

## 2-氨基对苯二甲酸根及 2-咪唑烷酮构筑的镉(II) 配位聚合物的合成、晶体结构及荧光性质

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**摘要:** 以一种尿素的衍生物 2-咪唑烷酮为溶剂, 采用脲热法合成了一个新的配位聚合物 $[\text{Cd}(\text{NH}_2\text{bdc})(\text{e-urea})]_n$  (**1**) ( $\text{H}_2\text{NH}_2\text{bdc}$  为 2-氨基对苯二甲酸,  $\text{e-urea}$  为 2-咪唑烷酮), 并对其结构和荧光性质进行了研究。单晶结构分析结果表明, 标题化合物的中心镉(II)离子分别与 2-氨基对苯二甲酸根配体的羧基氧原子和溶剂氧原子配位形成七配位的变形五角双锥结构。相邻的中心镉(II)离子通过溶剂氧原子和配体羧基基团的连接, 形成无限的一维链。这些一维的链进一步通过 2-氨基对苯二甲酸根配体的连接最终形成了具有一维孔道的三维框架结构。研究表明, 该化合物在室温下能发出较强的蓝色荧光。

**关键词:** 镉配位聚合物; 2-氨基对苯二甲酸; 2-咪唑烷酮; 脲热合成; 荧光性质

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## Synthesis, Crystal Structure and Luminescent Property of a Cd(II) Coordination Polymer Constructed by 2-Amino-1,4-benzenedicarboxylate and 2-Imidazolidinone

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**Abstract:** A new coordination polymer, namely  $[\text{Cd}(\text{NH}_2\text{bdc})(\text{e-urea})]_n$  (**1**) ( $\text{H}_2\text{NH}_2\text{bdc}$ =2-amino-1,4-benzenedicarboxylic acid,  $\text{e-urea}$ =2-imidazolidinone) has been urothermally synthesized by using urea derivative 2-imidazolidinone as solvent and its structure and fluorescence property have also been investigated. The crystallography analysis reveals that the centric Cd(II) ion is seven coordinated by carboxylate oxygen atoms from  $\text{NH}_2\text{bdc}$  ligands and oxygen atoms of  $\text{e-urea}$  molecules forming a distorted pentagonal-bipyramidal coordination geometry. The adjacent Cd(II) centers are bridged by oxygen atoms of  $\text{e-urea}$  molecules and carboxylate groups of  $\text{NH}_2\text{bdc}$  ligands forming an infinite 1D chain. Thus 1D chains are further connected together by  $\text{NH}_2\text{bdc}$  ligands into a 3D coordination framework with 1D tunnels. Luminescent study shows that complex **1** displays a strong blue emission at room temperature. CCDC: 902023.

**Key words:** cadmium coordination polymer; 2-amino-1,4-benzenedicarboxylic acid; 2-imidazolidinone; urothermal synthesis; photoluminescence

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In recent years, the design and construction of novel metal-organic frameworks (MOFs) have been under intense investigation for their fascinating structures and various potential applications such as gas storage and separation, magnetism, nonlinear optics and heterogeneous catalysis, etc<sup>[1-9]</sup>. In order to get such functional materials, the crucial step is to choose suitable organic ligands and constituent metal cations. The  $d^{10}$  metal ions especially the Cd(II) ion can adopt various coordination because of its big bond radius, its coordination numbers can vary greatly from four to eight. The Cd-based metal-organic frameworks not only show structural variety but also exhibit excellent photochemistry and photophysics property, so the coordination polymers based on Cd(II) ion have been widely studied recently because of their potential application in the areas of sensors and luminescent materials<sup>[10-13]</sup>. Meanwhile, The rigid aromatic organic bicarboxylate ligands are good for the construction of coordination polymers due to their diversity of the coordination modes and high structural stability<sup>[14-15]</sup>. Based upon this background information, we choose the  $d^{10}$  block metal Cd(II) to coordinate with 2-amino-1,4-benzenedicarboxylic acid ( $H_2NH_2bdc$ ).

On the other hand, the solvent plays an important role in the self-assembly of MOFs, and coordination polymers were predominantly prepared by employing hydrothermal, solvothermal and ionothermal synthetic methods<sup>[16-19]</sup>. Recently, a new synthetic method denoted as “urothermal synthesis” that uses urea derivatives as solvents is emerging and has been demonstrated to be a powerful method for the creation of framework materials with promising applications<sup>[20-22]</sup>. At the current stage, the urothermal syntheses of MOFs remain largely unexplored. Although the 2-amino-1,4-benzenedicarboxylic acid ligand has been well studied<sup>[23-25]</sup>, the construction of compounds based on it by using urothermal synthetic method has not been reported. Herein, we report the structural characterization and property of a new three-dimensional Cadmium(II) coordination polymer based on 2-amino-1,4-benzenedicarboxylic acid resulting from urothermal reaction by using urea derivative 2-

imidazolidinone (e-urea) as solvent.

## 1 Experimental

### 1.1 Materials and instruments

All reagents were purchased commercially and used without further purification. Elemental analyses for C, H and N were carried out on a Perkin-Elmer 240C elemental analyzer. The powder X-ray diffraction (PXRD) experiment was performed on a D/MAX-3CX diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 0.154\ 06\ \text{nm}$ ) at room temperature. Thermogravimetric analysis (TGA) experiment was carried out using a simultaneous SDT 2960 thermal analyzer in the temperature range of 25 ~650 °C under a flow of nitrogen with heating rate of 10 °C · min<sup>-1</sup>. Solid state emission spectrum of the title complex was recorded using 48000DSCF fluorescence spectrometer. Crystal structure determination was carried out on a Bruker SMART CCD diffractometer.

### 1.2 Synthesis of $[Cd(NH_2bdc)(e-urea)]_n$ (**1**)

A mixture of  $Cd(NO_3)_2 \cdot 4H_2O$  (90.0 mg, 0.292 mmol),  $H_2NH_2bdc$  (60.0 mg, 0.331 mmol) and e-urea · 0.5 $H_2O$  (1 840 mg, 21.4 mmol) was sealed in a 25 mL Teflon-lined stainless steel autoclave, which was heated at 120 °C for 72 h. After the reaction was cooled to room temperature, the product was washed by ethanol, then colorless single crystals were obtained in 68% yield (based on Cd). Anal. Calcd. for  $C_{11}H_9CdN_3O_5$  (%): C 35.17, H 2.42, N 11.19; Found (%): C 34.99, H 2.51, N 11.14.

### 1.3 Crystal structure determination

X-ray crystallography suitable single crystal of **1** was carefully selected under an optical microscope and glued to thin glass fiber. The diffraction data were collected at 293(2) K on a Bruker SMART CCD diffractometer equipped with a graphite-monochromatic Mo  $K\alpha$  radiation ( $\lambda = 0.071\ 073\ \text{nm}$ ). Intensities were collected by using a  $\omega$  scan mode in the range of  $3.09^\circ < \theta < 24.99^\circ$ . The structure was solved by direct method and refined with full-matrix least-squares technique (SHELXTL-97)<sup>[26]</sup>. The non-hydrogen atoms were refined anisotropically and all hydrogen atoms were located according to theoretical calculation. Crystallographic data for **1** is listed in Table 1.

**Table 1** Crystallographic data for complex **1**

Empirical formula	C <sub>11</sub> H <sub>9</sub> CdN <sub>3</sub> O <sub>5</sub>	$\mu$ / mm <sup>-1</sup>	1.763
Formula weight	375.61	<i>F</i> (000)	1472
Crystal size / mm	0.25×0.23×0.15	$\theta$ range for data collection / (°)	3.09~24.99
Crystal system	Monoclinic	<i>R</i> <sub>int</sub>	0.021 8
Space group	<i>C</i> 2/ <i>c</i>	Reflections collected	4 667
<i>a</i> / nm	2.188 79(17)	Unique reflections	2 191
<i>b</i> / nm	0.705 73(3)	Observed reflections	1 962
<i>c</i> / nm	1.924 14(13)	Parameters	199
$\beta$ / (°)	122.344 0(10)	Goodness-of-fit on <i>F</i> <sup>2</sup>	1.039
<i>V</i> / nm <sup>3</sup>	2.511 1(3)	<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.061 5, 0.175 2
<i>Z</i>	8	<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.065 8, 0.176 9
<i>D</i> <sub>c</sub> / (g·cm <sup>-3</sup> )	1.987	Largest difference peak and hole / (e·nm <sup>-3</sup> )	3 688, -1 713
<i>T</i> / K	293(2)		

**Table 2** Selected bond lengths (nm) and angles (°) for **1**

Cd(1)-O(3)	0.222 9(8)	Cd(1)-O(5) <sup>i</sup>	0.222 4(9)	Cd(1)-O(2) <sup>i</sup>	0.237 6(7)
Cd(1)-O(4) <sup>i</sup>	0.237 9(8)	Cd(1)-O(1)	0.239 5(9)	Cd(1)-O(4)	0.242 1(8)
Cd(1)-O(2)	0.245 7(8)	O(2)-Cd(1) <sup>ii</sup>	0.237 6(7)	O(4)-Cd(1) <sup>ii</sup>	0.237 9(8)
O(5)-Cd(1) <sup>ii</sup>	0.222 4(9)				
O(3)-Cd(1)-O(5) <sup>i</sup>	174.8(4)	O(3)-Cd(1)-O(2) <sup>i</sup>	83.0(3)	O(5)-Cd(1)-O(2) <sup>i</sup>	91.7(4)
O(3)-Cd(1)-O(4) <sup>i</sup>	92.2(3)	O(5)-Cd(1)-O(4) <sup>i</sup>	86.4(3)	O(2)-Cd(1)-O(4) <sup>i</sup>	71.2(3)
O(3)-Cd(1)-O(1)	96.3(4)	O(5)-Cd(1)-O(1)	88.6(4)	O(2)-Cd(1)-O(1)	154.6(3)
O(4) <sup>i</sup> -Cd(1)-O(1)	83.4(3)	O(3)-Cd(1)-O(4)	96.3(3)	O(5)-Cd(1)-O(4)	82.8(4)
O(2) <sup>i</sup> -Cd(1)-O(4)	83.2(3)	O(4) <sup>i</sup> -Cd(1)-O(4)	151.9(2)	O(1)-Cd(1)-O(4)	122.0(3)
O(3)-Cd(1)-O(2)	94.8(3)	O(5)-Cd(1)-O(2)	89.7(3)	O(2)-Cd(1)-O(2)	151.9(2)
O(4) <sup>i</sup> -Cd(1)-O(2)	136.8(3)	O(1)-Cd(1)-O(2)	53.5(3)	O(4)-Cd(1)-O(2)	69.2(3)
Cd(1) <sup>ii</sup> -O(2)-Cd(1)	98.0(2)	Cd(1) <sup>ii</sup> -O(4)-Cd(1)	99.0(3)		

Symmetry transformations used to generate equivalent atoms: <sup>i</sup>  $-x+0.5, y+0.5, -z+0.5$ ; <sup>ii</sup>  $-x+0.5, y-0.5, -z+0.5$ .

Selected bond lengths and bond angles are listed in Table 2.

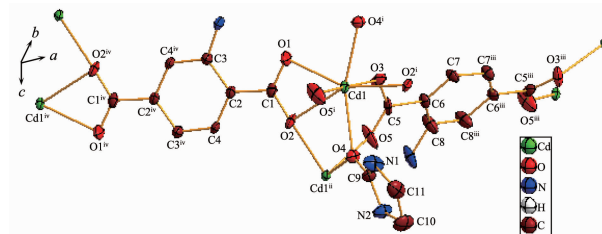
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## 2 Results and discussion

### 2.1 Description of the structure

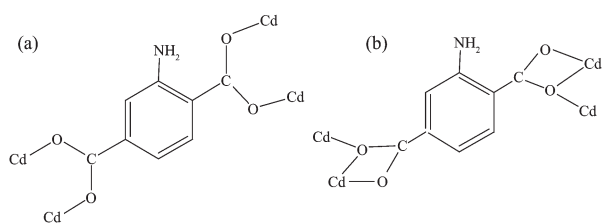
As shown in Fig.1, the asymmetric unit of **1** consists of one Cd(II) cation, two half NH<sub>2</sub>bdc<sup>2-</sup> anions and one coordinated e-urea molecule. In complex **1**, All carboxylate groups are all deprotonated and the NH<sub>2</sub>bdc ligands display two types of coordination modes with the Cd(II) centers. In the first mode, each carboxylate group bidentately bridges two Cd(II) centers in syn-syn fashion, and the whole NH<sub>2</sub>bdc<sup>2-</sup> behaviors as a tetradentate ligand linking four Cd(II) centers. In the second mode, each carboxylate group

adopts a chelating-bridging tridentate coordination mode, and the whole NH<sub>2</sub>bdc ligand connects four Cd(II) centers acting as a sexadentate ligand, as presented in Scheme 1. Based on above coordination modes, each centric Cd(II) ion is seven coordinated,



Hydrogen atoms are omitted for clarity; symmetry codes: <sup>i</sup>  $0.5-x, 0.5+y, 0.5-z$ ; <sup>ii</sup>  $0.5-x, -0.5+y, 0.5-z$ ; <sup>iii</sup>  $1-x, y, 0.5-z$ ; <sup>iv</sup>  $-x, -y, -z$

Fig.1 Asymmetric unit of **1** showing the coordination environment of Cd(II) atom and the coordination mode of NH<sub>2</sub>bdc ligand and e-urea

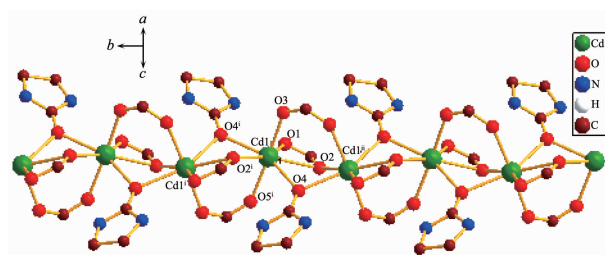


Scheme 1 Two coordination modes of  $\text{NH}_2\text{bdc}$  ligand observed in **1**

where the equatorial plane is completed by five oxygen atoms from two sexadentate  $\text{NH}_2\text{bdc}$  ligands (O(1), O(2) and O(2a)) and two coordinated e-urea molecules (O(4) and O(4a)) with five long Cd-O bonds: Cd(1)-O(1), Cd(1)-O(2), Cd(1)-O(4), Cd(1)-O(2a) and Cd(1)-O(4a). While the apical positions are occupied by two oxygen atoms (O(3) and O(5a)) from two tetradentate  $\text{NH}_2\text{bdc}$  ligands with shorter Cd-O distances: Cd(1)-O(5a) and Cd(1)-O(3). The total value of O(1)-Cd(1)-O(2), O(2)-Cd(1)-O(4), O(4)-Cd(1)-O(2a), O(4a)-Cd(1)-O(2a) and O(4a)-Cd(1)-O(1) is  $360.5^\circ$ , this shows that O(1), O(2), O(4), O(2a) and O(4a) are almost coplanar. The bond angles of O(5a)-Cd(1)-O(1), O(5a)-Cd(1)-O(2), O(5a)-Cd(1)-O(4), O(5a)-Cd(1)-O(2a), O(5a)-Cd(1)-O(4a), O(3)-Cd(1)-O(1), O(3)-Cd(1)-O(2), O(3)-Cd(1)-O(4), O(3)-Cd(1)-O(2a) and O(3)-Cd(1)-O(4a) all deviate from  $90^\circ$ , and the O(5a)-Cd(1)-O(3) bond angle is  $174.8(4)^\circ$ , so the coordination geometry of the seven-coordinated Cd(II) center can be regarded as a distorted pentagonal-bipyramid.

In the structure of **1**, the adjacent two Cd(II) centers are bridged by one  $\mu_2$ -bridging oxygen atom of e-urea molecule and two carboxylate groups from two different  $\text{NH}_2\text{bdc}$  ligands which adopt two different coordination modes, then forming an infinite 1D chain along the  $b$  axis with the nonbonding Cd  $\cdots$  Cd separation of 0.364 90(12) nm (Fig.2). Viewed along  $c$  axis, tetradentate  $\text{NH}_2\text{bdc}$  ligands connect 1D chains into 2D layers parallel to  $ab$  plane (Fig.3), which are further linked by sexadentate  $\text{NH}_2\text{bdc}$  ligands in the  $c$ -axial direction producing a 3D architecture with 1D rhomboid channels along the  $b$ -axial direction. In the 3D framework,  $\text{Cd}^{2+}$  ions located at the vertexes of the rhombus, while two tetradentate  $\text{NH}_2\text{bdc}$  ligands parallel to  $ab$  plane act as a pair of sides of the

rhombus and the other two sides of the rhombus are formed by sexadentate  $\text{NH}_2\text{bdc}$  ligands, generating rhomboid channels with the dimensions of approximately  $0.998\ 55\ \text{nm} \times 1.149\ 88\ \text{nm}$ . In the 1D channels, coordinated e-urea molecules occupy the cavities, and all e-urea molecules in the channels are parallel to each other viewed along  $b$  axis, shown as in Fig.4. The hydrogen bond interactions between e-urea molecules and carboxylate oxygen atoms of  $\text{NH}_2\text{bdc}$  ligands [ $\text{N}-\text{H}(\text{e-urea}) \cdots \text{O}(\text{NH}_2\text{bdc})$ ] further stabilize the resulting 3D framework structure (Table 3).



Symmetry codes: <sup>i</sup>  $0.5-x, 0.5+y, 0.5-z$ ; <sup>ii</sup>  $0.5-x, -0.5+y, 0.5-z$

Fig.2 View of 1D infinite chain along the  $b$  axis in complex **1**

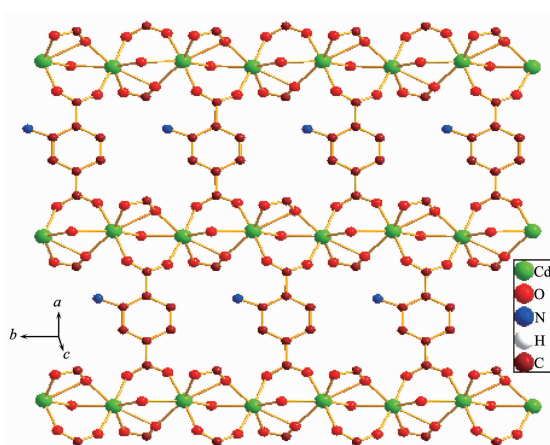


Fig.3 1D chains are contacted to yield 2D network parallel to  $ab$  plane

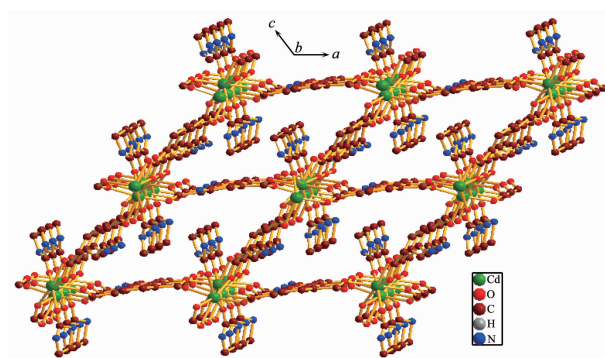


Fig.4 3D framework of **1**

**Table 3 Hydrogen bonding geometry for the complex 1**

D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$\angle \text{DHA} / (^{\circ})$
N(1)-H(1A)...O(5) <sup>i</sup>	0.086 0	0.314 4(19)	0.245	138.8
N(2)-H(2A)...O(1) <sup>ii</sup>	0.086 0	0.282 7(15)	0.209	143.7

Symmetry codes: <sup>i</sup>  $-x+0.5, y+0.5, -z+0.5$ ; <sup>ii</sup>  $-x+0.5, y-0.5, -z+0.5$ .

It is interesting to note that the e-urea solvent plays important roles in the construction of complex **1**. First of all, e-urea acts as the solvent dissolving the metal salts and organic ligands. Secondly, e-urea acts as an auxiliary ligand to help build the crystal structure. Lastly, e-urea can form rich hydrogen bonding interactions to help stabilize the structure.

## 2.2 PXRD and Thermogravimetric analysis

To investigate the phase purity of complex **1**, powder X-ray diffraction experiment was carried out on the as-synthesized sample (Fig.5). The powder XRD pattern of complex **1** matches well with the simulated pattern based on the single-crystal structure analysis. Together with the result of the elemental analyse, we can conclude that the synthesized bulk material of **1** has high purity.

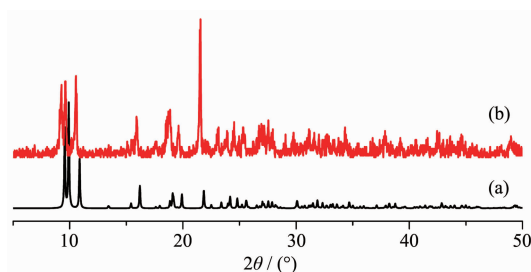


Fig.5 Powder XRD patterns of the simulation based on the single-crystal analysis (a) and as-synthesized sample (b) of **1**

The thermal stability of complex **1** was investigated through thermogravimetric analysis (TGA) experiment. The weight loss curve shows that complex **1** has high thermal stability, its framework maintains stability upon 340 °C. After that temperature, the framework begins to decompose, the continuous weight loss corresponding to the liberation water and carbon dioxide vapors of decomposed organic ligands occurs (Fig.6).

## 2.3 Fluorescence property

In the solid state, complex **1** has single broad emission spectra at 449 nm ( $\lambda_{\text{ex}}=350 \text{ nm}$ ) at room

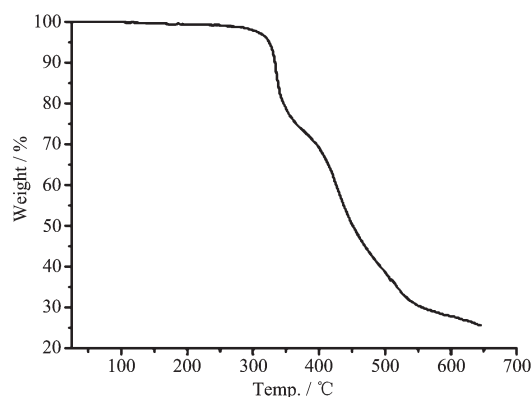


Fig.6 TGA diagram of **1**

temperature, as shown in Fig.7. According to the literature<sup>[25]</sup>, the free 2-amino-1,4-benzenedicarboxylic acid ( $\text{H}_2\text{NH}_2\text{bdc}$ ) ligand in the solid state has a broad fluorescent emission centered on 588 nm when excited at 358 nm. The blue shift of the emission at 449nm may be assigned as ligand-to-metal charge transfer (LMCT). Complex **1** may be a good candidate for potential photoactive materials because it is highly thermally stable and almost insoluble in common polar and nonpolar solvents.

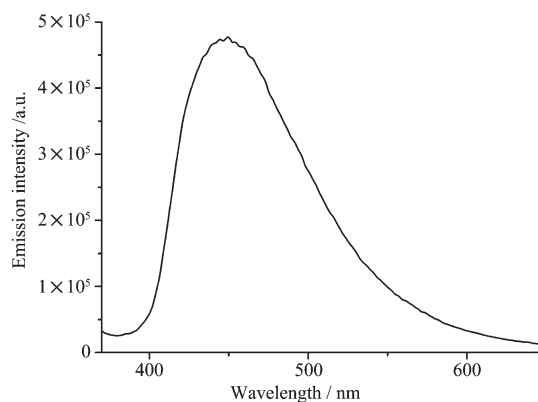


Fig.7 Solid-state emission spectrum of **1** at room temperature

## 3 Conclusions

In summary, one new 3D Cadmium(II) coordination polymer has been obtained by employing the urothermal synthetic method. The synthesized complex



has high stability and shows obvious photoluminescent emission at room temperature in the solid state. The experimental details show that the e-urea solvent plays important roles in the synthesis and crystallization of title complex. This study demonstrates that urothermal synthesis may be a promising method for the construction of MOFs with new architectures and functionalities.

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