

Molecular Tectonics of Four-Connected Network Topologies by Regulating the Ratios of Tetrahedral and Square-Planar Building Units

Ling Qin^{†,‡}, Hai-Lang Jia[†], Zi-Jian Guo[†], He-Gen Zheng^{*,†}

[†]*State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, P. R. China*

[‡]*Xuancheng Campus, Hefei University of Technology, Xuancheng, 242000, Anhui, P. R. China*

1.Experimental Section.

Preparation of N, N, N', N'-tetrakis(4-bromophenyl)biphenyl-4,4'-diamine: An oven-dried 500mL Schlenk flask was charged with tris(4-bromophenyl)amine (24.1 g, 50 mmol), then ether (350 mL) and N,N,N',N'-tetramethylethylenediamine (8.2 mL) were added through a rubber septum. The reaction mixture was cooled to -78 °C. Upon slow addition of a n-BuLi solution (34 mL, 1.6 M in hexanes, 55 mmol), and the mixture was stirred for 1 h at -78 °C. Solid CuCl₂ (10.8 g, 80 mmol) was added, and the reaction mixture was then allowed to slowly warm to room temperature and stirred for an additional 10 h. The reaction mixture was exposed to air, stirred for 30 min and concentrated in vacuo. Approximately chloroform (100 mL) and water (100 mL) were added, and the layers were separated. The aqueous layer was subsequently washed with chloroform (50 mL) three times. The organic extracts were combined, dried with MgSO₄, and filtered. The volatile chloroform was removed under vacuum to leave a green solid. Purification by column chromatography (petroleum ether)

yielded the pure product as a white solid (10.1 g, 50%). ¹HNMR (DMSO-d, 500 MHz, 25 °C): 7.61 (d, 4H), 7.49 (d, 8H), 7.09 (d, 4H), 7.0 (d, 8H).

Preparation of N,N,N',N'-tetrakis (4-(4-pyridine)-phenyl) biphenyl-4,4'-diamine (TPPBDA): A 500 mL Schlenk flask was evacuated and backfilled with nitrogen and charged with N, N, N', N'-tetrakis(4-bromophenyl)biphenyl-4,4'-diamine (8g, 10 mmol), the pyridine-4-boronic acid (8.41g, 70 mmol), and K₂CO₃ (9.66 mg, 70 mmol). The flask was evacuated and backfilled with nitrogen, then Pd(PPh₃)₄ (2.2 mg, 0.05 mmol, 5.0 mol %) and 1,4-dioxane / H₂O (V:V=3:2) were added through a rubber septum. The reaction mixture was heated to 95 °C with stirring until the starting N, N, N', N'-tetrakis(4-bromophenyl)biphenyl-4,4'-diamine had been completely consumed as judged by TCL. The reaction mixture was then cooled to room temperature and the 1,4-dioxane was removed under vacuum. The aqueous mixture was extracted with chloroform for three times (150 mL). The combined organic layers were dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. The crude material was purified by chromatography on silica gel (ethyl acetate / methanol = 10:1) yielded the pure product as a yellow solid (4.2 g, 53%). ¹HNMR (DMSO-d, 500 MHz, 25 °C): 8.60 (s, 8H), 7.80 (d, 8H), 7.68 (s, 12H), 7.19 (d, 12H). ¹³CNMR (DMSO-d): δ, [ppm]: 119.42, 120.41, 121.04, 124.33, 125.63, 128.15, 128.53, 131.85, 135.50, 145.91, 146.65, 148.12, 150.67. MS (ESI-Tof): Calcd for C₅₆H₄₀N₆, 796; found, 797.

Materials and Measurements. Reagents and solvents employed were commercially available. H₂tpdc ligand was prepared on the basis of palladium-catalyzed cross-coupling reactions.¹ IR absorption spectra of the compounds **1** - **3** were recorded in the range of 400–4000 cm⁻¹ on a Nicolet (Impact 410) spectrometer with KBr pellets (5 mg of sample in 500 mg of KBr). C, H and N analyses were carried out with a Perkin Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Mo-K_α radiation (λ = 0.71073 Å), in which the X-ray tube was operated at 40 kV and 40 mA. The as-synthesized samples were characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA up to 1023 K using a heating rate of 10 K min⁻¹ under N₂ atmosphere. Luminescent spectra were recorded with a SHIMAZU VF-320 X-ray fluorescence spectrophotometer at room temperature. The gas sorption isotherms were measured by Micromeritics ASAP 2020 M+C surface area analyzer.

Gas Sorption Measurements

In the gas sorption measurement, Ultra-high-purity grade, N₂, H₂, CO₂ and CH₄ (>99.999%) were used throughout the adsorption experiments. All of the measured sorption isotherms have been repeated several times to confirm the reproducibility within experimental error. Adsorption measurements (up to 1 bar) were performed on Micromeritics ASAP 2020 M+C surface area analyzer. About 140 mg of samples **2** were activated at 80 °C for 10 hours by using the “outgas” function of the surface area analyzer. Helium was used for the estimation of the dead volume, assuming that it is not adsorbed at any of the studied temperatures. To provide high accuracy and precision in determining P/P₀, the saturation pressure P₀ was measured throughout the N₂ analyses by means of a dedicated saturation pressure transducer, which allowed us to monitor the vapor pressure for each data point. The H₂ isotherm was measured at 77 K and the CO₂ isotherms were measured at 273 K and 298K, and CH₄ isotherm was measured at 273 K.

Synthesis of complex 1: A mixture of H₂O/DMA/CH₃CN containing the TPPBDA (79.6 mg, 0.1 mmol) and Cd(NO₃)₂·6H₂O (30.1 mg, 0.1 mmol) was mixed in a Teflon vessel within the autoclave. The vessel was heated at 85 °C for 72 h and then cooled to room temperature. The yellow block crystals were obtained. Yield of the reaction was ca. 50% based on TPPBDA ligand. Elemental analysis calcd. for C₇₂H₈₂CdN₁₀O₈ (**1**): C, 65.12; H, 6.22; N, 10.55, Found: C, 65.04; H, 6.41; N, 10.58. The IR spectrum of the corresponding complex is shown in the Figure S7.

Synthesis of complex 2: Compound **2** was synthesized by dissolving 39.8 mg of TPPBDA and 31.8 mg of tpdc in DMF (3mL) in a 10 mL glass vial. A solution of 0.1 mmol aqueous Cd(NO₃)₂ solution was then added and the solution heated at 85 °C for 3 days. Transparent pale yellow prismatic crystals were formed. Yield of the reaction was ca. 60% based on TPPBDA ligand. Elemental analysis calcd. for C₅₂H₄₁CdN₄O₅: C, 68.31; H, 4.52; N, 6.13, Found: C, 68.24; H, 4.49; N, 6.18. The IR spectrum of the corresponding complex is shown in the Figure S8.

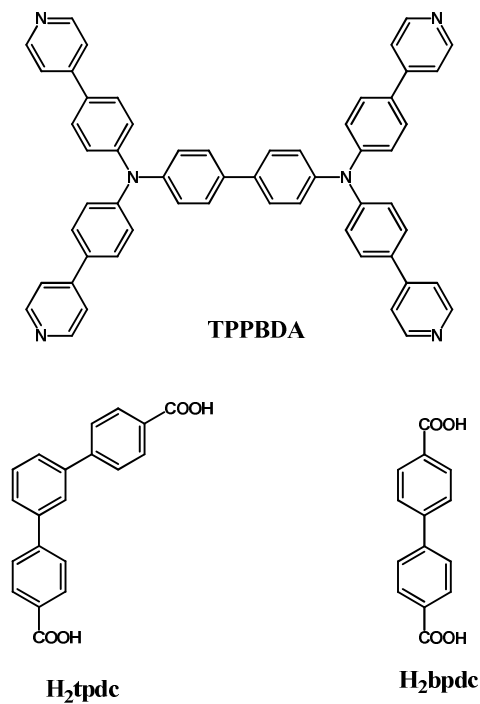
Synthesis of complex 3: A mixture of H₂O/DMA/CH₃CN containing the TPPBDA (79.6 mg, 0.1 mmol), H₂bpdc (48.4 mg, 0.1 mmol) and Zn(NO₃)₂·6H₂O (59.4 mg, 2

mmol) was mixed in a Teflon vessel within the autoclave. The vessel was heated at 85 °C for 72 h and then cooled to room temperature. The yellow crystals were obtained. Yield of the reaction were ca. 60% based on TPPBDA ligand. Elemental analysis calcd. for $C_{51}H_{55}N_6O_{10}Zn$ (**3**): C, 62.67; H, 5.67; N, 8.60, Found: C, 62.64; H, 5.32; N, 8.58. The IR spectrum of the corresponding complex is shown in the Figure S9.

X-ray Crystallography. Compounds **1** and **3** are unstable in the atmosphere. X-ray crystallographic data of **1** and **3** were collected at room temperature by way of sealing the better single crystals in a quartz tube with mother liquor, X-ray crystallographic data of **2** was collected using epoxy-coated crystals mounted on glass fiber. Crystallographic data were collected on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) using the ω -scan technique. The intensity data were integrated by using the SAINT program.² An empirical absorption correction was applied using the SADABS program.³ The structures were solved by direct method and the nonhydrogen atoms were located from the trial structures and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values. The positions of the non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically by using a riding model. The distribution of peaks in the channels of **1** and **3** was chemically featureless to refine, using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining solvent molecules was removed by the SQUEEZE routine in PLATON.⁴

Crystal data: for **1**: $[C_{72}H_{82}CdN_{10}O_8]$, $M_r = 1327.91$, orthorhombic, space group $Pbcn$, $a = 28.5893(10)$, $b = 41.9618(15)$, $c = 12.0642(4)$ Å, $V = 14472.9(9)$ Å³, $Z = 8$, $D_c = 1.219$ g·cm⁻³, $F(000) = 5605$, $\mu(\text{Mo-K}\alpha) = 0.360$ mm⁻¹, $T = 293(2)$ K, 13430 reflections measured, 7506 independent reflections ($R_{\text{int}} = 0.0798$), final $R_1 [I > 2\sigma(I)] = 0.0448$ and final $wR_2 = 0.1263$. For **2**: $[C_{52}H_{41}CdN_4O_5]$, $M_r = 914.29$, monoclinic, space group $P2_1/c$, $a = 8.8305(6)$, $b = 19.9787(15)$, $c = 25.7425(19)$, $\beta = 96.8210(10)$, $V = 4509.4(6)$ Å³, $Z = 4$, $D_c = 1.347$ g·cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.536$ mm⁻¹, $T = 296(2)$ K, 25124 reflections measured, 5471 independent reflections ($R_{\text{int}} = 0.0742$), final R_1

$[I > 2\sigma(I)] = 0.0431$ and final $wR_2 = 0.1072$. For **3**: $[C_{51}H_{55}N_6O_{10}Zn]$, $M_r = 977.42$, orthorhombic, space group $Pnna$, $a = 13.7355(12)$, $b = 40.624(4)$, $c = 20.8303(19)$, $V = 11623.1(19) \text{ \AA}^3$, $Z = 8$, $D_c = 1.117 \text{ g}\cdot\text{cm}^{-3}$, $F(000) = 4104$, $\mu(\text{Mo-K}\alpha) = 0.477 \text{ mm}^{-1}$, $T = 293(2) \text{ K}$, 83426 reflections measured, 6022 independent reflections ($R_{\text{int}} = 0.1016$), final $R_1 [I > 2\sigma(I)] = 0.0782$ and final $wR_2 = 0.2045$.



Scheme S1. The dicarboxylic acid and TPPBDA ligand.

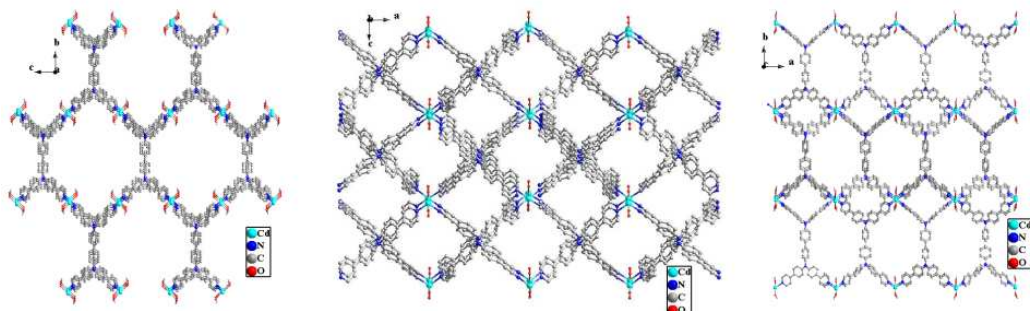
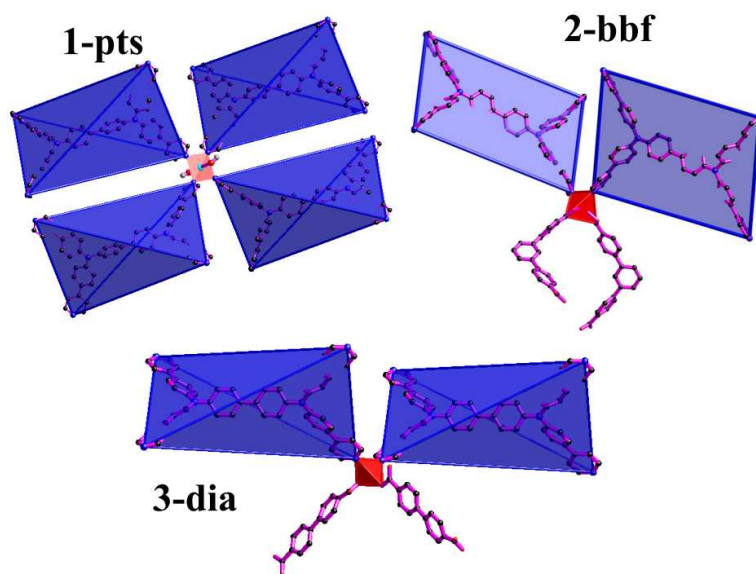


Figure S1. A perspective of 3D channels in net **1**.



Scheme S2 Different configurations of TPPBDA ligand and metal center result in the formation of different network topologies in compounds **1-3**.

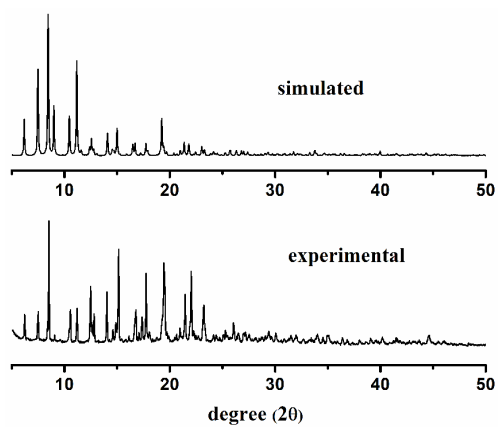


Figure S2 Powder X-ray diffraction patterns of complex **1**

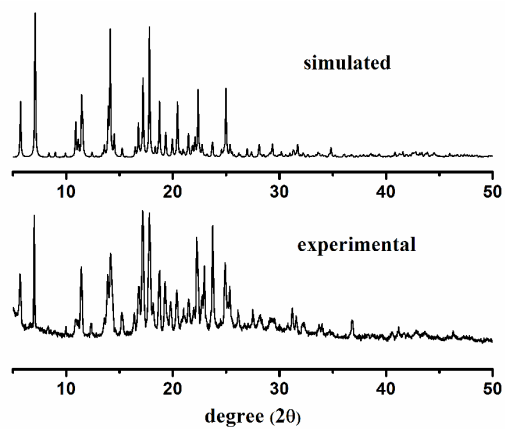


Figure S3 Powder X-ray diffraction patterns of complex 2

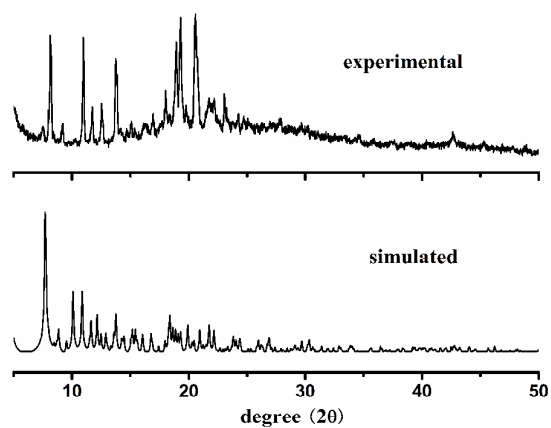


Figure S4 Powder X-ray diffraction patterns of complex 3

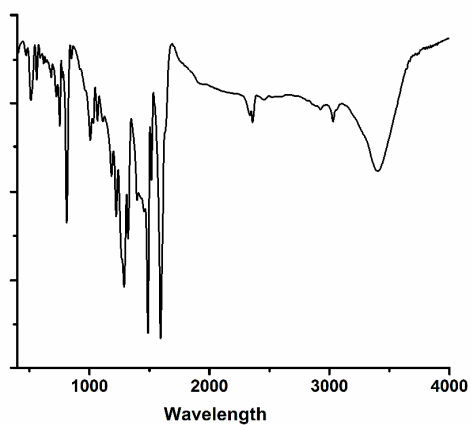


Figure S5 IR spectra of complex 1

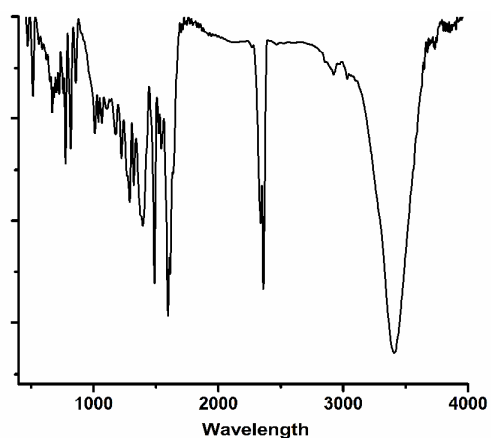


Figure S6 IR spectra of complex **2**

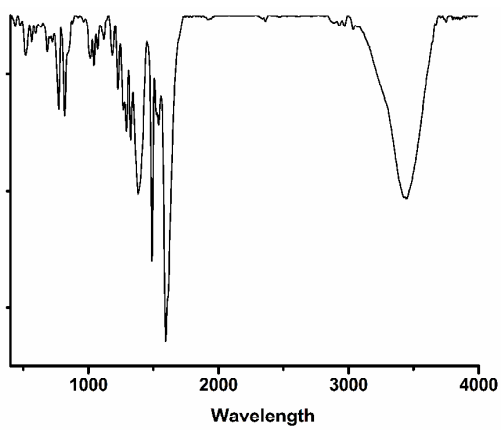


Figure S7 IR spectra of complex **3**

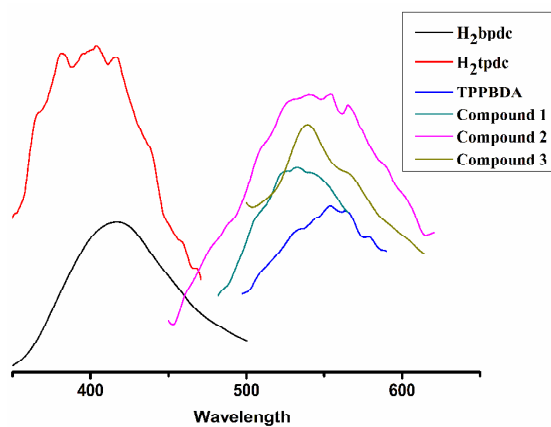


Figure S8 Solid-state photoluminescent spectra of **1-3** and ligands at room temperature.

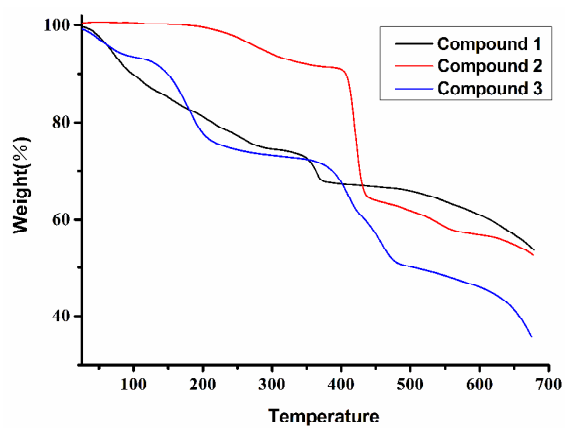


Figure S9 The TGA diagrams of complexes **1-3**.

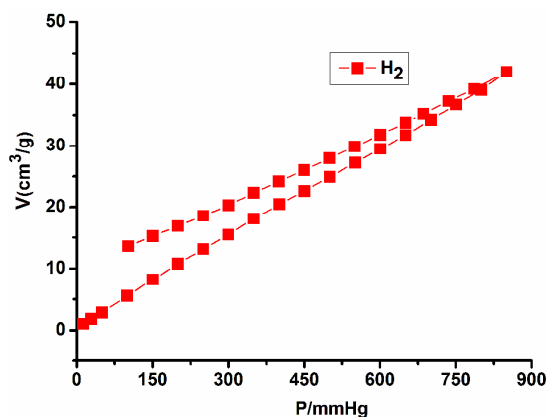


Figure S10 H₂ adsorption and desorption isotherms measured at 77 K.

Analysis of Gas Sorption Isotherms.

The CO₂ adsorption isotherms was fitted using the Langmuir-Freundlich equation according to the literature. The Langmuir-Freundlich model gives a better fit over the entire measured pressure range and predict the adsorption capacity of the compound **2** at saturation. The surface area of compound **2** was determined by fitting the nitrogen isotherm to the BET equation and the enthalpy of CO₂ adsorption was calculated using a modified version of the Clausius-Clapeyron equation.

$$\ln \frac{P_1}{P_2} = \Delta H_{ads} \times \frac{T_2 - T_1}{R \times T_1 \times T_2} \quad (I)$$

where T₁ and T₂ are the two isotherm temperatures (273 and 298 K), P₁ and P₂ are pressures at T₁ and T₂, respectively, for a given uptake, and R is the universal gas constant (R = 8.3147 J / (K· mol)). The equation (I) can be used to calculate the enthalpy of adsorption of a gas as a function of the quantity of gas adsorbed. Pressure as a function of the amount of gas adsorbed was determined using the Langmuir-Freundlich fit for the isotherms.

$$\frac{q}{q_m} = \frac{b p^{(1/t)}}{1 + b p^{(1/t)}} \quad (II) \quad \text{where } q = \text{the amount adsorbed}$$

q_m = the amount adsorbed at saturation

p = pressure

b and t = constants.

Equation (II) rearranges to:

$$p = \left(\frac{q / q_m}{b - bq / q_m} \right)^t \quad (\text{III})$$

$$\Delta H_{ads} = \frac{RT_1 T_2}{T_2 - T_1} \times \ln \frac{\left(\frac{q / q_{m1}}{b_1 - b_1 q / q_{m1}} \right)^{t_1}}{\left(\frac{q / q_{m2}}{b_2 - b_2 q / q_{m2}} \right)^{t_2}} \quad (\text{IV})$$

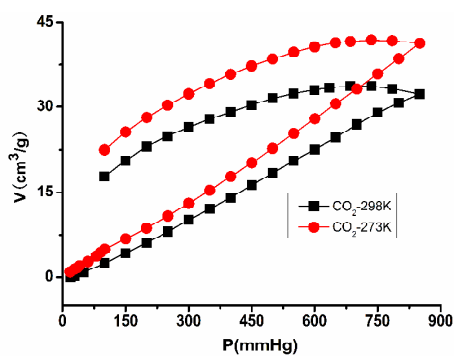


Figure S11 CO₂ adsorption isotherms in compound **2** at 273K (red) and 298 K (black).

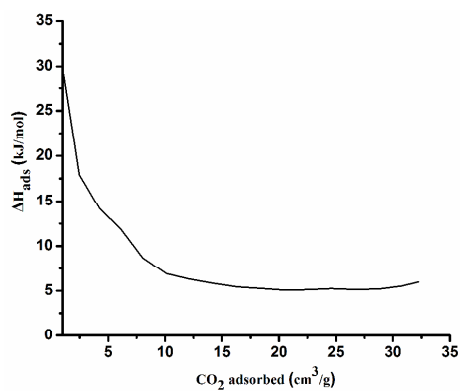


Figure S12 The isosteric heat of adsorption (Q_{st}) using CO₂ sorption isotherms measured at two temperatures (273K and 298K).

Table S1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1** - **3**

Complex 1			
Cd1-N1	2.358(2)	Cd1-N4 ^b	2.359(2)
Cd1-N5	2.349(2)	Cd1-N8 ^a	2.348(3)
Cd1-O1	2.427(3)	Cd1-O2	2.356(3)
N1- Cd1-N4 ^b	176.48(9)	N1- Cd1-N5	88.88(9)
N1- Cd1- N8 ^a	91.74(9)	N1- Cd1-O1	89.84(9)
N1- Cd1-O2	90.86(10)	N4 ^b - Cd1-N5	87.65(9)
N4 ^b - Cd1- N8 ^a	91.68(9)	N4 ^b - Cd1-O1	90.80(9)
N4 ^b - Cd1-O2	88.43(10)	N5 - Cd1- N8 ^a	175.63(11)
N5 - Cd1- O1	91.47(9)	N5 - Cd1- O2	87.47(9)
N8 ^a - Cd1- O1	92.86(10)	N8 ^a - Cd1- O2	88.19(10)
O1 - Cd1- O2	178.72(9)		
Complex 2			
Cd1-N2	2.273(3)	Cd1-N3 ^a	2.311(3)
Cd1-O1	2.430(3)	Cd1-O2	2.308(3)
Cd1-O3 ^b	2.377(3)	Cd1-O4 ^b	2.288(3)
N2- Cd1-N3 ^a	88.08(11)	N2- Cd1- O1	113.94(11)
N2- Cd1-O2	95.44(12)	N2- Cd1- O3 ^b	95.19(11)
N2- Cd1- O4 ^b	145.83(13)	N3 ^a - Cd1- O1	86.98(11)
N3 ^a - Cd1- O2	138.84(12)	N3 ^a - Cd1- O3 ^b	120.76(12)
N3 ^a - Cd1- O4 ^b	93.13(11)	O1 - Cd1- O2	54.17(10)
O1 - Cd1- O3 ^b	141.03(10)	O1 - Cd1-O4 ^b	100.21(11)
O2 - Cd1- O3 ^b	99.81(11)	O2 - Cd1-O4 ^b	105.58(13)

O3^b - Cd1-O4^b 55.33(10)

Complex 3

Zn1-N1	2.0501	Zn1- N4 ^a	2.057(6)
Zn1-O1	1.9491	Zn1-O3 ^b	1.933(3)
N1- Zn1-N4 ^a	108.7	N1- Zn1-O1	106.0
N1- Zn1-O3 ^b	106.5	N4 ^a - Zn1-O1	122.6
N4 ^a - Zn1- O3 ^b	107.4	O1- Zn1- O3 ^b	104.6

Symmetry Codes: for **1**: a = 0.5 + x, 0.5 + y, 0.5 - z. b = 0.5 + x, -0.5 + y, 0.5 - z. for **2**: a = -x, 0.5 + y, 1.5 - z; b = 1 - x, -0.5 + y, 0.5 - z. for **3**: a = 1.5 - x, 2 - y, -1 + z; b = 0.5 + x, 1.5 - y, -0.5 + z.

References

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