

Article

A Cd(II) Coordination Polymer Based on Mixed Ligands: Synthesis, Crystal Structure, and Properties

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Abstract: A new coordination polymer, namely, $[\text{Cd}(\text{L})(\text{frda})(\text{H}_2\text{O})]\cdot 0.5\text{L}\cdot \text{H}_2\text{O}$ (**1**) was synthesized by hydrothermal reaction based on mixed multi-N donor 1-(4-(1H-imidazol-5-yl) phenyl)-1H-1,2,4-triazole (L) and O-donor 2,5-furandicarboxylic acid ligands (H_2frda) with $\text{CdCl}_2\cdot 2.5\text{H}_2\text{O}$. Compound **1** was characterized by single-crystal x-ray diffraction, elemental analysis, and IR spectroscopy. In **1**, both the multi-N donor and O-donor frda^{2-} ligands act as linear two-connectors to bridge Cd(II) atoms, forming a two-dimensional (2D) layer. Interestingly, the parallel 2D layers stack in an AAA...mode, and the infinite one-dimensional (1D) channels formed along the *a*-axis direction, where the uncoordinated L molecules were embedded in the void. Furthermore, the weak interactions including the rich hydrogen bonding and π - π stacking interactions progress the 2D structure into a three-dimensional (3D) supramolecular polymer. Diffuse reflectance spectra and the luminescent property were also investigated.

Keywords: coordination polymer; characterization; optical property

1. Introduction

Coordination polymers (CPs) consisting of organic ligands and metal ions have attracted an upsurge in research during the past decades, due to their charming structures and their possibly applied domain of luminescence [1–4], gas adsorption/separation [5,6], proton conductivity [7], chemical separations [8], catalysis [9], and so on. Generally speaking, organic ligands act as linkers while metal ions act as connectors, and therefore, their orientation of the interacting sites for ligands and coordination numbers for metal ions, respectively, are the most fundamental two factors to decide the framework and properties of CPs [10–13]. In addition to these two core factors, other conditions such as the ligand–metal ratio, reaction solvent, template, pH value, and counteranion also have effects on the resulting structure [14,15]. Essentially, multidentate organic ligands with definite linking coordination sites result in the spatial arrangement for metal connectors in the final framework. Several important factors such as the length of organic ligands, their flexibility/ rigidity, decorated functional groups, varied coordination modes, or substituent groups of organic ligands have substantial effects on the resulting frameworks of CPs [16,17]. Therefore, the design and synthesis for organic compounds are key jobs to construct desirable CPs with specific structures, topologies, and functionalities. In this context, the effective ‘reticular synthesis’ put forward by Yaghi et al. was confirmed to be the most effective method to direct the assembly of desired frameworks with rigid organic linkers [18]. However, the flexible ligands are an important part in the assembly of interpenetrated structure by adopting fickle conformations and geometries via rotating, bending, or twisting transformation [19,20] because these flexible backbones often facilitate the stabilization of the framework through interpenetration to avoid the void within the structure. Generally speaking, the multi-N donor and O-donor carboxylic acids are two types of extensively used ligands because of their diverse coordination abilities [21,22]. For

example, N-donor polyazaheteroaromatic organic molecules are often used to form multipodal anions employed as chelating, bridging, and also acting as charge balance anionic building units for assembling polynuclear species. In our previous work, we deliberately designed a series of 4-imidazoly-containing organic molecules such as 1,3,5-tri(1H-imidazol-4-yl)benzene and 1,4-di(1H-imidazol-4-yl)benzene, which have been successfully employed to build metal-imidazolate CPs with favorable gas adsorption properties for CO₂ gas [23–25]. Apart from the polyazaheteroaromatic linkers, the aromatic polycarboxylate compounds are another kind of important O-donor ligands due to their diverse coordination modes for carboxyl groups, which can display chelating, mono/bis-bridging modes. Due to their good bridging abilities, a high connector of polynuclear metal centers can easily be formed, which can be employed to build higher node frameworks. Interestingly, we employed the mixed 4-imidazoly-containing ligands and various carboxylic acids to build diverse frameworks including cage structure, one-dimensional tube chain, two-dimensional layer structures, and three-dimensional interpenetrating and non-interpenetrating structures with different topologies, because the N-donor ligands can effectively adjust the coordination modes of polycarboxylate acids [26–28]. By virtue of their suitable adjustability for the mixed polyazaheteroaromatic and carboxylic ligands, we synthesized the multi-N donor ligand 1-(4-(1H-imidazol-5-yl)phenyl)-1H-1,2,4-triazole (L) (see Supplementary Materials), together with O-donor 2,5-furandicarboxylic acid ligand (H₂frda) to react with CdCl₂·2.5H₂O, and obtained a new Cd(II) coordination polymer [Cd(L)(frda)(H₂O)]·0.5L·H₂O (**1**) as a continual work. The diffuse reflectance spectra and luminescent property of **1** were also investigated.

2. Experimental Section

2.1. Materials and Instrumentation

The chemicals in this experiment were of reagent grade. The 1-(4-(1H-imidazol-5-yl) phenyl)-1H-1,2,4-triazole organic molecule was synthesized according to the related literature [29]. Infrared spectra was executed on a FT-IR spectrophotometer (Instrument Inc., Karlsruhe, Germany) using KBr pellets. Elemental analyses were analyzed on a Perkin-Elmer 240C Elemental Analyzer (PerkinElmer, Waltham, USA). Photoluminescence spectra were used with a HORIBA FluoroMax-4 (Edinburgh Instruments, Edinburgh, UK).

2.2. Synthesis of [Cd(L)(frda)(H₂O)]·0.5L·H₂O (**1**)

A mixture of L (0.042 g, 0.2 mmol), H₂frda (0.032 g, 0.2 mmol), CdCl₂·2.5H₂O (0.0456 g, 0.2 mmol), and NaOH (0.016 g, 0.4 mmol) in 8 mL H₂O was sealed in a Pyrex bottle (16 mL) and heated at 120 °C for 48 h. Colorless block crystals of **1** were isolated by filtration, with a yield of 68 %. Anal. Calcd. (%) for C₂₂H₁₆N₈O₇Cd: C, 47.30; H, 3.26; N, 18.39. Found (%): C, 47.16; H, 3.19; N, 18.48. IR(KBr): 3700–3050(s), 1581(m), 1399(m), 1373(m), 1278(w), 1158(w), 1066(m), 977(w), 837(w), 818(w), 786(w), 669(w), 636(w), 577(w), 487(w) cm^{−1}.

2.3. Crystal Structure Determination

The single crystal data of [Cd(L)(frda)(H₂O)]·0.5L·H₂O (**1**) suitable for analysis were selected and collected on a Rikaku XtaLAB Synergy diffractometer. The structure was solved and refined using the OLEX2 program suite, equipped with the ShelXT and ShelXL program [30]. The crystallographic refine data are displayed in Table 1.

Table 1. Crystallographic data and structure refinement for CP 1.

Empirical Formula	C ₄₅ H ₃₉ N ₁₅ O ₁₄ Cd ₂
Formula weight	1238.73
Temperature/K	293(2)
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	10.0552(2)
<i>b</i> /Å	10.1437(2)
<i>c</i> /Å	14.1937(2)
α /°	75.690(10)
β /°	69.664(2)
γ /°	62.167(2)
Volume/Å ³	1194.13(4)
<i>Z</i>	1
ρ_{calc} /mg/mm ³	1.723
μ /mm ^{−1}	0.976
<i>F</i> (000)	622
Index ranges	−12 ≤ <i>h</i> ≤ 13, −12 ≤ <i>k</i> ≤ 12, −13 ≤ <i>l</i> ≤ 18
Reflections collected	14832
Independent reflections	4980
Data/restraints/parameters	5560/0/396
Goodness-of-fit on <i>F</i> ²	1.030
Final <i>R</i> indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0310, <i>wR</i> ₂ = 0.0709
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0361, <i>wR</i> ₂ = 0.0742
Largest diff. peak/hole / e Å ^{−3}	0.470/−0.460

The CCDC number is 1957742 for **1**, deposited with the Cambridge Crystallographic Data Center. The data can be obtained on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

3. Results and Discussion

3.1. Structural of [Cd(L)(frda)(H₂O)]·0.5L·H₂O (**1**)

X-ray crystallographic analysis shows that CP **1** crystallizes in the triclinic *P*₁− space group (Table 1), and the asymmetric unit of **1** contains one unique Cd(II) atom, one coordinated L organic ligand, one deprotonated frda^{2−} molecule, one coordinated water molecule, a half of uncoordinated L ligand, and one lattice water molecule. The unsymmetrical polyazaheteroaromatic ligand of N2 and C8, N5 and C7, and N4 and C10 atoms can be defined according to their different atomic displacement parameters. The lattice of L lies an inversion center. The center Cd(II) atom is linked by two nitrogen atoms (N1 and N3A) from two different L ligands and four oxygen atoms (O1, O2, and O3B, O4B) from two pairs of carboxyl groups and one oxygen atom (O6) from the coordinated water ligand, thereby forming a seven-coordinated coordination geometry with a N₂O₅ donor set (Figure 1). The Cd–O bond lengths varied from 2.346(2) to 2.5866(18) Å and the Cd–N ones were 2.281(2) and 2.288(2) Å (Table 2), and the coordination angles were around the Cd1 range from 52.90(6) to 175.41(7)°. The L ligands adopt linear bidentate bridging mode to combine Cd(II) ions to form one-dimensional (1D) chains. The adjacent 1D chains are connected by frda^{2−} ligands to form a two-dimensional (2D) layer (Figure 2). From a topological perspective, the 2D layers can be simplified to 4-connected **sql** nets with point symbol (4⁴·6²). The parallel 2D layers are stacked in an AAA···mode, and the infinite 1D channels are created along the *a*-axis, where the uncoordinated L molecules are embedded in the void of **1** (Figure 3). The solvent-accessible volume of these channels without considering guest L molecules was estimated to be 387.8 Å³, approximately 32.5% of the total crystal volume of 1194.1 Å³, calculated with the PLATON program [31]. It is noteworthy that the nitrogen and oxygen atoms from multi-N donor or carboxyl groups, can easily be employed as acceptors of hydrogen bonding, and as a return, the weak interaction can easily benefit the formation of a supramolecular polymer. In the packing diagram,

rich hydrogen bonding interaction are found in CP **1**, and the C–H...O, O–H...O hydrogen bonding including (C(2)...O(2)^c 3.142(3) Å, C(2)–H(2)...O(2) 148°; C(10)...O(2)^c 3.101(4) Å, C(10)–H(10)...O(2) 155°; C(11)...O(6) 3.410(4) Å, C(11)–H(11)...O(6) 151°; C(6)...O(6) 2.738(3) Å, C(6)–H(6B)...O(6) 169°; O(6)...O(5) 2.872(4) Å, O(6)–H(6A)...O(5) 167°; C(9)...O(4) 3.086(3) Å, C(9)–H(9)...O(4) 118°) exist among the adjacent 2D layers (Table 3). In addition to the rich hydrogen bonding, classic weak π – π stacking interactions could also be found between the neighboring 2D packing layers. The five-membered furan rings of the frda²⁻ ligands were completely parallel with the centroid–centroid distance of 3.49 Å, indicating the existence of strong π – π stacking interactions [32,33]. On the whole, the weak interactions including the hydrogen bonding and π – π stacking interactions progress adjacent 2D layers into a three-dimensional (3D) supramolecular polymer (Figure 4).

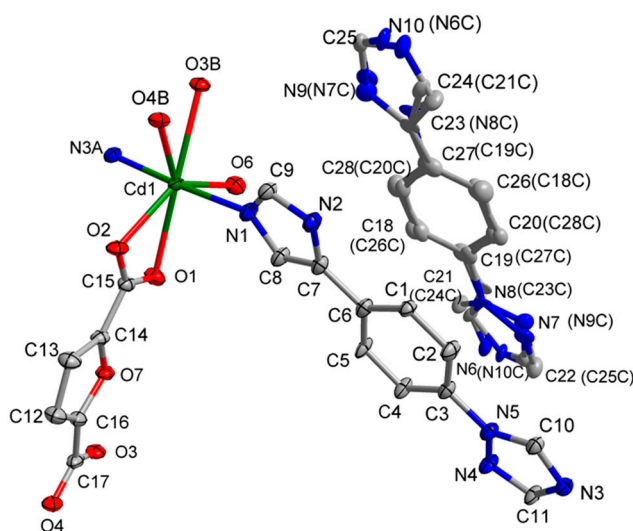


Figure 1. The coordination environment of Cd(II) ion and free L ligand in **1**. Symmetry code: A $x, y, 1 + z$, B $x, 1 + y, z$, C $1 - x, 2 - y, 1 - z$.

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

Bond	<i>d</i>	Bond	<i>d</i>
Cd(1)–N(1)	2.288(2)	Cd(1)–N(3) ⁱ	2.281(2)
Cd(1)–O(6)	2.346(2)	Cd(1)–O(2)	2.3470(16)
Cd(1)–O(4) ⁱⁱ	2.3871(19)	Cd(1)–O(3) ⁱⁱ	2.5427(18)
Cd(1)–O(1)	2.5866(18)		
Angle	ω	Angle	ω
N(3) ⁱ –Cd(1)–N(1)	175.41(7)	N(3) ⁱ –Cd(1)–O(6)	90.86(8)
N(1)–Cd(1)–O(6)	84.94(8)	N(3) ⁱ –Cd(1)–O(2)	93.45(6)
N(1)–Cd(1)–O(2)	90.84(7)	O(6)–Cd(1)–O(2)	135.86(7)
N(3) ⁱ –Cd(1)–O(4) ⁱⁱ	99.08(7)	N(1)–Cd(1)–O(4) ⁱⁱ	82.57(7)
O(6)–Cd(1)–O(4) ⁱⁱ	133.33(7)	O(2)–Cd(1)–O(4) ⁱⁱ	89.19(6)
N(3) ⁱ –Cd(1)–O(3) ⁱⁱ	83.11(7)	N(1)–Cd(1)–O(3) ⁱⁱ	94.58(7)
O(6)–Cd(1)–O(3) ⁱⁱ	83.62(7)	O(2)–Cd(1)–O(3) ⁱⁱ	140.50(6)
O(4) ⁱⁱ –Cd(1)–O(3) ⁱⁱ	53.03(6)	N(3) ⁱ –Cd(1)–O(1)	87.07(7)
N(1)–Cd(1)–O(1)	94.26(7)	O(6)–Cd(1)–O(1)	83.57(7)
O(2)–Cd(1)–O(1)	52.90(6)	O(4) ⁱⁱ –Cd(1)–O(1)	142.01(6)
O(3) ⁱⁱ –Cd(1)–O(1)	163.71(6)		

Symmetry codes: (i) $x, y, z + 1$; (ii) $x, y + 1, z$.

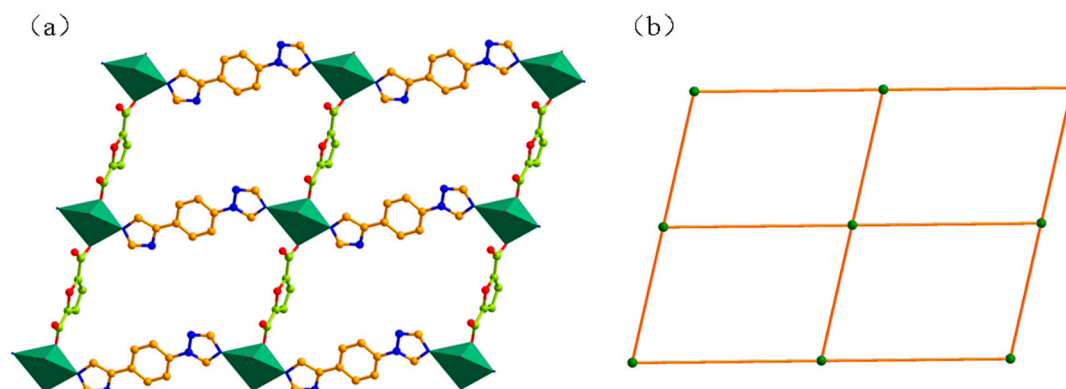


Figure 2. (a) 2D layer of $[\text{Cd}(\text{L})(\text{frda})(\text{H}_2\text{O})]$. (b) 2D network of (4, 4) topology in CP 1.

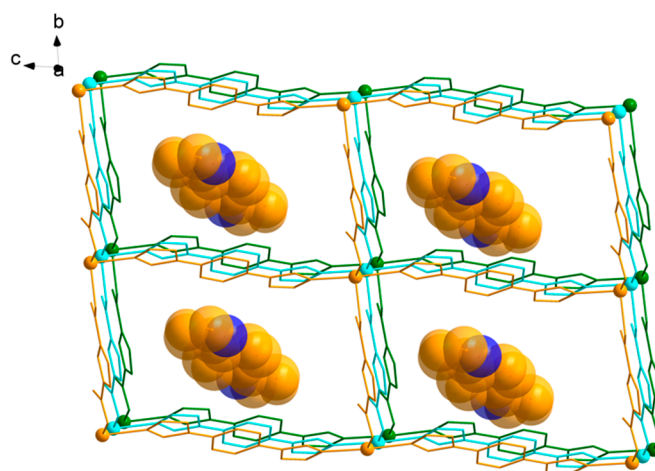


Figure 3. The 2D parallel packing layers with infinite 1D void channels embedded with uncoordinated L guest molecules.

Table 3. Hydrogen bond lengths (\AA) and bond angles ($^\circ$) for **1**.

D–H \cdots A	d(D–H)	d(H \cdots A)	d(D \cdots A)	$\angle\text{DHA}$
O(6)–H(6A) \cdots O(5) ^a	0.70(4)	2.18(4)	2.872(4)	167(5)
C(6)–H(6B) \cdots O(6) ^b	0.79(4)	1.96(4)	2.738(3)	169(5)
C(2)–H(2) \cdots O(2) ^c	0.9300	2.3200	3.142(3)	148.00
C(4)–H(4) \cdots N(4)	0.9300	2.5100	2.826(4)	100.00
C(9)–H(9) \cdots O(4) ^a	0.9300	2.5400	3.086(3)	118.00
C(10)–H(10) \cdots O(2) ^c	0.9300	2.2300	3.101(4)	155.00
C(11)–H(11) \cdots O(6) ^d	0.9300	2.5700	3.410(4)	151.00

Symmetry codes: ^a $x, 1 + y, z$; ^b $1 - x, 1 - y, 2 - z$; ^c $2 - x, 1 - y, 1 - z$; ^d $1 - x, 1 - y, 1 - z$.

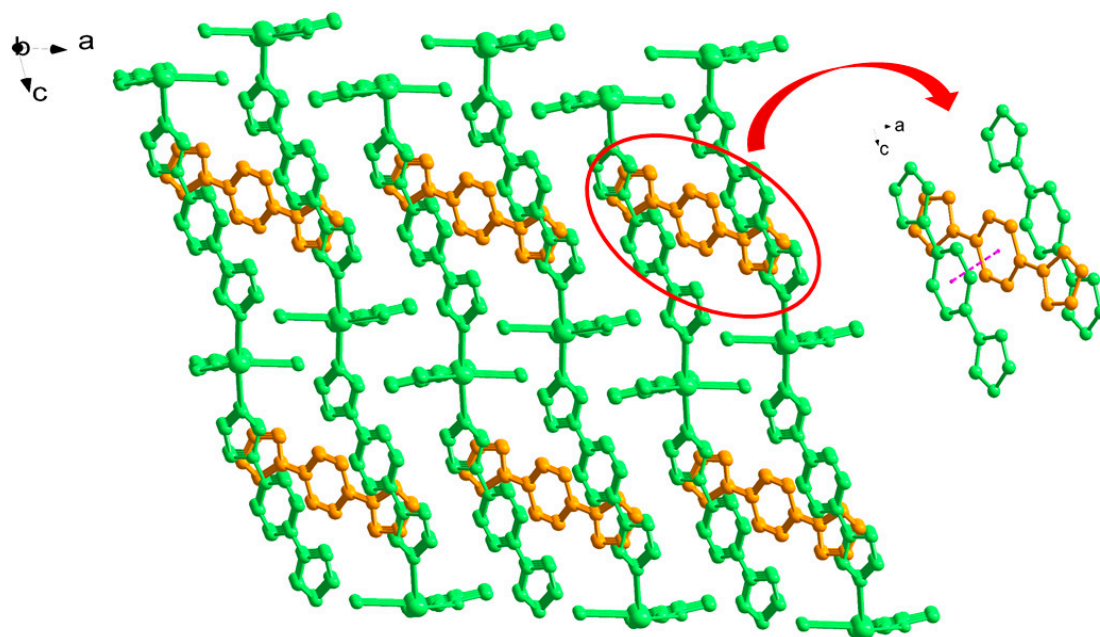


Figure 4. 3D supramolecular structure of **1** packed by $\pi\cdots\pi$ stacking interactions.

3.2. Thermal Analysis and Powder X-Ray Diffraction Analysis

Figure 5 shows that a 6.28% weight loss corresponds to one coordinated and one lattice water molecule in a temperature range of 185–245 °C (calcd: 6.32%), and the framework collapsed at about 350 °C. Powder x-ray diffraction (PXRD) data can be used to testify the purity of as-synthesized samples. Therefore, the PXRD data of CP **1** were directly collected at room temperature. The diffraction peaks of the as-synthesized **1** were consistent with the simulated PXRD patterns from the single crystal results. The result confirms that the as-synthesized crystals of **1** were phase purities as shown in Figure 6.

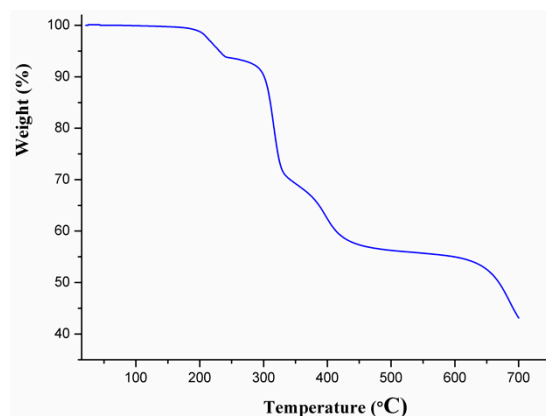


Figure 5. Thermal analysis curve of CP **1**.

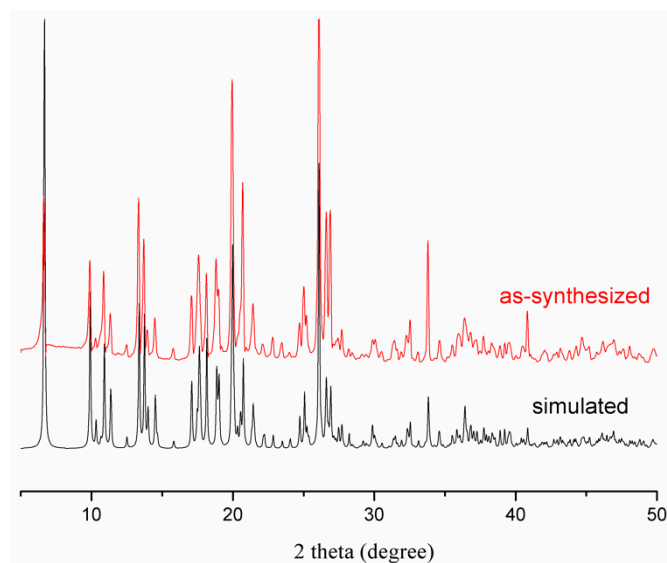


Figure 6. Simulated and experimental powder X-Ray diffraction patterns of CP 1.

3.3. Diffuse Reflectance Spectra

The UV–Vis spectra in the solid-state were investigated for the CP 1 together with the organic compound L (Figure 7). The CP 1 and L molecules showed the same absorption peaks ranging from 275 to 345 nm in the UV region, which belongs to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligand. Furthermore, the diffuse reflectance data obtained were transformed into a Kubelka–Munk function to get their band gaps (E_g), which can be employed to evaluate the semiconductivity of the CPs. The values of E_g for 1 and L were estimated as 3.55 and 3.35 eV (Figure 8), which can be determined by the theory of optical absorption for the direct band gap semiconductor: $(Ah\nu)^2 = B(h\nu - E_g)$ [34], indicating that the as-synthesized crystalline material is an optical semiconductor [35].

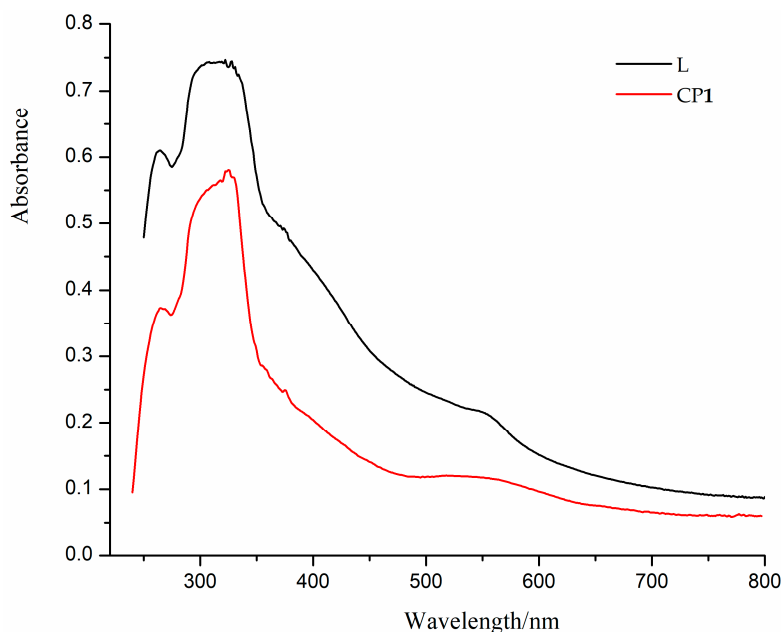


Figure 7. The UV–Vis spectra in the solid-state of the L ligand and CP 1.

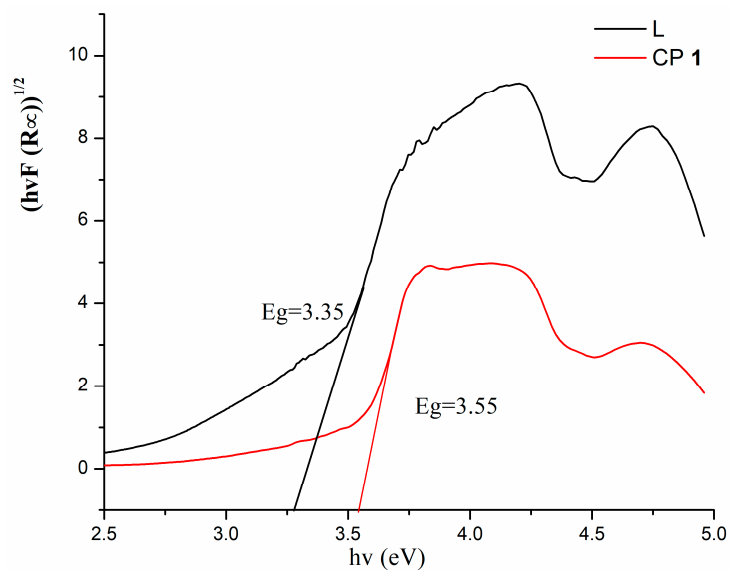


Figure 8. The band gap E_g values for L and CP 1.

3.4. Photoluminescent Property

Luminescent coordination polymers containing a d^{10} metal center and π -conjugated organic ligands can often exhibit favorable photoluminescent properties because of their tunable factors between metal and ligands [36,37]. Therefore, we carried out the relevant studies on the Cd(II) coordination polymer in the solid-state together with the L organic ligand (Figure 9). The L ligand showed no fluorescence, however, compound 1 appeared as a strong broad emission band at 415 nm upon excitation at 361 nm on complexation of the ligands with Cd(II) atoms, which may be attributable to the coordination interactions between the ligand and central metal Cd(II) atom [38].

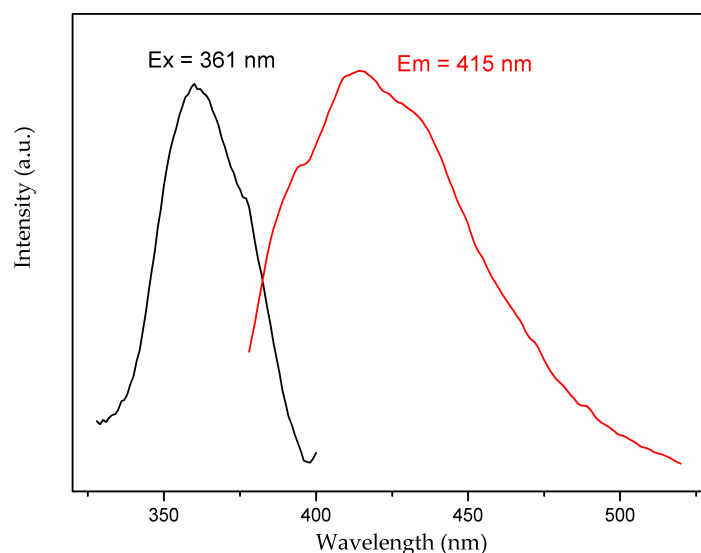


Figure 9. Photoluminescent spectra of CP 1.

The good photoluminescent property of CP 1 provided the impetus to further investigate the quantum yield (QY) and corresponding decay lifetimes. The QY value of CP 1 was 4.28 % (Figure 10), similar to some reported CPs [39]. Furthermore, the luminescence decay curve was fitted by exponential function as $I(t) = A \exp(-t/\tau)$, and the luminescence lifetime of CP 1 was 48.87 ns. The value of luminescence lifetime for CP 1 was fairly shorter than a triplet state ($>10^{-3}$ s), in this context, the luminescence emission of CP 1 should derive from a singlet state [40].

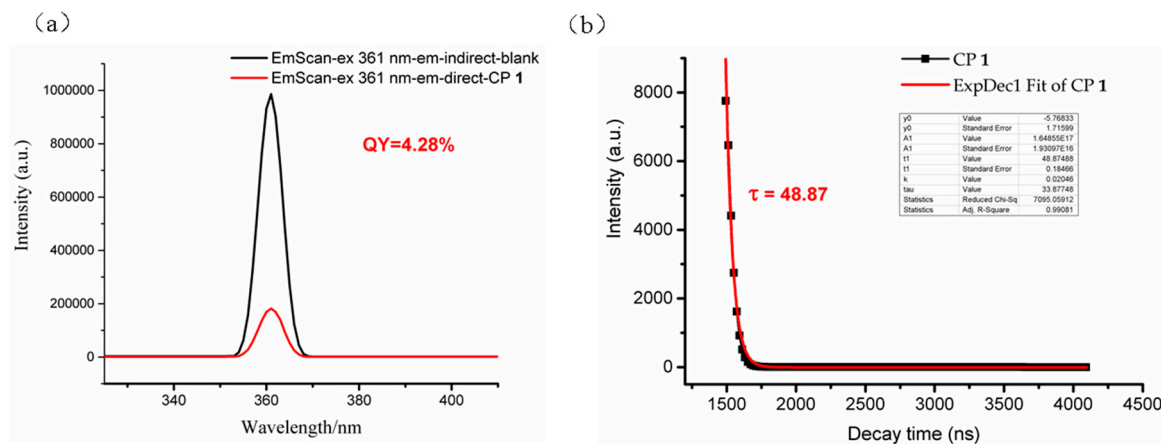


Figure 10. (a) The quantum yield curves and (b) luminescence decay curve for CP 1 (black line: experimental data; red line: fitting result).

4. Conclusions

In summary, a new CP of $[\text{Cd}(\text{L})(\text{frda})(\text{H}_2\text{O})] \cdot 0.5\text{L} \cdot \text{H}_2\text{O}$ (**1**) was obtained by the reaction of $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ salt with mixed multi-N-donor and auxiliary polycarboxylate ligands. The coordination polymer was a 2D layer structure with a large 1D void filled with uncoordinated L ligands. CP **1** showed absorption peaks at 304 nm in the UV region with the value E_g of 3.55 eV. The crystalline material exhibited the maximal emission peak at 415 nm, upon excitation at 361 nm. Additionally, the QY and luminescence lifetime of CP **1** were 4.28 % and 48.87 ns, respectively. The study further confirmed that the mixed multi-N donor and carboxylate ligands are an effective moiety to generate desired architectures in self-assembly coordination polymers.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/9/12/625/s1>. Scheme S1. The synthesis method of 1-(4-(1H-imidazol-5-yl) phenyl)-1H-1,2,4-triazole.

Author Contributions: S.-S.H. and Z.-W.H. synthesized the organic molecule and CP **1**, and tested the properties of CP **1**. L.L. characterized the Cd(II) coordination polymer. S.-S.C. guided the project.

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Conflicts of Interest: The authors declare no conflict of interest.

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