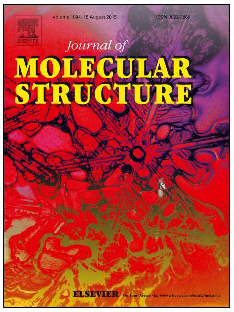

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Three Coordination Polymers Based on 9,10-Di(pyridine-4-yl)anthracene Ligands: Syntheses, Structures and Fluorescent Properties

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To *Journal of Molecular Structure*

Abstract

Three new mixed-ligand divalent coordination polymers (CPs) $\{[Zn_3(\mathbf{L})(1,4\text{-bdc})_3]\cdot 2DMF\}_n$ (**1**), $\{[Zn_2(\mathbf{L})(2,6\text{-ndc})_2]\cdot 3DMF\}_n$ (**2**) and $\{[Cd_2(\mathbf{L})_3(2,6\text{-ndc})_2]\}_n$ (**3**) [**L** = 9,10-di(pyridine-4-yl)anthracene, 1,4-H_2bdc = 1,4-benzenedicarboxylic acid, 2,6-H_2ndc = 2,6-naphthalenedicarboxylic acid] have been prepared and well characterized by elemental analyses, infrared spectroscopy, single-crystal X-ray diffraction techniques, powder X-ray diffraction patterns and thermogravimetric analyses. The crystal structure analyses of coordination polymers (CPs) reveal that all the complexes **1-3** have the three-dimensional (3D) coordination networks. The structure of **1** can be simplified as a ***sqc3*** 3D 8-connected framework with the point symbol of ($4^{24}\cdot 6^4$). Particularly, in the presence of the linear 2,6-H_2ndc auxiliary ligand, a double-deck interpenetrating ***pcu*** 3D network of **2** is assembled by 6-connecting framework with the point symbol of ($4^{12}\cdot 6^3$). Complex **3** exhibits a ***ttd*** 3D 5-connected net with a point symbol of ($4^6\cdot 6^4$). Further, the solid-state luminescent properties of the complexes **1-3** were measured and studied at room temperature.

Keywords: coordination polymers, 9,10-di(pyridine-4-yl)anthracene, crystal structure, fluorescent properties

1. Introduction

Over the past few decades, metal-organic coordination polymers (MOCPs) has a rocket-like speed of development, and the self-assembly of transition metal salts with mixed ligands of carboxylate and multidentate N-donor have been employed to construct MOCPs displaying intriguing architectures and various potential applications in the fields of catalysis, luminescence, magnetism, nonlinear optics, gas storage, and so on [1-5]. The self-assembly of MOCPs with yearning for intriguing structures and properties is still facing many difficulties, because the structures of complexes may be easily affected by organic ligands, metal ions, solvent, metal-ligand ratio, reaction temperature, counterions and many more [6-8]. Among them, the selection of suitable multifunctional ligands as building blocks is crucial to determining the structural outcome of target MOCPs [9]. Among various organic ligands, the flexible bis(pyridine) derivatives with remarkable coordination ability and versatile conformations, have attracted great interest within coordination chemistry [10].

Recently, the mixed-ligand systems generated from polycarboxylic acids and N-donor linkers have been widely adopted for the assembly of new coordination networks. Compared with the single ligand, the mixed-ligand is more likely to form frameworks with the desired structure [11]. However, the MOCPs based on aromatic dicarboxylate have been extensively investigated in the past decades due to their strong coordination capability, large conjugated-system and the possibility of offering new functional materials [12-15]. The 2,6-naphthalenedicarboxylic acid (2,6-H_2ndc) and 1,4-benzenedicarboxylic acid (1,4-H_2bdc) are typical aromatic dicarboxylic acids, which have attracted tremendous attention in constructing MOCFs with elegant architectures and desired properties, and they can be attributed to their various coordinating modes, high symmetry and structural rigidity [16].

In this study, we designed and synthesized such a ligand, 9,10-di(pyridine-4-yl)anthracene (**L**), to construct coordinative networks. On the basis of the **L** and two assistant carboxylic ligands, 1,4-H_2bdc and 2,6-H_2ndc, we got three complexes: namely, $\{[Zn_3(\mathbf{L})(1,4\text{-bdc})_3]\cdot 2DMF\}_n$ (**1**), $\{[Zn_2(\mathbf{L})(2,6\text{-ndc})_2]\cdot 3DMF\}_n$ (**2**), and $\{[Cd_2(\mathbf{L})_3(2,6\text{-ndc})_2]\}_n$ (**3**). All complexes were structurally characterized by elemental analyses, IR spectra, single crystal X-ray diffraction techniques and powder X-ray diffraction patterns (PXRD). As we know, the topological analyses of complexes can simplify complicated frameworks of coordination polymers, and it plays an instructive role in the rational design of some predicted functional materials [17]. In the present work, topological analyses reveal that complexes **1-3** display three-dimensional (3D) frameworks with different topological structures. Furthermore, the photoluminescence properties and thermal stabilities have been investigated.

(Insert Scheme 1)

2. Experimental Section

2.1 Materials and Measurements

All reagents and solvents were commercially available and used without further purification. FT-IR spectra were recorded by a Thermo Scientific Nicolet 6000 FT-IR spectrophotometer with KBr pellets in the 400-4000 cm^{-1} region. Elemental analyses for C, H, and N were performed by Perkin-Elmer 240 analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/Max-2500 diffractometer. Thermogravimetric analyses were carried out by the Japan's neo-confucianism standard TG-DTA analyzer. The fluorescent spectra were carried out by Hitachi F-4500 fluorescence spectrometer.

2.2 Preparation of ligand ***L***

9,10-dibromoanthracene (2.0 g, 5.95 mmol), Pyridine-4-boronic acid (2.4 g, 17.8 mmol), K_2CO_3 (11.6 g, 35.5 mmol), $Pd(PPh_3)_4$ (0.68 g, 0.59 mmol) and PhMe:DMF (6:1 300 ml) were successively add to a 500 ml flask. Under N_2 conditions, the reaction mixture was heated to 130 °C in the dark for 48 h. After the reaction mixture was cooled to room temperature and filtered to remove the catalyst by diatomaceous earth. The removal of solvent under reduced pressure yielded crude solid. The crude solid was dissolved in dichloromethane and washed with distilled water, then dried over anhydrous magnesium sulfate and concentrate dichloromethane under reduced pressure. A HCl solution was added and adjusted the pH to 2-3. Solid precipitation was produced and then filtered, the solid was dissolved in water and adjusted the pH to 8-9 by the addition of NaOH (10 M) solution. The pale yellow solid thus obtained by filtration and was washed with distilled water. Yield (1.4 g, 70%). MS (333.1387). ^{1}H NMR (CDCl3-*d*6, δppm): 8.879 (m, 4H, pyridine-2), 7.609 (m, 4H, anthracene-1), 7.456 (m, 4H, pyridine-3), 7.405 (t, 4H, anthracene-2).

*2.3 Synthesis of complexes **1~3***

*2.3.1 Preparation of [Zn_3(**L**)(1,4-bdc)$_3$]·2DMF (**1**)*

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (30 mg, 0.1 mmol), **L** (16.6 mg, 0.05 mmol), 1,4-H_2bdc (16.6 mg, 0.1 mmol) was put in a reaction vessel (10 ml) and DMF (3 ml) was added to it, then sealed, with ultrasonic processing for 30 min the solid completely dissolved in DMF giving a clear solution. The reaction solution was heated at 70 °C for five days then cooled to room temperature and filtered, after the solid was washed with DMF and dried to obtain many yellow petals crystals (ca. 51.2% yield based on **L**). Anal.Calcd (%) for $C_{48}H_{28}N_2O_{12}Zn_3$ (%): C, 54.73; H, 3.53; N, 4.91. Found: C,54.71; H, 3.58; N, 4.89. IR (KBr pellets, cm^{-1}): 3062(m), 2926(s), 2856(s), 1954(m), 1829(m), 1671(s), 1607(s), 1506(s), 1390(s), 1262(m), 1134(s), 1096(s), 1023(m), 951(s), 885(s), 825(s), 750(s), 644(m).

*2.3.2 Preparation of [Zn_2(**L**)(2,6-ndc)$_2$]·3DMF (**2**)*

The preparation of complex **2** was similar to that of **1**, except that 2,6-H_2ndc (21.6 mg, 0.1 mmol) was used instead of 1,4-H_2bdc (16.6 mg, 0.1 mmol), and heated at 95 °C for four days. Resulting in the formation of orange square crystals of **2** that were obtained.Yield: 62.1% based on **L**. Anal Calcd (%) for $C_{117}H_{105}N_{11}O_{23}Zn_4$ (%): C, 61.69; H, 4.36; N, 5.05. Found: C, 61.63; H, 4.37; N, 5.02. IR (KBrpellets，cm^{-1}): 3300(m), 3055(m), 2933(s), 1949(m), 1662(s), 1608(s), 1514(m), 1457(m), 1418(s), 1358(s), 1259(s), 1217(s),1158(s), 1091(s), 1068(s), 1030(s), 859(m), 824(s).

*2.3.3 Preparation of [Cd_2(**L**)$_3$(2,6-ndc)$_2$] (**3**)*

The preparation of complex **3** was similar to that of **1**, except that $Cd(NO_3)_2 \cdot 4H_2O$ (31 mg, 0.1 mmol) was used instead of $Zn(NO_3)_2 \cdot 6H_2O$ (30 mg, 0.1 mmol), and heated at 95 °C for 3 days. Resulting in the formation of yellow particles and crystals of **3** were obtained. Yield: 50.5% based on **L**. Anal Calcd (%) for $C_{48}H_{30}N_3O_4Cd$ (%): C, 69.87; H, 3.66; N, 5.09. Found: C, 69.85; H, 3.68; N, 5.07. IR (KBrpellets, cm^{-1}): 3320(m), 3057(s), 2933(s), 1956(m), 1834(m), 1654(s), 1603(s), 1564(s), 1491(s), 1400(s), 1359(s), 1219(s), 1192(s), 1143(s), 1097(s), 1013(s), 931(s), 797(s).

2.4. X-ray crystallography

Single-crystal X-ray data for complexes **1-3** were collected with a Bruker APEX2 Smart CCD diffractometer using Mo-Kα (λ = 0.71073 Å) radiation at room temperature. All the structures were solved by direct methods and refined by the full-matrix least-squares methods on F^2 using the SHELXTL software [18]. Metal atoms in the complexes were located from the *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses by refining with anisotropic thermal parameters on F^2. All of the hydrogen atoms were placed in the calculated position. Crystallographic datas and experimental details for structure determination are presented in **Table 1**. Selected bond lengths and bond angles are listed in Table S1 of Supplementary 1.

(Insert **Table 1)**

3. Results and Discussion

3.1. Syntheses and General Characterization

Despite solvothermal reaction being in a “black box” and being somewhat complicated, it has been proven to be an effective method in preparing MOCPs. A series of experiments were carried out in order to get the optimal reaction temperature and solvents for single crystal growth. Herein, complexes **1-3** were successfully prepared by solvothermal reactions at 70-95 °C. The crystal structures of these coordination polymers were analyzed in terms of network geometries, the thermogravimetric analyses and fluorescence properties were studied on base of their structural aspects. The pertinent crystallographic details for complexes **1-3** were given in Table 1 and Table S1 respectively.

The infrared spectra of **1-3** exhibit characteristic absorption for corresponding ligand with a slight shift due to coordination. For complexes **1-3**, the weak bands observed in the range 3064-2922 cm^{-1} are attributed to aromatic stretching vibrations. The bands observed at 1675 and 1358 cm^{-1} are due to asymmetric and symmetric stretching vibrations of carboxylate groups in H_2bdc and H_2ndc, respectively. The asymmetric vibration at 1675 cm^{-1} of H_2bdc and H_2ndc disappeared after conversion to complexes **1-3**, indicating the full deprotonation of carboxylate groups in H_2bdc and H_2ndc.

3.2. Description of the crystal structure

3.2.1. Structure of $\{[Zn_3(\mathbf{L})(1,4\text{-}bdc)_3]\cdot 2DMF\}_n$(***1***)

X-ray crystallographic analysis shows that complex **1** crystallizes in the monoclinic space group *C*2/*c* and features a 3D framework structure, and it consists of three Zn(II) ions (Zn1, Zn2 and Zn1$^{\#5}$, symmetry code: #5 -x+1,-y,-z+1), one **L** ligand, three bdc^{2-} anions and two uncoordinated DMF molecules. The Zn(II) ions show different coordination geometries. The Zn1 (Zn1$^{\#5}$) ion is five coordinated with a distorted pentahedron coordination geometry, which is fulfilled by four oxygen atoms (O1, O2, O4 and O5) originating from three independent 1,4-H_2bdc ligands and one nitrogen atom (N1) of the **L** ligand with the coordination angles varying from 99.9(9)° to 121.9(6)°. The Zn-N bond lengths are 2.004(3) Å, and the lengths of Zn-O bonds are 1.975(3) Å, 1.955(3) Å and 1.930(3) Å, respectively, four oxygen atoms and one nitrogen atom are located on the five vertices of pentahedron, and the Zn1(Zn1$^{\#5}$) is located in the center of pentahedron **(Fig. 1a)**. The Zn2 center is six coordinated by six O atoms from six 1,4-bdc^{2-} ions to complete an octahedral geometry with the coordination angles varying from 81.9(6)° to 120.0(0)°. The Zn-O bond lengths are 2.036(3) Å, 2.058(3) Å and 2.181(3) Å, severally. The four oxygen atoms (O3, O3$^{\#5}$, O6, and O6$^{\#5}$) are located in the equatorial plane location of octahedral and the two oxygen atoms (O1, O1$^{\#5}$) are located in the axial location of octahedral **(Fig. 1b)**. Three Zn(II) ions (Zn1, Zn2 and Zn1$^{\#5}$) are bridged by μ_2-1,3-carboxylate and μ_2-carboxylate oxygen atoms to form a trimer **(Fig. 1c)**, with the Zn···Zn distance is 3.205 Å. The dihedral angle between one pyridine ring and one anthracene ring in the same **L** is 63.9°. The trimers are joined through the scaffolds of 1,4-H_2bdc ligands, leading to the formation of a 4^4-***sqc*** coordination layer and two trimers in a diagonal position are linked by 1,4-H_2bdc **(Fig. 1d)**. The **L** ligand adopts bidentate bridging coordination, linking the 2D layers to form a 3D framework **(Fig. 1e)**. Meanwhile, from the topological point of view, Zn2 can be described as 8-connected nodes, and the ligands are regarded as linear linkers. Thus, the structure of **1** can be simplified as a 3D 8-connected framework with the point symbol of $(4^{24}\cdot 6^{4})$ **(Fig. 1f)**.

(Insert **Fig. 1**)

*3.2.2. Structure of {[Zn$_2$(**L**)(2,6-ndc)$_2$]·3DMF}$_n$ (**2**)*

Single crystal X-ray diffraction analysis reveals that complex **2** crystallizes in the triclinic space group *P*-1 and features a 3D framework structure. The complex **2** contains two Zn(II) ions, one **L** ligand, two 2,6-ndc^{2-} anions and three uncoordinated DMF molecules. The all Zn(II) ions are five coordinated with a slightly distorted quadrangular pyramid coordination geometry, which is coordinated by four O atoms (O2, O3, O5, and O7) originating from four independent 2,6-ndc^{2-} anions and one N atoms (N1) from **L** ligand with the coordination angles varying from 87.3(5)° to 110.4(3)° **(Fig. 2a)**. The four oxygen atoms are located in the equatorial plane of quadrangular pyramid and are coplanar, and the N1 atom is in the axial location of quadrangular pyramid. The Zn-N bond lengths are 2.027(3) Å and 2.035(3) Å, respectively, and the lengths of Zn-O bond lengths range from 2.021(3) Å to 2.079(2) Å. Two adjacent Zn ions are bridged by μ_2-1,3-carboxylate to form a dimer and the Zn···Zn distance is 2.977 Å. The dihedral angle between one pyridine ring and one anthracene ring in the same **L** is 63.9°. However, the dimers are joined through the scaffolds of 2,6-H_2ndc ligands, leading to the formation of a 4^4-***pcu*** coordination 2D layer **(Fig. 2b)**, which is different with complex **1**. In complex **2**, the distance between adjacent dimers is equal and the two dimers in the diagonal position are not linked by the 2,6-H_2ndc ligands. Then the 2D layer is bridged to give 3D framework by **L** ligands **(Fig. 2c)**.

For a better understanding of the intricate framework, a topological analysis of complex **2** was performed. In the 2D layer, we can define the [Zn$_2$(**L**)(2,6-ndc)$_2$] dimer as six-connected nodes with all crystallographically independent **L** ligands and 2,6-ndc^{2-} anions as linkers. Thus, the network topology of **2** can be represented as a two-dimensional layer interpenetrating 6-connected framework with the point symbol of $(4^{12}\cdot 6^{3})$ **(Fig. 2d)**.

(Insert **Fig. 2**)

3.2.3. Structure of $\{[Cd_2(\mathbf{L})_3(2,6\text{-}ndc)_2]\}_n$ ***(3)***

Single crystal X-ray diffraction structural analysis reveals that complex **3** crystallizes in the triclinic space with group *P*-1 and features a 3D net. Complex **3** includes an asymmetric unit consisting of one Cd(II) ion, one and half of **L** ligands and one 2,6-ndc^{2-} anion, As shown in **Fig. 3a**, each Cd(II) ion is coordinated by three nitrogen atoms (N1, N2, N3) from three different **L** ligands (Cd-N 2.361(2) Å, 2.377(2) Å and 2.444(2) Å) and four oxygen atoms (O1, O2, O3 and O4) from two 2,6-ndc^{2-} anions (Cd-O 2.253(2)-2.697(2) Å) to generate a distorted pentagonal bipyramid geometry with the coordination angles varying from 55.29(7)° to 119.95(9)°, and the equatorial plane is occupied by the above four oxygen atoms and one nitrogen atom (N3) (the O1, O2 and O3 are coplanar, the O1, O4 and N3 are coplanar, and the dihedral angle between two different planes is 32.31°), while N1 and N2 occupy axial positions with the N1-Cd-N2 bond angle of 172.20(3)°. The Cd(II) ions are connected by 2,6-H_2ndc ligands to generate a 4^4-***ttd*** coordination 2D layer **(Fig. 3b)**, which is further bridged to form 3D framework by **L** ligands **(Fig. 3c)**. In contrast, in complex **3**, the difference of 4^4-***ttd*** with those complexes of **1** and **2** is a ladder-like structure. From the viewpoint of structure topology, Cd(II) ions can be considered as 5-connected nodes, the **L** and 2,6-ndc^{2-} anions are simply viewed as linkers. Therefore, the whole 3D framework should be simplified as a 5-connected net with a point symbol of $(4^6 \cdot 6^4)$ **(Fig. 3d)**.

(Insert **Fig. 3**)

3.3. Powder X-ray diffraction (PXRD) and Thermogravimetric Analysis

PXRD is a reliable technique to characterize the nature of the new solid forms in crystallization experiment. The PXRD experimental and computer-simulated patterns of the corresponding complexes were shown in Supplementary 2 Fig. S1, which showed good agreement with that of the simulated ones, indicating that the as-synthesized products are in pure phase. The preferred orientation of the powder sample may cause the differences in intensity.

For the sake of researching the framework stability of the complexes **1-3** were shown in Supplementary 2 Fig. S2. The TG shows that the complex **2** undergoes decomposition in two stages, and the complex **3** undergoes decomposition in three stages [19]. For **1**, in the whole process of stepwise decomposition until the temperature rise to 500 °C, the final residual of 19.05% may be the mixture of $ZnCO_3$ and ZnO (Calcd 20.17%). For **2**, the first loss of 39.34%, occurs between 25 °C and 150 °C, corresponding to the loss of three lattice DMF molecules and two **L** molecules (Calcd 38.49%). The second that occurs between 300° and 475° are ascribed to the collapse of the framework. The final residual of 9.08% may be the mixture of $ZnCO_3$ and ZnO (Calcd 7.33%). For **3**, the first loss, of 9.42%, occurs between 25 °C and 80 °C, corresponding to the loss of one lattice DMF molecule (Calcd 9.02%). The second occurs between 130 °C and 240 °C, amounting to about 10.09%, corresponding to escape of one lattice DMF molecule (Calcd 9.02%), and the third weight loss between 350 °C and 500 °C amounts to about 60.02%, which is ascribed to the collapse of the framework (Calcd 60.35%), and the final residual of 19.37% may be $CdCO_3$ (Calcd 20.84%).

3.5. Fluorescent Properties

It is known that many d^{10} metal complexes exhibit luminescence properties. The coordination complexes with the rational selection and design of conjugated organic spacers with metal centers can be efficient for obtaining new luminescent materials [20]. To investigate the luminescence properties of complexes **1-3**, the solid-state fluorescent properties of **1-3** as well as the ligand **L** have been studied at room temperature under the same experimental condition and their emission spectra are given in Supplementary 2 Fig. S3. When excited with 390 nm light, the free **L** ligand exhibited an emission peak at 470 nm, which originated from ligand internal change transfer. Upon excitation with 390 nm light, complexes **1-3** all display intense photoluminescence, with emission maxima at 474, 440 and 440 nm, respectively. Compared with the free **L** Ligand, the introduction of Zn(II) and Cd(II) to ligand **L** led to a weak blue-shift for complexes **2** and **3**. On the one hand, because the N atoms coordination to the metal centre, the electron transfer to the metal ions and occurs Ligand-to-Metal Charge Transition (LMCT). Moreover, the ligand π^* track as the highest occupied molecular orbital (HOMO) and the metal *d* track for the lowest unoccupied molecular orbital (LUMO), the electron transfer when subjected to external excitation, resulting in the maximum absorption wavelength of the compounds blue shift. On the other hand, the differences of the peaks for **1** may be resulted from different coordination environments around Zn(II) and Cd(II) center [21]. In addition, the high-dimensional structures of complexes **2** and **3** lead to significant enhancement of fluorescence intensity compared to that of the free ligand. The enhancement of fluorescence intensity of complexes **1-3** can be attributed to the following aspects: firstly, anthracene is a kind of polycyclic aromatic hydrocarbons with strong fluorescence emission; secondly, the ligand coordination to the metal centre and increase plane conjugated system of ligands, which the intraligand $\pi \rightarrow \pi^*$ transition occurs more easily; on the other hand, the ligand rigidity enhancement and thus reduces the loss of energy through a radiationless pathway[22], however, fluorescence enhancement of complexes **1-3**.

4. Conclusion

In summary, three new Zn(II)/Cd(II) complexes with 9,10-di(pyridine-4-yl)anthracene have been successfully constructed and characterized by single-crystal X-ray diffraction, element analysis, IR and PXRD. Complexes **1-3** have the 3D network structure. The central metals, reaction solvents and temperatures play crucial roles in the formation of complexes **1-3**. The X-ray powder diffraction (PXRD) of the complexes **1-3** demonstrate that they have high phase purity. In addition, we studied thermal stabilities and fluorescent properties of complexes **1-3**. We believe that this study reveals the effectiveness of general solvothermal processing methods which are influenced by the nature of the solvent and reaction temperature. Because of the multi ring structure of the ligand molecule, the solubility of the ligand is reduced and the difficulty coefficient is enhanced. Complex **1-3** has a novel structure and strong fluorescence properties, which indicated that those complexes can be used as a potential functional materials, for example used in LED lamps. For another, the coordination of the carboxylate group from auxiliary ligand to metal center effectively increase the dimension of the coordination polymers, which provides a potential guiding significance for the synthesis of coordination polymers with multi dimensions.

Appendix A. Supplementary data

CCDC 1528618-1528620 contains the supplementary crystallographic data for complexes $\{[Zn_3(\mathbf{L})(1,4\text{-bdc})_3]\cdot 2DMF\}_n$ (**1**), $\{[Zn_2(\mathbf{L})(2,6\text{-ndc})_2]\cdot 3DMF\}_n$ (**2**), and $\{[Cd_2(\mathbf{L})_3(2,6\text{-ndc})_2]\}_n$ (**3**) respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data

Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Captions to Figures

Fig. 1 View of (a) (b) and (c) the coordination environment of Zn(II) atoms in complex **1;** (d) the 2D sheet structure of **1;** (e) the 3D architecture of **1;** (f) the 8-connected net topology with the Schläfli symbol of ($4^{24}\cdot 6^{4}$).

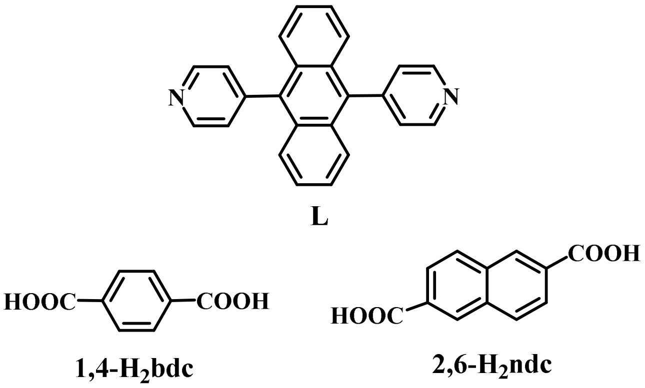
Fig. 2 View of (a) the coordination environment of Zn(II) atoms in complex **2;** (b) the 2D sheet of **2;** (c) the 3D sheet of **2;** (d) the 6-connected net topology with the Schläfli symbol of ($4^{12}\cdot 6^{3}$).

Fig. 3 View of (a) the coordination environment of Cd(II) atoms in complex **3;** (b) and (c) the 3D sheet of **3;** (d) the 5-connected net topology with the Schläfli symbol of ($4^{6}\cdot 6^{4}$).

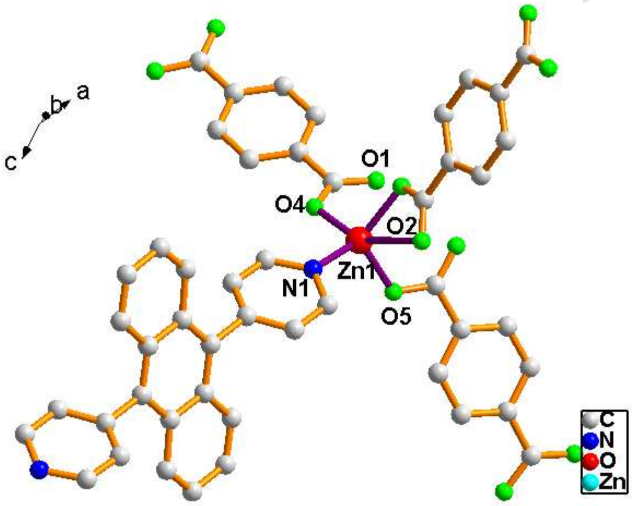
Table 1 Crystal data and structure refinement summary for complexes **1-3**

	1	**2**	**3**
Formula	$C_{52}H_{40}N_4O_{14}Zn_3$	$C_{57}H_{48}N_5O_{11}Zn_2$	$C_{96}H_{60}N_6O_8Cd_2$
Formula wt	1141.05	1109.78	1650.32
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	*P*-1	*P*-1
T (K)	386(2)	386(2)	386(2)
a (Å)	42.213(3)	12.997(3)	9.1668(12)
b (Å)	9.4323(9)	13.106(3)	13.6510(16)
c (Å)	46.063(3)	17.213(4)	22.598(3)
α（°）	90	93.895(4)	74.887(5)
β（°）	156.243(2)	107.639(6)	84.345(6)
γ（°）	90	95.018(6)	88.071(8)
V (Å^3)	7388.7(10)	2769.6(12)	2716.6(6)
Z	4	1	2
D (Mg/m^3)	0.918	1.376	1.009
μ (mm^{-1})	1.006	0.932	0.437
F(000)	2064	1188	838
Crystal size (mm^3)	0.22 × 0.20 × 0.18	0.22 × 0.20 × 0.18	0.22 × 0.20 × 0.18
Theta rang (deg)	3.12—27.52	3.00—27.53	3.05—27.55
Goof(F^2)	0.810	0.990	1.194
Messuredrefins	45774	35205	34869
Obsdreflns	8455	12435	12238
R_{int}	0.0321	0.0290	0.0192
R^a/wR^b	0.0625/0.1453	0.0578/0.1547	0.0363/0.1105

[a] $R = \Sigma(||F_0|-|F_C||)/\Sigma|F_0|$; [b] $wR = [\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0^2)]^{1/2}$



Scheme 1 The ligand **L** and organic acids used in this work.



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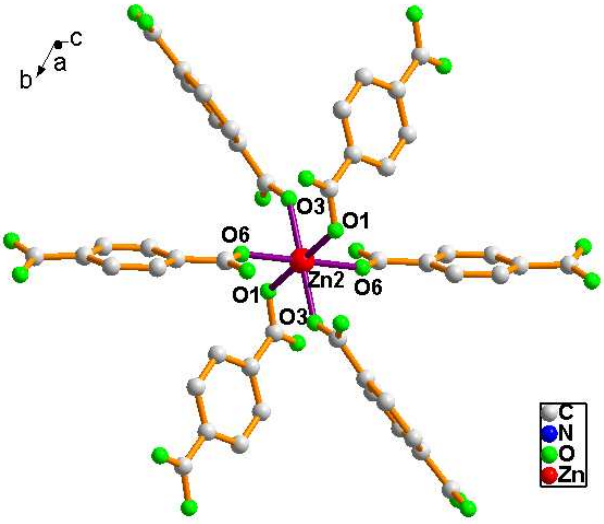

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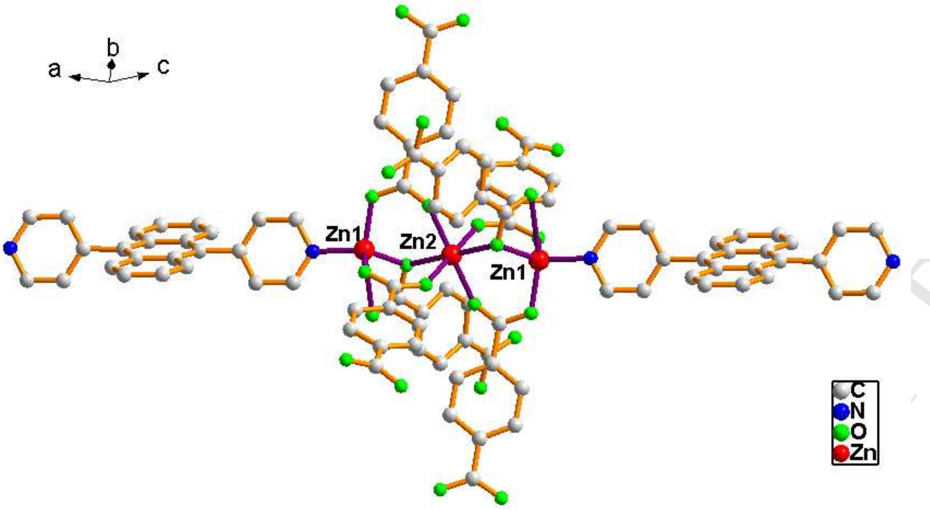

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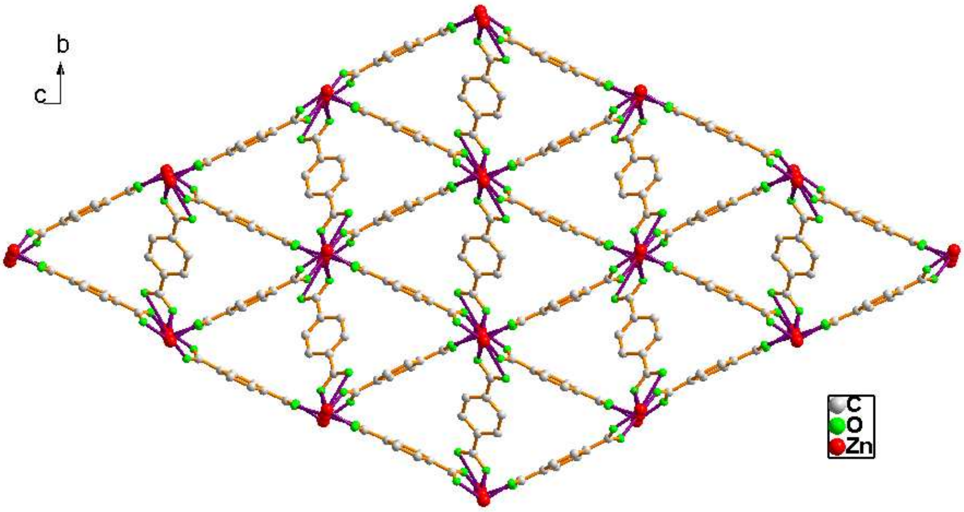

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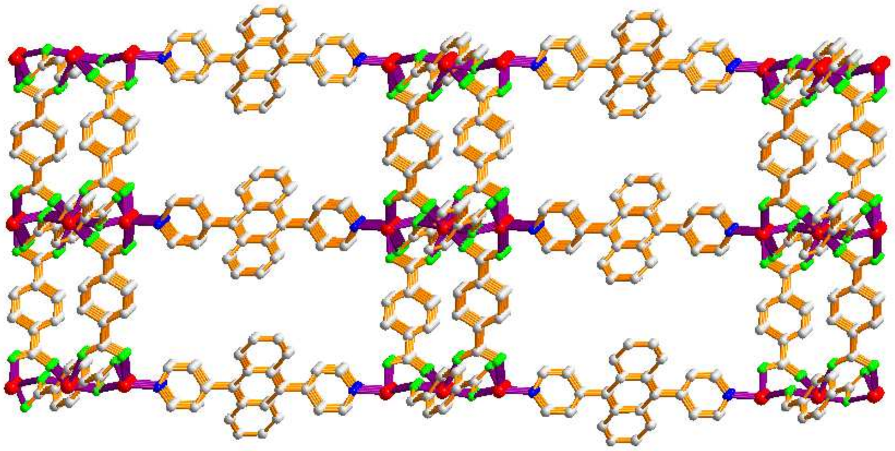

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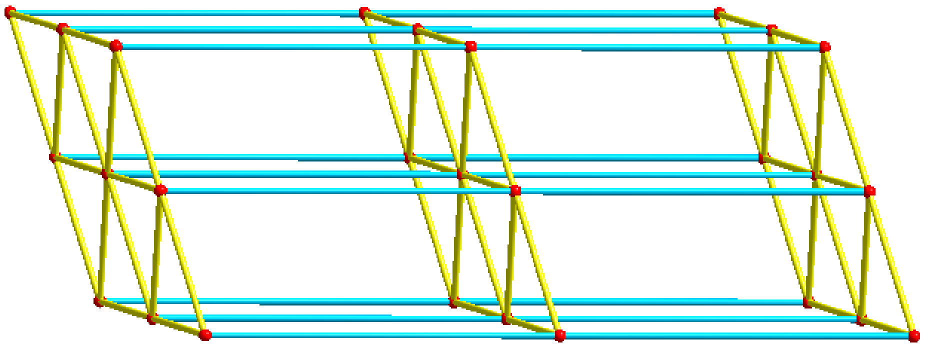

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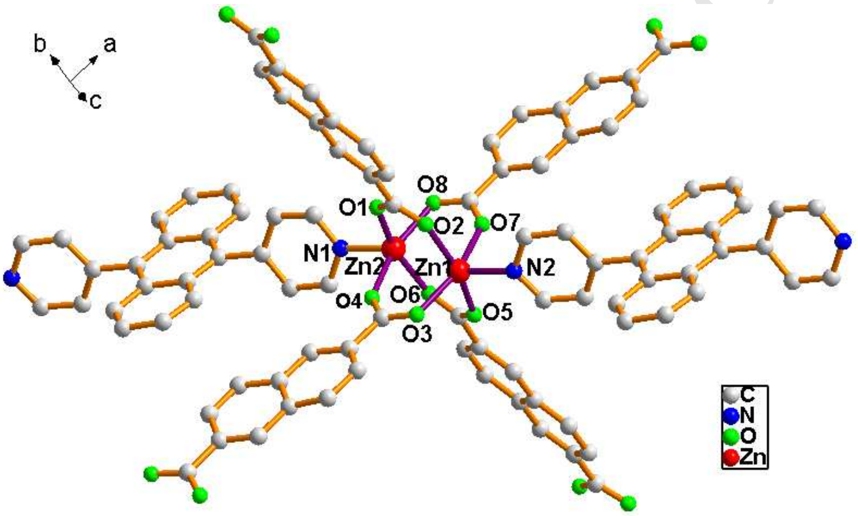
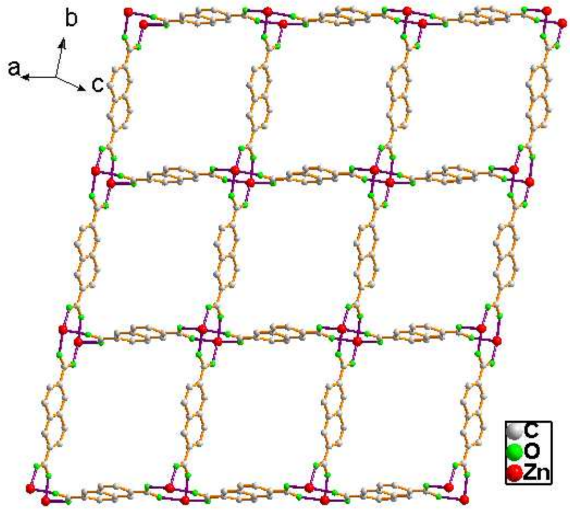
Fig. 1



(a)



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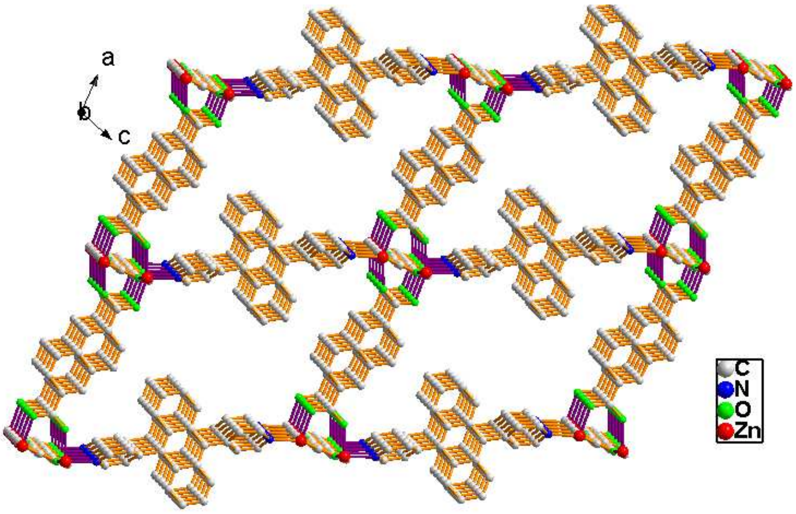

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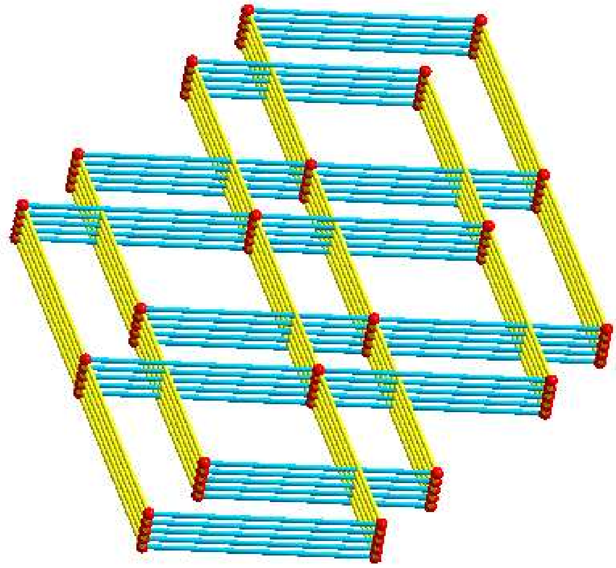

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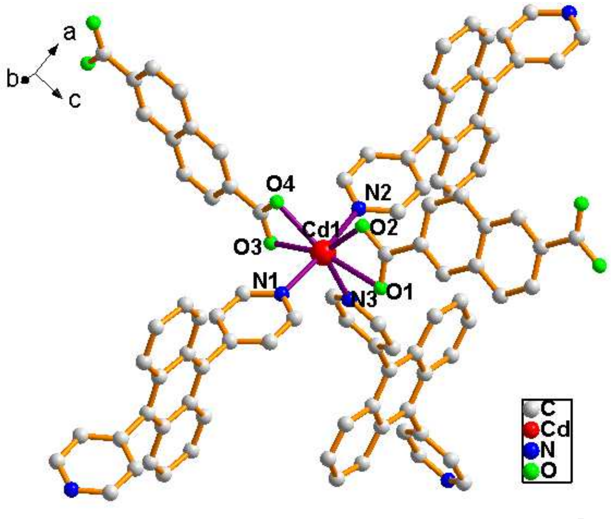
Fig. 2



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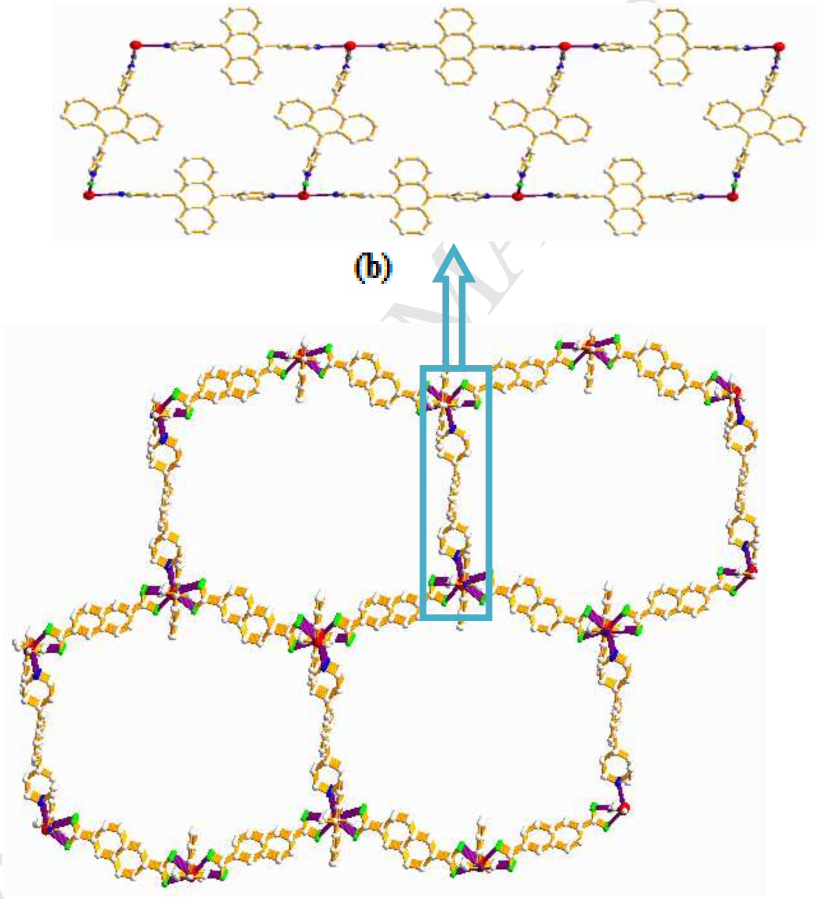

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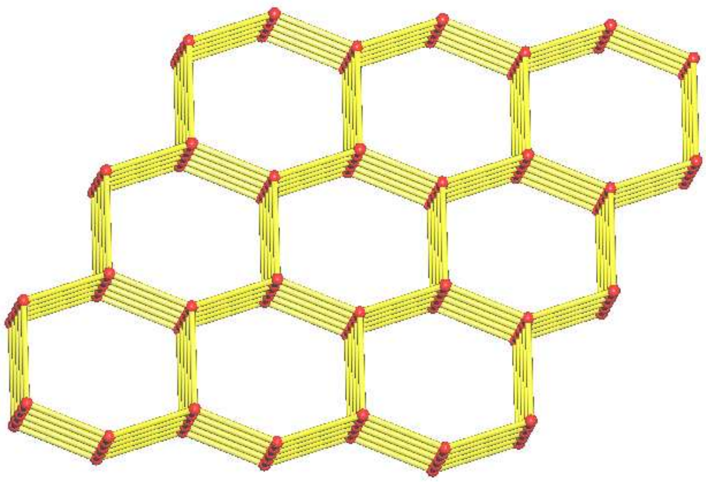


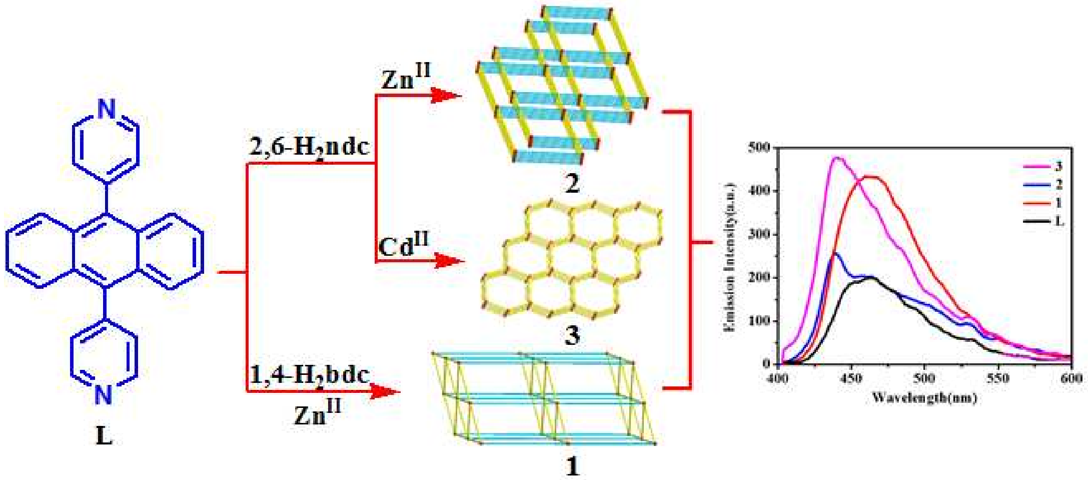
(d)

Fig. 3

Graphical Abstract

Three Coordination polymers based on 9,10-di(pyridine-4-yl)anthracene Ligands: Syntheses, Structures and Fluorescent properties

Jun-Liang Dong[a], Duo-Zhi Wang*[a, b], Yan-Yuan Jia[c], Dan-Hong Wang[d]*



Three new Zn(II)/Cd(II) complexes with 9,10-di(pyridine-4-yl)anthracene have been successfully constructed and characterized by single-crystal X-ray diffraction, element analyses, IR, PXRD. Complexes **1-3** have a 3D network structure. In addition, the network topology of **2** can be represented as a two-dimensional layer interpenetrating 6-connected framework with the point symbol of $(4^{12}\cdot 6^{3})$. Moreover, the solid-state luminescence properties and thermogravimetric analysis of complexes **1-3** have been investigated and discussed.

- 9,10-Di(pyridine-4-yl)anthracene Ligands.
- Mixed-ligand divalent coordination polymers.
- Structural analysis of all complexes.
- Fluorescent Properties.