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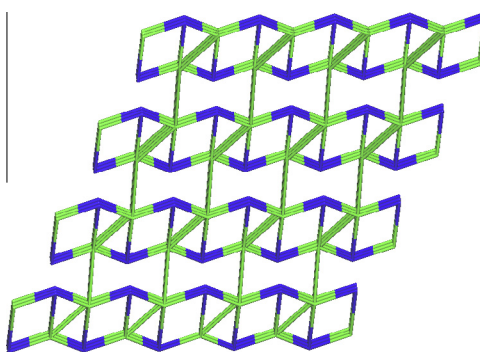
## Synthesis, crystal structures, luminescence properties of two metal coordination polymers derived from 5-substituted isophthalate and flexible bis (triazole) ligands

Chun-lun Ming<sup>a</sup>, Li-na Wang<sup>a</sup>, Kristof Van Hecke<sup>b</sup>, Guang-hua Cui<sup>a,\*</sup><sup>a</sup> College of Chemical Engineering, Hebei United University, 46 West Xinhua Road, Tangshan 063009, Hebei, PR China<sup>b</sup> Department of Inorganic and Physical Chemistry, Ghent University, Krijgslaan 281 S3, B-9000 Ghent, Belgium

### HIGHLIGHTS

- Two new metal coordination polymers have been synthesized.
- IR, PXRD, TG technique for the polymers.
- X-ray single-crystal structure analyses and discussion for two polymers.
- Luminescence properties of two complexes have been investigated.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Two new metal complexes,  $[\text{Ni}(\text{btx})(\text{nip})(\text{H}_2\text{O})]_n$  (**1**),  $\{[\text{Cd}(\text{btx})(\text{mip})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$  (**2**) (btx = 1,4-bis(1,2,4-triazol-1-ylmethyl)benzene,  $\text{H}_2\text{nip}$  = 5-nitroisophthalic acid,  $\text{H}_2\text{mip}$  = 5-methyisophthalic acid) were synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction methods, IR spectroscopy, TGA and elemental analysis. Complex **1** features a 3D metal-organic framework with three-fold interpenetrating  $\text{CdSO}_4$ -type topology. Complex **2** exhibits a 2D network with square grid units, which is further extended into a rare **3,5T1** three-dimensional supramolecular network via three modes of classical  $\text{O} \cdots \text{H} \cdots \text{O}$  hydrogen bonds. In addition, luminescence properties of **1** and **2** have also been investigated in the solid state.

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### Introduction

Metal organic coordination polymers (MOCs) assembled from the linkage of metal center atoms through organic ligands have vital applications in luminescent devices, gas storage, ion exchange, separations, biomedicine, catalysis and so on [1–6]. In order to get

such intriguing topologies and functional materials, the crucial step is to employ appropriate organic building blocks as well as metal ions. However, construction of MOCs with expected structures and properties in hydrothermal reactions is still a challenge, owing to the fact that the assembly of such complexes can be easily influenced by the geometrical and electronic properties of metal ions and ligands, temperature, pH value of the solution, etc. In recent years, 1,2,4-triazole and its derivatives have often been chosen as ligands for the construction of interesting and

\* Corresponding author. Tel.: +86 0315 2592169; fax: +86 0315 2592170.

E-mail address: [tscghua@126.com](mailto:tscghua@126.com) (G.-h. Cui).

fascinating structures [7–11]. Especially, the flexible 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene (btx) not only possesses the merits of triazole, but can also freely bend and rotate to interact with metal ions. [12–14]. A series of Cd–btx complexes with the third-order NLO (nonlinear optics) properties and Co–btx coordination polymers with novel topologies have been studied [15,16]. In addition, aromatic carboxylates such as 1,2,4,5-benzenetetracarboxylate, 1,3,5-benzenetricarboxylate, terephthalate, 5-substituted isophthalate, ligands are of particular interest due to their multi-carboxylate groups and the versatile coordination modes of these carboxylate groups, such as monodentate, bis-monodentate or chelating modes, leading to diverse structures of the resulting MOCPs [17]. The combination of flexible btx and aromatic polycarboxylate ligands may induce novel architectures and versatile properties. Wang and co-workers have presented a rare example of entangled coordination polymer containing both interpenetrating and polythreading features coordination polymer  $[\text{Zn}(\text{CH}_3\text{O-ip})(\text{btx})_2 \cdot \text{H}_2\text{O}]_n$  ( $\text{CH}_3\text{O-ip}$  = 5-methoxyisophthalate) [18]. We have reported three unprecedented binodal high-connected metal-organic frameworks constructed from btx and 1,2,4,5-benzenetetracarboxylate [19,20]. As a part of our ongoing studies on ternary transition metal complexes based on btx and aromatic carboxylate ligands, two new coordination polymers with interesting luminescence properties were prepared and structurally characterized.  $[\text{Ni}(\text{btx})(\text{nip})(\text{H}_2\text{O})]_n$  (**1**) ( $\text{H}_2\text{nip}$  = 5-nitroisophthalic acid,  $\text{H}_2\text{mip}$  = 5-methyisophthalic acid) reveals a 3-fold interpenetrating 3D  $\text{CdSO}_4$ -type network, while  $\{[\text{Cd}(\text{btx})(\text{mip})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$  (**2**) shows a 2D (4, 4) sheet-like network, which is finally extended into a 3D **3,5T1** supramolecular framework through multiple strong hydrogen bond interactions. To the best of our knowledge, coordination polymers exhibiting such **3,5T1** supramolecular network have only rarely been reported [21].

## Experimental

### Materials and measurements

All reagents were obtained from commercial sources and used without further purification. The ligand btx was prepared according to literature procedures [22]. Elemental analysis (C, H, and N) was performed on a Perkin–Elmer 240C Elemental Analyzer. Power X-ray diffraction (XRD) data were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. FT-IR spectra were recorded on an Avatar 360 (Nicolet) spectrophotometer between 400 and 4000  $\text{cm}^{-1}$ , using the KBr pellet method. Thermogravimetric analyses (TGA) were conducted on a Netzsch TG 209 thermal analyzer in  $\text{N}_2$  environmental at a heating rate of 10  $^\circ\text{C}/\text{min}$  up to 800  $^\circ\text{C}$ . The fluorescence spectra were collected with a Hitachi F-4500 spectrophotometer at room temperature.

### Preparation of the complexes **1** and **2**

#### $[\text{Ni}(\text{btx})(\text{nip})(\text{H}_2\text{O})]_n$ (**1**)

A mixture of  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.1 mmol, 24.9 mg), btx (0.1 mmol, 24.0 mg),  $\text{H}_2\text{nip}$  (0.1 mmol, 105.5 mg) was added in 20 mL  $\text{H}_2\text{O}$ . It was then sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 160  $^\circ\text{C}$  for 3 days; then, the reaction system was cooled to room temperature at 5  $^\circ\text{C}/\text{h}$ . Green block-shaped crystals were collected by filtration and washed with distilled water in 45% yield (based on  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ). Anal. Calcd. for  $\text{C}_{20}\text{H}_{17}\text{N}_7\text{NiO}_7$  (%): C, 45.66, H, 3.26, N, 18.64. Found (%): C, 45.32, H, 3.12, N, 18.39. IR (KBr,  $\text{cm}^{-1}$ ): 3420(vs), 3120(w), 2368(w), 1617(s), 1532(s), 1461(s), 1353(s), 1282(s), 1125(w), 733(w), 677(w).

#### $\{[\text{Cd}(\text{btx})(\text{mip})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**2**)

The synthetic procedure of **2** was analogous to the synthesis of **1**, except that  $\text{H}_2\text{nip}$  and  $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  were used instead of  $\text{H}_2\text{mip}$  (0.1 mmol, 18.0 mg) and  $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (0.1 mmol, 26.7 mg), respectively. Colorless block-shaped crystals of **2** (yield: 43%) could be obtained. Anal. Calcd. for  $\text{C}_{21}\text{H}_{22}\text{CdN}_6\text{O}_6$  (%): C, 44.50, H, 3.91, N, 14.83. Found (%): C, 44.36, H, 3.82, N, 14.55. IR (KBr,  $\text{cm}^{-1}$ ): 3427(vs), 3103(w), 2948(w), 1640(s), 1542(s), 1483(s), 1348(s), 1284(w), 1064(s), 733(w), 683(w).

### X-ray crystallography

The crystallographic data for the single crystal of compound **1** was collected at 100 K on an Agilent SuperNova Dual Source diffractometer with Atlas CCD detector, microfocus sources and focusing multilayer optics, using Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å). CrysAlis PRO [23] software was used to collect, index, scale and apply analytical absorption correction based on faces of the crystal with multi-scan mode. X-ray diffraction data for **2** was collected on a Bruker Smart 1000 CCD diffractometer using graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature with  $\omega$ -scan mode. A semi-empirical absorption correction was applied using the SADABS program [24]. Both structures were solved by direct methods with SHELXS-97 and refined by full-matrix least squares on  $F^2$  with SHELXTL [25]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The H-atoms of organic ligands were generated theoretically onto the specific atoms and refined isotropically. The aqua hydrogen atoms in **1** and **2** were located from difference Fourier maps and refined with isotropic displacement parameters. The crystallographic data for **1** and **2** are listed in Table 1, and selected length and angle parameters for **1** and **2** are presented in Table 2, respectively.

## Results and discussion

### Crystal structures

#### Crystal structures of compound **1**

The structure of **1** is a 3D MOF. X-ray analysis reveals that **1** crystallized in the monoclinic space group Cc. The asymmetric unit

**Table 1**  
Crystal and refinement data for complexes **1** and **2**.

	1	2
Empirical formula	$\text{C}_{20}\text{H}_{17}\text{N}_7\text{NiO}_7$	$\text{C}_{21}\text{H}_{22}\text{CdN}_6\text{O}_6$
Formula weight	526.12	566.85
Crystal system	Monoclinic	Triclinic
Space group	Cc	P $\bar{1}$
<i>a</i> (Å)	16.1760(3)	10.2021(7)
<i>b</i> (Å)	16.9691(3)	11.4351(8)
<i>c</i> (Å)	7.3806(2)	11.8614(8)
$\alpha$ (deg)	90	69.2300(8)
$\beta$ (deg)	94.459(2)	68.8065(8)
$\gamma$ (deg)	90	67.0920(7)
<i>V</i> (Å <sup>3</sup> )	2019.77(7)	1150.98(14)
<i>Z</i>	4	2
<i>D</i> <sub>calc</sub> (g/m <sup>3</sup> )	1.730	1.636
$\mu$ (mm <sup>-1</sup> )	1.025	0.999
<i>F</i> (000)	1080	572
Crystal size (mm)	0.28 × 0.21 × 0.15	0.27 × 0.23 × 0.22
Total reflections	21,862	7039
Unique reflections	4784	5062
<i>R</i> <sub>int</sub>	0.0635	0.0164
GOF	0.851	1.002
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0366	0.0254
<i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0805	0.0622
$\Delta\rho$ max (eÅ <sup>-3</sup> )	0.393	0.341
$\Delta\rho$ min (eÅ <sup>-3</sup> )	-0.330	-0.421

$$R_1 = \sum |F_o| - |F_c| / \sum |F_o|; wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$$

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