### Accepted Manuscript

Accepted Date:

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PII:	\$0277-5387(17)30680-0
DOI:	https://doi.org/10.1016/j.poly.2017.10.019
Reference:	POLY 12882
To appear in:	Polyhedron
Received Date:	8 September 2017

12 October 2017



Please cite this article as: B-D. Wu, X-Y. Li, J. Liang, X-H. Geng, H-S. Huang, H. Huang, J-Y. Wang, W-H. Hu, 1D Energetic Metal–organic Frameworks Assembled with Energetic Combination of Furazan and Tetrazole, *Polyhedron* (2017), doi: https://doi.org/10.1016/j.poly.2017.10.019

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### 1D Energetic Metal-organic Frameworks Assembled with Energetic Combination of

### **Furazan and Tetrazole**

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**Abstract:** Two novel 1D Cd(II) energetic MOFs  $[Cd(NH_2NH_2)(AFT)_2 \cdot 0.7H_2O]_n$  (1) and  $[Cd(ODH)_{1.5}(AFT)_2 \cdot 5H_2O]_n$  (2), combining the advantages of tetrazole-ring and furazan-ring, were successfully synthesized based on 2D energetic MOF  $[Cd(H_2O)_2(AFT)_2]_n$  (3, AFT=4-amino-3-(5-tetrazolate)-furazan, ODH=NH\_2NHCOCONHNH\_2= oxalyl-dihydrazide). The crystal structures were determined by single-crystal X-ray diffraction, and fully characterized by elemental analysis and FT-IR spectroscopy. The thermal stability and impact sensitivity were also investigated. For 1, 1D energetic MOF had an outstanding thermal stability ( $T_p>300$  °C) and insensitivity (IS>24.5 J). In addition, the non-isothermal kinetics parameters, critical temperature of thermal explosion, entropy of activation, enthalpy of activation and free energy of activation were discussed in detail. For 2, it was revealed that the each Cd(II) cation is located in a unique hepta-coordination environment. Noticeably, tetrazole-ring of AFT group presents typical monodentate coordination mode, and ODH molecule presents typical tridentate and tetradentate coordination modes, featuring a one-dimensional chain structure. Therefore, the reasonable assembly strategy plays a decisive role in energetic properties of MOF-based energetic materials.

Keywords: Tetrazole; Furazan; MOF; Crystal structure; Thermal behaviour

### **1. Introduction**

High-energetic metal-organic frameworks (HE-MOFs) have been achieved by the self-assembly of metal ions (such as Ag<sup>+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>3+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, etc) and energetic bidentate and (or) multidentate ligands, which will significantly influence the designing MOFs structures and ultimately the energetic properties. By virtue of this strategy, a new class of one-, two- and three-dimensional (1D, 2D and 3D) energetic MOFs are emerging, which are expected to possess the desired physical (such as high density, reasonable fluidity) and chemical properties (such as high thermal stability, high energetic output, low sensitivity and low environmental impact)[1-12]. Shreeve et al. highlighted the application prospects and development potentials of HE-MOFs in the field of energetic materials [13, 14]. Physicochemical properties of 37 HE-MOFs from 1D to 3D, based on various nitrogen-rich energetic ligands, had been summarized by Chen et al.[1]. It was found that, oxygen-containing energetic groups ameliorate oxygen balance of the whole system to fully release the energy. Therefore, in regard to the requirements of detonation performance and safety, very promising is furazan-ring (185 kJ·mol<sup>-1</sup>) conjugated with tetrazole  $(200 \text{ kJ} \cdot \text{mol}^{-1})$ , heats of formation of which are more than the 1,2,4-oxadiazole  $(51 \cdot \text{kJ mol}^{-1})$ , pyrazole (171 kJ·mol<sup>-1</sup>), imidazole (124 kJ·mol<sup>-1</sup>), and 1,2,4-triazole (182 kJ·mol<sup>-1</sup>)[15]. Undoubtedly, it is propitious to constructing high-dimensional energetic frameworks with more outstanding physicochemical properties by 4-amino-3-(5-tetrazolate)-furazan (HAFT). Prof. Shreeve had reported energetic salts by HAFT, all of which possess relatively high density, acceptable impact and friction sensitivities, and good detonation pressure and velocity[15]. On the other hand, 3D energetic MOF  $[Ag_{16}(BTFOF)_9]_n \cdot [2(NH_4)]_n$ assembled with Ag(I)ions and 4,4'-oxybis[3,3'-(1H-5-tetrazol)]furazan (H<sub>2</sub>BTFOF) had an outstanding insensitivity (IS>40J), an ultrahigh detonation pressure of 65.29 GPa and a detonation velocity of 11.81 km  $\cdot$  s<sup>-1</sup>[2]. Therefore, synthesizing the ligands above is a feasible and promising route to construct HE-MOFs.

Herein, we had reported a 2D energetic MOF  $[Cd(H_2O)_2(AFT)_2]_n$  (3)[5]. On this basis, we report two 1D energetic MOFs  $[Cd(NH_2NH_2)(AFT)_2 \cdot 0.7H_2O]_n$  (1) and  $[Cd(ODH)_{1.5}(AFT)_2 \cdot 5H_2O]_n$  (2, ODH=NH<sub>2</sub>NHCOCONHNH<sub>2</sub>= oxalyl-dihydrazide) by replace coordination water molecules of 3, which of synthesis, crystal structures, the thermal decomposition mechanism and explosive performance were studied in the present work.

### 2. Experimental Section

#### 2.1 Materials and Physical Techniques

All the reagents and solvents were of analytical grade and used without further purification as commercially obtained. Elemental analyze was performed on a Flash EA 1112 full-automatic trace element analyzer. The FT-IR spectra was recorded on a PerkinElmer Spectrum 100 infrared spectrometer

(KBr pellets) in the range of 4000~400 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. DSC measurement was carried by using DSC-131 differential scanning calorimeter (SETARAM).

### 2.2 The synthesis of 1 and 2 was as follows (Scheme 1)

HAFT (20 mmol) was dissolved in distilled water (20 ml), and charged into a glass reactor with a water bath. It was kept under mechanical stirring and heated to the temperature of 60  $^{\circ}$ C. Cd(NO<sub>3</sub>)<sub>2</sub> (1 mol/L, 12ml) was added to the HAFT solution during 15 min with continuous stirring. Then, acidified hydrazine hydrate (10 mmol) or acidified oxalyl-dihydrazide (15mmol), dissolved in distilled water (30 ml), was added to the solution during 5 min and keeping for 30 min. In the end, the solution was cooled to room temperature naturally. Single crystal suitable for X-ray measurement was obtained by evaporation of the mother liquor at room temperature for one week.

 $[Cd(NH_2NH_2)(AFT)_2 \cdot 0.7H_2O]_n$  (1): Yield: 50% (based on AFT).  $CdN_{16}C_6H_{9,4}O_{2.7}$  (461.35): calcd. C 15.62, H 2.05, N 48.59; found C 15.72, H 2.23, N 48.52. IR (KBr): 3429, 3327, 3167, 2150, 1784, 1605, 1568 and 768 cm<sup>-1</sup> (-NH and -NH<sub>2</sub>), 1633cm<sup>-1</sup> (N=N), 1242cm<sup>-1</sup> (-CN), 1153 and 1034 cm<sup>-1</sup> (tetrazole-ring).

 $[Cd(ODH)_{1.5}(AFT)_2 \cdot 5H_2O]_n$  (2): Yield: 30% (based on AFT).  $CdN_{20}C_9H_{13}O_{10}$  (673.79): calcd. C 16.04, H 1.94, N 41.58; found C 15.86, H 2.34, N 41.32. IR (KBr): 3465, 3335, 3286, 1596 and 784 cm<sup>-1</sup> (-NH and -NH<sub>2</sub>), 1732 cm<sup>-1</sup> (-C=O), 1249cm<sup>-1</sup> (-CN), 1124 and 1066 cm<sup>-1</sup> (tetrazole-ring).



#### 2.3 X-ray data collection and structure refinement

The X-ray diffraction data collection was performed with a Rigaku AFC-10/Saturn724<sup>+</sup>CCD and Bruker APEX-II CCD detector diffractometer with graphite monochromated Mo-K $\alpha$  radiation. The structure was solved by direct method using *SHELXS-97* and refined by full-matrix least-squares method on  $F^2$  with *SHELXL-97*. All non-hydrogen atoms were obtained from the difference Fourier map and subjected to anisotropic refinement by full-matrix least squares on  $F^2$ . Detailed information concerning crystallographic data collection and structure refinement are summarized in Table 1.

**Table 1**. Crystallographic data and structure determination details.

Compound	1	2	3 [5]
Empirical formula	$CdN_{16}C_{6}H_{9.4}O_{2.7}$	$CdN_{20}C_9H_{13}O_{10}$	$Cd_{0.25}N_{3.50}C_{1.50}H_2O$

Formula weight	461.35	673.79	113.17
T/K	153.15	100(2)	153(2)
Crystal system	monoclinic	triclinic	monoclinic
Space group	C2/ <i>c</i>	P-1	$P2_{1}/c$
a/Å	28.359(8)	9.0126(18)	7.857(3)
$b/ m \AA$	7.8563(16)	9.982(2)	9.409(3)
$c/ m \AA$	15.790(3)	15.045(3)	9.046(3)
α/(°)	90	87.125(3)	90
$eta/(^\circ)$	120.72(2)	85.468(3)	93.560(4)
γ/(°)	90	68.265(3)	90
$V/\text{\AA}^3$	3024.3(12)	1253.0(4)	667.4(4)
Ζ	8	2	8
$D_c/(g \cdot cm^{-3})$	2.026	1.786	2.252
$ heta/(^{\circ})$	1.67~27.48	2.20~25.00	3.13 ~31.48
h, k, l	-36~35,-10~9,-20~20	-10~5, -11~11, -17~15	-11~11, -9~13, -12~13
Reflections collections	4248	6246	6408
Independent reflection	3408	4360	2200
S	1.248	1.058	1.000
$R_1, wR_2[I \ge 2\sigma(I)]$	0.0629, 0.1707 <sup>[a]</sup>	0.0587, 0.1422 <sup>[b]</sup>	0.0227, 0.0532 <sup>[c]</sup>
$R_1, wR_2$ (all data)	0.0789, 0.2024 <sup>[a]</sup>	$0.0677, 0.1464^{[b]}$	$0.0307, 0.0570^{[c]}$
<i>F</i> (000)	1816	670	444
CCDC	1523833	1561476	1488809

<sup>[a]</sup> w =  $1/[\sigma^2(F_o^2) + (0.0852P)^2 + 66.3515P]$ , <sup>[b]</sup> w =  $1/[\sigma^2(F_o^2) + (0.0100P)^2 + 14.0000P]$ , <sup>[c]</sup> w =  $1/[\sigma^2(F_o^2) + (0.0298P)^2 + 0.0000P]$ , wR<sub>2</sub> =  $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ , P =  $(F_o^2 + 2F_c^2)/3$ .

### **3 Results and Discussion**

### 3.1 Structure Description

In the previous work, we had reported a 2D energetic MOF  $[Cd(H_2O)_2(AFT)_2]_n$  (3)[5], which of each two Cd(II) cations can mutual connect through bidentate coordination tetrazole-ring of AFT group, and form #-shape structure (Supporting Information Figure 1). The crystal structure of **1** belongs to *monoclinic*, pertains to *P*2<sub>1</sub>/c space group, *a*= 7.857(3) Å, *b*= 9.409(3) Å, *c*= 9.046(3) Å, *β*= 93.560(4)<sup>o</sup> and *D*<sub>c</sub>=2.252 g·cm<sup>-3</sup>[5]. The purpose is to verify that we can design and synthesis the more complex structures by adding energetic bidentate or multidentate ligands, such as hydrazine and ODH, to replace two coordination water molecules of **3**.

In **1**, the crystal structure belongs to *monoclinic*, pertains to C2/*c* space group, a = 28.359(8) Å, b = 7.8563(16) Å, c = 15.790(3) Å,  $\beta = 120.72(2)^{\circ}$  and  $D_c = 2.026$  g·cm<sup>-3</sup> (Table 1). There are one cadmium(II) cation, four AFT ligands and two hydrazine molecules from Figure 1. Furazan-ring is not take part in coordination. Moreover, tetrazole-rings and hydrazine molecules present typical

bidentate coordination modes, and connect with two cadmium cations, featuring a one-dimensional chain structure (Figure 2). The six basically equivalent Cd–N bonds are approximately equal about 2.33-2.45 Å from the Table 2. The bond angles of two contraposition hydrazine molecules and Cd(II) cation are close to  $180^{\circ}$  (<N12-Cd1-N11=179.3°), but the bond angles of two N atoms of contraposition AFT groups and Cd(II) cation are close to  $157^{\circ}$  (<N1A-Cd1-N2=156.8° and <N13-Cd1-N8=157.2°). The nitrogen atoms from two border upon ligands and Cd(II) cation's bond angles are all departure from 90°. Therefore, all above data demonstrate that the each Cd(II) cations of **1** exhibit appreciably distorted–octahedral configuration. In addition, the distance of two Cd(II) cations (4.08 Å) for **1** is more shorter than **3** (6.53 Å), owing to shortening the distance of two cadmium ions by hydrazine molecule. But **1** has zero point seven crystal waters compared with **3**, which is one reason of lower density. From the packing diagram (Figure 3), intermolecular hydrogen bonds make an important contribution to extend the structure into a 3D supramolecule and enhance the thermal stability.







Figure 2. Coordination mode of  $Cd^{2+}$  in 1, omit amino-furazan and water molecular for clarity.



Figure 3. Packing structure of 1 along *b*-axis of the unit cell.

In 2, the crystal structure belongs to *triclinic*, pertains to P-1 space group, a = 9.0126(18) Å, b =9.982(2) Å, c = 15.045(3) Å,  $\alpha = 87.125(3)^{\circ}$ ,  $\beta = 85.468(3)^{\circ}$ ,  $\gamma = 68.265(3)^{\circ}$  and  $D_c = 1.786$  g·cm<sup>-3</sup> (Table 1). Each Cd(II) cation is located in a hepta-coordination environment with two AFT groups and three ODH molecules (Figure 4). In addition, Cd(II) cation is related to different hexadentate coordination mode, such as  $[Cd(DAT)_6](PA)_2 \cdot 4H_2O$  (DAT= 1,5-diaminotetrazole,  $[Cd(DAT)_6](ClO_4)_2[16], [Cd(DAT)_6](NO_3)_2[17],$ PA=picrate)[11],  $[Cd(DAT)_2(N_3)_2]_n[18],$  $[Cd(en)(N_3)_2]_n$  (en=ethylenediamine),  $[Cd(IMI)_2(N_3)_2]_n$  (IMI=imidazole), 1 and 3. Noticeably, furazan-ring is also not take part in coordination, and tetrazole-ring presents typical monodentate coordination mode, which is different in 1 and 3. In addition, ODH molecule presents typical tridentate coordination mode and tetradentate coordination mode, and each ODH molecule is also connected with two cadmium cations (Figure 5), featuring a one-dimensional chain structure. For 2, the distance of two Cd(II) cations (7.43Å) is more than 1 (4.08 Å), resulted tetrazole-ring presenting single coordination mode. And 2 has more crystal waters, which is also one reason of lower density. The seven basically equivalent Cd-N and Cd-O bonds are approximately equal about 2.33-2.45 Å from the Table 3. Cd(II) ions and ODH ligands are basically in the same plane, and the bond angles of two N atoms (contraposition AFT groups) and Cd(II) cation are close to 180° (<N1-Cd1-N8=174.2°). Therefore, all above data demonstrate that each Cd(II) cations exhibit appreciably distorted-decahedral configuration for 2. From the packing diagram (Figure 6), the all furazan-ring and tetrazole-ring are coplanar or in parallel, and the offset face-to-face  $\pi$ - $\pi$  stacking distance is about 3.4 Å, resulted a lower impact sensitivity. And intermolecular

hydrogen bonds also make an important contribution to extend the structure into a 3D supramolecule.



Figure 4. Molecular structure of 2, thermal ellipsoids drawn at 50% probability level.



**Figure 5.** Coordination mode of  $Cd^{2+}$  and ODH in **2**, omit AFT group and water molecular for clarity.



**Figure 6.** Packing structure of **2**.

bond	length/ Å	bond	angle/(°)	bond	angle/(°)			
Cd1-N1	2.337(7)	N1A-Cd1-N2	156.8(2)	N11-Cd1-N2	95.2(2)			
Cd1-N2	2.447(7)	N12-Cd1-N11	179.3(2)	N11-Cd1-N8	84.7(2)			
Cd1-N8	2.429(7)	N13-Cd1-N8	157.2(2)	N12-Cd1-N2	85.1(2)			
Cd1-N11	2.350(7)	N1A-Cd1-N8	85.0(2)	N12-Cd1-N8	94.8(2)			
Cd1-N12	2.339(7)	N1A-Cd1-N11	96.6(2)	N13-Cd1-N1A	116.3(2)			
Cd1-N13	2.336(7)	N1A-Cd1-N12	82.9(2)	N13-Cd1-N2	84.6(2)			
N12-N11A	1.456(9)	N8-Cd1-N2	76.4(2)					
	Table 3.       Selected bond lengths and bond angles for 2.							
bond	length/ Å	bond	angle/(°)	bond	angle/(°)			
Cd1-N1	2.303(6)	N1-Cd1-N8	174.2(2)	N1-Cd1-N19	96.3(2)			
Cd1-N8	2.320(6)	N15-Cd1-N19	136.4(2)	N8-Cd1-N19	88.6(2)			
Cd1-N19	2.415(6)	N1-Cd1-O3	88.23(18)	O3-Cd1-N19	153.90(18)			
Cd1-N15	2.450(6)	N8-Cd1-O3	86.00(18)	O5-Cd1-N19	68.83(18)			
Cd1-N18A	2.488(5)	N1-Cd1-O5	80.06(19)	N1-Cd1-N15	96.2(2)			
Cd1-O3	2.374(4)	N8-Cd1-O5	104.72(19)	N8-Cd1-N15	82.3(2)			
Cd1-O5	2.383(5)	O3-Cd1-O5	137.17(15)	N15-Cd1-N19	136.4(2)			

**Table 2**Selected bond lengths and bond angles for 1.

#### 3.2 Thermal decomposition analysis

In order to investigate the thermal behavior of **1** and **2**, it was analyzed by differential scanning calorimetry (DSC) with a linear heating rates of 5, 10, 15 and 20  $^{\circ}C \cdot min^{-1}$  in a flowing N<sub>2</sub> atmosphere with flowing rate 20 ml·min<sup>-1</sup> and shown in Figure 7.

In **1**, a melting point could not be observed in the DSC curves, in spite of the presence of coordination water molecules. The peaks of exothermic decomposition stages were observed at 306.3°C, 320.5 °C, 327.0 °C and 340.2 °C, and onset temperatures were observed at 302.5 °C, 308.5 °C, 315.7 °C and 339.9 °C, respectively, corresponding to the linear heating rates of 5, 10, 15 and 20 °C·min<sup>-1</sup>. Compared with **3**, compound **1** has only one exothermic process, and is one of the few thermally stable energetic materials at temperature higher than 300 °C.

In 2, there were two endothermic peaks in the temperature ranges of 50-100 °C and 180-200 °C, which are coincident with the loss of all lattice water molecules. Then, the cleavage of amino- and ODH groups and the breaking of tetrazole and furazan rings are destroyed, so it gets unstable and begins to decompose. It can be seen from the DSC curve, the decomposition occurs in the temperature range of 220~400 °C with one endothermic and two exothermic steps. The peaks of first exothermic decomposition stages were observed at 271.3°C, 287.8 °C, 300.0 °C and 308.5 °C, respectively, corresponding to the linear heating rates of 5, 10, 15 and 20 °C·min<sup>-1</sup>. Therefore, **2** was more unstable than that of **1**.



**Figure 7.** DSC curves for **1** and **2** with  $\beta = 5$ , 10, 15 and 20 °C·min<sup>-1</sup> in a N<sub>2</sub> atmosphere.

#### 3.3 Non-isothermal kinetics analysis

It is widely used to determine the Arrhenius Equation for main exothermic peak for **1** with the apparent activation energy *E*, pre–exponential factor *A*, linear coefficient *R* and standard deviation *S* corresponding to Kissinger's method[19], Ozawa's method[20] and Starink's method[21], respectively (See Supporting Information), and was showed in Table 5. So, the Arrhenius equation of **1** can be expressed as follows: (*E* is the average number):  $lnk = 15.22 - 117.59 \times 10^{3}/(RT)$ . Then, critical temperature of thermal explosion,  $\Delta S^{\neq}$ ,  $\Delta H^{\neq}$  and  $\Delta G^{\neq}$  of **1** were calculated (See Supporting Information).

**Table 5.** Peak temperatures of main exothermic and the chemical kinetics parameters for 1.

Heating rates $\beta / {}^{\circ}C \cdot \min^{-1}$	$T_{\rm p}/{\rm ^oC}$	parameters	Kissinger's method	Ozawa's method	Starink's method
5	306.3	$E/kJ \cdot mol^{-1}$	113.96	123.86	114.95
10	320.5	lgA	6.61	-	-
15	327.0	R	-0.9802	-0.9833	-0.9806
20	340.2	S	0.1344	0.1340	0.1344

### 3.4 Impact Sensitivity Test

The impact sensitivity was determined by fall hammer apparatus. **1** and **2**(30 mg) was placed between two steel poles and was hit by a 5.0 kg drop hammer at a height of 50 cm. The test result showed that the firing rate was 0% (>24.5 J), which was less sensitive to impact than TNT (15.0 J) and RDX (7.5 J).

The physicochemical properties are tabulated in Table 6.

Compound	Ν	OB	$D_c$	E	$T_{\rm p0}$	$T_{\rm b}$	$\Delta S^{ eq}$	$\Delta H^{\! \neq}$	$\Delta G^{ eq}$	IS
compound	(%)	(%)	$/(g \cdot cm^{-3})$	$(kJ \cdot mol^{-1})$	$(^{\circ}C)$	$(^{\circ}C)$	$(J \cdot K^{-1} \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	$(kJ \cdot mol^{-1})$	(J)
1	48.59	-52.02	2.026	117.59	260.0	281.77	-131.52	119.43	189.55	>24.5
2	41.58	-36.81	1.786	-	-	-	-	-	-	>24.5
3	43.30	-45.95	2.252	189.5	296.4	300.23	-0.67	183.46	183.65	>24.5

**Table 6.** Physicochemical properties of 1, 2 and 3.

### 4. Conclusions

**Synthesis** and characterization of two novel 1D **MOFs** compounds  $[Cd(NH_2NH_2)(AFT)_2 \cdot 0.7H_2O]_n$  (1) and  $[Cd(ODH)_{1.5}(AFT)_2 \cdot 5H_2O]_n$  (2) were reported, which have 2.026 g cm<sup>-3</sup> of crystal density and 48.59% nitrogen content for **1**, and 1.786 g cm<sup>-3</sup> of crystal density and 48.59% nitrogen content for 2. They have their respective advantages: (1) 1 is one of the few thermally stable energetic materials at temperature higher than 300  $^{\circ}$ C; (2) 2 is located in a unique hepta-coordination mode. Therefore, based on 2D MOF compound 3, we only obtain 1D MOFs compounds 1 and 2. There is no doubt that we can also design and synthesis the 3D energetic MOFs by adding energetic bidentate ligands (eg. ethylenediamine) or multidentate ligands (eg. azido-group).

#### Acknowledgments

The project was supported by Shanxi Province Science Foundation for Youths (No.201701D221048), the Advantage Disciplines Climbing Plan of Shanxi Province, Science Foundation of North University of China (2015) and Chongqing Key Laboratory of Inorganic Special Functional Materials (Yangzte Normal University, No. KFKT201503).

### Appendix A. Supplementary data

CCDC 1523833 and 1561476 contains the supplementary crystallographic data for compounds 1 and 2. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found at Supporting Information.

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### **Supporting Information**

### **Structure Description**



Figure 1. Molecular structure of **3**, thermal ellipsoids drawn at 70% probability level (left), and coordination mode of Cd<sup>2+</sup>, omit amino-furazan and water molecular for clarity (right).

#### Thermal decomposition analysis



DSC curves for **3** with  $\beta = 5$ , 10, 15 and 20 °C·min<sup>-1</sup> in a N<sub>2</sub> atmosphere. Figure 2.

### Non-isothermal kinetics analysis

The equations of Kissinger's method, Ozawa's method and Starink's method are as follows:

$$\ln(\beta/T^s) = -(BE/RT) + C \tag{1}$$

Where *T* is the peak temperature in K. *E* is the apparent activation energy in kJ·mol<sup>-1</sup>. *R* is the gas constant (8.314 J·K<sup>-1</sup>·mol<sup>-1</sup>).  $\beta$  is the linear heating rate in K·min<sup>-1</sup>. B and C are constant. When s=2 and B=1, equation (1) is according to Kissinger's method. When s=0 and B=1.0516, equation 12/14

(1) is according to Ozawa's method. When s=1.8 and B=1.0037, equation (1) is according to Starink's method. Based on the exothermic peak temperature measured with four different heating rates of 5, 10, 15 and 20 °C·min<sup>-1</sup>, three methods were applied to study the kinetics parameters of the title compound. From the original data, the apparent activation energy *E*, pre–exponential factor *A*, linear coefficient *R* and standard deviation *S* were determined based on the relationship of  $\ln(\beta/T^2)$ ,  $\ln(\beta/T^{1.8})$  and  $\ln\beta$  to 1/T, corresponding to Kissinger's method, Starink's method, and Ozawa's method, respectively.

### Calculation of critical temperature of thermal explosion, $\Delta S \neq$ , $\Delta H \neq$ and $\Delta G \neq$

The value of the peak temperature corresponding to  $\beta \rightarrow 0$  ( $T_0$ ), the corresponding critical temperature of thermal explosion ( $T_b$ ), entropy of activation ( $\Delta S^{\neq}$ ), enthalpy of activation ( $\Delta H^{\neq}$ ), and free energy of activation ( $\Delta G^{\neq}$ ) were obtained by the following equations (2), where *a*, *b* and *c* are coefficients,  $k_B$  is the Boltzmann constant ( $1.381 \times 10^{-23}$  J/K) and *h* is the Planck constant ( $6.626 \times 10^{-34}$  J·s).

$$T_{i} = T_{0} + a\beta + b\beta^{2}$$

$$T_{b} = \left(E - \sqrt{E^{2} - 4ERT_{0}}\right)/2R$$

$$A = \left(k_{B}T_{0}/h\right)\exp\left(1 + \Delta S^{\neq}/R\right)$$

$$\Delta H^{\neq} = E - RT_{0}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T_{0}\Delta S^{\neq}$$
(2)



- Based on 2D MOF compound 3, we only obtain 1D MOFs compounds 1 and 2. 1 is one of the few thermally stable energetic materials at temperature higher than 300 °C; 2 is located in a unique hepta-coordination mode.
- There is no doubt that we can also design and synthesis the 3D energetic MOFs by adding energetic

bidentate ligands (eg. ethylenediamine) or multidentate ligands (eg. azido-group).

Accepted MANUSCAR