Supporting Information

Conversion of Nonporous Helical Cadmium Organic Framework to a Porous Form

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Materials and physical measurements: All reagents were commercially available and used without further purification. Infrared spectra were obtained from KBr pellets on a Bruker TENSOR 27 Fourier transformation infrared spectrometer in the 400-4000 cm^{-1} region. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/M-2200T automated diffractometer. The luminescent spectra for the solid state were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5.0 nm. Thermal analyses (under oxygenated atmosphere, heating rate of 5 °C/min) were carried out in a Labsys NETZSCH TG 209 Setaram apparatus.

Crystallographic Studies: X-ray diffraction data were collected on a Bruker Apex II diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 298 K. Absorption corrections were applied by using multiscan program SADABS. All

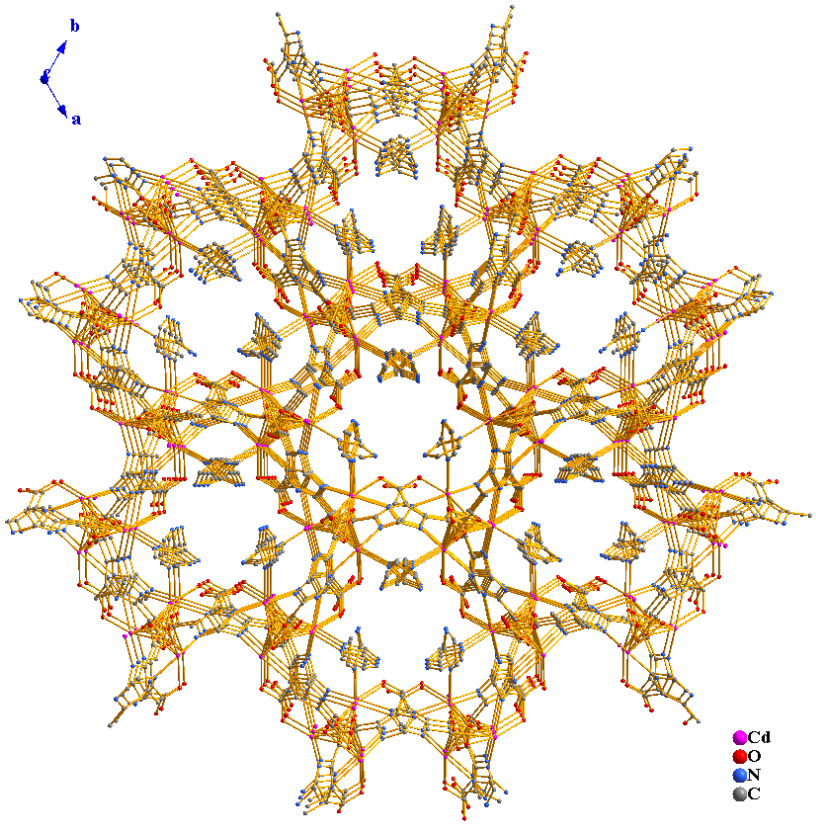
the structures were solved by direct methods and refined with full-matrix least-squares technique using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms on organic ligands were generated by the riding mode (C-H 0.96 Å), and hydrogen atoms on water molecules were located from difference maps.

Synthesis of compound [Cd(HImDC)(Im)]$_n$ (1). A mixture of H_3ImDC (0.078 g, 0.50 mmol), Im (0.066 g, 1 mmol), and $Cd(NO_3)_2$ (0.122 g, 0.5 mmol), deionized water 10 mL were sealed in 20 mL Teflon-lined stainless steel vessel and heated to about 170 ºC for 72 h, and then cooled to room temperature (at a rate of 0.5 ºC min^{-1}). The pH values of the solution before and after reactions are ca. 6, respectively. The colorless crystals obtained were washed twice with Et_2O to give pure product with the formula $C_8H_6CdN_4O_4$ and dried in air.C, H, N analysis (%) for the compound: calcd: C 28.69, H 1.79, N 16.74; found: C 28.61, H 1.82, N 16.83. IR (KBr, cm^{-1}): ν 3438 (br, m), 3168 (br, m), 3124 (w), 2952 (w), 2716 (w), 1672(m), 1541 (vs), 1491(vs), 1436 (s), 1328(m), 1256(s), 1111(m), 1070(s), 1009 (m), 941 (w), 873 (w), 840 (w), 786(w), 759(m), 658(m), 622(w), 526(w).

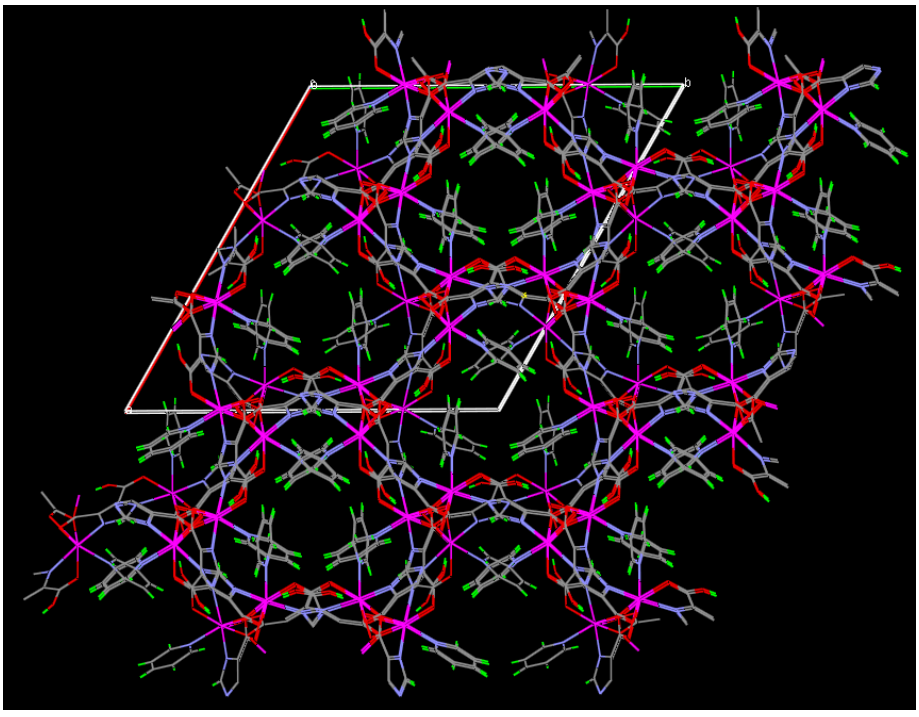
Synthesis of compound [Cd(HImDC)(Py)]$_n$ (2). Similar to the method for the preparation of compound **1**, compound **2** can not be obtained. Accordingly, compound **2** was only synthesised by the colorless single crystals of compound **1** being immersed in pyridine under refluxing for 5 hours, during the process the crystals was gradually dissolved. When temperature decreased to room temperature at 10 °C h^{-1} and pale yellow single crystals of **2** with the formula $C_{10}H_7CdN_3O_4$ were obtain and dried in air. C, H, N analysis (%) for the compound: calcd: C 34.72, H 2.03, N 12.15; found: C 34.63, H 2.11, N 12.23. IR (KBr, cm^{-1}): ν 3448 (br, s), 2968 (br, s), 2334 (m), 1672(m), 1574 (vs), 1477(vs), 1379 (s), 1308(m), 1254 (m), 1238 (w), 1110(s), 999 (m), 945 (w), 862(m), 829 (w), 814 (w), 793 (w), 783(m), 663(m), 521(w), 491 (w).

Figure S1 A view of 3D metal-organic open framework in compound [Cd(HImDC)(Im)]n in *ab* plane for **1** (a) and **2** (b), respectively. (c) A 8^3 topology of the three-connected network of the complex [Cd(HImDC)(Im)]n viewed along the *a* axis.

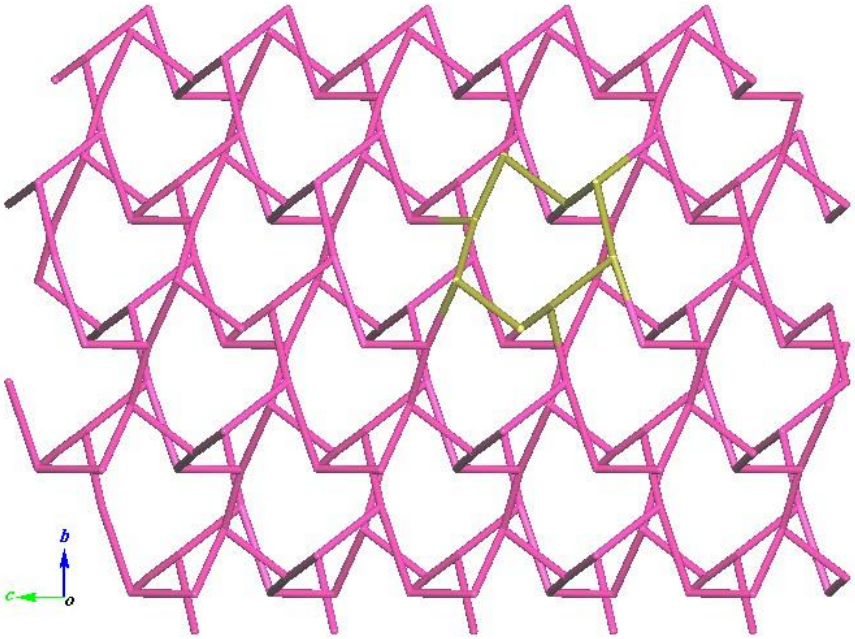
(**a**)

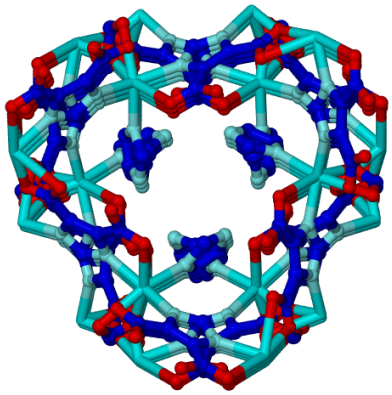


(**b**)

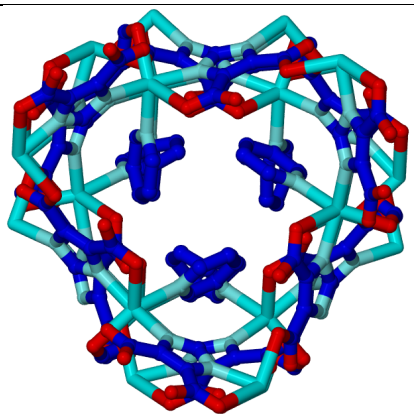


(c)

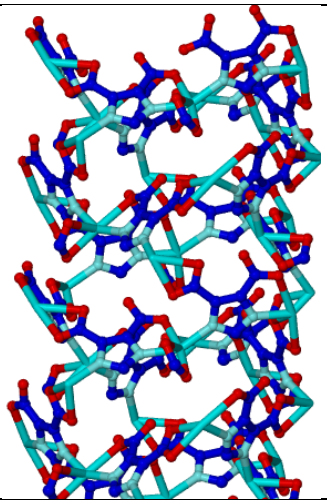




Complex 1



Complex 2



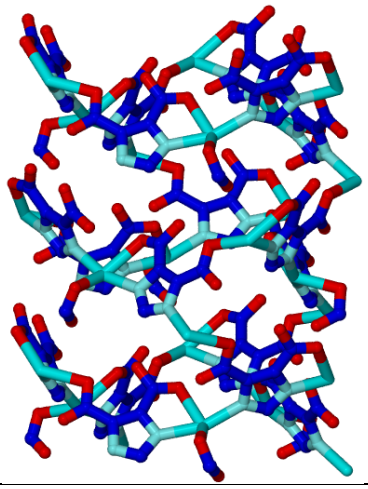


Table **S1** Crystal data and structure refinement for compounds **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_8H_6N_4O_4Cd$	$C_{10}H_7N_3O_4Cd$
Formula weight	334.57	345.59
Temperature	298(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Trigonal	Trigonal
Space group	*R*3*c*	*R*3*c*
Unit cell dimensions		
a (Å)	20.6556(6)	21.1266(16)
b (Å)	20.6556(6)	21.1266(16)
c (Å)	13.3915(7)	13.967(2)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
V (Å^3)	4948.1(3)	5398.9(10)
Z	18	18
ρ (cald.) (mg m^{-3})	2.021	1.913
μ (m^{-1})	1.995	1.830
F(000)	2916	3024
Crystal size (mm)	0.26 × 0.22 × 0.15	0.22 × 0.16 × 0.11
θ range for data collection (°)	1.97 to 25.48	1.93 to 25.16
h/k/l (max, min)	-21,24/-24,18/-16,12	-24,14/-24,25/-16,16
Reflections collected	8347	8802
Unique	1913[R(int) = 0.0283]	2151[R(int) = 0.0235]
Completeness to θ = 27.13	100 %	100 %
Absorption correction	empirical	empirical
Max. and min. transmission	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data / restraints / parameters	1913 / 1 / 155	2151 / 1 / 164
Goodness-of-fit on F^2	1.048	1.043
Final *R*1[a],*wR*2 [b] indices [$I > 2\sigma(I)$]	0.0180, 0.0373	0.0.0168, 0.0407
*R*1, *wR*2 indices (all data)	0.0196, 0.0380	0.0177, 0.0413
Largest diff. Peak and hole (e Å^{-3})	0.326/ -0.209	0.256/-0.481

[a] $R = \Sigma||F_o|-|F_c||/S|F_o|$. [b] $wR = [\Sigma w(|F_o|^2-|F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2)+(0.0214P)^2+4.1856P]$ for **1** and $w = 1/[\sigma^2(F_o^2)+(0.0213P)^2+3.8889P]$ for **2**, where $P = (F_o^2 + 2F_c^2)/3$.

Table S**2**. Selected atomic distances (Å) and bond angles (°) for compounds **1** and **2**[a].

		1	
Cd(1)-N(2)#1	2.180(3)	N(1)-Cd(1)-N(3)	102.63(13)
Cd(1)-N(1)	2.191(3)	N(2)#1-Cd(1)-O(4)#2	101.66(12)
Cd(1)-N(3)	2.295(4)	N(1)-Cd(1)-O(4)#2	99.28(12)
Cd(1)-O(4)#2	2.404(3)	N(3)-Cd(1)-O(4)#2	95.21(12)
Cd(1)-O(3)#2	2.553(3)	N(2)#1-Cd(1)-O(3)#2	97.26(12)
Cd(1)-O(1)	2.576(3)	N(1)-Cd(1)-O(3)#2	80.99(12)
N(2)#1-Cd(1)-N(1)	151.89(12)	N(3)-Cd(1)-O(3)#2	147.14(12)
N(2)#1-Cd(1)-N(3	93.96(14)	O(4)#2-Cd(1)-O(3)#2	52.29(11)
N(2)#1-Cd(1)-O(1)	88.58(11)	N(1)-Cd(1)-O(1)	68.87(11)
N(3)-Cd(1)-O(1)	90.86(12)	O(4)#2-Cd(1)-O(1)	167.68(10)
O(3)#2-Cd(1)-O(1)	120.12(11)		
		2	
Cd(1)-N(2)#3	2.205(2)	N(2)#3-Cd(1)-N(1)	161.61(9)
Cd(1)-N(1)	2.221(2)	N(2)#3-Cd(1)-O(3)#4	100.67(9)
Cd(1)-N(3)	2.363(3)	N(1)-Cd(1)-O(3)#4	86.43(9)
Cd(1)-O(3)#4	2.322(2)	N(2)#3-Cd(1)-N(3)	88.13(9)
Cd(1)-O(1)	2.526(3)	N(1)-Cd(1)-N(3)	98.28(9)
N(2)#3-Cd(1)-O(1)	93.26(9)	O(3)#4-Cd(1)-N(3)	136.94(10)
N(1)-Cd(1)-O(1)	69.73(8)	O(3)#4-Cd(1)-O(1)	131.40(9)
N(3)-Cd(1)-O(1)	89.35(10)		

[a]Symmetry transformations used to generate equivalent atoms: #1 x-1/3,x-y+1/3,z-1/6; #2 -y+4/3,-x+5/3,z+1/6; #3 -y+1/3,-x+2/3,z+1/6; #4 x-1/3,x-y-2/3,z-1/6.

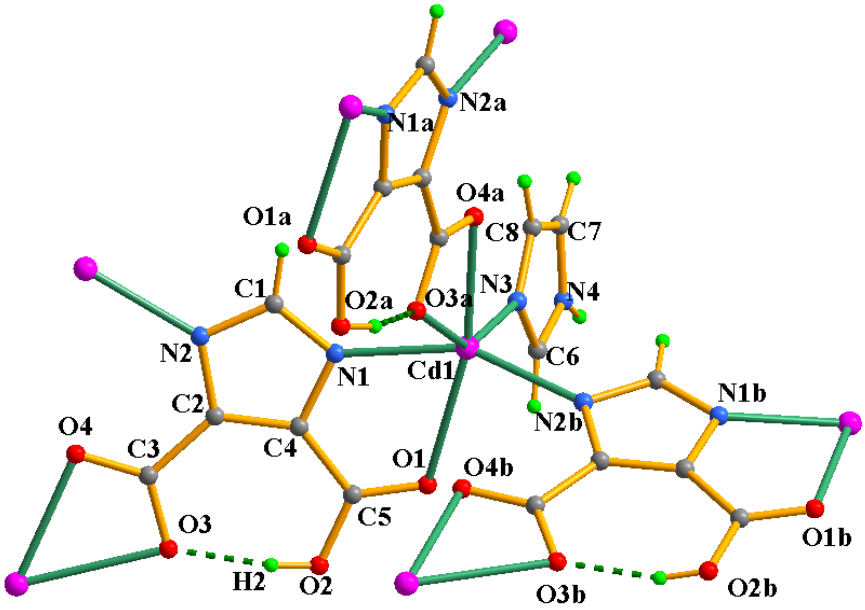
Table **S3** Distances (Å) and angles (°) of hydrogen bonds for the compounds **1**-**2**.

D-H···A	d(H···A)	d(D···A)	□D-H···A
		1	
O(2)-H(2)···O(3)	1.702(2)	2.485(5)	159(6)
N(4)-H(7)···O(1)#1	1.978(2)	2.833(4)	173(6)
		2	
O(2)-H(2)···O(3)	1.720(2)	2.523(3)	164(5)
O1W-H1W···O1W#2	2.163(2)	2.774(3)	132(6)

*Symmetry transformation used to generate equivalent atoms: #1 –y+1,-x+1,-z+1/2; #2 y+1/4,-x+1/4,z+1/4.

Figure S2. The coordination environments of Cd1 in two compounds **1** and **2** with symmetric codes: a) 5/3-x,4/3-y,1/6+z; b) -1/3+x,1/3+x-y,-1/6+z; c) -1/3+x,-2/3+x-y,-1/6+z; d) -1/3-y,2/3-x,1/6+z; e) 2/3-x+y,1/3-x,1/3+z; f) 2/3-y,1/3-x,-1/6+z; g) 1/3+x,-1/3+x-y,1/6+z; h) 1/3-x,-1/3+x-y,-1/3+z.

(a)



(b)

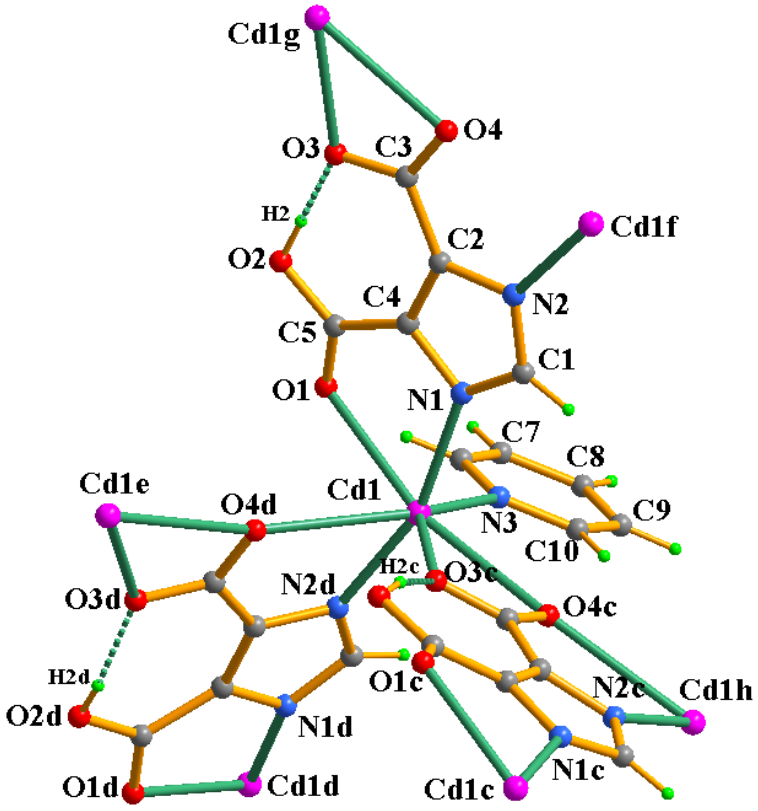


Figure S3. The new coordination mode (μ^3-) of the ligand $HImDC^{2-}$ in compounds **1** and **2**.

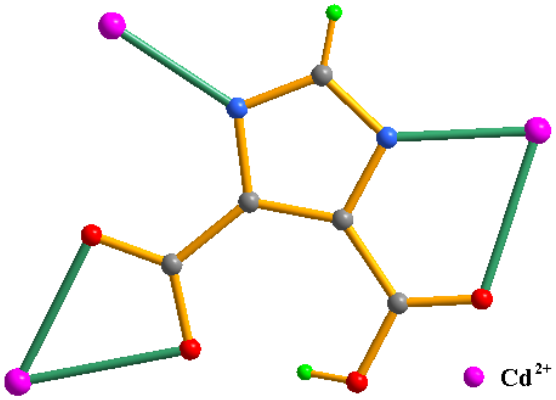
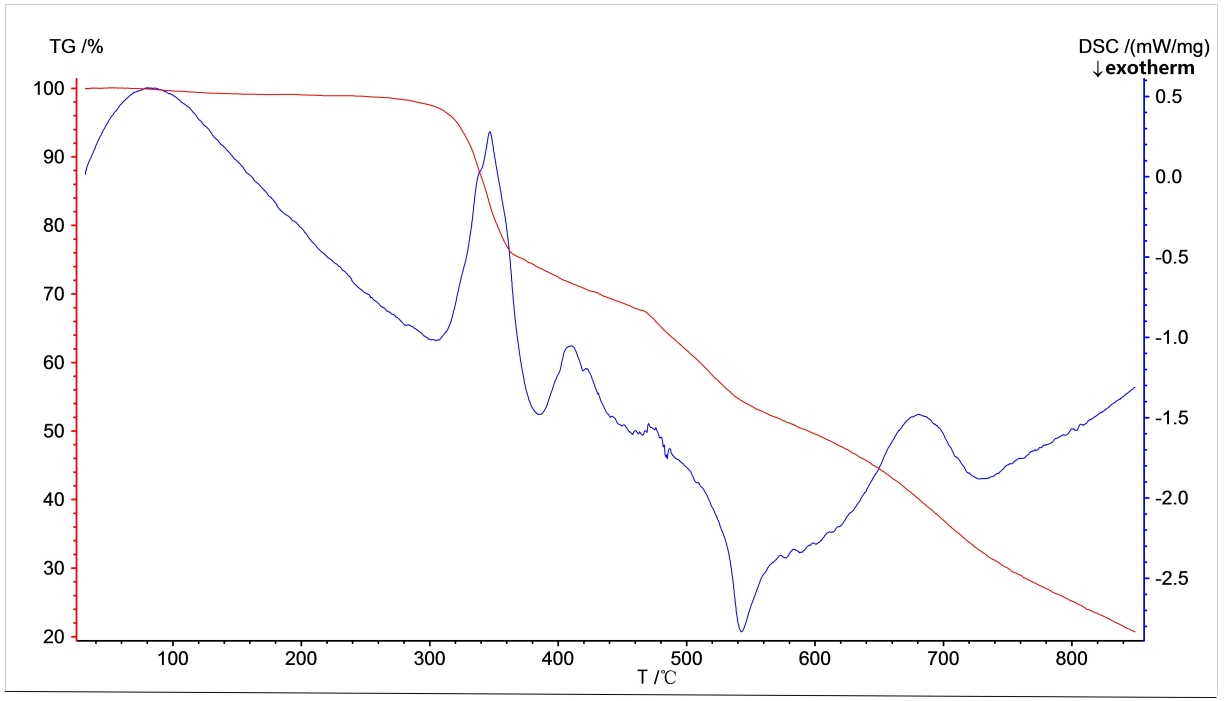


Figure S4. The TG and DSC curves of two compounds: (a) for **1** and (b) for **2**.

(a)



Supplementary Material (ESI) for Chemical Communications
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(b)

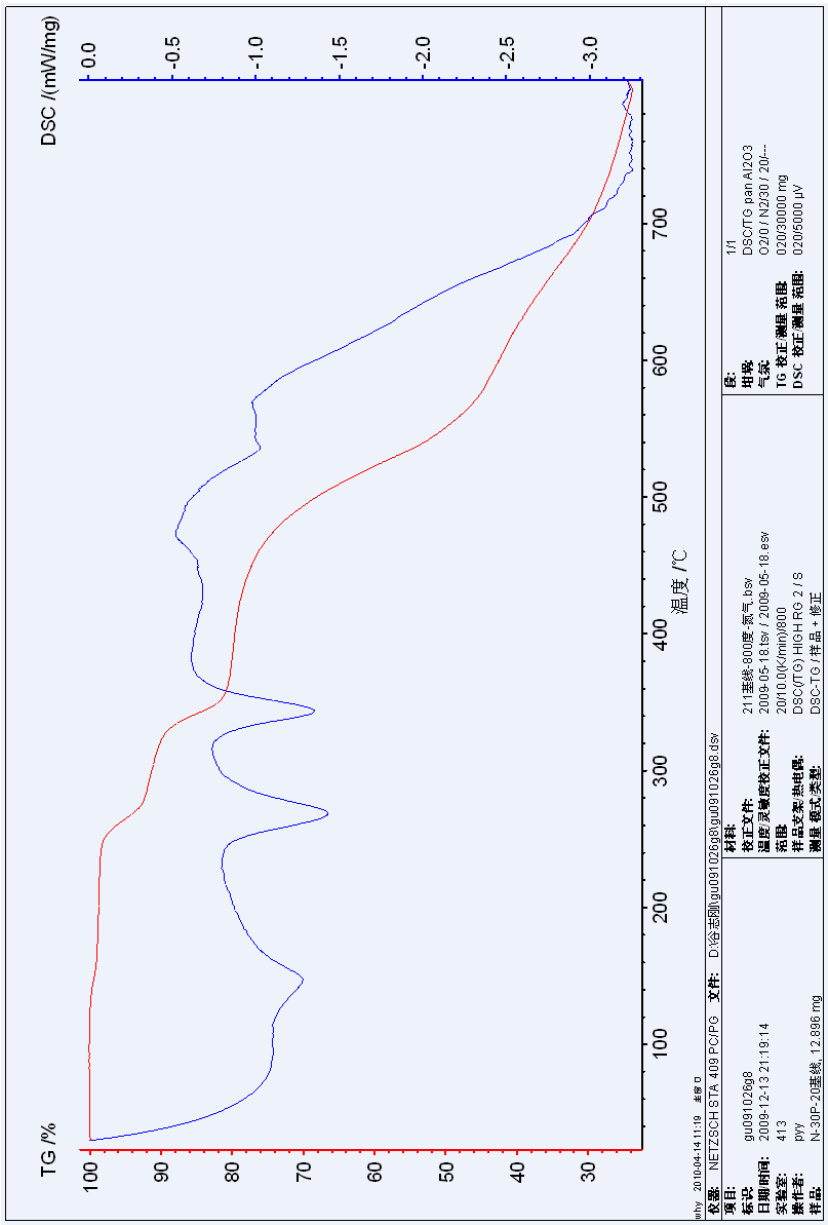
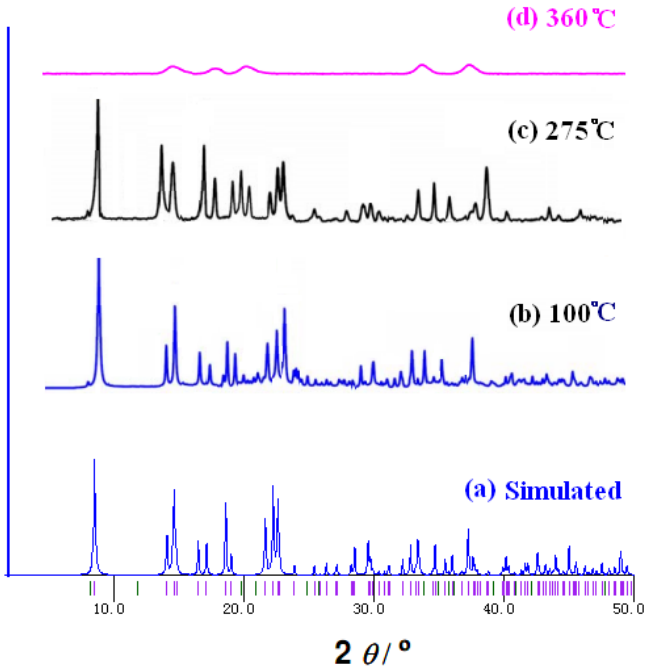
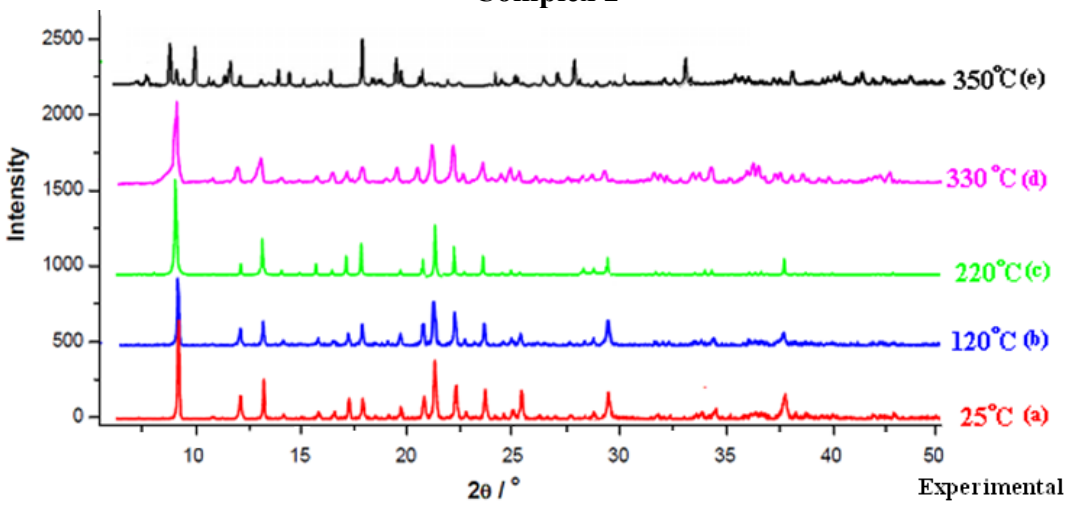

TG /%
DSC /(mW/mg)
温度 /℃
100
90
80
70
60
50
40
30
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
100
200
300
400
500
600
700
仪器: NETZSCH STA 409 PC/PG 文件: D:\徐志刚\gu091026g8\gu091026g8.dsv
项目: 材料:
标识: gu091026g8 校正文件: 211基线-800度_氮气.bsv
日期/时间: 2009-12-13 21:19:14 温度/灵敏度校正文件: 2009-05-18.tsv / 2009-05-18.esv
实验室: 413 范围: 20/10.0(K/min)/800
操作者: pyy 样品支架/热电偶: DSC(/TG) HIGH RG 2 / S
样品: N-30P-20基线, 12.896 mg 测量 模式/类型: DSC-TG /样品 + 修正
坩埚: 1/1
气氛: DSC/TG pan Al2O3
TG 校正 测量 范围: O2/0 / N2/30 / 20/---
DSC 校正 测量 范围: 020/30000 mg
020/5000 µV

Figure S5. Powder X-ray diffraction (PXRD) patterns for complexes **1** and **2** collected at different temperatures.
for complex **1**: (a) Simulated; (b) 100°C; (c)275°C; (d) 360°C.
for complex **2**: (a) 25 °C; (b) 120 °C; (c) 220 °C; (d) 330 °C; (e) 350 °C and simulated at the bottom.

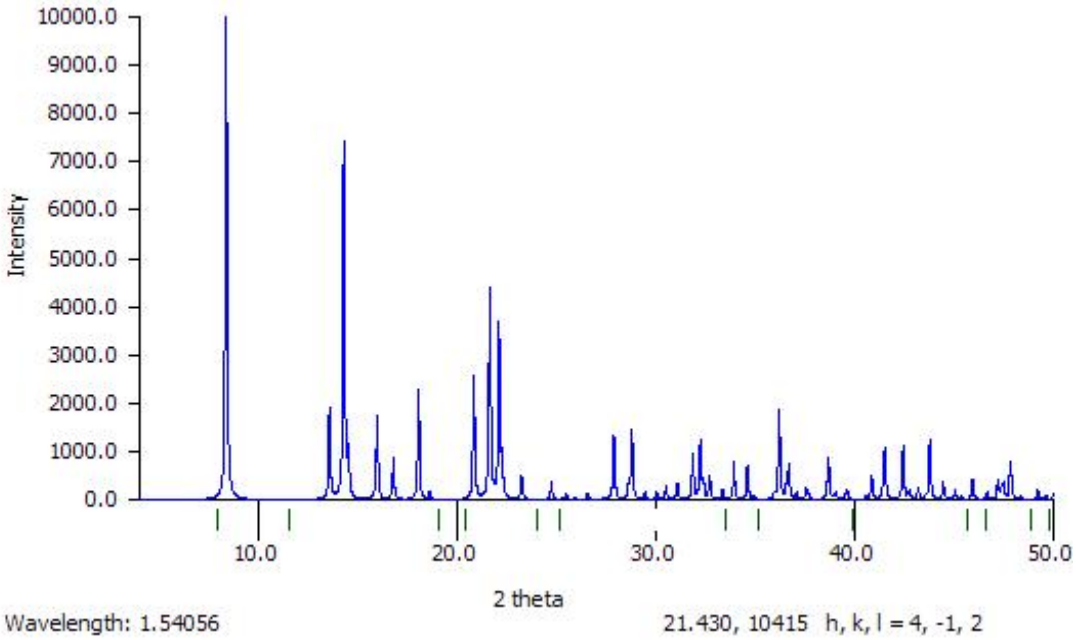
Complex 1



Complex 2



Complex 2 simulated



S6 Report of cif check for two compounds **1** and **2**.

checkCIF/PLATON report (publication check)

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: CCDC 717400

Bond precision: C-C = 0.0060 A Wavelength=0.71073
Cell: a=20.6556(6) b=20.6556(6) c=13.3915(7)
alpha=90 beta=90 gamma=120
Temperature: 298 K

	Calculated	Reported
Volume	4948.1(3)	4948.1(3)
Space group	R 3 c	R 3 c
Hall group	R 3 -2"c	R 3 -2"c
Moiety formula	C8 H6 Cd N4 O4	C8 H6 Cd N4 O4
Sum formula	C8 H6 Cd N4 O4	C8 H6 Cd N4 O4
Mr	334.58	334.57
Dx,g cm-3	2.021	2.021
Z	18	18
Mu (mm-1)	1.995	1.995
F000	2916.0	2916.0
F000'	2902.66	
h,k,lmax	24,24,16	24,24,16
Nref	1002[1992]	1870
Tmin,Tmax	0.601,0.741	0.625,0.754
Tmin'	0.589	

Correction method= MULTI-SCAN
Data completeness= 1.87/0.94 Theta(max)= 25.240
R(reflections)= 0.0180(1794) wR2(reflections)= 0.0380(1870)
S = 1.048 Npar= 155

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Cd1 -- O1 .. 6.12 su
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Cd1 -- O3_i .. 5.34 su
PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Cd1 -- O4_i .. 5.68 su
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 48.00 A**3

Alert level G

REFLT03_ALERT_4_G Please check that the estimate of the number of Friedel pairs is
correct. If it is not, please give the correct count in the
_publ_section_exptl_refinement section of the submitted CIF.
From the CIF: _diffrn_reflns_theta_max 25.24
From the CIF: _reflns_number_total 1870
Count of symmetry unique reflns 1002
Completeness (_total/calc) 186.63%
TEST3: Check Friedels for noncentro structure
Estimate of Friedel pairs measured 868
Fraction of Friedel pairs measured 0.866
Are heavy atom types Z>Si present yes
PLAT764_ALERT_4_G Overcomplete CIF Bond List Detected (Rep/Expd) . 1.14 Ratio
PLAT850_ALERT_4_G Check Flack Parameter Exact Value 0.00 and su .. 0.02

0 ALERT level A = In general: serious problem
0 ALERT level B = Potentially serious problem
4 ALERT level C = Check and explain
3 ALERT level G = General alerts; check

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4 ALERT type 2 Indicator that the structure model may be wrong or deficient
0 ALERT type 3 Indicator that the structure quality may be low
3 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

checkCIF/PLATON report (publication check)

No syntax errors found. CIF dictionary
Please wait while processing .... Interpreting this report

Datablock: CCDC 773501

Bond precision: C-C = 0.0051 A Wavelength=0.71073
Cell: a=21.1266(16) b=21.1266(16) c=13.967(2)
alpha=90 beta=90 gamma=120
Temperature: 298 K

	Calculated	Reported
Volume	5398.8(10)	5398.9(10)
Space group	R 3 c	R3c
Hall group	R 3 -2"c	?
Moiety formula	C10 H7 Cd N3 O4	C10 H7 Cd N3 O4
Sum formula	C10 H7 Cd N3 O4	C10 H7 Cd N3 O4
Mr	345.60	345.59
Dx,g cm-3	1.913	1.913
Z	18	18
Mu (mm-1)	1.830	1.830
F000	3024.0	3024.0
F000'	3010.74	
h,k,lmax	25,25,16	25,25,16
Nref	1090[2168]	2151
Tmin,Tmax	0.711,0.818	0.689,0.824
Tmin'	0.662	

Correction method= MULTI-SCAN
Data completeness= 1.97/0.99 Theta(max)= 25.160
R(reflections)= 0.0168(2085) wR2(reflections)= 0.0413(2151)
S = 1.043 Npar= 164

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT232_ALERT_2_C Hirshfeld Test Diff (M-X) Cd1 -- O1 .. 7.57 su
PLAT241_ALERT_2_C Check High Ueq as Compared to Neighbors for O1
PLAT601_ALERT_2_C Structure Contains Solvent Accessible VOIDS of . 59.00 A**3
PLAT125_ALERT_4_C No _symmetry_space_group_name_Hall Given ..... ?

Alert level G

REFLT03_ALERT_4_G Please check that the estimate of the number of Friedel pairs is correct. If it is not, please give the correct count in the _publ_section_exptl_refinement section of the submitted CIF.
From the CIF: _diffrn_reflns_theta_max 25.16
From the CIF: _reflns_number_total 2151
Count of symmetry unique reflns 1090
Completeness (_total/calc) 197.34%
TEST3: Check Friedels for noncentro structure
Estimate of Friedel pairs measured 1061
Fraction of Friedel pairs measured 0.973
Are heavy atom types Z>Si present yes
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Cd1 -- O4_p .. 19.85 su

Crystallographic Data

Crystal data: For **1**, 298(2) K, rhombohedral *R*3*c*, a = 20.6556(6) Å, b = 20.6556(6) Å, c = 13.3915(7) Å, γ=120º, V = 4948.1(3) Å^3, Z = 18, Dc = 2.021 Mg/m^3, final R_1 = 0.0204 [$I>2\sigma(I)$], wR_2 = 0.0467 (all data), S = 1.082. For **2**, 298(2) K, rhombohedral *R*3*c*, a = 21.1266(16) Å, b = 21.1266(16) Å, c = 13.967(2) Å, γ=120º, V = 5398.9(10) Å^3, Z = 18, Dc = 1.913 Mg/m^3, final R_1 = 0.0168 [$I>2\sigma(I)$], wR_2 = 0.0407 (all data), S = 1.043. CCDC-717400 and-773501 for **1** and **2** contain the supplementary crystallographic data for this paper.