

# Isomer transformation and photoluminescence in novel coordination polymers constructed from 1,4-cyclohexanedicarboxylic acid and imidazole

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## Abstract

Three novel coordination polymers  $[M(\text{chdc})(\text{imi})]_n$  (chdc = 1,4-cyclohexanedicarboxylic dianion, imi = imidazole,  $M = \text{Ni}$  **1**,  $\text{Co}$  **2** and  $\text{Zn}$  **3**) have been synthesized by solvothermal technique and characterized by elemental analysis, IR and single-crystal X-ray diffraction. The *trans*-chdc have been partially transformed into *cis*-chdc and the *cis*-chdc have been separated from the mixture of *cis*- and *trans*-chdc in the synthetic reactions of the three compounds. The three compounds exhibit similar one dimension chain-like architecture constructed by their  $M(\text{II})$  dimers interconnected via double strands of *cis*-chdc-bridge.  $M(\text{II})$  atom of the dimer exhibits a square-pyramidal geometry and interaction happens within two metal centers. Both compounds **1** and **2** do not exhibit emission spectra whereas compound **3** shows intense photoluminescence property at room temperature.

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**Keywords:** 1,4-cyclohexanedicarboxylic acid; Solvothermal synthesis; Imidazole; Transformation; Photoluminescence

## 1. Introduction

The rational design and synthesis of novel coordination polymers is of current interest in the field of supramolecular chemistry and crystal engineering, not only because of their intriguing structural motifs but also because of their potential applications in catalysis, molecular adsorption, magnetism, nonlinear optics, and molecular sensing [1–11]. Consequently, a variety of coordination polymers with interesting compositions and topologies have been prepared through taking certain factors into account, such as the coordination nature of the metal ion and the shape, functionality, flexibility, and symmetry of organic ligand [12–20]. A

guiding principle of our work is the attempt to control the conformations of flexible spacer ligands in the architecture of the products. 1,4-cyclohexanedicarboxylic acid ( $\text{chdcH}_2$ ) possesses a chair-type structure with *cis*- and *trans*-conformations, it can connect metal ions in different directions and attracts researchers' great interest. A serial of metal–chdc complexes with different coordination networks have been reported previously [21–27]. If some organic nitrogen donors such as 1,10-phenanthroline, 2,2'-bipyridine [28–30] are introduced into the framework of metal–chdc complexes, it is expected that novel coordination polymer with special properties can be constructed. Imidazole as an *exo*-bidentate rigid nitrogen donor is rarely investigated in the architecture of flexible chdc system. Previous chdc-involved complexes were usually synthesized by hydrothermal technique [21–30], but water as a good coordination ligand or hydrogen bonding synthon is easily incorporated into the final product. In the

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present work we utilized solvothermal technique, replacing water by ethanol and synthesized three novel coordination polymers  $[M(\text{chdc})(\text{imi})]_n$  ( $M = \text{Co}$  **1**,  $\text{Ni}$  **2** and  $\text{Zn}$  **3**). The *trans*-chdc have been partially transformed into *cis*-chdc and the *cis*-chdc have been separated from the mixture of *cis*- and *trans*-chdc in the synthetic reactions of the three compounds. The three compounds exhibit similar one-dimensional chain-like structure constructed by their  $M(\text{II})$  dimers interconnected via double strands of *cis*-chdc-bridge. Due to the different metal ions in the structure, only compound **3** shows intense photoluminescence property.

## 2. Experimental section

### 2.1. Synthesis and characterization

All chemicals purchased were of reagent grade and used without further purification. C, H, N elemental analyses were performed on Perkin-Elmer 240c elemental analyzer. Infrared spectra were recorded as KBr pellets on a Nicolet 170SXFT/IR spectrometer. X-ray power diffraction (XRD) analyses were obtained on a Japan Rigaku D/max  $\gamma$ A X-ray diffractometer equipped with graphite monochromatized  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154056 \text{ nm}$ ). The  $2\theta$  range used was from  $5^\circ$  to  $40^\circ$  in steps of  $4^\circ \text{ min}^{-1}$ . Excitation and emission spectra were obtained on a Spex FL-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source. Luminescence lifetimes were measured with a Spex 1934D phosphorimeter using a 7 W pulsed xenon lamp as the excitation source. All measurements were performed at room temperature.

### 2.2. Synthesis of $[M(\text{chdc})_2(\text{imi})_2]_n$

A mixture of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol, 0.119 g),  $\text{chdcH}_2$  (mixture of *cis* and *trans* 99%) (1 mmol, 0.172 g), imidazole (0.5 mmol, 0.034 g),  $\text{NaOH}$  (0.75 mmol, 0.30 g) and ethanol (10 mL) was sealed in Teflon-lined autoclaves and heated at  $160^\circ\text{C}$  for 3 days, followed by slow cooling to room temperature. The resulting green block crystals of **1** were isolated by mechanical separation from a blue amorphous solid, then washed with ethanol (yield: ca. 30% based on  $\text{chdcH}_2$ ). Elemental Analysis Calculated for  $\text{C}_{11}\text{H}_{14}\text{NiN}_2\text{O}_4$ : C, 44.44; H, 4.71; N, 9.43%. Found: C, 44.59; H, 4.80; N, 9.48%.

The syntheses of **2** and **3** were similar to that described above except using  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol, 0.119 g) or  $\text{ZnCl}_2$  (0.5 mmol, 0.068 g) instead of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , and blue crystals of **2** and pink crystals of **3** were yielded (yields: ca. 30% based on  $\text{chdcH}_2$ ). Elemental Anal. Calculated for  $\text{C}_{11}\text{H}_{14}\text{CoN}_2\text{O}_4$ : C, 44.44; H, 4.71; N, 9.43%. Found: C, 44.51; H, 4.78; N, 9.58%. Calculated

for  $\text{C}_{11}\text{H}_{14}\text{ZnN}_2\text{O}_4$ : C, 43.56; H, 4.62; N, 9.24%. Found: C, 43.51; H, 4.80; N, 9.40%.

### 2.3. X-ray crystallography

Single crystals of dimensions  $0.25 \times 0.18 \times 0.13 \text{ mm}^3$  for **1**,  $0.38 \times 0.32 \times 0.21 \text{ mm}^3$  for **2**,  $0.42 \times 0.40 \times 0.38 \text{ mm}^3$  for **3** were used for structure determination. XRD data of **1**, **2** and **3** were collected on a Bruker-AXS CCD area detector-equipped diffractometer with graphite-monochromatized  $\text{MoK}\alpha$  ( $\lambda = 0.07103 \text{ \AA}$ ) radiation at room temperature. A total of 6345 (2171 unique,  $R_{\text{int}} = 0.0248$ ) reflections of **1** ( $-16 \leq h \leq 11$ ,  $-12 \leq k \leq 12$ ,  $-20 \leq l \leq 20$ ,  $2.35 < \theta < 25.03$ ), a total of 6116 (2163 unique,  $R_{\text{int}} = 0.0698$ ) reflections of **2** ( $-16 \leq h \leq 16$ ,  $-8 \leq k \leq 12$ ,  $-20 \leq l \leq 20$ ,  $2.34 < \theta < 25.03$ ), a total of 6376 (2181 unique,  $R_{\text{int}} = 0.0286$ ) reflections of **3** ( $-16 \leq h \leq 13$ ,  $-12 \leq k \leq 12$ ,  $-20 \leq l \leq 17$ ,  $2.33 < \theta < 25.02$ ) were measured. An empirical absorption correction from  $\psi$  scan was applied. All the structure was solved by direct methods and expanded using Fourier techniques. The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were added in their calculated positions. All calculations were performed using the SHELXTL-97 program [31,32]. The CCDC reference numbers are the following: 257 267 for **1**, 258 191 for **2**, 259 389 for **3**. Crystal data and structure refinements for compounds **1**, **2** and **3** are listed in Table 1. Selected bond lengths and angles for **1** are listed in Table 2. Bond lengths and angles for **2** and **3** are available in supplementary information.

## 3. Results and discussion

### 3.1. Synthesis

Hydrothermal or solvothermal synthesis has recently been proved a useful technique in preparation of organic–inorganic hybrid materials. In a relatively low temperature and autogenous pressure environment, problems of different solubility for ligands are minimized. In our cases, the species of solvent is of crucial important for the crystallization of the three compounds. If water was involved in the preparations, the crystals obtained were not in good quality. The mole ratio of  $\text{chdcH}_2$  and imidazole can range from 1: 1 to 1:0.3, which indicates the amount of imidazole is not very crucial if that of  $\text{chdcH}_2$  is fixed. The preparations of the three compounds were not susceptible to the reaction temperature. The temperature can range from  $80$  to  $170^\circ\text{C}$  if only boiling state of solvent ethanol is kept constant.

Table 1  
Crystal data and structure refinements for **1**, **2** and **3**

Compound	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>11</sub> H <sub>14</sub> NiN <sub>2</sub> O <sub>4</sub>	C <sub>11</sub> H <sub>14</sub> CoN <sub>2</sub> O <sub>4</sub>	C <sub>11</sub> H <sub>14</sub> ZnN <sub>2</sub> O <sub>4</sub>
Formula weight	296.95	297.17	303.61
Temperature (K)	298(2)	298(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	C2/c	C2/c
<i>a</i> (Å)	13.946(3)	13.870(4)	13.930(4)
<i>b</i> (Å)	10.181(2)	10.178(3)	10.181(3)
<i>c</i> (Å)	17.369(3)	17.410(3)	17.458(5)
$\alpha$ (°)	90	90	90
$\beta$ (°)	90.433(3)	90.053(2)	91.249(5)
$\gamma$ (°)	90	90	90
Volume (Å <sup>3</sup> )	2466.0(8)	2457.6(11)	2475.2(13)
<i>Z</i>	8	8	8
$\rho_{\text{calc}}$ (Mg m <sup>-3</sup> )	1.600	1.606	1.629
Absorption coefficient (mm <sup>-1</sup> )	1.581	1.404	1.992
<i>F</i> (000)	1232	1224	1248
Crystal size (mm <sup>3</sup> )	0.25 × 0.18 × 0.13	0.38 × 0.32 × .21	0.42 × 0.40 × 0.38
$\theta$ range (deg)	2.35–25.03	2.34–25.03	2.33–25.02
Limiting indices	−16 ≤ <i>h</i> ≤ 11, −12 ≤ <i>k</i> ≤ 12, −20 ≤ <i>l</i> ≤ 20,	−16 ≤ <i>h</i> ≤ 16, −8 ≤ <i>k</i> ≤ 12, −20 ≤ <i>l</i> ≤ 20	−16 ≤ <i>h</i> ≤ 13, −12 ≤ <i>k</i> ≤ 12, −20 ≤ <i>l</i> ≤ 17
Reflections collected	6345	6116	6376
Independent reflections	2171	2163	2181
Absorption correction	$\psi$ -scan	$\psi$ -scan	$\psi$ -scan
Max. and min. transmission	0.8208 and 0.6933	0.7569 and 0.6174	0.8410 and 0.7033
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data, restraints, parameters	2171, 0, 163	2163, 0, 163	2181, 0, 163
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.079	1.011	1.077
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0265, <i>wR</i> <sub>2</sub> = 0.0585	<i>R</i> <sub>1</sub> = 0.0469, <i>wR</i> <sub>2</sub> = 0.1106	<i>R</i> <sub>1</sub> = 0.0341, <i>wR</i> <sub>2</sub> = 0.0886
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0360, <i>wR</i> <sub>2</sub> = 0.0634	<i>R</i> <sub>1</sub> = 0.0760, <i>wR</i> <sub>2</sub> = 0.1272	<i>R</i> <sub>1</sub> = 0.0427, <i>wR</i> <sub>2</sub> = 0.0927
Largest diff. peak and hole	0.291 and −0.287	0.672 and −0.618	0.598 and −0.266

$$R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; wR_2 = \Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)]^{1/2}.$$

Table 2  
Selected bond lengths (Å) and angles (°) for [Ni(chdc)<sub>2</sub>(imi)<sub>2</sub>]<sub>n</sub>, **1**

Bond lengths			
Ni(1)–N(1)	1.983(2)	Ni(1)–O(1)	2.0301(17)
Ni(1)–O(2)#3	2.0163(17)	Ni(1)–O(3)#2	2.0087(16)
Ni(1)–O(4)#1	2.0056(17)	Ni(1)–Ni(1)#3	2.6549(7)
O(3)–Ni(1)#4	2.0087(16)	O(4)–Ni(1)#1	2.0056(17)
Bond angles			
O(4)#1–Ni(1)–O(1)	87.87(7)	O(2)#3–Ni(1)–O(1)	167.12(7)
O(4)#1–Ni(1)–O(3)#2	166.86(7)	O(3)#2–Ni(1)–O(1)	93.04(7)
N(1)–Ni(1)–O(1)	94.77(8)	N(1)–Ni(1)–O(2)#3	97.83(8)
N(1)–Ni(1)–O(4)#1	96.87(8)	N(1)–Ni(1)–O(3)#2	96.11(8)
O(1)–Ni(1)–Ni(1)#3	74.28(5)	O(2)#3–Ni(1)–Ni(1)#3	93.22(5)
O(4)#1–Ni(1)–Ni(1)#3	85.15(5)	O(3)#2–Ni(1)–Ni(1)#3	82.49(5)
N(1)–Ni(1)–Ni(1)#3	168.82(6)	C(7)–O(1)–Ni(1)	135.09(17)
C(7)–O(2)–Ni(1)#3	112.94(16)	C(8)–O(3)–Ni(1)#4	125.16(16)

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

### 3.2. Structure description

The X-ray crystal structure analyses of **1**, **2** and **3** reveal that the three compounds are isostructural

(Table 1). Therefore, we will restrict our description to the nickel compound **1** and only mention pertinent points for the cobalt and zinc compounds **2**, **3** where appropriate.

In compound **1**, there is one crystallographically unique Ni (II), one unique imidazole and one unique chdc. As shown in Fig. 1, Ni (II) exhibits a square-pyramidal coordination sphere and is five coordinated by one nitrogen atom from imidazole (Ni(1)–N(1) 1.983(2) Å) and four oxygen atoms from different chdc ligands (Ni(1)–O(1) 2.0301(17) Å, Ni(1)–O(2A) 2.0163(17) Å, Ni(1)–O(3B) 2.0087(16) Å, Ni(1)–O(4C) 2.0056(17) Å). The O–Ni–O bond angles range from 87.87(7) to 167.12 (7)° and the N–Ni–O bond angles range from 94.77(8) to 97.83(8)° (Table 2). Each carboxylate group of chdc exhibits bi-dentate coordination mode and connects two Ni(II). A lantern-like dimer is formed via two Ni(II) connected by four carboxylate groups from four different chdc ligands, in which two carboxylate groups and two Ni(II) constitute an approximately coplanar ten membered ring. The dimer consists of two approximately perpendicular ten membered rings (dihedral angle: 92.3°) (Fig. 1). The Ni

(1)⋯Ni(1A) distance is 2.6549(7) Å and the Ni⋯Ni–O angles range from 74.28(5)° to 93.22(5)°, it is expected that magnetic coupling will happen within the two nickel centers [33]. The Co (1)⋯Co (1A) and Zn (1)⋯Zn (1A) distances in compounds 2 and 3 are 2.756 and 2.651 Å, respectively.

Compounds 1, 2 and 3 exhibit similar one dimension chain-like architecture that is constructed by their *M*(II) dimers interconnected via double strands of chdc-bridge. The interesting feature in the structure of the three compounds is that the flexible chdc ligands possess only one kind of *e, a*-*cis*-form and empty cavity is left

within the double strands of chdc-bridge (Figs. 1 and 2). No solvent molecules occupy the cavity in the three compounds. The empty channel in compound 1 is ca. 18 Å<sup>2</sup> in terms of the C (7)⋯C (8) (5.035 Å) and C (7)⋯C (8C) distance (3.574 Å).

As well known, chdcH<sub>2</sub> possesses one *cis*- and two *trans*-conformations, that is, *e, a*-*cis*-, *e, e*-*trans*- and *a, a*-*trans*-chdcH<sub>2</sub> (Scheme 1). The *e, e*-*trans*-form is the most thermodynamically stable due to its two equatorial substituents and the *a, a*-*trans*-form is the least stable because of 1,3-diaxial hindrance [34]. Due to the rotation of flexible C–C bond and the spontaneous

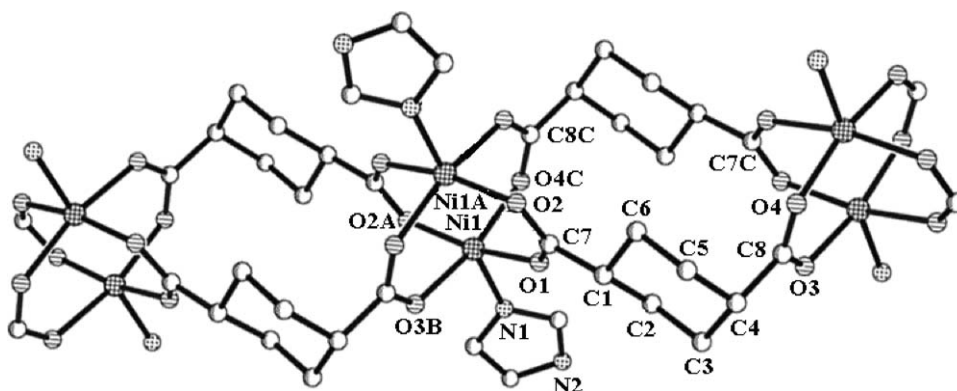


Fig. 1. ORTEP drawing of [Ni(chdc)<sub>2</sub>(imi)<sub>2</sub>]<sub>n</sub> 1 with the atoms labeled (H atoms omitted for clarity). Atoms with additional labels A, B and C referring to symmetry operations: (A)  $-x+1, -y+2, -z+1$ ; (B)  $x+1/2, y+1/2, z$ ; and (C)  $-x+3/2, -y+5/2, -z+1$ .

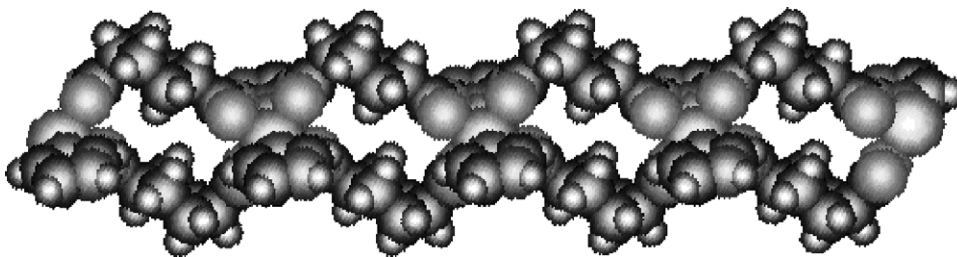
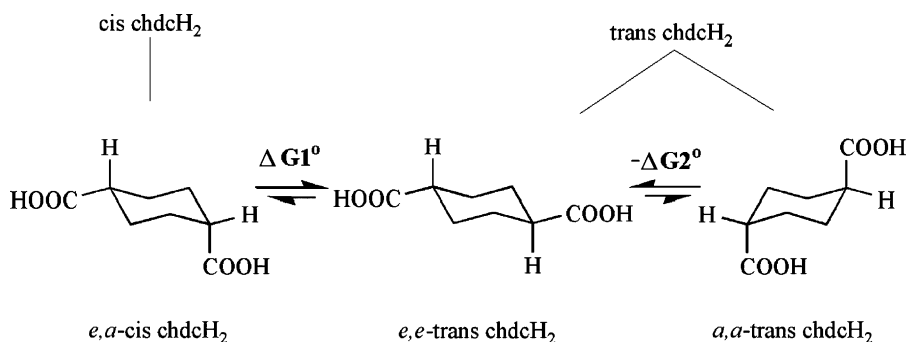


Fig. 2. Space-filling diagram of compound 1 viewed down *c*-axis showing empty cavity within double strands of chdc-bridge.



Scheme 1. Three conformations of 1,4-chdcH<sub>2</sub>.



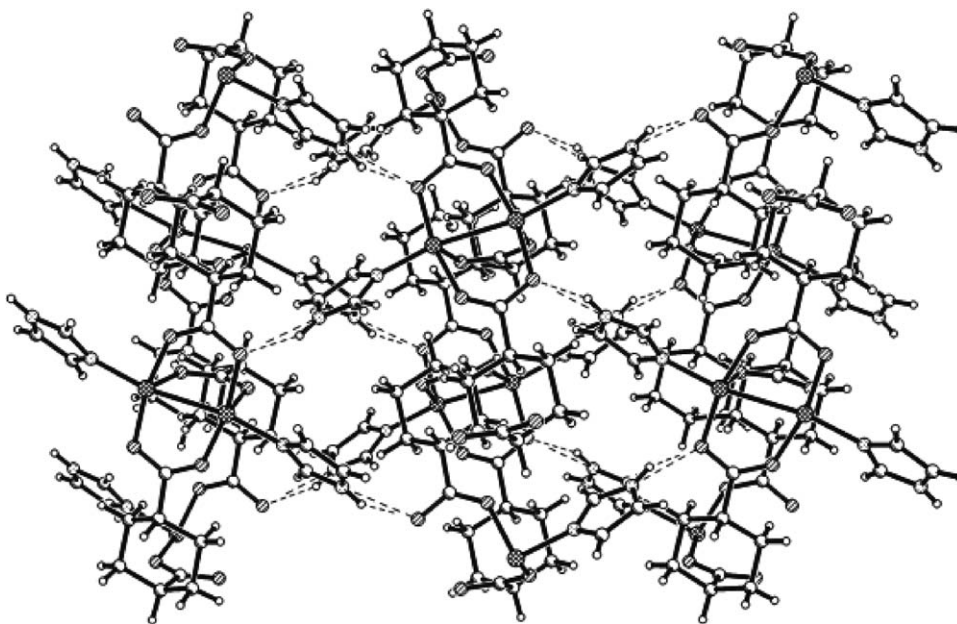


Fig. 3. Crystal packing of compound **1** viewed down *a*-axis.

conformational inversion of  $\text{chdcH}_2$ , the *e*- and *a*-positions of  $\text{chdcH}_2$  can be interconverted. Therefore, thermodynamic equilibrium exists among the three conformations of  $\text{chdcH}_2$  though the *e,e*-*trans*-form is the preferential conformation (Scheme 1) [22,35–38]. As shown in Scheme 1, the  $\Delta G_1^\circ$  and  $\Delta G_2^\circ$  are  $-1.4$  and  $-2.8 \text{ kcal mol}^{-1}$ , respectively. Such low  $\Delta G^\circ$  value theoretically indicates the possibility of conformational inversion [34]. According to  $-\Delta G^\circ = RT \ln K_a$ , it is calculated that the amount of *a,a*-*trans*- $\text{chdcH}_2$  is so little as to be neglected at normal temperature ( $20^\circ\text{C}$ ) and the mole ratio of *e*, *a*-*cis*- and *e,e*-*trans*- $\text{chdcH}_2$  is ca. 1: 11 [39]. Therefore, the *cis*- and *trans*- $\text{chdc}$  always co-exist at normal temperature and 1 mmol  $\text{chdcH}_2$  contains ca. 0.08 mmol *cis*- and 0.92 mmol *trans*- $\text{chdc}$ .

The introduction of imidazole ligands, which blocks the extension of two- or three-dimensional architectures caused  $\text{chdc}$  adopted the *cis*-conformation to be incorporated into the products for less steric hindrance to form one dimension chain. The yields of compounds **1–3** are all 30% based on  $\text{chdcH}_2$ , which indicates that 0.3 mmol *cis*- $\text{chdc}$  can be obtained in the solid state of compounds **1–3** from 1 mmol initial  $\text{chdcH}_2$  (in which *cis*- $\text{chdc}$  is 0.08 mmol). It is inferred that ca. 0.22 mmol (0.3–0.08 leaves 0.22) *trans*- $\text{chdc}$  have been transformed into *cis*- $\text{chdc}$  in the solid state. The solution is still the mixture of *cis*- and *trans*- $\text{chdc}$  in which thermodynamic equilibrium has been arrived. Only *cis*- $\text{chdc}$  is found in compounds **1–3**, which indicates that *cis*- $\text{chdc}$  has been separated from the mixture of *cis*- and *trans*- $\text{chdc}$  [28]. Furthermore, the present work shows the isomer of  $\text{chdc}$

transformation and separation can be achieved by different metal ions under same conditions.

Besides occupying one coordination position of  $M(\text{II})$ , imidazole can utilize its uncoordinated protonated nitrogen atom to form hydrogen bonding with oxygen atom of  $\text{chdc}$  ligand (Fig. 3). For example:  $\text{H}(2)\cdots\text{N}(2)$ : 0.860 Å,  $\text{H}(2)\cdots\text{O}(2)$ : 2.083 Å,  $\text{N}(2)\cdots\text{O}(2)$ : 2.892 Å,  $\text{N}(2)\text{--H}(2)\cdots\text{O}(2)$ :  $156.3^\circ$ . Viewed down *c*-axis, undulated chains are formed by lantern-like  $M(\text{II})$  dimers connected each other via intermolecular weak interactions (Fig. 4).

### 3.3. IR spectrum

The IR spectrum of compound **1** shows characteristic bands of carboxylate groups at  $1608$  and  $1514 \text{ cm}^{-1}$  for the antisymmetric stretching and at  $1413 \text{ cm}^{-1}$  for symmetric stretching. The separations ( $\Delta$ ) between  $\nu_{\text{asym}}(\text{CO}_2)$  and  $\nu_{\text{sym}}(\text{CO}_2)$  bands indicate the presence of bidentate coordination mode [40]. The IR spectra of compounds **2** and **3** exhibit similar characteristic bands at  $1618$ ,  $1508$ ,  $1413 \text{ cm}^{-1}$  and  $1612$ ,  $1503$ ,  $1414 \text{ cm}^{-1}$ , respectively. Single-crystal X-ray diffractions show that carboxylate groups coordinate to the metal atoms in compounds **1**, **2** and **3** in an absolutely same fashion, the shifts of the characteristic bands result from their different metal atoms. The absence of the characteristic bands at around  $1700 \text{ cm}^{-1}$  in compounds **1**, **2** and **3** attributed to the protonated carboxylate group indicates that the complete deprotonation of  $\text{chdc}$  ligand upon reaction with Ni, Co and Zn ions [41]. The IR spectra of

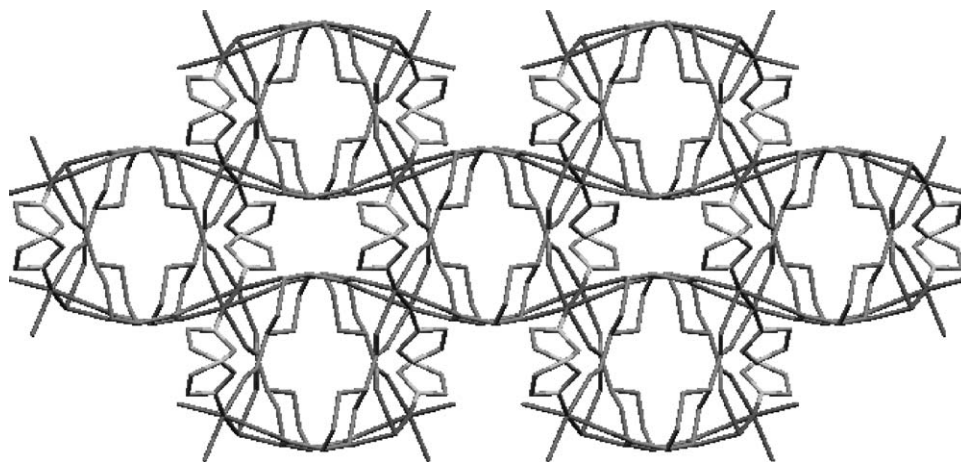


Fig. 4. Undulated chains of compound **1** viewed down *c*-axis (H atoms omitted for clarity).

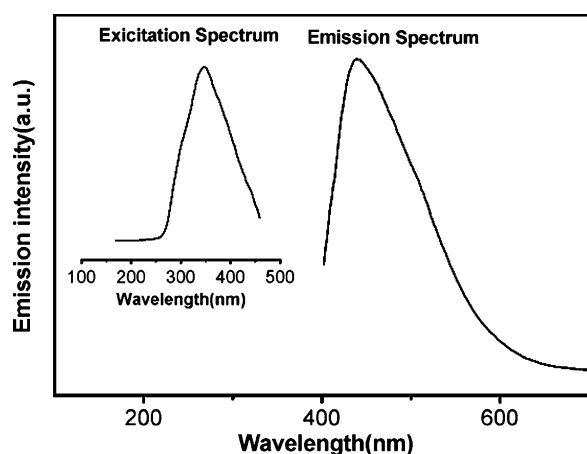


Fig. 5. Solid-state emission spectrum of compound **3** at room temperature.

compounds **1**, **2** and **3** exhibit a serial of characteristic peaks of imidazole in the  $740\text{--}1360\text{ cm}^{-1}$  range.

### 3.4. Photoluminescence property

The powder X-ray diffraction patterns of compounds **1**, **2** and **3** are shown in Fig. S1 in the supporting information. All the peaks of the three compounds can be indexed to their respective simulated XRD powder pattern, which indicates each of the three compounds is pure phase. In the solid state, compound **3** exhibits an intense emission at 430 nm in the blue region ( $\lambda_{\text{ex}} = 356\text{ nm}$ ) at room temperature (see Fig. 5). To understand the nature of the emission band, we analyzed the photoluminescence properties of the chdc and imidazole ligands and found that imidazole is a nonphotoluminescent ligand and the strongest emission peak for chdc is at about 446 nm, which is attributable to the  $\pi^* \rightarrow n$  transition [42]. According to literatures in

which similar emission bands at about 430 nm have been previously reported for other zinc-organic polymers [43], the emission band observed in compound **3** might be attributable to the ligand-to-metal charge transfer (LMCT). The existence of dinuclear Zn(II), double strands of chdc-bridge and the supramolecular interactions in the structure cause the intense photoluminescence in compound **3**. It suggests that compound **3** may be an excellent candidate for potential photoactive materials. Whereas for different metal atoms in compounds **1** and **2**, LMCT cannot happen in the blue region and compounds **1** and **2** do not exhibit photoluminescence properties.

## 4. Conclusion

In summary, using solvothermal technique we have synthesized and characterized three novel isostructural coordination polymers **1**, **2** and **3**. The *trans*-chdc have been partially transformed into *cis*-chdc and the *cis*-chdc have been separated from the mixture of *cis*- and *trans*-chdc in the synthetic reactions of the three compounds. Double strands of *e*, *a*-*cis*-chdc-bridge with empty cavity link *M*(II) dimers to form one dimension chain. The solid-state emission spectra of the three compounds have been measured and this work shows metal ion has great influence on its photoluminescence property. Compound **3** may be an excellent candidate for potential photoactive materials.

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## Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2005.07.023](https://doi.org/10.1016/j.jssc.2005.07.023).

## References

- [1] S. Leininger, B. Olenyuk, P.J. Stang, *Chem. Rev.* 100 (2000) 853.
- [2] G.F. Swiegers, T.J. Malefetse, *Chem. Rev.* 100 (2000) 3483.
- [3] P.J. Hagrman, D. Hagrman, J. Zubietta, *Angew. Chem. Int. Ed.* 38 (1999) 2638.
- [4] Q.D. Liu, J.R. Li, S. Gao, B.Q. Ma, H.Z. Kou, L. Ouyang, R.L. Huang, X.X. Zhang, K.B. Yu, *Eur. J. Inorg. Chem.* (2003) 731.
- [5] B.Q. Ma, S. Gao, G. Su, G.X. Xu, *Angew. Chem. Int. Ed.* 40 (2001) 434.
- [6] W.F. Yeung, W.L. Man, W.Y. Wong, T.C. Lau, S. Gao, *Angew. Chem. Int. Ed.* 40 (2001) 3031.
- [7] J.S. Seo, D. Whang, H. Lee, I. Jun, J. Oh, Y.J. Jeon, K. Kim, *Nature (London)* 404 (2000) 982.
- [8] W. Lin, O.R. Evans, R.G. Xiong, Z. Wang, *J. Am. Chem. Soc.* 120 (1998) 13272.
- [9] J. Pang, E.J.P. Marcotte, C. Seward, R.S. Brown, S.N. Wang, *Angew. Chem. Int. Ed.* 40 (2001) 4042.
- [10] K. Inoue, H. Imai, P.S. Ghalsasi, K. Kikuchi, M. Ohba, H. Okawa, J.V. Yakhmi, *Angew. Chem. Int. Ed.* 40 (2001) 4242.
- [11] D. Cave, J.M. Gascon, A.D. Bond, S.J. Teat, P.T. Wood, *Chem. Commun.* (2002) 1050.
- [12] D.L. Reger, T.D. Wright, R.F. Semeniuc, T.C. Grattan, M.D. Smith, *Inorg. Chem.* 40 (2001) 6212.
- [13] M.B. Zaman, M.D. Smith, H.C. Zurloye, *Chem. Commun.* (2001) 2256.
- [14] R. Kitaura, K. Seki, G. Akiyama, S. Kitagawa, *Angew. Chem. Int. Ed.* 42 (2003) 428.
- [15] R. Kitaura, K. Fujimoto, S. Noro, M. Kondo, S. Kitagawa, *Angew. Chem. Int. Ed.* 41 (2002) 133.
- [16] X.H. Bu, W. Chen, S.L. Lu, R.H. Zhang, D.Z. Liao, W.M. Bu, M. Shionoya, F. Brisse, J. Ribas, *Angew. Chem. Int. Ed.* 40 (2001) 3201.
- [17] B. Moulton, M.J. Zaworotko, *Chem. Rev.* 101 (2001) 1629.
- [18] D. Braga, F. Grepioni, G.R. Desiraju, *Chem. Rev.* 98 (1998) 1375.
- [19] H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, *Nature* 402 (1999) 276.
- [20] S.O.H. Gutschke, D.J. Price, A.K. Powell, P.T. Wood, *Angew. Chem. Int. Ed.* 40 (2001) 1920.
- [21] W.H. Bi, R. Cao, D.F. Sun, D.Q. Yuan, X. Li, M.C. Hong, *Inorg. Chem. Commun.* 6 (2003) 1426.
- [22] Y. Kim, D.Y. Jung, *Chem. Commun.* 8 (2002) 908.
- [23] M. Kurmoo, H. Kumagai, S.M. Hughes, C.J. Kepert, *Inorg. Chem.* 42 (2003) 6709.
- [24] S. Takamizawa, W. Mori, M. Furihata, S. Takeda, K. Yamaguchi, *Inorg. Chim. Acta* 283 (1998) 268.
- [25] W.H. Bi, R. Cao, D.F. Sun, D.Q. Yuan, X. Li, Y.Q. Wang, X.J. Li, M.C. Hong, *Chem. Commun.* (2004) 2104.
- [26] J.K. Bera, R. Clérac, P.E. Fanwick, R.A. Walton, *J. Chem. Soc. Dalton Trans.* (2002) 2168.
- [27] F.A. Cotton, L.M. Daniels, C. Lin, C.A. Murillo, S.Y. Yu, *J. Chem. Soc. Dalton Trans.* (2001) 502.
- [28] Y.J. Qi, Y.H. Wang, C.W. Hu, M.H. Cao, L. Mao, E.B. Wang, *Inorg. Chem.* 42 (2003) 8519.
- [29] A.Q. Ma, M.X. Yu, L.G. Zhu, *Z. Kris. Allg.* 219 (2004) 117.
- [30] A.Q. Ma, M.X. Yu, L.G. Zhu, *Z. Kris. Allg.* 219 (2004) 63.
- [31] G.M. Sheldrick, SHELXS 97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, 1997.
- [32] G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, 1997.
- [33] D. Min, S.S. Yoon, D.Y. Jung, C.Y. Lee, Y.J. Kim, W.S. Han, S.W. Lee, *Inorg. Chim. Acta* 324 (2001) 293.
- [34] E.L. Eliel, N.L. Allinger, S.J. Angyal, G.A. Morrison, *Conformational Analysis*, Wiley, New York, 1996.
- [35] J.T. Wang, *Organic Chemistry*, Nankai University Press, Tian Jin, 1998.
- [36] E.L. Eliel, S.H. Schroeter, *J. Am. Chem. Soc.* 87 (1965) 5031.
- [37] N.L. Allinger, M.A. Miller, F.A. Vancatledge, J.A. Hirsch, *J. Am. Chem. Soc.* 89 (1967) 4345.
- [38] E.M. Engler, J.D. Andose, P.R. Schleyer, *J. Am. Chem. Soc.* 95 (1973) 8005.
- [39] X.C. Fu, *Physical Chemistry*, Advanced Education Press, Beijing, 1990.
- [40] K. Nakamoto, *Infrared Spectra and Raman Spectra of Inorganic and Coordination Compound*, Wiley, New York, 1986.
- [41] L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1958.
- [42] W. Chen, J.Y. Wang, C. Chen, Q. Yue, H.M. Yuan, J.X. Chen, S.N. Wang, *Inorg. Chem.* 42 (2003) 944.
- [43] L.Y. Zhang, G.F. Liu, S.L. Zheng, B.H. Ye, X.M. Zhang, X.M. Chen, *Eur. J. Inorg. Chem.* (2003) 2965.