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Blue luminescent complexes based on 5-aminodiacetic isophthalic ligand

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Abstract

The reactions of $Cd(CH_3COO)_2\cdot 2H_2O$ or $Zn(CH_3COO)_2\cdot 2H_2O$ and 5-aminodiacetic isophthalic acid (H_4adip) with 1,10′-phenanthroline (phen) ligand gave rise to two blue luminescent coordination mononuclear complexes: $[Cd(phen)(H_3adip)_2(H_2O)_2]\cdot 0.5H_2O$ (**1**) and $Zn(phen)(H_3adip)_2$ (**2**), respectively. **1** crystallizes in the triclinic space group P-1, with $a=6.2889(2)$, $b=16.1556(5)$, $c=18.4277(7)$ Å, $\alpha=97.722(12)$, $\beta=94.338(9)$, $\gamma=95.039(7)°$, $V=1840.86(11)$ Å^3, $Z=2$. Complex **2** crystallizes in monoclinic, space group $C2/c$ with $a=22.639(8)$, $b=9.813(3)$, $c=15.708(6)$ Å, $\beta=110.928(4)°$, $V=3259(2)$ Å^3, $Z=4$. Carboxylic groups in both structures are involved in strong hydrogen bonding interactions. At room temperature, complex **1** exhibits an intense emission at 474 nm upon 380 nm excitation, while complex **2** exhibits an intense emission at 485 nm upon 365 nm excitation, which are contributed from ligand-to-metal charge-transfer (LMCT).

Keywords: Mononuclear; Supramolecule; Carboxylate; Hydrogen bond; Luminescence

1. Introduction

In recent years, chemists have devoted a great deal of effort to metal-organic coordination polymers [1–5]. In particular, aromatic multi-carboxylate ligands have been shown to be good building blocks in the design of metal-organic materials with desired topologies owing to their rich coordination modes [6–9]. However, most adopted ligands possesses rigid carboxylate arms, e.g. 1,3,5-benzenetricarboxylate [10], 1,2,4,5-benzenetetracarboxylate [11], 1,4,5,8-naphthalenetetracarboxylate [12], etc. Relative fewer compounds are reported derive from flexible carboxylate arms [13,14]. But as known that the crystal structure formation is sensitive to the flexibility of carboxylate arms, and such flexibility may increase the probability of making tube-like or cage-like structure. Taking account of these, we feel it significant to take on the exploration on carboxylate ligand with flexible carboxylate arms. So, we designed and synthesized a new bridging chelating multi-carboxylate ligand 5-aminodiacetic isophthalic acid (H_4adip). H_4adip not only has two rigid carboxyl groups, but also has two flexible acetic groups with suitable lengths. Moreover, the nitrogen atom of aminodiacetic group is also possible to participate in the coordination sphere. In addition, like other multi-carboxylate ligands, it can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor, depending upon the number of deprotonated carboxyl groups, which contribute to the stability of supramolecular network. Recently, we began to assemble H_4adip and transition metal ions into polymeric complexes under hydrothermal conditions. We hope the rich information stored in H_4adip will induce novel polymeric structures. Through carefully controlling the reaction conditions, we have found that H_4adip is a versatile building block for the construction of metal-organic complexes through complete or partial deprotonation of its carboxyl groups. A series of interesting structures from 1D to 3D architectures have been successfully obtained in our experiments [15]. Herein, we reported two transition metal complexes derived from H_4adip and phen under strong acidic conditions: $[Cd(phen)(H_3adip)_2(H_2O)_2]\cdot 0.5H_2O$ (**1**) and $Zn(phen)(H_3adip)_2$ (**2**). Such discrete molecules are further linked together by hydrogen bonds or $\pi\cdots\pi$ interactions to generate interesting supramolecular architectures, and both show intense blue luminescence in solid state at room temperature.

2. Experimental section

2.1. General

The H_4adip were prepared as described in our work elsewhere [15], and the other starting materials were purchased commercially and used without further purification. Elemental

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analyses were determined on an Elemental Vario ELIII elemental analyzer. IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT IR spectrometer in the range of 200–4000 cm^{-1}. Fluorescent spectra were measured on an Edinburgh Instruments analyzer model FL920.

2.2. Synthesis of $[Cd(phen)(H_3L)_2(H_2O)_2]\cdot 0.5H_2O$ (**1**)

A mixture of $Cd(CH_3COO)_2\cdot 2H_2O$ (0.134 g, 0.5 mmol), H_4adip (0.148 g, 0.5 mmol) and 1,10-phen (0.099 g, 1.0 mmol) dissolved in distilled water (6 ml)/CH_3COOH (6 ml) was sealed in a 25 ml Teflon-lined autoclave and heated under autogenous pressure at 90 °C for 3 days. The resulting colorless prismatic crystals of **1** were filtered, and air-dried at room temperature. Yielded (0.157 g), produced in 67.6% (based on H_4adip). IR (KBr pellet, cm^{-1}): 3425(br), 2972(w), 2911(w), 2844(w), 1696(s), 1602(s), 1468(s), 1423(s), 1383(m), 1325(s), 1383(m), 1293(m), 995(m). Anal. Calcd for $C_{36}H_{33}CdN_4O_{18.5}$: C 46.49, H 3.58, N 6.02%. Found: C 46.42, H 3.71, N 5.98%.

2.3. Synthesis of $Zn(phen)(H_3L)_2$ (**2**)

Complex **2** was synthesized by the same procedure as above but adding $Zn(CH_3COO)_2\cdot 2H_2O$ instead of $Cd(CH_3COO)_2\cdot 2H_2O$. Pale-yellow prism crystals are obtained by filtration. Yielded (0.075 g), produced in 36.2% (based on H_4adip). IR (KBr pellet, cm^{-1}): 3436.9(br), 3075.6(w), 2921.54(w), 2865.02(w), 2361.7(w), 1718.63(vs), 1597.8(m), 1555.49(m), 1467.63(m), 1421.97(m), 1383.83(m), 1267.9(w), 1216.5(m), 1192.47(m), 990.58(m), 846.79(w). Anal. Calcd for $C_{36}H_{28}N_4O_{16}Zn$: C 51.60, H 3.37, N 6.69%. Found: C 51.52, H 3.42, N 6.64%.

Table 1
Crystallographic data for the complexes **1** and **2**

	1	2
Empirical formula	$C_{36}H_{33}CdN_4O_{18.5}$	$C_{36}H_{28}N_4O_{16}Zn$
Temp. (K)	173(2)	173(2)
Cryst. color	Colorless	Colorless
Cryst. size (mm^3)	0.20×0.10×0.08	0.20×0.10×0.05
Mr	930.06	837.99
Crystal system	Triclinic	Monoclinic
Space group	$P-1$	$C2/c$
a (Å)	6.2889(2)	22.639(8)
b (Å)	16.1556(5)	9.813(3)
c (Å)	18.4277(7)	15.708(6)
α (°)	97.722(12)	90
β (°)	94.338(9)	110.928(4)
γ (°)	95.039(7)	90
V (Å^3)	1840.86(11)	3259(2)
Z	2	4
Density (mg/m^3)	1.678	1.708
Abs. coeff. (mm^{-1})	0.684	0.846
F(000)	946	1712
Refln collections	14204	12279
Indep. Reflns	8293 [R(int)=0.0259]	3719 [R(int)=0.0315]
Params	547	314
S on F^2	1.142	1.076
$R1$, $wR2$ [$I>2\sigma(I)$]	0.0534, 0.1176	0.0393, 0.0928
$R1$, $wR2$ (all data)	0.0609, 0.1216	0.0459, 0.0973

Table 2
Selected bond lengths (Å) and bond angles (°) of complexes **1** and **2**

	Bond length (Å)		Bond angle (°)
Complex 1			
Cd(1)–O(18)	2.274(3)	N(2)–Cd(1)–N(1)	70.67(11)
Cd(1)–O(8)	2.306(3)	O(8)–Cd(1)–O(14)	152.75(11)
Cd(1)–N(2)	2.336(3)	O(18)–Cd(1)–O(17)	89.80(13)
Cd(1)–O(14)	2.340(3)	O(8)–Cd(1)–N(1)	87.36(11)
Cd(1)–N(1)	2.403(3)	O(18)–Cd(1)–N(2)	162.06(11)
Cd(1)–O(17)	2.412(3)	O(18)–Cd(1)–N(1)	113.45(12)
O(13)–C(36)	1.247(5)	O(14)–Cd(1)–N(1)	118.94(10)
O(14)–C(36)	1.278(5)	N(1)–Cd(1)–O(17)	152.48(12)
O(7)–C(13)	1.272(6)		
O(8)–C(13)	1.235(5)		
Complex 2			
Zn(1)–N(2A)#1	2.0641(17)	N(2A)#1–Zn(1)–N(2)	81.92(9)
Zn(1)–N(2)	2.0641(17)	O(1)–Zn(1)–O(2)	59.97(6)
Zn(1)–O(1A)#1	2.1252(16)	O(1A)#1–Zn(1)–O(1)	153.73(8)
Zn(1)–O(1)	2.1252(16)	N(2A)#1–Zn(1)–O(2A)#1	153.19(6)
Zn(1)–O(2A)#1	2.2347(15)	N(2)–Zn(1)–O(1A)#1	105.37(6)
Zn(1)–O(2)	2.2347(15)	O(1)–Zn(1)–O(2A)#1	101.43(6)
Zn(1)–C(8A)#1	2.517(2)	N(2)–Zn(1)–O(2A)#1	96.43(6)
O(1)–C(8)	1.257(2)		
O(2)–C(8)	1.262(3)		

Symmetry code: #1 $-x,y,-z+1/2$.

2.3.1. X-ray structure analyses

X-ray intensity data of both complexes were collected on a Mercury CCD diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda=0.71073$ Å) at 173 K. Empirical absorption corrections were applied to the data using the SADABS program [16]. The structures were solved by the direct method and refined by the full-matrix least squares on F^2 using the SHELXTL-97 program [17]. All of the non-hydrogen atoms were refined anisotropically. The H atoms bonded to C atoms were positioned geometrically and refined using a riding model [C–H 0.93 Å and $U_{iso}(H)=1.2\ U_{eq}(C)$]. The H atoms bonded to O atoms were located from difference maps and refined isotropically. Crystallographic data and structure refinements for **1** and **2** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2. CCDC numbers are 290056 for compound **1** and 290057 for compound **2**, respectively.

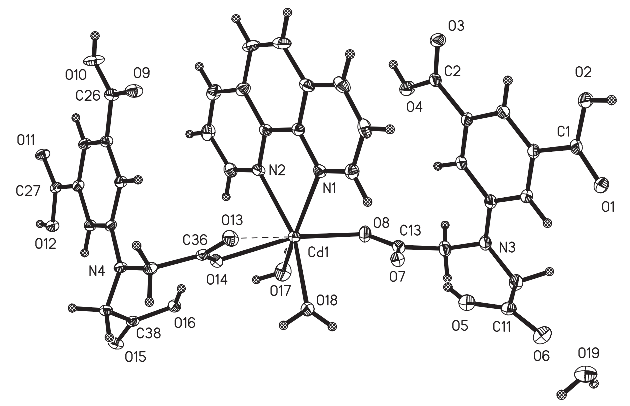


Fig. 1. ORTEP drawing of **1**, drawn with displacement ellipsoids at the 30% probability.

Table 3
Parameters (Å, °) for hydrogen-bonding interaction of complexes **1** and **2**

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠DHA (°)
*Complex **1***				
O(5)–H(5)···O(7)	0.84	1.69	2.489(5)	158.6
O(16)–H(16A)···O(14)	0.84	1.73	2.524(4)	158.1
O(17)–H(17A)···O(16)	0.85	2.63	3.431(5)	157.3
O(2)–H(2)···O(11F)#1	0.84	1.75	2.592(4)	174.7
O(4)–H(4A)···O(3A)#2	0.84	1.74	2.574(4)	170.2
O(10)–H(10)···O(9B)#3	0.84	1.78	2.603(4)	165.9
O(12)–H(12)···O(1G)#4	0.84	1.73	2.567(4)	175.6
O(18)–H(18A)···O(6D)#6	0.85	2.14	2.838(5)	139.6
O(18)–H(18B)···O(15E)#7	0.85	1.97	2.745(4)	151.2
O(19)–H(19A)···O(5C)#8	0.85	2.09	2.811(7)	142.7
*Complex **2***				
O(6)–H(6A)···O(1B)#2	0.97(4)	1.77(4)	2.721(2)	164(3)
O(8)–H(8A)···O(4C)#3	0.90(3)	1.82(4)	2.667(2)	158(3)
O(3)–H(1)···O(2)	0.95(4)	1.63(4)	2.581(2)	177(3)

Symmetry transformations used to generate equivalent atoms: for complex **1**: #1 $x+2, y+1, z$; #2 $-x+1, -y+2, -z+1$; #3 $-x+1, -y+1, -z+1$; #4 $x-2, y-1, z$. #5 $x-1, y, z$; #6 $-x+1, -y+2, -z$; #7 $-x, -y+1, -z$; #8 $-x+2, -y+2, -z$. for complex **2**: #2 $-x, -y, -z$; #3 $-x+1/2, -y-1/2, -z+1$.

3. Results and discussion

Single-crystal X-ray diffraction analysis reveals that **1** is a mononuclear complex. As shown in Fig. 1, the Cd^{II} center is ligated by two nitrogen atoms from 1,10′-phen, two carboxylate oxygen atoms from two different H_3L^- ligands in a trans arrangement, together with two oxygen atoms from coordinated water molecules. The bond lengths of Cd–O in **1** vary from 2.274(3) to 2.412(3) Å and bond lengths of Cd(1)–N(1)/Cd(1)–N(2) are 2.336(3)/2.403(3) Å, which are comparable to those in reported Cd compounds [18–20]. However, the Cd1···O13 distance of 2.774 Å suggests a non-negligible interaction between them, as may be described as a semi-chelating coordination mode. Thus, one of H_3L^- ligand adopts a bis-monodentate chelating coordinate mode, the other adopts monodentate mode. Hence, the Cd^{II} center may be also regarded as in distorted pentagonal bipyramidal geometry. The face-to-face distances between phenyl ring of H_3adip^- and 1,10′-phen ligand are 3.632 and 3.680 Å, indicating the existence of π···π stacking interactions.

Different kinds of hydrogen bonds are observed in the complex **1** in Table 3: (i) hydrogen bonds between two uncoordinated carboxylate oxygen atoms with an O···O distance of 2.489(5)–2.603(4) Å; (ii) hydrogen bonds of uncoordinated water molecules/carboxylate oxygen atoms (O···O distance: 2.811(7) Å); (iii) hydrogen bonds of coordinated water molecules/carboxylate oxygen atoms (O···O distances: 2.745(4)–2.838(5) Å). As shown in Fig. 2a, the mononuclear units are linked together into a zigzag chain by hydrogen bonds$^{\mathrm{i}}$ of O4···O3A (2.574(4) Å; A: $-x+1, -y+2, -z+1$); O10···O9B, (2.603(4) Å; B: $-x+1, -y+1, -z+1$). Meanwhile, the hydrogen bonds$^{\mathrm{i}}$ of O5···O7 2.489(5) and O16···O14 2.524(4) Å, together with hydrogen bonds$^{\mathrm{ii}}$ of O5···O19C (2.811(7) Å; C: $2-x, 2-y, -z$), further

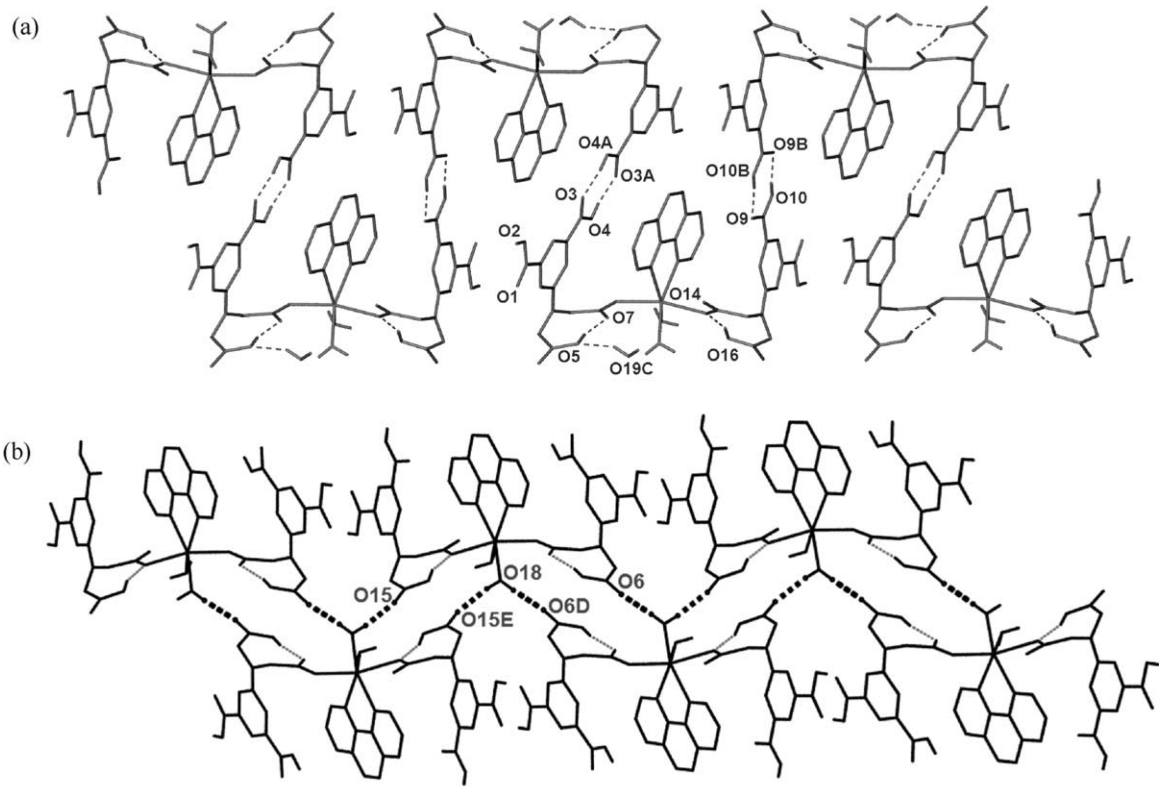


Fig. 2. (a) View of 1D chain formed by H_3adip^- extending along *b*-axis; (b) The coordinated water oxygen atom forms bifurcated hydrogen bonds$^{\mathrm{ii}}$ to link zigzag chain along *c*-axis.

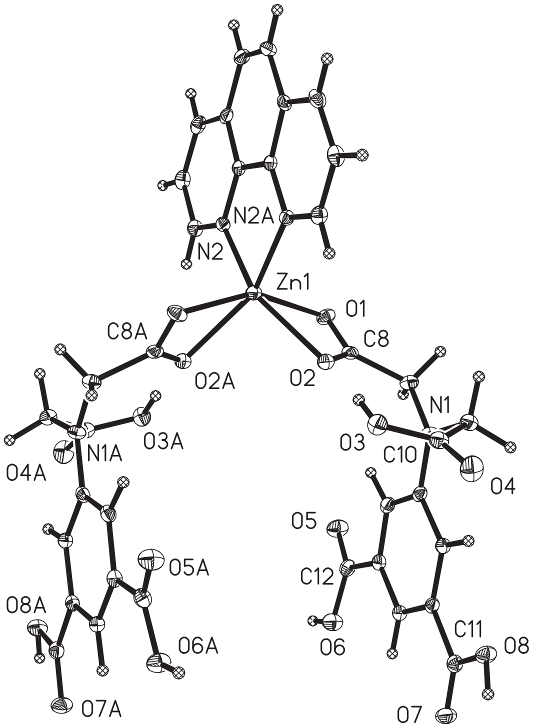


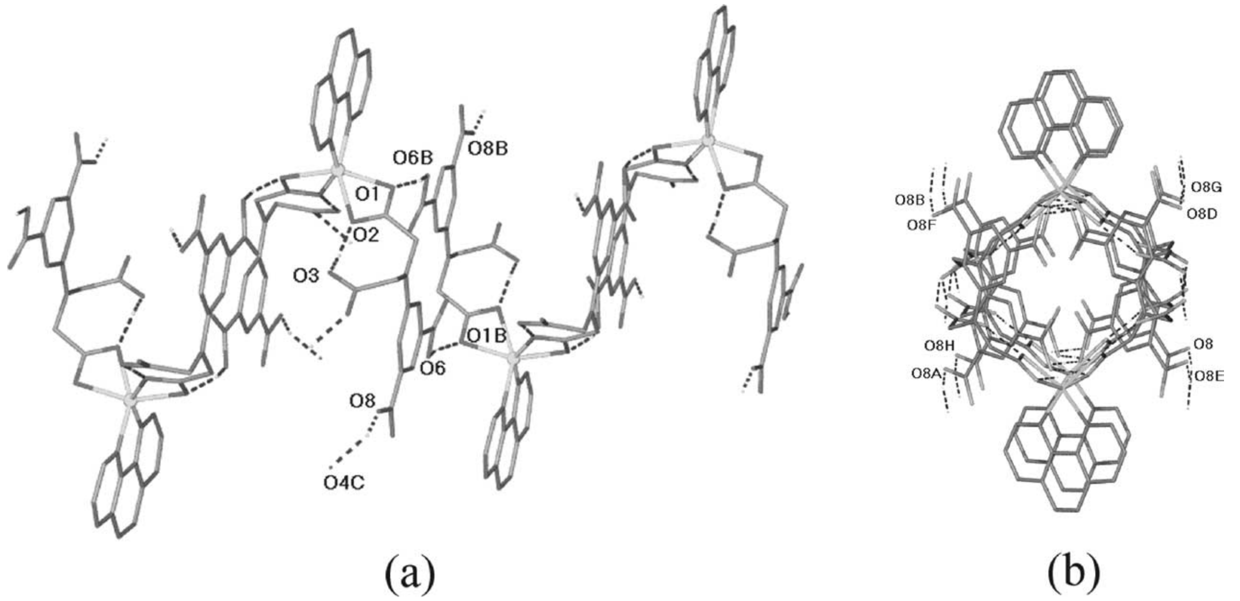
Fig. 3. ORTEP drawing of **2**, drawn with displacement ellipsoids at the 30% probability.

consolidate the chain framework. Moreover, these zigzag chains are cross-linked along *oc* direction by the bifurcated hydrogen bonds^{iii} of $O18\cdots O6D$ (2.838(5) Å; D: $-x+1$, $-y+2$, $-z$)) and $O18\cdots O15E$ (2.745(4) Å; E: $-x$, $-y+1$, $-z$) to generate 2D layer. Fig. 2b affords the view of the bifurcated hydrogen bonds^{iii} connectivity. The 2D layers are linked by hydrogen bonds^{i} of $O2\cdots O11F$ (2.592(4) Å; F: $2+x$, $1+y$, z) and $O12\cdots O1G$ (2.567(4) Å; G: $x-2$, $y-1$, z) to give rise to 3D architecture, as is shown in Fig. S1.

Single crystal X-ray analyses show that complex **2** also features a mononuclear structure, which is composed of Zn^{II} center, one phen and two H_3L^-. Zn^{II} is six-coordinated by two nitrogen atoms from one phen and four oxygen atoms from two H_3L^- ligands, as is shown in Fig. 3. The bond lengths of Zn–O in **1** vary from 2.1252(16) to 2.2347(15) Å and bond lengths of Zn(1)–N(1)/Zn(1)–N(2) are 2.0641(17) Å, which are comparable to those in reported Zn compounds [21–23]. But the two H_3L^- ligands arrange in a cis way and deviate from phen rings. As a result, no $\pi\cdots\pi$ interactions exist in such an isolated molecule. Moreover, for the lack of the water molecules, only hydrogen bonds^{i} mentioned above was found in this structure. As shown in Fig. 4a, $O1\cdots O6B$ (2.721(2) Å; B: $-x$, $-y$, $-z$) functions as linkage to link the mononuclear into a zigzag chain along *oc* direction. The intramolecular hydrogen bonds $O2\cdots O3$ with the distance of 2.581(2) Å consolidate the framework. The perspective of the chain viewed along *oc* is shown in Fig. 4b. The 1D chain extends by intermolecular hydrogen bonds in *ab* plane ($O8\cdots O4C$ 2.667(2) Å; C $-x+1/2$, $-y-1/2$, $-z+1$; D: x, $-y$, $1/2+z$; E: x, y, $z-1$; F: $-x$, $-y$, $1-z$; G: x, $-y$, $z-1/2$; H: $-x$, y, $-z-1/2$) and generate a 3D architecture, as shown in Fig. S2.

3.1. Luminescent properties

As shown in Fig. 5, the free H_4adip ligand exhibits a broad strong green-fluorescent emission around 521 nm upon excitation at 410 nm. Complex **1** exhibits an intense blue emission at 474 nm upon 380 nm excitation, while complex **2**



(a) (b)

Fig. 4. (a) 1D zigzag chain extend along *oc* direction; (b) perspective view down *c*-axis.

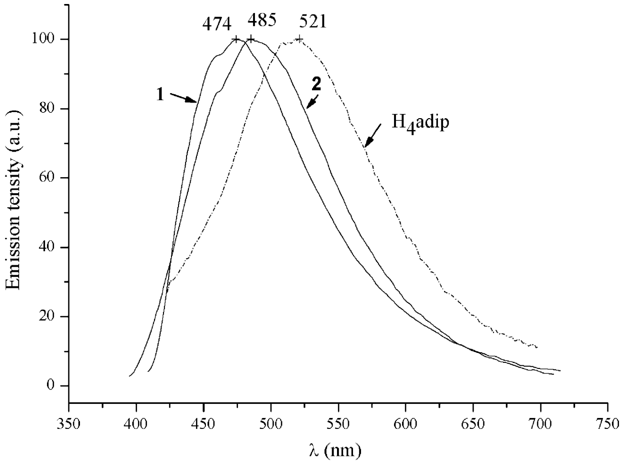


Fig. 5. The emission spectra of **1**,**2** and free ligand H_4adip in the solid state.

exhibits an intense blue emission at 485 nm upon 365 nm excitation. Both were determined to be photoluminescence based on their nanosecond-order decay lifetime (3.15 ns for **1** and 19.06 ns for **2**). Since, a similar emission was observed for $[Zn_7(adip)_4(H_2O)_{10}K_2(H_2O)_2]_n \cdot 4nH_2O$ [15], they may be assigned to blue-fluorescent emissions derived from ligand-to-metal charge transfer (LMCT).

In summary, two coordination polymers formed by different metal salts and H_4adip with the same auxiliary ligand phen have been prepared and characterized. Various sizes of metal centers induce different array of H_4adip ligand, which result in distinct supramolecular structures in both compounds. Researches indicate that the low pH value condition is crucial to the formation of 0D metal-H_4adip compounds, besides, the nitrogen atom is not active in the coordination sphere under strong acid condition.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2005.12.023

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