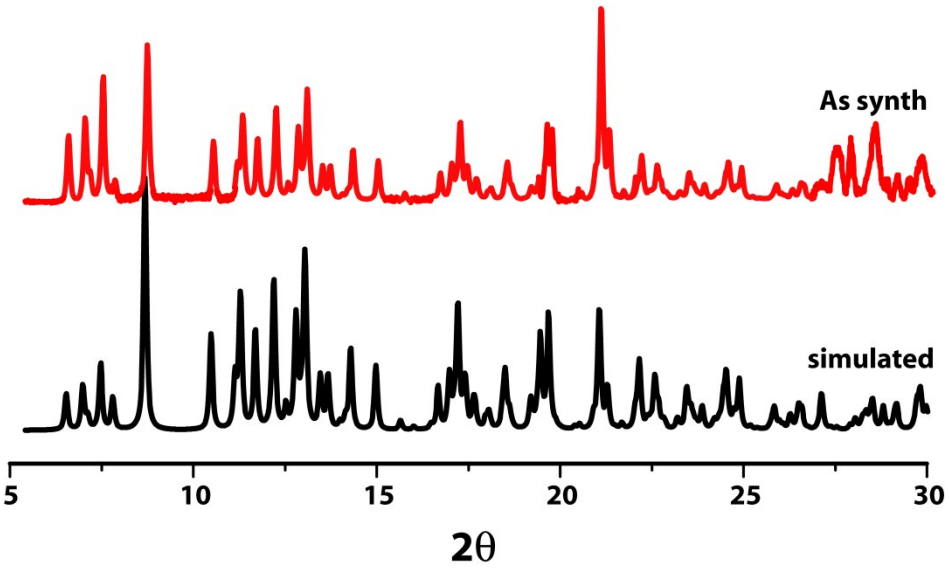

Figure S15. PXRD patterns of compound **1**.

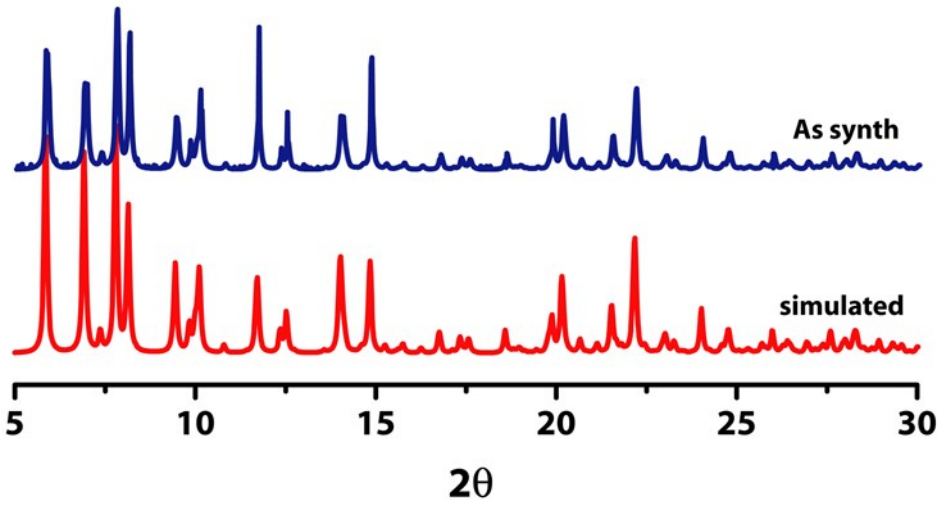

Figure S16. Pxrd patterns of compound **2**.

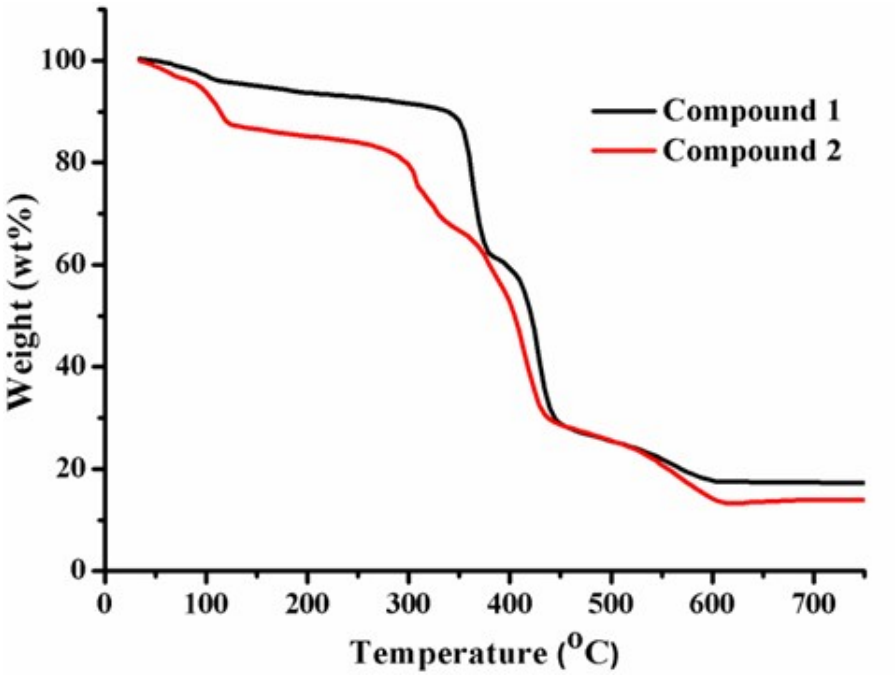

Figure S17. TGA graph of Compounds **1**(black) and **2** (red).

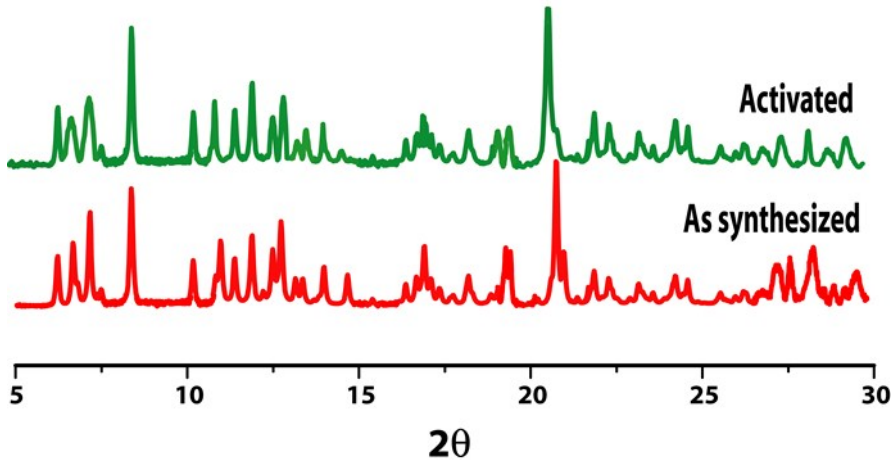

Figure S18. Pxrd patterns of assynthesized and activated frameworks (after removal guest molecules) of compound **1.**

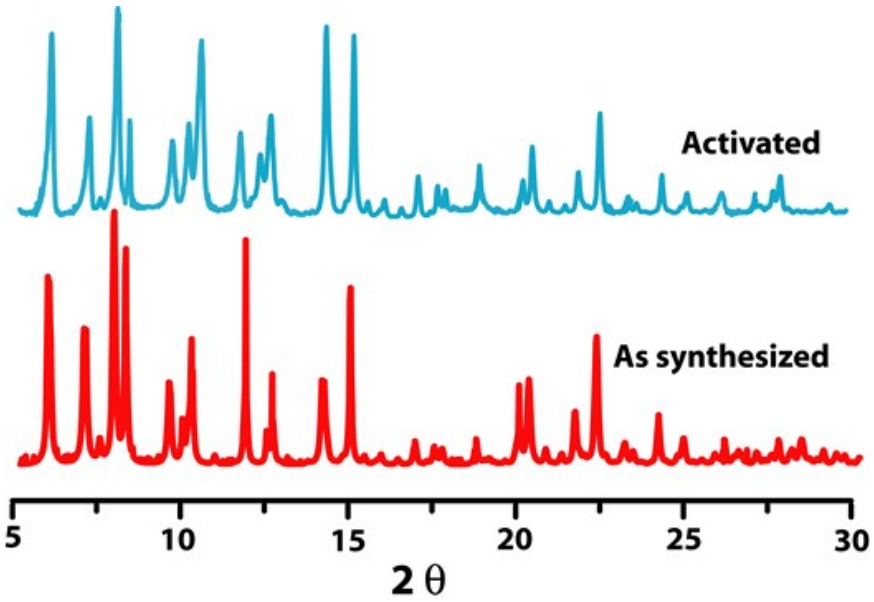

Figure S19. Pxrd patterns of assynthesized and activated frameworks (after removal guest molecules) of compound **2.**

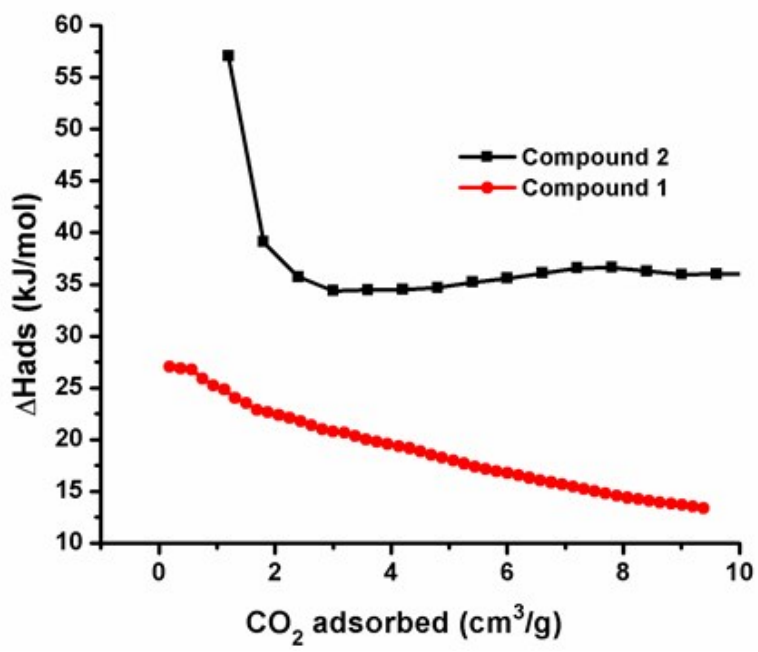

Figure S20. Isosteric heats (Q_{st}) of CO_2 adsorption are calculated based on the adsorption data collected at 273 K and 298 K by using Clapeyron method.

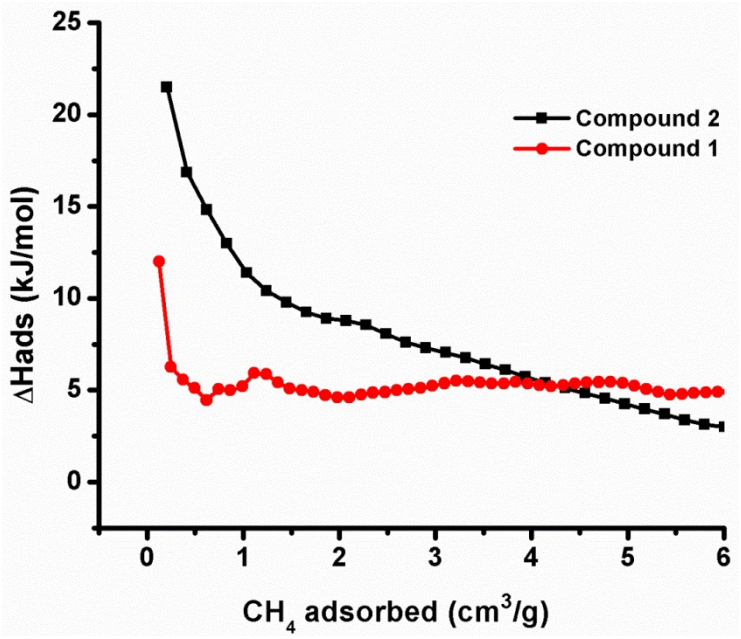

Figure S21. Isosteric heats (Q_{st}) of CH_4 adsorption are calculated based on the adsorption data collected at 273 K and 298 K by using Clapeyron method.

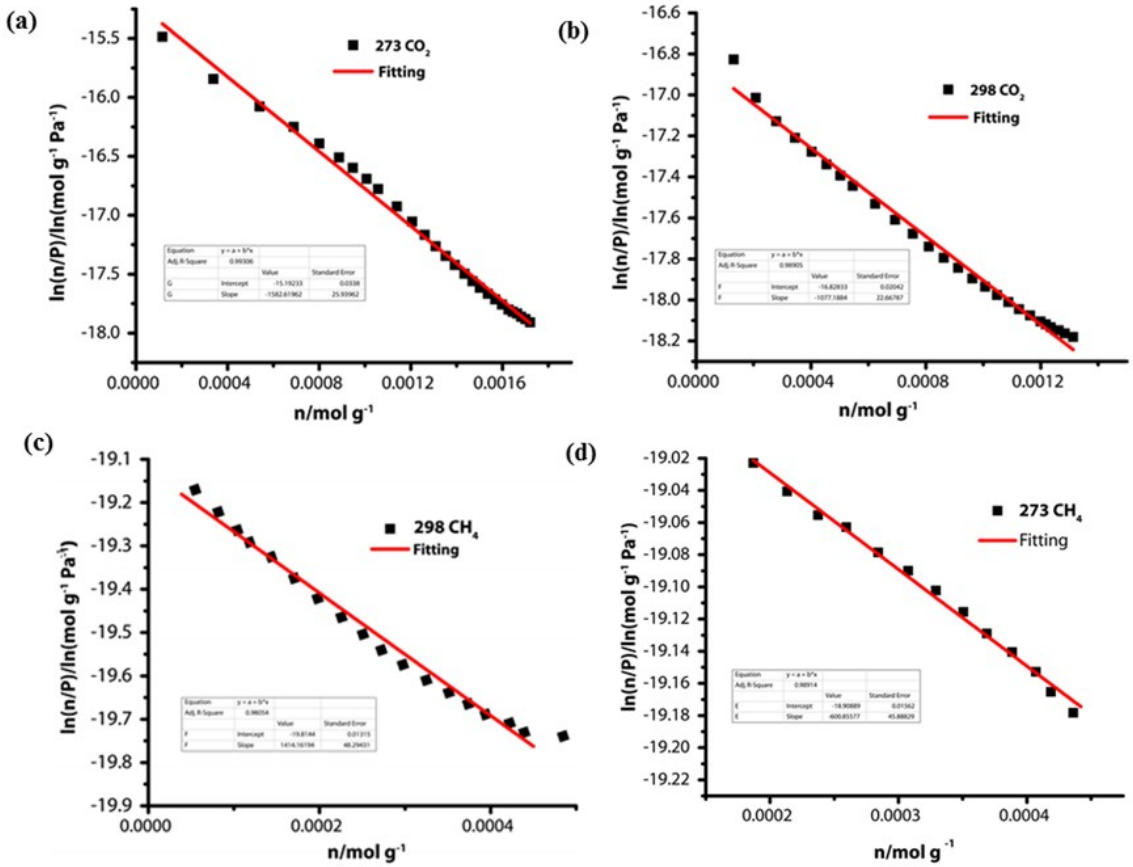

Figure S22. The virial graphs for adsorption of CO_2 and CH_4 on compounds **1** and **2** at 273 K and 298 K.

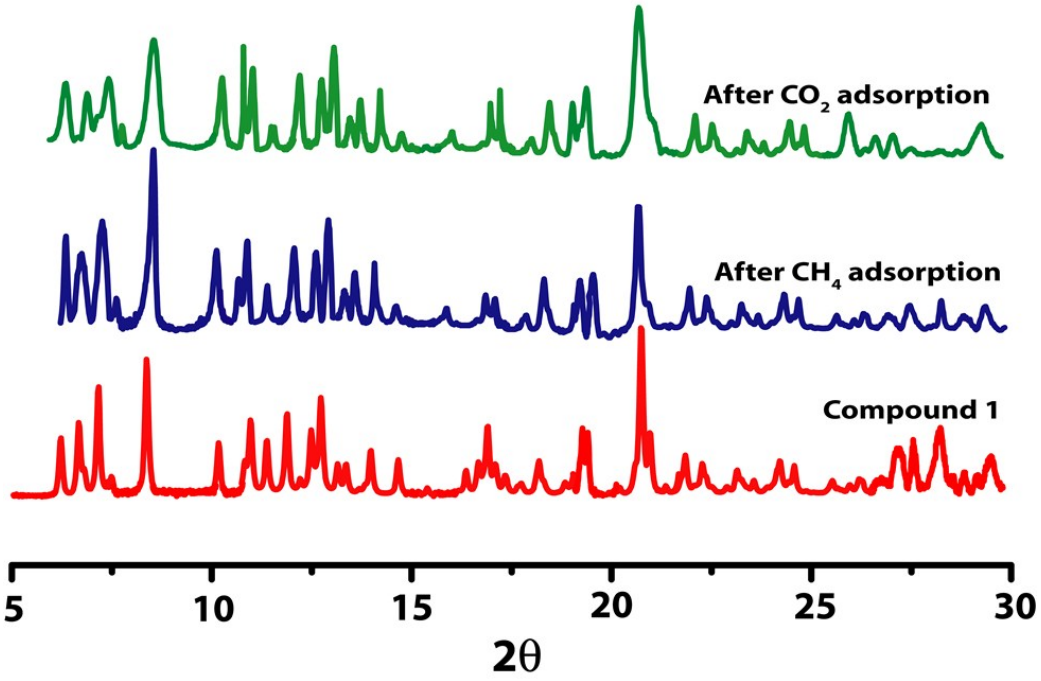

Figure S23. Pxrd patterns of compound **1** and after adsorption of CO_2 and CH_4.

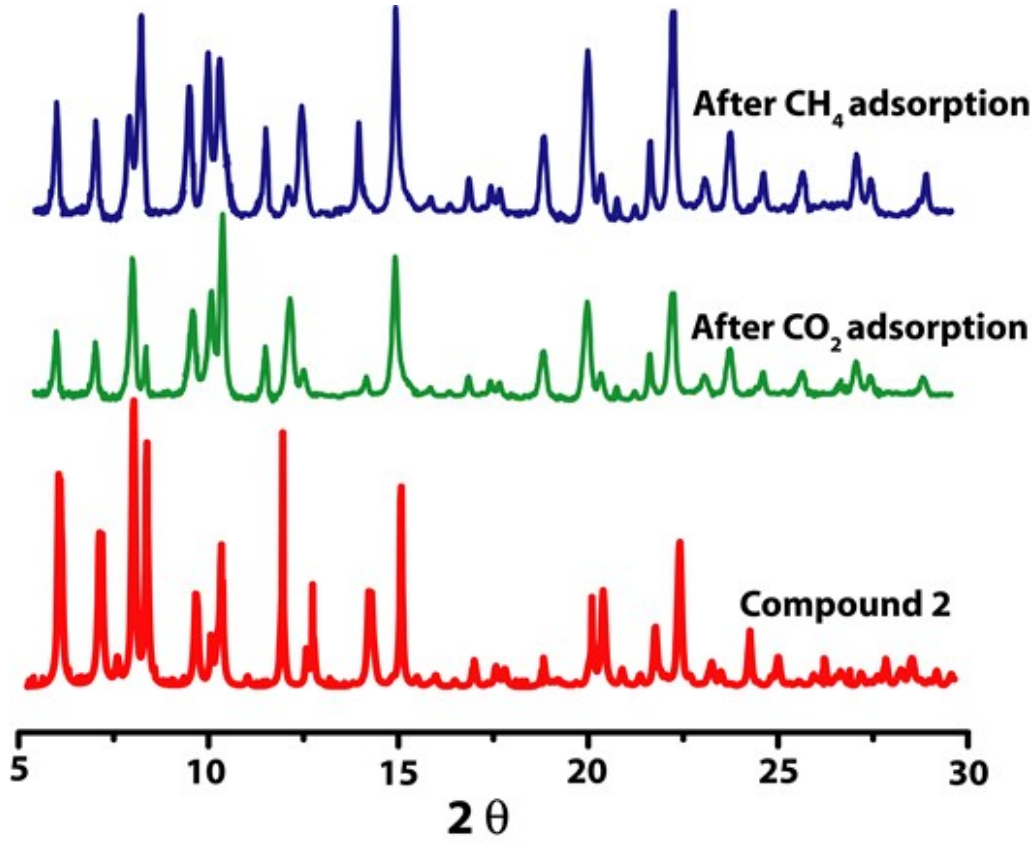

Figure S24. Pxrd patterns of compound **2** and after adsorption of CO_2 and CH_4.

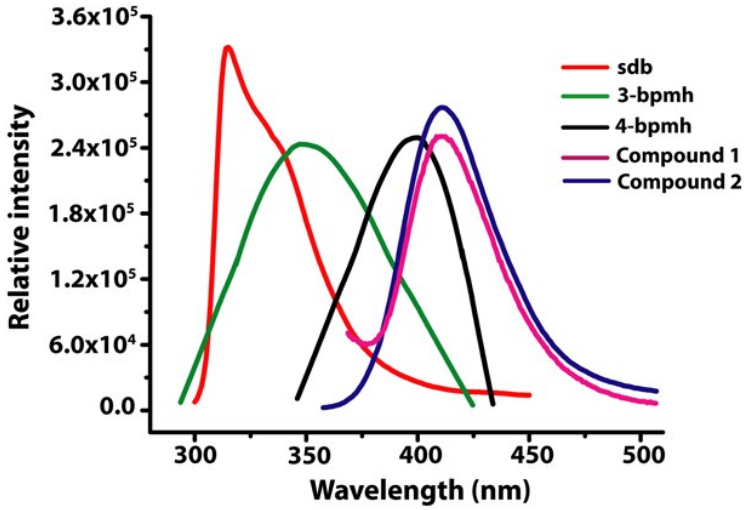

Figure S25. Solid-state emission spectra for the ligands used and for compounds **1** and **2.**

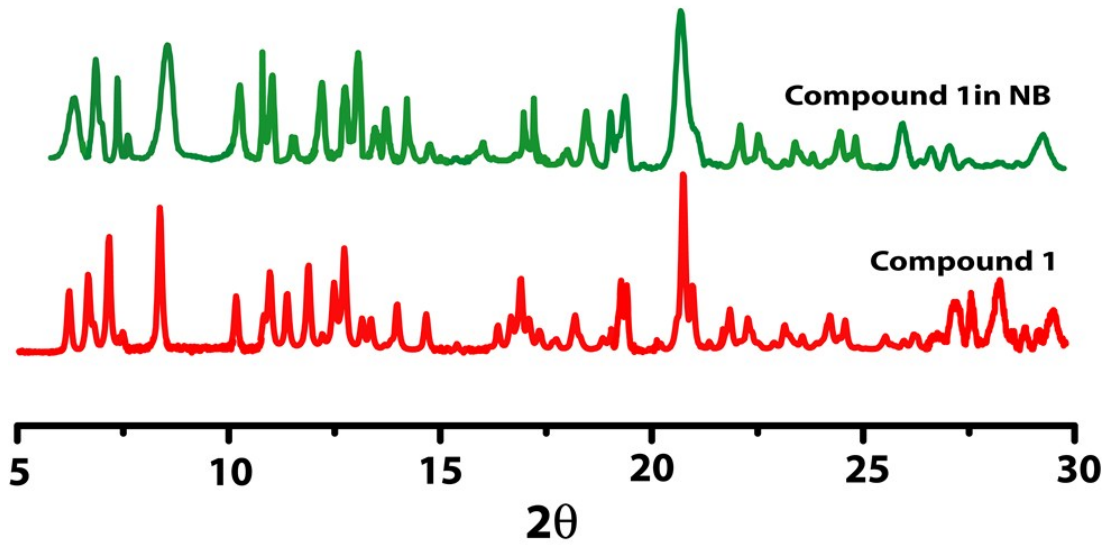

Figure S26. PXRD pattern of compound **1** obtained after immersing in NB.

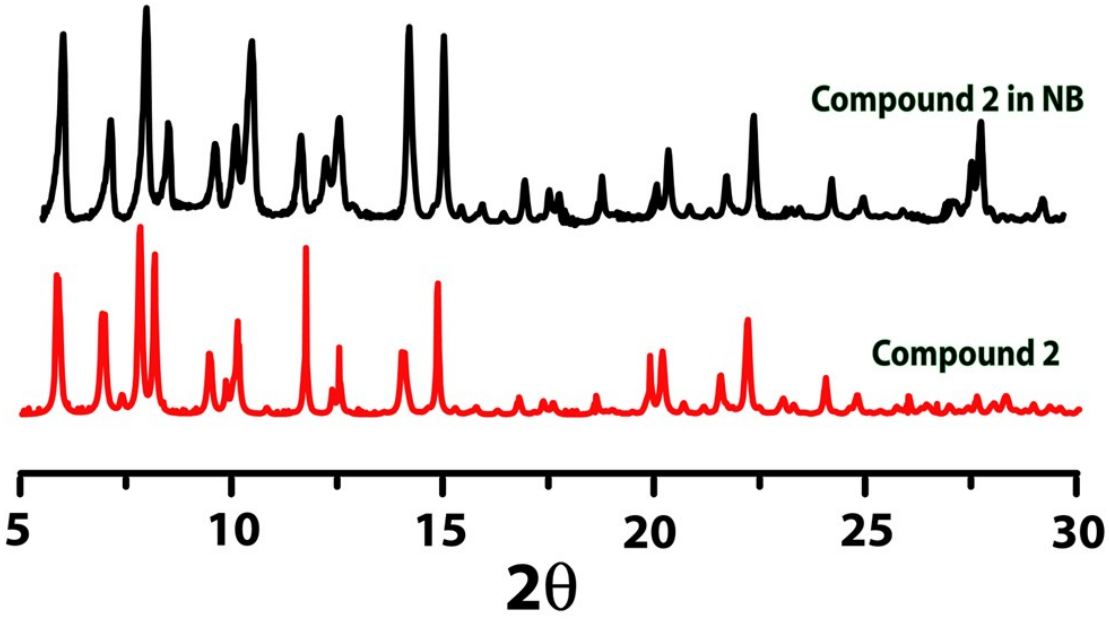

Figure S27. PXRD pattern of compound **2** obtained after immersing in NB.

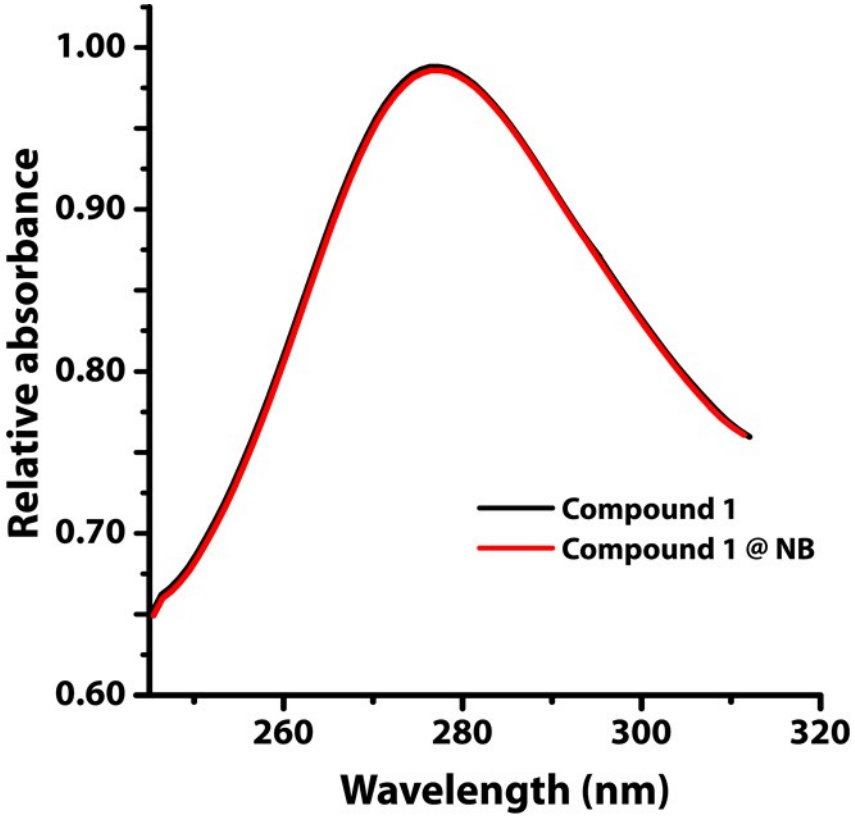

Figure S28. Excitaton spectra of compound **1** upon addition of NB.

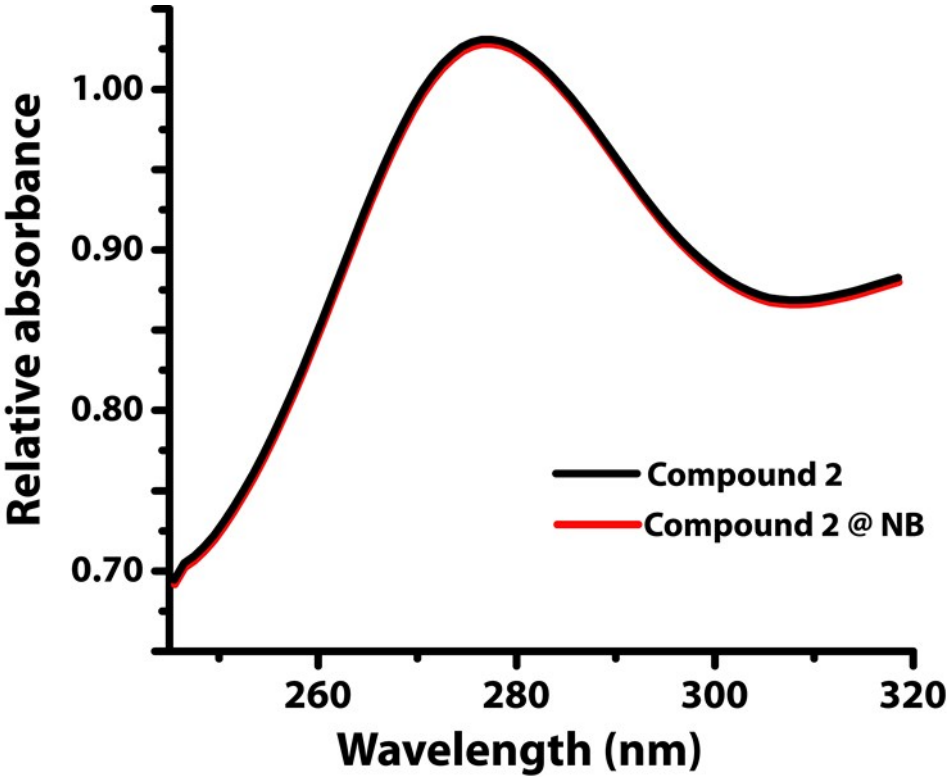

Figure S29. Excitaton spectra of compound **2** upon addition of NB.

Table S1. Comparison of CO_2/CH_4 Selectivity for compound **2** with reported MOFs which are calculated by using henry equation.

S.No	**MOFs**	**CO_2/CH_4 Selectivity**
1	[Cu3(BTB^{6-}), Cu3($TATB^{6-}$)][1]	8.6
2	[$Cu_2(HBTB)^{2-}$][2]	12.4
3	[NJU-Bai][3]	14.7
4	[HKUST-1/PSf][4]	21.5
5	[Cu-BPY-HFS][4]	22.5
6	[HKUST-1/PI][5]	27.5
7	[CuTPA MOF][6]	34.9
8	[CuTPA][6]	40
9	[NJU-Bai8][3]	40.8
10	ZIF-78[7]	45
11	[Cd-$(NDC)_{0.5}$(PCA)]·Gx[8]	28
12	ZIF-82[7]	32
13	{[Cu(tdc)(bpe)]$_n$·2n(H_2O)·n(MeOH)}[9]	32
14	**Present work (Compound 2)**	**41**

Table S2. Selected bond angles and bond lengths of compound **1**

Cd1-N2	2.3708	N1-Cd1-O10	88.8(3)
Cd1-O6	2.3519	N3-Cd2-O3	105.5(4)
Cd1-O7	2.2411	N3-Cd2-N7	167.6(4)
Cd1-O9	2.3970	N3-Cd2-O13	95.3(5)
Cd1-N1	2.3265	N3-Cd2-O12	87.7(5)
Cd1-O10	2.2425	O3-Cd2-N7	86.6(4)
Cd2-N3	2.3036	O3-Cd2-O13	90.5(5)
Cd2-O3	2.1903	O3-Cd2-O12	140.4(5)
Cd2-N7	2.3354	N7-Cd2-O13	87.2(5)
Cd2-O13	2.3046	N7-Cd2-O12	84.5(5)
Cd2-O12	2.6945	O13-Cd2-O12	50.6(5)
N2-Cd1-O6	84.5(3)	O13-Cd2-O12	50.6(5)
N2-Cd1-O7	94.1(3)	O9-Cd1-O10	90.3(3)
N2-Cd1-O9	86.0(3)	O6-Cd1-N1	96.5(3)
N2-Cd1-N1	179.1(3)	O6-Cd1-O10	144.7(3)
N2-Cd1-10	90.5(3)	O7-Cd1-O9	143.5(3)
O6-Cd1-O7	89.1(3)	O7-Cd1-N1	85.9(3)
O6-Cd1-O9	54.5(3)	O7-Cd1-O10	126.1(3)
O6-Cd1-N1	96.5(3)	O9-Cd1-N1	94.6(3)

Table S3. Selected bond angles and bond lengths of compound **2**

Cd1-N1	2.313(8)	Cd1-O3-Cd2	106.5(3)
Cd1-O13	2.479(8)	O4-Cd2-O3	50.3(2)
Cd1-O12	2.296(8)	O5-Cd2-O3	83.1(2)
Cd1-O11	2.231(7)	O2-Cd2-O5	84.3(3)
Cd1-N8	2.365(9)	O4-Cd2-O3	50.3(2)
Cd1-O3	2.272(7)	O4-Cd2-N7	97.8(3)
N8-Cd1	2.365(9)	O4-Cd2-O5	129.8(3)
O3-Cd1	2.272(7)	O3-Cd2-N7	78.8(2)
O3-Cd2	2.785(8)	O3-Cd2-O5	83.1(2)
Cd2-N6	2.33(1)	N7-Cd2-O5	88.9(3)
Cd2-O1	2.337(8)	N6-Cd2-O1	90.2(3)
Cd2-O2	2.457(8)	N6-Cd2-O2	86.9(3)
Cd2-O4	2.275(7)	N6-Cd2-O4	86.7(3)
Cd2-O3	2.785(8)	N6-Cd2-O3	99.0(3)
Cd2-N7	2.321(8)	N6-Cd2-N7	171.6(3)
Cd2-O5	2.284(7)	N6-Cd2-O5	82.8(3)
N7-Cd2	2.321(8)	O1-Cd2-O2	54.3(3)
O5-Cd2	2.284(7)	O1-Cd2-O4	90.4(3)
O3-Cd2	2.785(8)	O1-Cd2-O3	138.4(2)
N1-Cd1-O13	91.2(3)	O1-Cd2-N7	96.8(3)
N1-Cd1-O12	95.8(3)	O1-Cd2-O5	138.4(3)
N1-Cd1-O11	101.5(3)	O2-Cd2-O4	144.0(3)
N1-Cd1-N8	169.7(3)	O2-Cd2-O3	165.3(2)
N1-Cd1-O3	85.0(3)	O2-Cd2-N7	93.4(3)
O13-Cd1-O12	55.0(2)	O12-Cd1-N8	88.7(3)
O13-Cd1-O11	149.2(3)	O12-Cd1-O3	149.2(3)
O13-Cd1-N8	83.8(3)	O11-Cd1-N8	87.3(3)
O13-Cd1-O3	94.1(3)	O11-Cd1-O3	114.6(3)
O12-Cd1-O11	95.5(3)	N8-Cd1-O3	86.4(3)

References.

1. B. Mu, F. Li and K. S. Walton, *Chem. Commun.,* 2009, 2493.
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