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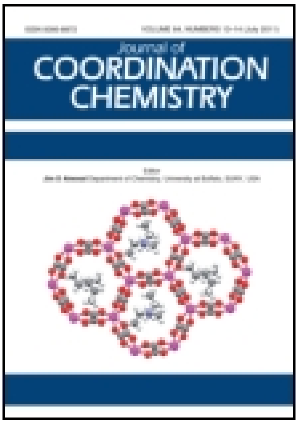

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1-D chain Cd(II) compound based on flexible phenylenediacetic ligand: synthesis, crystal structure, and fluorescent properties

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1-D chain Cd(II) compound based on flexible phenylenediacetic ligand: synthesis, crystal structure, and fluorescent properties

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A coordination polymer of Cd^{II} with a flexible ligand in $[Cd(Hpda)_2(4,4'\text{-bipyridyl})_2]\cdot(H_2O)_2$ (**1**) ($H_2pda = 1,2$-phenylenediacetic acid) has been synthesized by hydrothermal reactions and characterized by IR, TG, fluorescent spectrum, X-ray powder diffraction, and single-crystal X-ray diffraction techniques. The results show that **1** is monoclinic, with space group $P2(1)/c$, $a = 1.1704(7)$, $b = 1.7206(1)$, and $c = 2.2073(1)$ nm, $\beta = 120.881(2)°$. In **1**, the Cd(II) ions are linked by 4,4′-bipyridyl ligands to form 1-D chain with the arms of 1,2-pda ligands. These chains are imbedded into each other to form 2-D supramolecular sheets through hydrogen bonds. Adjacent 2-D sheets are assembled to 3-D network architecture through the crystallization of water molecules. Photoluminescence properties of **1** were investigated in the solid state at room temperature. The spectrum shows intense photoluminescence at 300 nm ($\lambda_{ex} = 275$ nm).

Keywords: Phenylenediacetic compound; Network; Crystal structure; Fluorescence

1. Introduction

The designed construction of novel coordination polymers has attracted more and more intense interest from chemists not only for functional material purposes [1, 2], but also for fascinating structures [3]. A successful approach to build metal-organic frameworks is to select suitable multidentate ligands as building blocks. Multicarboxylate ligands are often employed as bridging ligands because of their versatile coordination modes and ability to act as H-bond acceptors and donors to assemble supramolecular structures [4]. Phenylenediacetic acids are difunctional ligands with two carboxyl groups that possess three isomers of 1,2-, 1,3-, and 1,4-phenylenediacetic acids. As symmetrical and flexible dicarboxylate ligands, the acids are expected to display versatile coordinated modes and provide potential sites of hydrogen bonds and π–π stacking interactions to expand to high-dimension frameworks. A search of the Cambridge Structural Database (CSD, May 2011) reveals a total of 109 coordination complexes containing phenylenediacetic acid ligands (27 for 1,2-pda, 34 for 1,3-pda, and 48 for 1,4-pda). The 1,3- and 1,4-phenylenediacetitic acids have been widely investigated for the larger separation distances of the two carboxylate groups and are, thus, apt to form

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porous materials [5]. However, several compounds with 1,2-phenylenediacetic acid are still reported [6].

Considering the points above and following our previous studies [7], in this research we choose 1,2-phenylenediacetic acid (H_2pda) as a dicarboxylate ligand and 4,4′-bipyridyl as an N-containing auxiliary ligand. A mixed-ligand Cd(II) coordination polymer, namely $[Cd(Hpda)_2(4,4'\text{-bipyridyl})_2]\cdot(H_2O)_2$ (**1**), has been synthesized under hydrothermal conditions. The structure of the solid has been determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, IR spectra, and thermogravimetric analyses (TGA). The fluorescence properties of **1** have been also investigated in the solid state at room temperature.

2. Experimental

2.1. *General*

All reagents and solvents employed were commercially available and used as received. Elemental analyses for carbon, hydrogen, and nitrogen were performed with a Vario EL III elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Bruker EQUINOX-55 spectrometer. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. TGA were performed under nitrogen with a heating rate of 10°C min^{-1} using a NETZSCH STA 449 C thermogravimetric analyzer. X-ray powder diffraction (XRPD) was used to check the purity of **1**.

2.2. *Syntheses*

A mixture of $Cd(NO_3)_2$ (0.3 mmol), H_2pda (0.3 mmol), 4,4′-bipyridine (0.3 mmol), NaOH (0.3 mmol), and water (8 mL) was stirred for 20 min in air. The mixture was then transferred to a 23 mL Teflon reactor and kept at 120°C for 5 days under pressure and then cooled to room temperature at a rate of 5°C h^{-1}. Colorless block crystals of **1** were obtained (yield: 65% based on Cd). Elemental Anal. Calcd for $C_{40}H_{38}N_4O_{10}Cd$ (%): C, 56.59; H, 4.52; N, 6.60. Found (%): C, 56.18; H, 4.87; N, 6.56. IR data (KBr cm^{-1}): 3420(br), 3063(w), 1720(w), 1580(s), 1414(s), 1290(w), 1224(w), 812(m), 717(m), 632(w).

2.3. *Crystal structure determination*

Diffraction intensities for **1** were collected at 297 K on a Bruker SMART 1000 CCD diffractometer employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A semi-empirical absorption correction was applied using the SADABS program [8]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXS 97 and SHELXL 97 programs, respectively [9, 10]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in geometrically calculated positions. The crystallographic data for **1** are listed in table 1 and selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{40}H_{38}N_4O_{10}Cd$
Formula weight	847.14
Temperature (K)	297(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimensions (Å, °)	
a	11.7042(7)
b	17.2061(1)
c	22.0731(1)
α	90.00
β	120.88(2)
γ	90.00
Calculated density ($Mg\,m^{-3}$)	1.475
Absorption coefficient (mm^{-1})	0.636
$F(000)$	1736
Crystal size (mm^3)	$0.30 \times 0.27 \times 0.24$
θ range for data collection (°)	1.60–27.58
Index range	$-15 \le h \le 7$; $-22 \le k \le 20$; $-24 \le l \le 28$
Reflections collected	22,860
Reflections unique	8730 ($R(\text{int}) = 0.0603$)
Completeness to $\theta = 27.58$	98.7%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8730/130/541
Goodness-of-fit on F^2	0.979
Final R indices $[I > 2\sigma(I)]$[a]	$R_1 = 0.0451$, $wR_2 = 0.0930$
R indices (all data)[a]	$R_1 = 0.0965$, $wR_2 = 0.1088$
Largest difference peak and hole ($e\,Å^{-3}$)	0.497 and −0.610

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

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

Cd(1)–O(1)	2.308(3)
Cd(1)–N(3)	2.317(3)
Cd(1)–N(4)#1	2.340(3)
Cd(1)–N(1)	2.351(3)
Cd(1)–O(5)	2.385(3)
Cd(1)–O(6)	2.486(3)
O(1)–Cd(1)–N(3)	94.25(10)
O(1)–Cd(1)–N(4)#1	87.24(10)
N(3)–Cd(1)–N(4)#1	176.14(11)
O(1)–Cd(1)–N(1)	129.86(10)
N(3)–Cd(1)–N(1)	90.06(10)
N(4)#1–Cd(1)–N(1)	86.26(11)
O(1)–Cd(1)–O(5)	86.93(10)
N(3)–Cd(1)–O(5)	90.00(10)
N(4)#1–Cd(1)–O(5)	93.63(11)
N(1)–Cd(1)–O(5)	143.08(10)
O(1)–Cd(1)–O(6)	139.03(9)
N(3)–Cd(1)–O(6)	94.27(10)
N(4)#1–Cd(1)–O(6)	86.89(10)
N(1)–Cd(1)–O(6)	90.11(11)
O(5)–Cd(1)–O(6)	53.08(10)

Symmetry operations: #1: $x + 1$, y.

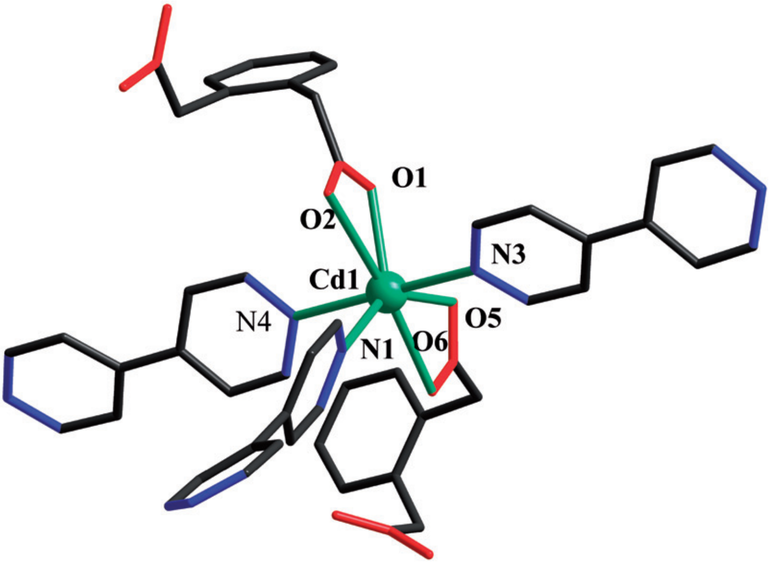

Figure 1. The coordination environment of Cd in **1**.

3. Results and discussion

3.1. *Crystal structure*

Single-crystal X-ray diffraction analysis of **1** reveals the monoclinic space group $P2_1/c$ with $Z = 4$ (table 1). The asymmetric unit consists of one crystallographically independent Cd^{II} cation, two $Hpda^-$ anions, two 4,4′-bipyridines, and two lattice water molecules. Each Cd^{II} is surrounded by three N-atoms from three 4,4′-bipyridines and four O-atoms from two $Hpda^-$ anions, which make up a slightly distorted penta-bipyramidal geometry (figure 1) that involves O1, O2, O5, O6, N1 that form a equatorial pentagon plane and N3 and N4 that form the axially coordination. The Cd–N bond lengths are 2.317(3), 2.340(3), 2.351(3) Å, respectively, and the Cd–O bond lengths are in the range 2.308(3)–2.486(3) Å, which compare favorably to expected Cd–N and Cd–O bond lengths [11].

Cd(II) ions are alternately linked by 4,4′-bipyridines to form a 1-D chain (figure 2). The 1,2-pda ligand exhibits a *syn*-configuration, wherein only one carboxylate group adopts bidentate coordination with the other group not coordinated. Consequently, 1,2-pda ligands are located at both sides of the 1-D chain. Furthermore, the 1-D arrays are extended to a wavy 2-D supramolecular architecture through hydrogen bonds between two adjacent 1-D arrays (figure 3). In this arrangement, O2 of the carboxylate group from one 1,2-pda ligand acts as an H-bond acceptor for O4 of carboxylate of another 1,2-pda molecule (O4–H $\cdots$ O2, 2.577 Å) and N2 of 4,4′-bipyridine is an H-bond acceptor for O8 of carboxylate (O8–H $\cdots$ N2, 2.687 Å) (figure 3, table 3).

In **1**, adjacent lattice water molecules are connected to form a $(H_2O)_4$ cluster *via* hydrogen-bonding (figure 4). The water tetramer is composed by O9, O10, O9#, O10#. The average O $\cdots$ O distance is 2.928 Å (table 3), which is slightly longer than liquid

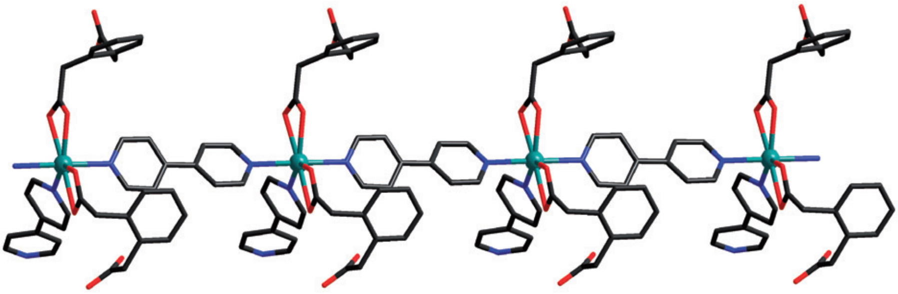

Figure 2. 1-D chain of **1**.

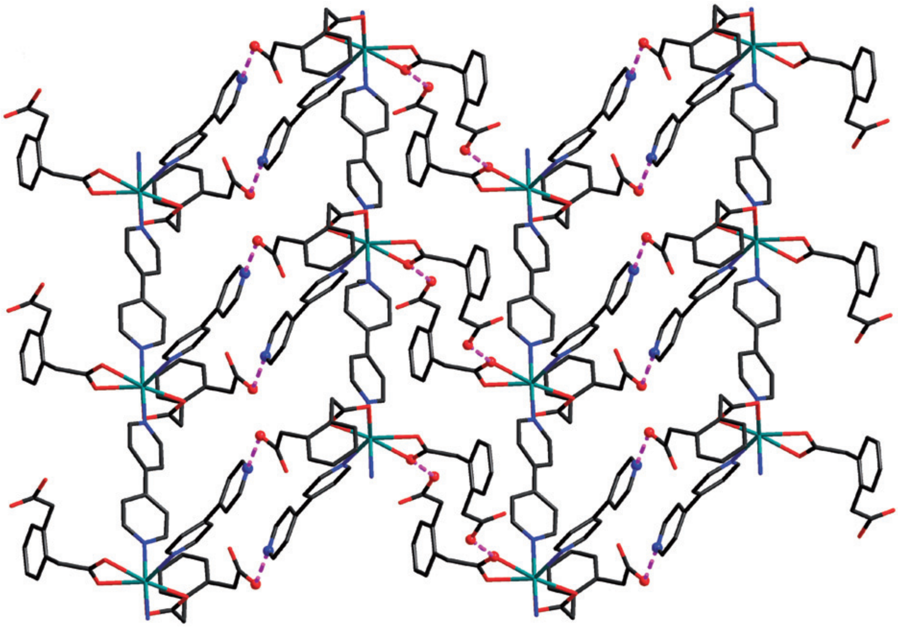

Figure 3. The 2-D wavy supramolecular network of **1**.

Table 3. Selected hydrogen-bond distances and angles for **1**.

D–H···A	H···A (Å)	D···A (Å)	∠D–H···A (°)	D···H (Å)
O(4)–H(4 A)···O(2)	1.785	2.577	161.92	0.8200
O(8)–H(8 A)···N(2)	1.879	2.687	168.25	0.8200
O(9)–H(9WA)···O(10)	2.105	2.927	158.47	0.865
O(9)–H(9WB)···O(10)	2.183	2.930	145.32	0.858
O(10)–H(10WB)···O(5)	1.959	2.741	158.15	0.8233
O(10)–H(10WA)···O(1)	2.153	2.843	138.12	0.8500

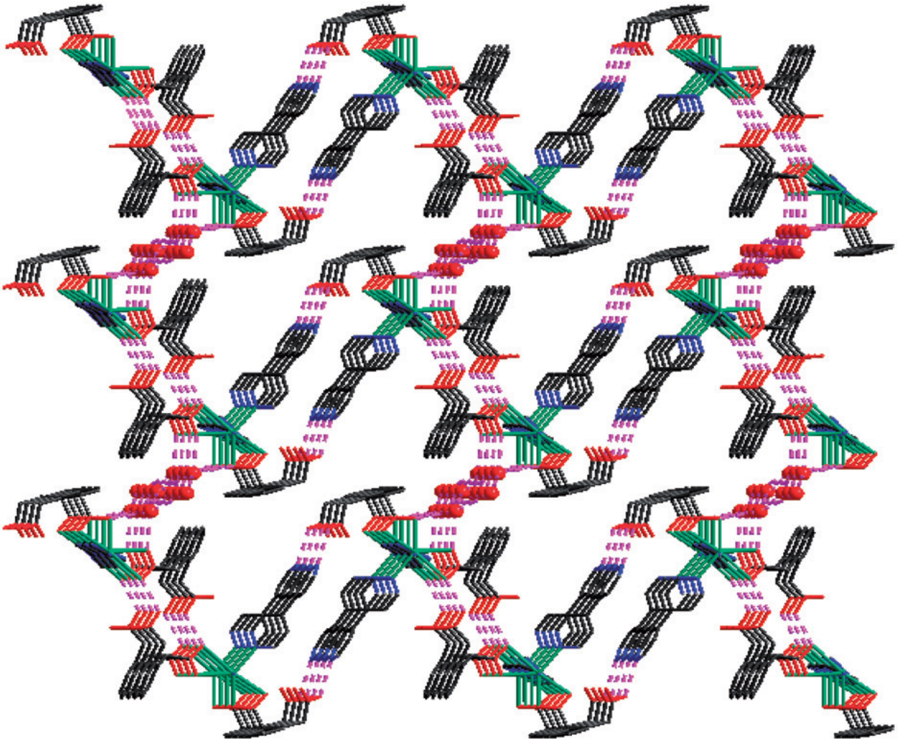

Figure 4. 3-D supramolecular framework of **1**.

water (2.85 Å) [12]. It must be remarked that the water tetramers are discrete and extend the 2-D wavy sheets *via* hydrogen-bonding to give a 3-D network (figure 4).

3.2. *Thermogravimetric analyses*

TGA were performed in air for **1** between 20°C and 800°C. For **1**, the TGA curve showed three weight losses. The first loss was 4.21% in the temperature range of 20–100°C, which corresponds to two lattice H_2O molecules (calcd 4.59%). The next and final steps are losses of 1,2-pda$^-$ anion and 4,4′-bipyridyl ligand in the range 300–500°C (calcd 80.63%, obsd 78.92%) (figure 5).

3.3. *X-ray powder diffraction*

XRPD was used to investigate the purity of **1**, as shown in figure 6. Although the experimental patterns have slight irregularities in the indexed peaks and some that are slightly broadened in comparison to the simulated single-crystal data, the solid can be regarded as the bulk as-synthesized material. Moreover, the XRPD patterns at different temperatures indicate that **1** is stable at 100–275°C. The dissimilar curves at 275°C and 300°C demonstrates that **1** decomposes above 300°C, which is in good agreement with

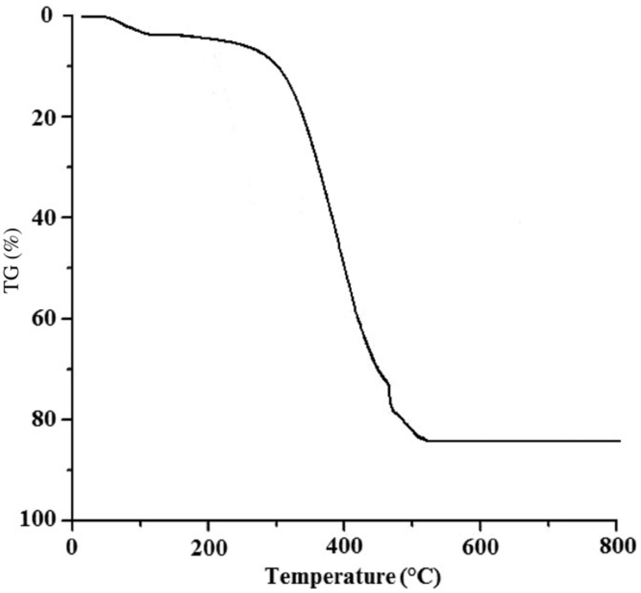

Figure 5. TGA curve for **1**.

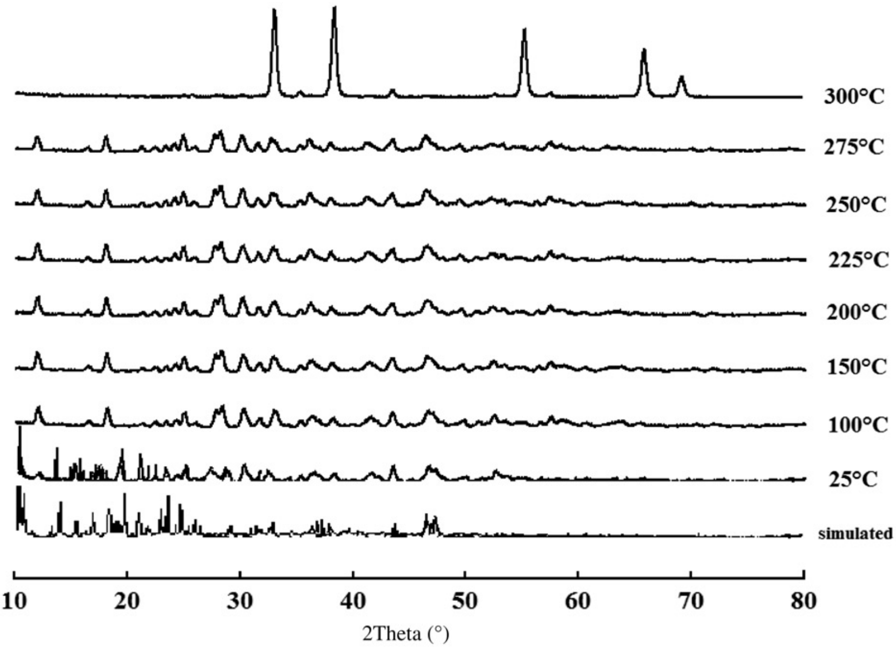

Figure 6. XRPD pattern of the single crystal of **1** under different conditions.

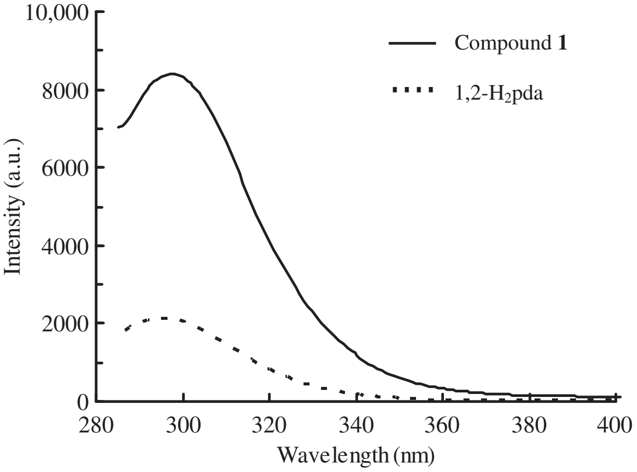

Figure 7. Solid-state emission spectra of **1** and 1,2-H_2pda at room temperature.

the TGA data. TGA curves for **1** revealed that the release of non-coordinated water occurs in the range 20–100°C while the decomposition of the networks begins above 300°C. The remaining final residue is likely CdO.

3.4. *Fluorescent properties*

Emission spectra of **1** and 1,2-H_2pda in the solid state at room temperature are shown in figure 7. Intense emissions occur at 300 nm upon excitation at 275 nm for **1**. To understand the nature of the emission band, the photoluminescence properties of H_2pda were determined. Weak emissions at 294 nm were observed for free H_2pda ligand ($\lambda_{max} = 277$ nm). In comparison to the free ligand, the emission maximum of **1** has changed, which is neither metal-to-ligand charge transfer nor ligand-to-metal charge transfer, since Cd^{II} is difficult to oxidize or reduce. Thus, it may be assigned to intraligand (π–π^*) fluorescent emission [13]. Many aromatic ligands that are not strongly emissive as pure compounds exhibit significant luminescence when coordinated to Cd^{II} [14]. The enhanced luminescence is, perhaps, a result of coordination of the ligands to the metal center, which effectively increases the molecular rigidity and, thereby, reduces non-radiative decay of the intraligand (π–π^*) excited state [15].

4. Conclusion

$[Cd(Hpda)_2(4,4'\text{-bipyridyl})_2]\cdot(H_2O)_2$ (**1**) was prepared and characterized using single-crystal X-ray crystallography and fluorescence measurements. Compound **1** is composed of 1-D Cd(II) chain bridged by alternating 4,4′-bipyridyl ligands. Hydrogen-bonding between two 1-D chains and the water tetramer $(H_2O)_4$

adjoin 2-D wavy sheets to an extended 3-D supramolecular structure. Fluorescence measurements reveal that **1** exhibits intense photoluminescence at 300 nm ($\lambda_{ex} = 275$ nm).

Supplementary material

Additional crystallographic data sets for the structures are available through the Cambridge Structural Data Base as supplementary publication reference number CCDC-822074 for **1**. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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