Electronic Supplementary Material for

Metal-Organic Frameworks Constructed from Mixed Infinite Inorganic Units and Adenine

Yuna Song,[a] Xinbo Yin,[b] Binbin Tu,[c] Qingqing Pang,[c] Haiwei Li,[a] Xiaoqian Ren,[a] Bo Wang*[a] and Qiaowei Li*[c]

[a]Key Laboratory of Cluster Science, Ministry of Education of China, School of Chemistry, Beijing Institute of Technology, 5 Zhongguancun South Street, Beijing 100081, China. Email: bowang@bit.edu.cn

[b]Laboratory of Advanced Materials, Fudan University, 2205 Songhu Road, Shanghai 200438, China.

[c]Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China. Email: qwli@fudan.edu.cn

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1 Materials and Methods

All the chemicals were commercially available reagent of analytical grade and used without further purifications. IR spectra were recorded on an IR Prestige-21 spectrophotometer as KBr pellets between 4000 and 450 cm^{-1}. Thermogravimetric analysis (TGA) was carried out using a TA Q600 analyzer from room temperature to 800 °C under air atmosphere. Powder X-ray diffraction (PXRD) data were collected on a Bruker AXS D8 Advance diffractometer operated at 1600 W power (40 kV, 40 mA) using Cu $K\alpha_1$ radiation. Simulated PXRD patterns were calculated using Mercury 3.0 from the corresponding single crystal structural data. Fluorescence spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer at room temperature.

2 Synthesis of Metal-Organic Frameworks (MOFs)

$Cd(HAd)_2Cl_2$ (**1**; HAd = adenine): HAd (5.4 mg, 0.04 mmol) and $CdCl_2{\cdot}2.5H_2O$ (9.1 mg, 0.04mmol) were mixed with *N*,*N*-dimethylformamide/ EtOH/ H_2O (1:1:1, 2 mL) in a 5-mL vial. After being sonicated for 10 minutes at room temperature, the vial was capped tightly and placed into an isothermal oven at 60 °C for 3 d. Colorless needle-shaped crystals were obtained. Yield: 85% based on $CdCl_2{\cdot}2.5H_2O$. Elemental Analysis: calcd. N 34.88, C 24.47, H 2.21; found N 34.47, C 24.54, H 2.74. IR data (KBr): ν = 3307(w), 3236(w), 3105(br), 1701(vs), 1616(vs), 1589(s), 1427(w), 1352(s), 1300(s), 1232(m), 1139(s), 1089(w), 1022(w), 916(vw), 790(w), 729(m), 677(w), 605(w), 601(m), 551(w).

$Cd_3(Ad)_2(OAc)_4(EtOH)_2$ (**2**): This structure was synthesized by a reaction condition similar to that of **1**, except with the replacement of $CdCl_2{\cdot}2.5H_2O$ by $Cd(OAc)_2{\cdot}2H_2O$ (10.6 mg, 0.04 mmol). Colorless block crystals were collected. Yield: 76% based on $Cd(OAc)_2{\cdot}2H_2O$. Elemental Analysis: calcd. N 15.02, C 28.33, H 3.43; found N 15.05, C 27.93, H 3.16. IR data (KBr): ν = 3317(w), 3111(br), 2977(w), 1675(s), 1609(s), 1561(vs), 1470(w), 1398(s), 1344(w), 1318(w), 1276(m), 1221(s), 1150(s), 1044(m), 988(vw), 896(w), 799(m), 736(w), 665(s), 620(w), 578(m), 550(w).

$HCd_4Cl(Ad)_2Cl_6$ (**3**): The same solid mixture and reaction procedure as **1** were used in the synthesis of **3**, and the reaction temperature was elevated to 110 °C instead. Colorless rod-like

crystals were collected. Yield: 57% based on HAd. Elemental Analysis: calcd. N 14.48, C 12.42, H 0.94; found N 14.93, C 13.38, H 1.93. IR data (KBr): ν = 3506(w), 3414(br), 3340(w), 1656(vs), 1604(vs), 1544(w), 1504(w), 1469(m), 1406(s), 1340(w), 1319(w), 1273(w), 1215(s), 1145(w), 1028(w), 856(w), 786(m), 729(w), 638(m), 557(w).

3 Single Crystal Structure Determinations

Crystals of **1**, **2** and **3** coated with Paratone oil on a Cryoloop pin were mounted on a Bruker SMART Apex II single-crystal x-ray diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo $K\alpha$ radiation (λ = 0.71073 Å). The crystal structures were solved by Direct Methods and refined on F^2 by full-matrix least-squares using the Shelxtl-97 program systems. Details of crystal data, data collection, structure solution, and refinement are given in Table S1, S2, and S3. CCDC 974455-974457 contains the crystallographic data for these structures. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

For structure **1**: The model shows relatively high R factor, due to the low quality of the crystals. Multiple crystals from different reaction conditions have been tried, and the quality improvement was not obvious. The crystals are in thin needle shape. A large residue peak can be found in the square center formed by Cd and Cl. This place is not possible for any atom due to the close distance to Cd and Cl. Splitting atoms such as C5 does not lead to stable refinement. Nevertheless, the infinite chain of CdCl can be clearly located.

In structure **3**: Very little remaining electron density was left, because of the highly disordered nature of solvent molecules. Cations in the pores could not be located. The model shows relatively high R factor, due to the low quality of the crystals. ISOR was used for C1 with relative high ADP max/min ratio. Some void space remains in the structure, even after SQUEEZE was applied.

Table S1. Crystal data and structure refinement for **1**.

Identification code	**1**	
Empirical formula	C10 H10 N10 Cd Cl2	
Formula weight	453.58	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P*21/*c*	
Unit cell dimensions	a = 3.694(4) Å	α = 90.00°
	b = 8.184(9) Å	β = 94.49(0)°
	c = 23.62(3) Å	γ = 90.00°
Volume	712.1(14) $Å^3$	
Z	2	
Density (calculated)	2.115 Mg/m^3	
Absorption coefficient	1.925 mm^{-1}	
F(000)	444	
Crystal size	0.35 x 0.02 x 0.02 m^3	
Theta range for data collection	1.73 to 26.41°	
Index ranges	-4 <= h <= 4, -7 <=k<= 10, -29 <=l<= 25	
Reflections collected	3837	
Independent reflections	1451 [R(int) = 0.1500]	
Completeness to theta = 26.41°	99.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1451 / 6 / 107	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.1511, wR2 = 0.4242	
R indices (all data)	R1 = 0.2346, wR2 = 0.4467	
Largest diff. peak and hole	4.760 and -1.119 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **2**.

Identification code	**2**	
Empirical formula	C22 H32 N10 O10 Cd3	
Formula weight	933.78	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P*21/*c*	
Unit cell dimensions	a = 9.1560(12) Å	α = 90.00°
	b = 12.1449(16) Å	β = 95.271(2)°
	c = 14.1202(19) Å	γ = 90.00°
Volume	1563.5(4) $Å^3$	
Z	2	
Density (calculated)	1.983 Mg/m^3	
Absorption coefficient	2.089 mm^{-1}	
F(000)	916	
Crystal size	0.15 x 0.05 x 0.05 mm^3	
Theta range for data collection	1.95 to 21.76°	
Index ranges	-7 <=h<=11, -15 <=k<=15, -17<=<=17	
Reflections collected	8415	
Independent reflections	3187 [R(int) = 0.0699]	
Completeness to theta = 21.76°	99.7 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3187 / 1 / 212	
Goodness-of-fit on F^2	0.487	
Final R indices [I>2sigma(I)]	R1 = 0.0294, wR2 = 0.0726	
R indices (all data)	R1 = 0.0467 , wR2 = 0.0817	
Largest diff. peak and hole	0.658 and -0.446 $e.Å^{-3}$	

Table S3. Crystal data and structure refinement for **3**.

Identification code	**3**	
Empirical formula	C10 H8 Cd4 Cl7 N10	
Formula weight	966.01	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbam*	
Unit cell dimensions	a = 14.857(5) Å	α = 90°
	b = 23.615(9) Å	β = 90°
	c = 3.7317(13) Å	γ = 90°
Volume	1309.2(8) $Å^3$	
Z	2	
Density (calculated)	2.450 Mg/m^3	
Absorption coefficient	3.938 mm^{-1}	
F(000)	898	
Crystal size	0.05 x 0.02 x 0.02 mm^3	
Theta range for data collection	2.19 to 20.47°	
Index ranges	-18 <=h<=15, -29 <=k<=24, -4 <=l<=4	
Reflections collected	6994	
Independent reflections	1562 [R(int) = 0.1426]	
Completeness to theta = 20.47°	100 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1562 / 6 / 95	
Goodness-of-fit on F^2	0.854	
Final R indices [I>2sigma(I)]	R1 = 0.0918, wR2 = 0.2457	
R indices (all data)	R1 = 0.1518, wR2 = 0.2693	
Largest diff. peak and hole	1.767 and -1.960 $e.Å^{-3}$	

4 X-ray Powder Diffraction of the MOFs

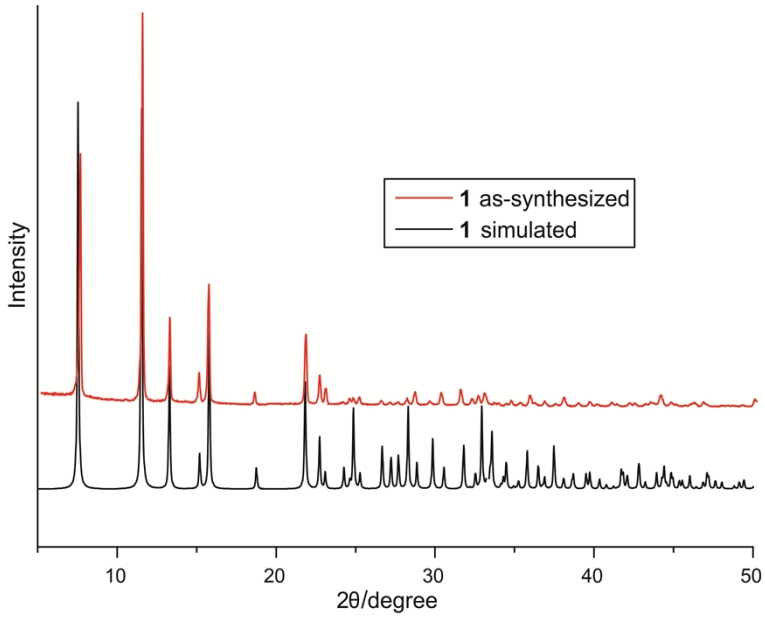

Fig. S1. XRD pattern for the as-synthesized **1**, compared with simulated pattern calculated from single crystal data.

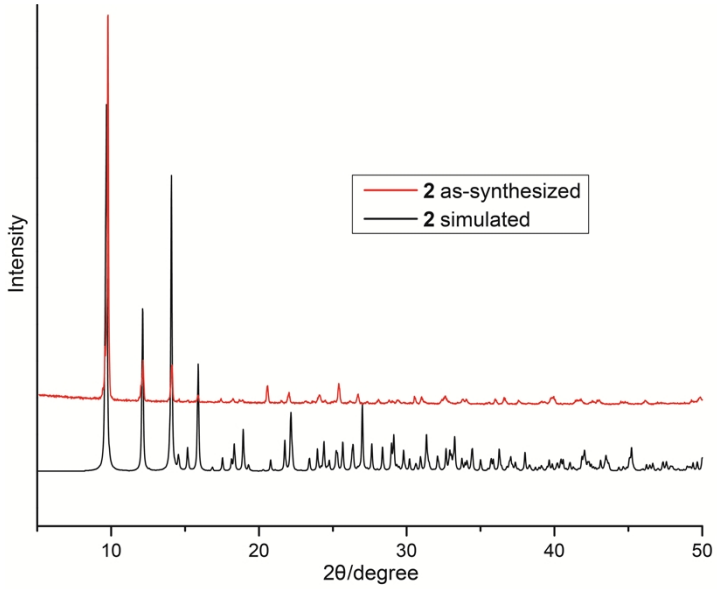

Fig. S2. XRD pattern for the as-synthesized **2**, compared with simulated pattern calculated from single crystal data.

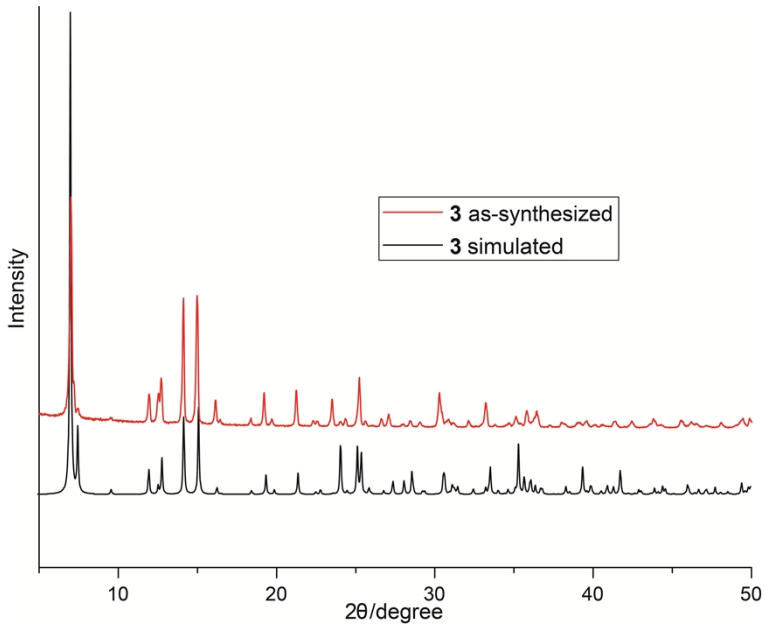

Fig. S3. XRD pattern for the as-synthesized **3**, compared with simulated pattern calculated from single crystal data.

5 Thermogravimetric analysis of the MOFs

The crystals of structure **1-3** were rinsed with DMF for three times, followed by solvent exchange with acetone for three times over one day. The crystals of structure **1-3** were further dried in vacuum at 85 °C over 24 hours.

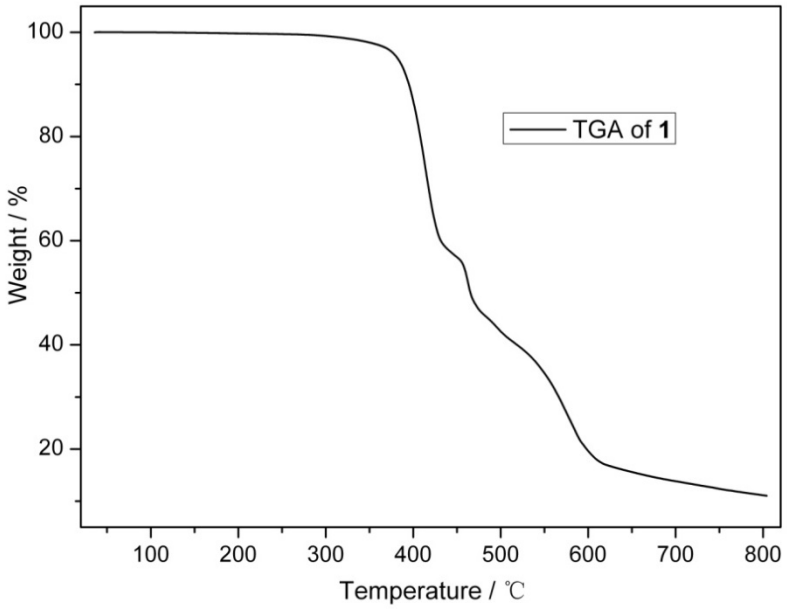

Fig. S4. TGA characterization of **1**.

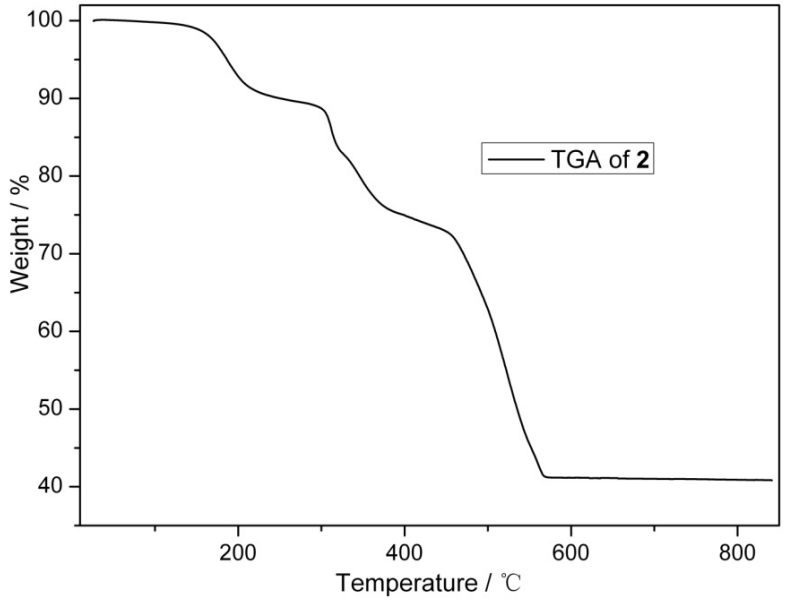

Fig. S5. TGA characterization of **2**.

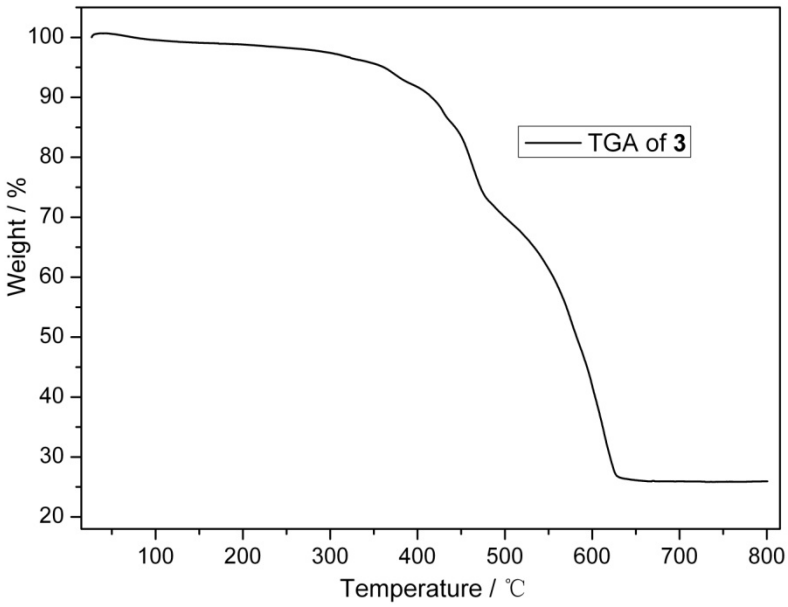

Fig. S6. TGA characterization of **3**.

6 Adsorption Isotherm of the MOFs

Before the isotherm measurement, structure **3** was rinsed with DMF for three times, followed by solvent exchange with acetone for three times over one day. The crystals of structure **3** were further dried in vacuum at 100 °C over 24 hours.

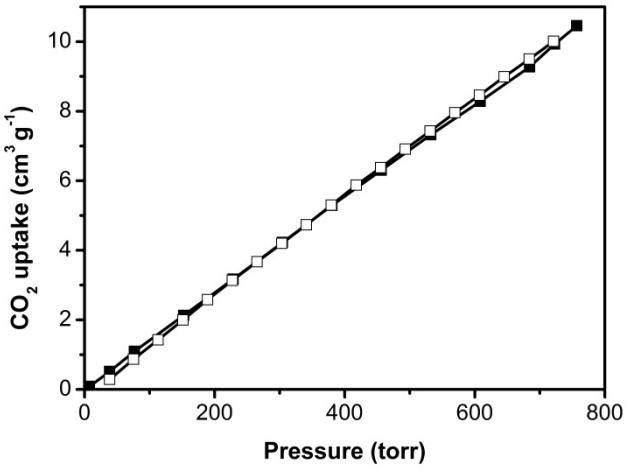

Fig. S7. Low pressure CO_2 adsorption isotherm of structure **3** at 273 K. Adsorption, filled squares; desorption, open squares.