

Rapid Communication

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Synthesis and crystal structure of one new cadmium coordination polymer constructed by phenanthroline derivate and 1,4-naphthalenedicarboxylic acid

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Abstract: A cadmium coordination polymer, $[\text{Cd}(1,4\text{-NDC})(\text{L})]_n$ (**1**), has been hydrothermally synthesized by using 1-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)naphthalen-2-ol (L) and 1,4-naphthalenedicarboxylic acid (1,4- H_2NDC). The complex **1** was characterized by diffraction and elemental analyses. In complex **1**, the cadmium ion is distorted octahedral coordinated linking the deprotonated 1,4-NDC anion to form a two-dimensional (2D) layer, and the 2D layer are associated into 3D supramolecular structure via the strong π - π stacking interactions from the conjugated L ligands. In addition, thermogravimetry, powder X-ray diffraction, and the solid-state photoluminescent properties of complex **1** were also studied.

Keywords: cadmium(II), 1,10-phenanthroline derivate, N-containing ligand, crystal structure

Coordination polymers (CPs) (Tang et al., 2006; Zhao et al., 2004; Li et al., 2020) have attracted considerable research interest due to their intriguing architectures and potential applications as functional materials in the areas of chemical separation, ion-exchange, magnetism, heterogeneous catalysis, gas adsorption, and so on (Bloch et al., 2012; Fan et al., 2021; Gómez et al., 2002; Li et al., 2021; Zhang et al., 2020; Zhao et al., 2021). The design and synthesis of functional cadmium CPs (including metal-organic frameworks) have paid great attention owing to their instinct electronic, luminescent, and biological properties (Lan et al., 2009; Liu et al., 2016). Recent research studies in this field have primarily focused on constructing novel frameworks with the typical N-donor ligands, which exhibit excellent coordination ability (including various coordination modes) and interesting properties (Pasán et al., 2009; Qiu et al., 2015; Song et al., 2021). Especially, 1,10-phenanthroline (phen) as an excellent N-donor bidentate chelating ligand, not only endowed the substituents with richer coordination properties, but also widely used in the field of metal catalysis (Zhang et al., 2000). In 2021, Hendrich's team synthesized two novel three-dimensional (3D) lanthanide dicyanoaurate CPs by reacting the bidentate ligand 1,10-phenanthroline oxide in the presence of lanthanide nitrate salts with phen and potassium dicyanoaurate (Hendrich et al., 2021).

Based on the abovementioned, 1,4-naphthalenedicarboxylic acid (1,4- H_2NDC) and the derivative 1-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)naphthalen-2-ol ligands (L) were selected as organic carboxylate and auxiliary ligands to react with $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, the novel 3D complex $[\text{Cd}(1,4\text{-NDC})(\text{L})]_n$ (**1**) has been successfully synthesized (Kong et al., 2015).

As described in Figure 1, the asymmetric unit of **1** contains one unique Cd(II) atom, one L ligand, and one unique 1,4-NDC anion. Each Cd(II) atom adopts a distorted tetragonal-octahedral geometry coordinated by two N atoms from one L ligands, and four O atoms of

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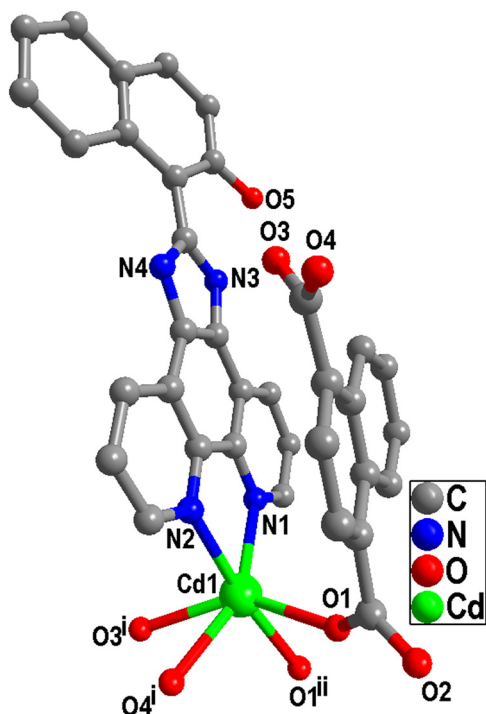


Figure 1: Coordination environment of the Cd(II) atom in **1** (symmetry codes: ⁱ x, y, z ; ⁱⁱ $-x + 1/2, y + 1/2, -z + 1/2$; ⁱⁱⁱ $-x, -y, -z$; and ^{iv} $x - 1/2, -y - 1/2, z - 1/2$).

the three different 1,4-NDC anions. Two nitrogen atoms (N(1), N(2)) and two oxygen atoms (O(1ⁱ), O(4ⁱ)) make up the basal plane, and the axial position is occupied by two O atoms (O(1), O(3ⁱ)). The Cd–N distances range from 2.298(3) to 2.346(3) Å, and the Cd–O vary from 2.268(2) to 2.340(2) Å (Table 1). The Cd–O and Cd–N distances are very close to the ones reported in other analogous complex $\{[\text{Cd}_5(\text{BTC})_2(\text{L}^1)_4(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}$ (H_3BTC = 1,3,5-benzenetricarboxylic acid, HL^1 = 3-(2-pyridyl)pyrazole; Wang et al., 2019). The two carboxylate groups of the 1,4-NDC anion display different coordination manners: one carboxylate chelates one Cd(II) atoms with $\mu_1\text{-}\eta^1\text{:}\eta^1$ coordination manners, while the another one bridges two Cd(II) atoms through a $\mu_2\text{-}\eta^2$ coordination model. In this way, the deprotonated 1,4-NDC anion connecting three adjacent Cd(II) atoms to give a 2D layer structure, as a μ_3 bridging ligand, is shown in Figure 2, and the farthest Cd \cdots Cd distance is 11.281 Å. The L ligands are attached on both sides of the layer in chelating coordination modes (Figure 3).

As it has been reported that stacking interactions between pyridine rings with benzene rings can exist at a very long Cg \cdots Cg distances with 4.50 Å (Ninković et al., 2013). Therefore, the conjugated L ligands from the layers generate strong $\pi\text{-}\pi$ stacking interactions between the L

Table 1: Selected bond lengths (Å) and angles (°) for the complex **1**

N(1)–Cd(1)	2.298(3)
N(2)–Cd(1)	2.346(3)
O(1)–Cd(1) ⁱⁱ	2.268(2)
O(1)–Cd(1)	2.337(2)
O(3)–Cd(1) ⁱ	2.359(2)
O(4)–Cd(1) ⁱ	2.340(2)
N(1)–Cd(1)–O(1)	111.33(9)
N(1)–Cd(1)–O(1) ⁱⁱ	107.53(8)
N(2)–Cd(1)–O(3) ⁱⁱⁱ	91.10(10)
N(1)–Cd(1)–O(4) ⁱⁱⁱ	152.76(9)
N(1)–Cd(1)–O(3) ⁱⁱⁱ	104.54(9)
N(2)–Cd(1)–O(1)	99.99(8)
N(2)–Cd(1)–O(1) ⁱⁱ	171.22(8)
N(2)–Cd(1)–O(4) ⁱⁱⁱ	88.57(9)
N(1)–Cd(1)–N(2)	72.18(9)
O(1)–Cd(1)–O(1) ⁱⁱ	71.77(8)
O(1) ⁱⁱ –Cd(1)–O(4) ⁱⁱⁱ	92.48(8)
O(1)–Cd(1)–O(4) ⁱⁱⁱ	64.49(11)
O(1) ⁱⁱ –Cd(1)–O(3) ⁱⁱⁱ	97.40(9)
O(1)–Cd(1)–O(3) ⁱⁱⁱ	144.12(9)
O(4) ⁱⁱⁱ –Cd(1)–O(3) ⁱⁱⁱ	55.55(8)

Symmetry codes: ⁱ x, y, z ; ⁱⁱ $-x + 1/2, y + 1/2, -z + 1/2$; ⁱⁱⁱ $-x, -y, -z$; ^{iv} $x - 1/2, -y - 1/2, z - 1/2$.

ligands of neighboring layers [N(2)/C(6)–C(10), C(18)–C(23) at $(-x, -y + 1, -z + 1)$, centroid-to-centroid distance of 4.283(2) Å and face-to-face distance of 3.6659(12) Å, and dihedral angle of 13.37(17)°], as shown in Figure 4, forming a 3D supramolecular structure (Figure 5). In addition, O–H \cdots N hydrogen bonds (O(5)–H(5) = 0.82,

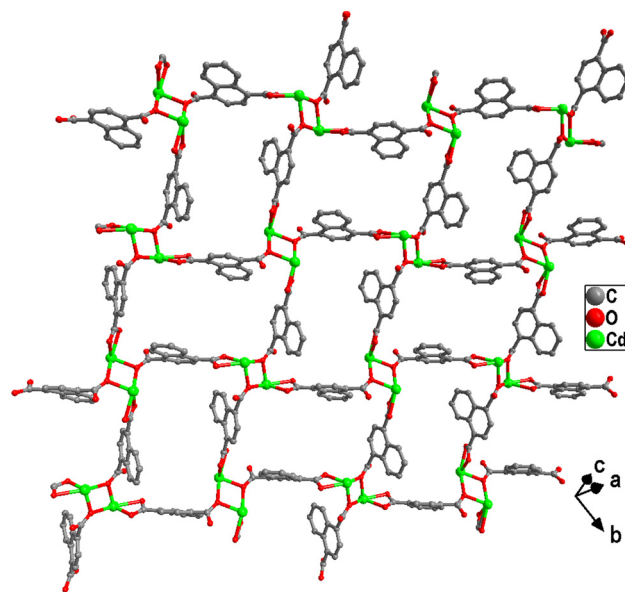


Figure 2: View of the 2D layer structure of **1** constructed by the 1,4-NDC.

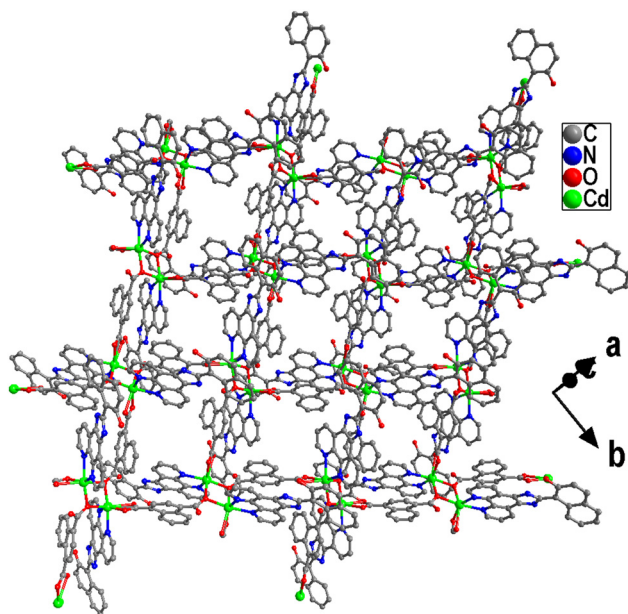


Figure 3: View of the 2D layer structure of **1** constructed by the 1,4-NDC and L ligands.

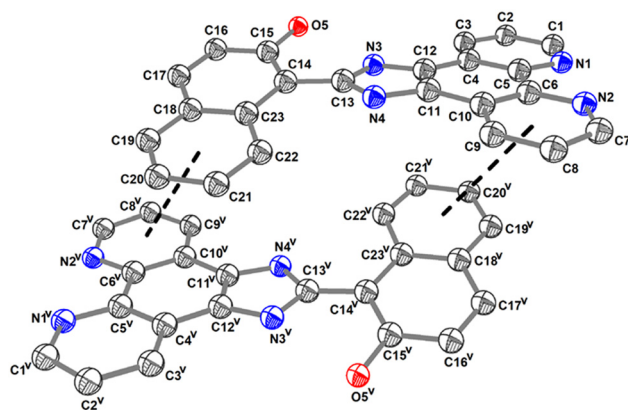


Figure 4: View of the π - π interactions between two L ligands of neighboring layers (symmetric code: (v) $-x, -y + 1, -z + 1$).

$H(5) \cdots N(3) = 1.79$, $O(5) \cdots N(3) = 2.525(4)$ Å, $\angle O(5)-H(5) \cdots N(3) = 147.9^\circ$) consolidates the 2D layer structure, and the $N-H \cdots O$ hydrogen bond ($N(4)-H(4) = 0.86$, $H(4) \cdots O(2)^{iv} = 2.07$, $N(4) \cdots O(2)^{iv} = 2.877(3)$ Å, $\angle N(4)-H(4) \cdots O(2)^{iv} = 156.9^\circ$) (symmetric codes: $^{iv} -x + 1/2, y + 1/2, -z + 1/2$) further stabilizes the 3D supramolecular structure.

The synthesized products of **1** have been characterized by powder X-ray diffraction (PXRD). The diffraction peaks of **1** are consistent with the simulated PXRD patterns from single-crystal diffraction analysis results, which indicates the high purity of the synthesized samples (Figure 6).

To determine the thermal stability of **1**, the thermal behavior was investigated under nitrogen atmosphere

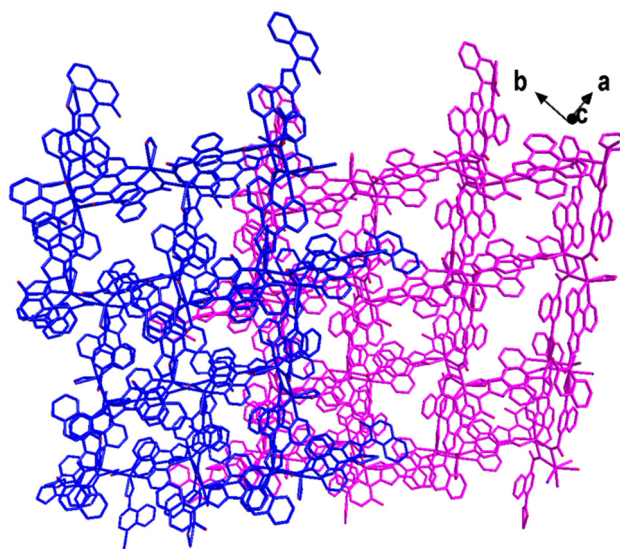


Figure 5: View of the 3D supramolecular structure of **1** formed by π - π interactions.

with a heating rate of $10^\circ\text{C min}^{-1}$ in temperatures ranging from room temperature to 900°C by thermogravimetric analysis (TGA). As depicted in Figure 7, the TGA curve of **1** reveals that the sample is stable up to 366°C , lost its organic group $C_{12}H_6O_3$ of 1,4-NDC anion in the range of 367 – 565°C (observed: 28.6%; calculated: 28.8%), and followed by decomposition.

The solid-state photoluminescent properties of 1,4- H_2 NDC, L ligand, and **1** have been studied in solid state at room temperature. Their emission peaks are shown in Figure 8. The main emission peaks of 1,4- H_2 NDC and free L occur at 501 nm ($\lambda_{ex} = 325$ nm) and 546 nm ($\lambda_{ex} = 325$ nm),

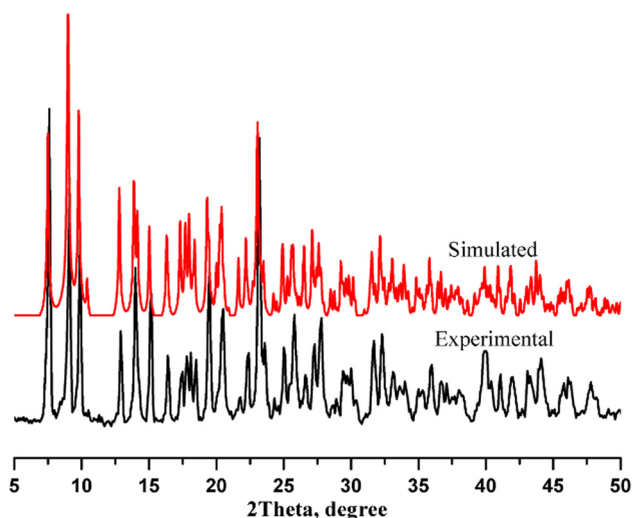


Figure 6: Powder X-ray diffraction patterns of **1**.

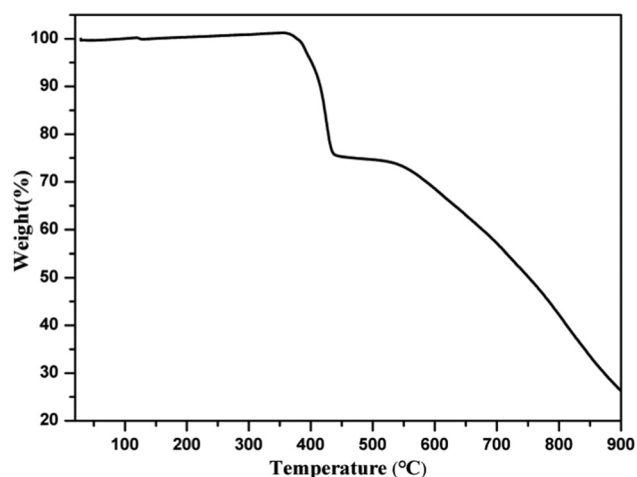


Figure 7: Thermal analysis curve of 1.

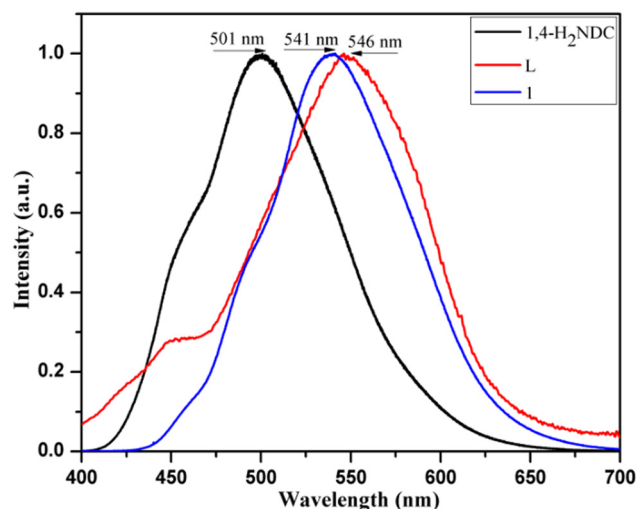


Figure 8: The solid-state photoluminescent properties of 1.

respectively, which are probably attributable to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transition. The 1 shows an emission band at 541 nm ($\lambda_{\text{ex}} = 325$ nm). This emission is similar to that of the free L ligand ($\lambda_{\text{ex}} = 546$ nm). Therefore, the emission of 1 should originate from the L ligand.

In conclusion, a novel 3D supramolecular polymer $[\text{Cd}(\text{1,4-NDC})(\text{L})]_n$ (**1**) has been successfully synthesized and characterized under hydrothermal conditions. In the complex, each deprotonated 1,4-NDC anion is connected to infinite 2D layers by three adjacent Cd(II) atoms, in which the L ligands occupy both sides of the layer. The π - π stacking interactions among the L ligands of neighboring 2D layers extend the chains into a 3D supramolecular structure. In addition, the presence of these hydrogen bonds contributes considerably to the stability of 3D networks.

Experimental

All PXRD analyses were recorded on a Rigaku Dmax 2000 X-ray diffractometer with graphite-monochromatized CuK α radiation (Rigaku, Japan). The emission spectra were measured on a Renishaw inVia Raman Microscope (Renishaw inVia, UK). Thermal stability studies were carried out on a TG SDT2960 thermal analyzer under a nitrogen atmosphere (TA, USA). All reagents and solvents used in the synthesis procedure were bought from the commercial companies (Shanghai Yiyang Biological Technology Co. Ltd and Tianjin Yuzhou Chemical Sales Co., Ltd, China). Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240 CHN elemental analyzer (Perkin Elmer, North Waltham, USA).

Preparation of $[\text{Cd}(\text{1,4-NDC})(\text{L})]_n$ (**1**)

A mixture of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.4 mmol, 0.091 g), L (0.3 mmol, 0.0108 g), and 1,4-H₂NDC (0.4 mmol, 0.086 g) and 1 mL anhydrous ethanol were added to a 50 mL flask. And the pH value was adjusted to 4–5 with 1 mol L⁻¹ NaOH (about 0.2 mL) solution. The solution is weakly acidic, and the hydroxyl groups on the naphthalene rings of the L ligands are partially deprotonated. Then the mixture was transferred to the sealed 15 mL Teflon-lined Parr and heated at

Table 2: Crystalline data and refinement parameters for complex 1

Empirical formula	$\text{C}_{35}\text{H}_{20}\text{N}_4\text{O}_5\text{Cd}$
Formula weight	688.95
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	14.471(3)
b (Å)	14.060(3)
c (Å)	14.579(3)
β (°)	108.47(3)
Volume (Å ³)	2,813.6(11)
Z	4
D_c (g cm ⁻³)	1.626
μ (mm ⁻¹)	0.830
$F(000)$	1,384
θ range (°)	3.196 to 27.480
Crystal size (mm)	0.302 × 0.181 × 0.145
Tot. reflections	26,622
Uniq. reflections, R_{int}	6,375, 0.0477
GOF on F^2	1.074
R_1 indices [$I > 2\sigma(I)$]	0.0363
wR_2 indices (all data)	0.1012
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ (e Å ⁻³)	−0.377, 0.529
CCDC No.	2,130,660

GOF: Goodness-of-fit on F_2 .

180°C for 4 days, and then the autoclave was gradually cooled to room temperature. Yellow flake shaped crystals of complex **1** were collected. Yield: 41% (based on the L). Analytical calculated for $C_{35}H_{20}N_4O_5$: C, 61.02%; H, 2.93%; N, 8.13%; found: C, 60.39%; H, 2.88%; N, 8.01%.

X-ray crystallography

A yellow flake shaped crystal of complex **1** was selected for diffraction data collection at 296(2) K on a Bruker-AXS Smart CCD diffractometer with graphite-monochromatized $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using the ϕ and ω scan technique. The structure was solved by direct methods with SIR2014 (Burla *et al.*, 2014) and refined by full-matrix least-squares techniques with SHELXL2018/3 program (Sheldrick, 2015), refining on F^2 . All nonhydrogen atoms were refined anisotropically. All hydrogen atoms were generated geometrically and refined isotropically using the riding model. Detailed crystal data and structure refinement are listed in Table 2. The selected bond lengths and angles are listed in Table 1. Crystallographic data have been deposited with the Cambridge Crystallographic Centre as supplementary publication number CCDC-2130660.

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