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以对苯二氧基二乙酸和咪唑基化合物为配体的镍、镉配合物的合成和晶体结构

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摘要: 以对苯二氧基二乙酸(H_2BDOA)和 4,4′-二咪唑基二苯醚(BIDPE)为原料,分别与氯化镍、氯化镉在水热条件下反应,得到 2 个结构不同的配位聚合物$[Ni(BDOA)(BIDPE)(H_2O)]_n$ (**1**)和$[Cd(BDOA)_{0.5}(BIDPE)Cl]_n$ (**2**)。对它们进行了元素分析、红外光谱分析,并利用 X-射线衍射测定了它们的单晶结构。配合物 **1** 属于三斜晶系,$P\bar{1}$ 空间群,a=0.934 97(8) nm,b=1.032 31(9) nm,c=1.352 91(12) nm,α=96.398 0(10)°,β=90.729 0(10)°,γ=102.027 0(10)°,V=1.268 31(19) nm^3,Z=2,M_w= 603.22,D_c=1.580 g·cm^{-3},μ=0.827,F(000)=624,R_1=0.039 5,wR_2=0.089 5(I>2σ(I))。配合物 **2** 也属于三斜晶系,$P\bar{1}$ 空间群,a=1.017 51(7) nm,b=1.042 99(7) nm,c=1.173 38(8) nm,α=68.723 0(10)°,β=71.826 0(10)°,γ=76.091 0(10)°,V=1.091 05(13) nm^3,Z=2,M_w=562.26,D_c=1.711 g·cm^{-3},μ=1.163,F(000)=562,R_1=0.021 0,wR_2=0.053 7(I>2σ(I))。配合物 **1** 中镍离子通过 2 种配体桥联成二维波浪形层状结构,而配合物 **2** 中镉离子通过 2 个 Cl 离子连接成一个双核 Cd_2 单元,双核单元再通过 2 种配体连接成一维链状结构。结果说明了金属离子在配合物组装过程中起着非常重要的作用。此外,研究了它们的荧光性质。

关键词: 配位聚合物; 双咪唑配体; 芳香羧酸配体; 晶体结构

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Syntheses and Crystal Structures of Nickel(Ⅱ) and Cadmium(Ⅱ) Coordination Polymers Constructed by Benzene-1,4-dioxydiacetate and 4,4-Bis(imidazole-l-yl)diphenyl Ether

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Abstract: Two coordination polymers, $[Ni(BDOA)(BIDPE)(H_2O)]_n$ (**1**) and $[Cd(BDOA)_{0.5}(BIDPE)Cl]_n$ (**2**), (H_2BDOA= benzene-1,4-dioxydiacetic acid and BIDPE=4,4′-bis(imidazole-l-yl)diphenyl ether), have been synthesized and characterized by IR spectroscopy, elemental analysis and single-crystal X-ray diffraction. Complex **1** crystallizes in triclinic, space group $P\bar{1}$ with a=0.934 97(8) nm, b=1.032 31(9) nm, c=1.352 91(12) nm, α=96.398 0(10)°, β=90.729 0(10)°, γ=102.027 0(10) °, V=1.268 31(19) nm^3, Z=2, M_w=603.22, D_c=1.580 g·cm^{-3}, μ=0.827, F(000)=624, R_1=0.039 5, wR_2=0.089 5 (I>2σ (I)). Complex **2** belongs to triclinic, space group $P\bar{1}$ with a=1.017 51 (7) nm, b=1.042 99(7) nm, c=1.173 38(8) nm, α=68.723 0(10)°, β=71.826 0(10)°, γ=76.091 0(10)°, V=1.091 05(13) nm^3, Z=2, M_w=562.26, D_c=1.711 g·cm^{-3}, μ=1.163, F (000)=562, R_1=0.021 0, wR_2=0.053 7 (I>2σ (I)). Structural analyses reveal that complex **1** exhibits a two-dimensional (2D) corrugated layer structure, whereas complex **2** possesses a one-dimensional (1D) chain structure which is generated by joining binuclear Cd_2 units by BIDPE and BDOA ligands. The results show that the nature of metal ions plays an important role in governing the molecular

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frameworks. The photochemical properties of two complexes have also been studied. CCDC: 1018030, **1**; 1018031, **2**.

Key words: coordination polymer; bis(imidazole) ligands; polycarboxylate; crystal structure

0 Introduction

Construction of coordination polymers (CPs) is experiencing great growth in crystal engineering due to their fascinating structural topologies and potential applications as functional materials in the fields of catalysis, gas absorption, magnetism, nonlinear optics, and luminescence[1-9]. However, it would still be a challenge for a long time to design and construct coordination compounds with the desired topologies and properties, because the molecular architectures of coordination compounds are affected by many factors, such as organic ligands, metal ions, metalligand ratio, solvents, counter ions, pH value, and temperature[10-17]. Of all these influential factors, the intrinsic geometric preferences of central metal atom and various coordination sites of bridging ligands are the pivotal factors in determining the supramolecular architectures[18-21]. Therefore, through the choice of organic ligands and metal ions, it is possible to develop a targeted architecture. Among various organic ligands, aromatic polycarboxylate ligands have been extensively employed in the preparation of such metal-organic complexes with multidimensional networks and interesting properties[22-28]. Hence, the reported coordination polymers are mostly constructed by rigid polycarboxylate ligands[22-24]. Recently, more and more attention has been paid to the flexible polycarboxylate ligands[25-28], because the flexible ligands have different conformations when they react with metal salts, and thus can form metal complexes with great structural diversity.

Recently, a large number of mixed-ligand coordination compounds have been reported[29-31], most of which contain N-containing ligands introduced into metal-polycarboxylate systems. The combination of different ligands may result in greater tunability of structural frameworks than that present with single ligands. Hence, a mixed-ligand is undoubtedly a good choice for the construction of new polymeric structures. Imidazole ligands have been used in the synthesis of unique CPs which possess excellent coordination ability and allow free rotation of the imidazole ring to meet the requirement of coordination geometries of metal ions. Until now, a great number of ingenious CPs have been synthesized based on imidazole ligands[32-33]. Syntheses of new imidazole ligands are still a long-standing fascination of chemists, and we have designed and synthesized a new V-shape imidazole ligand, 4,4′-bis (imidazol-1-yl)diphenyl ether (BIDPE), which may be regarded as a semi-rigid ligand. To test the ability of this ligand to give new architectures and topologies, we have selected a new ligand, H_2BDOA ligand(H_2BDOA= benzene-1,4-dioxydiacetic acid), and different bivalent metal salts to prepare two coordination polymers with intriguing structures, namely, $[Ni(BDOA)(BIDPE)(H_2O)]_n$ (**1**) and $[Cd(BDOA)_{0.5}(BIDPE)Cl]_n$ (**2**). Herein, we report their syntheses, crystal structures and photochemical properties.

1 Experimental

1.1 Materials and general methods

All reagents for syntheses and analyses were purchased from commercial sources and used as received without further purification. The BIDPE ligand was synthesized according to the reported method[34]. Elemental analyses (C, H and N) were performed on a Vario EL Ⅲ elemental analyzer. Infrared spectra were performed on a Nicolet AVATAR-360 spectrophotometer with KBr pellets in the 4 000~400 cm^{-1} region. Solid-state UV-Vis diffuse reflectance spectra were obtained at room temperature using a Shimadzu UV-3600 double monochromator spectrophotometer, and $BaSO_4$ was used as a 100%

reflectance standard for all materials. The luminescent spectra for the powdered solid samples were measured at room temperature on a Horiba FluoroMax-4P-TCSPC fluorescence spectrophotometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm. All the measurements were carried out under the same experimental conditions.

1.2 Synthesis of $[Ni(BDOA)(BIDPE)(H_2O)]_n$ (1)

A mixture containing $NiCl_2 \cdot 6H_2O$ (23.7 mg, 0.1 mmol), H_2BDOA (22.6 mg, 0.1 mmol), BIDPE (30.2 mg, 0.1 mmol) and $LiOH \cdot H_2O$ (8.4 mg, 0.2 mmol) in 15 mL of deionized water was sealed in a 25 mL Teflon lined stainless steel container and heated at 140 ℃ for 3 days. Green block crystals of **1** were collected by filtration and washed with water and ethanol several times with a yield of 59% based on BIDPE ligand. Anal. Calcd. for $C_{28}H_{24}N_4O_8Ni$ (%): C, 55.75; H, 4.01; N, 9.29. Found (%): C, 55.73; H, 4.03; N, 9.31. IR spectrum (cm^{-1}): 3 445(s), 3 138(m), 2 927(w), 1 609(s), 1 559(s), 1 519(m), 1 422(m), 1 371(s), 1 289(s), 1 241(m), 1 172(w), 1 072(s), 1 032(m), 973(w), 832(w), 788(w), 689(w), 572(w) and 537(w).

1.3 Synthesis of $[Cd(BDOA)_{0.5}(BIDPE)Cl]_n$ (2)

A mixture containing $CdCl_2 \cdot 2.5H_2O$ (45.6 mg, 0.2 mmol), H_2BDOA (22.6 mg, 0.1 mmol), BIDPE (60.4 mg, 0.2 mmol) and $LiOH \cdot H_2O$ (8.4 mg, 0.2 mmol) in 15 mL of deionized water was sealed in a 25 mL Teflon lined stainless steel container and heated at 140 ℃ for 3 days. Colorless block crystals of **2** were collected by filtration and washed with water and ethanol several times with a yield of 61% based on BIDPE ligand. Anal. Calcd. for $C_{23}H_{18}N_4O_4ClCd$(%): C, 49.13; H, 3.23; N, 9.64. Found(%): C, 49.11; H, 3.25; N, 9.62. IR spectrum (cm^{-1}): 3427(s), 3166(m), 2 827(w), 1 595(s), 1 519(s), 1 422(m), 1 362(s), 1 249(m), 1 126(m), 1 089(s), 1 012(w), 965(w), 929(w), 857(w), 822(w), 755(w), 657(w) and 562(w).

1.4 X-ray crystallography

Two block single crystals with dimensions of 0.22 mm×0.16 mm×0.14 mm for 1 and 0.18 mm×0.16 mm×0.12 mm for **2** were mounted on glass fibers for measurement, respectively. X-ray diffraction intensity data were collected on a Bruker APEX Ⅱ CCD diffractometer equipped with a graphite-monochromatic Mo-$K\alpha$ radiation (λ =0.071 073 nm) using the ϕ-ω scan mode at 293(2) K. Data reduction and empirical absorption correction were performed using the SAINT and SADABS program[35], respectively. The structures were solved by the direct method using SHELXS-97[36] and refined by full-matrix least squares on F^2 using SHELXL-97[37]. All of the non-hydrogen atoms were refined anisotropically. The details of the crystal parameters, data collection and refinement for **1** and **2** are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are listed in Table 2.

CCDC: 1018030, **1**; 1018031, **2**.

Table 1　Crystal data and structure refinement for 1 and 2

Empirical formula	$C_{28}H_{24}N_4O_8Ni$	$C_{23}H_{18}ClN_4O_4Cd$
Formula weight	603.22	562.26
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	0.934 97(8)	1.017 51(7)
b / nm	1.032 31(9)	1.042 99(7)
c / nm	1.352 91(12)	1.173 38(8)
α / (°)	96.398 0(10)	68.723 0(10)
β / (°)	90.729 0(10)	71.826 0(10)
γ / (°)	102.027 0(10)	76.091 0(10)
V / nm^3	1.268 31(19)	1.091 05(13)
Z	2	2
D_c / ($g \cdot cm^{-3}$)	1.580	1.711

Continued Table 1

Absorption coefficient / mm^{-1}	0.827	1.163
θ range / (°)	2.03~25.50	2.12~25.50
F(000)	624	562
Reflections collected	10 144	8 690
Independent reflections	4 702(R_{int}=0.034 7)	4 043(R_{int}=0.016 2)
Reflections observed ($I>2\sigma(I)$)	3 716	3 750
Data / restraints / parameters	472/2/378	4 043/0/298
Goodness-of-fit on F^2	1.048	1.053
R_1, wR_2 ($I>2\sigma(I)$)	0.039 5, 0.089 5	0.021 0, 0.053 7
R_1, wR_2 (all data)	0.054 0, 0.097 1	0.023 3, 0.055 1
Largest difference peak and hole / ($e\cdot nm^{-3}$)	312 and −302	292 and −405

Table 2 Selected bond lengths(nm) and angles(°) for 1 and 2

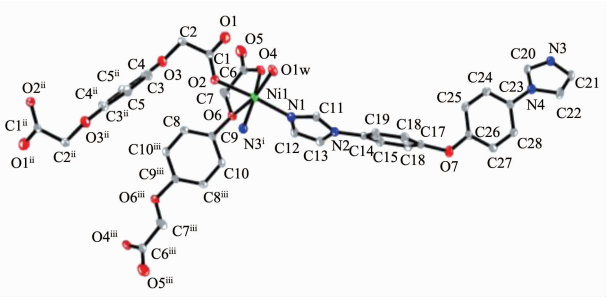
			1		
Ni1-O1W	0.202 58(19)	Ni1-N1	0.205 8(2)	Ni1-O4	0.204 41(18)
Ni1-N3i	0.207 2(2)	Ni1-O2	0.205 13(17)	Ni1-O6	0.226 44(18)
O1W-Ni1-O4	92.83(8)	O2-Ni1-N3i	87.93(8)	O1W-Ni1-O2	93.19(8)
N1-Ni1-N3i	93.33(8)	O4-Ni1-O2	88.11(7)	O1W-Ni1-O6	165.76(8)
O1W-Ni1-N1	94.59(9)	O4-Ni1-O6	75.04(7)	O4-Ni1-N1	89.65(8)
O2-Ni1-O6	79.21(7)	O2-Ni1-N1	172.00(8)	N1-Ni1-O6	92.79(8)
O1W-Ni1-N3i	94.36(9)	N3i-Ni1-O6	97.35(8)	O4-Ni1-N3i	171.97(8)
			2		
Cd1-N1	0.229 54(17)	Cd1-O2	0.244 32(16)	Cd1-N4i	0.229 62(18)
Cd1-Cl1ii	0.261 50(6)	Cd1-O1	0.233 93(17)	Cd1-Cl1	0.262 95(5)
N1-Cd1-N4i	94.55(7)	O1-Cd1-Cl1ii	101.06(4)	N1-Cd1-O1	163.06(6)
O2-Cd1-Cl1ii	155.23(4)	N4i-Cd1-O1	86.58(7)	N1-Cd1-Cl1	89.61(5)
N1-Cd1-O2	108.49(6)	N4i-Cd1-Cl1	175.54(5)	N4i-Cd1-O2	81.00(6)
O1-Cd1-Cl1	89.91(5)	O1-Cd1-O2	54.93(5)	O2-Cd1-Cl1	99.22(4)
N1-Cd1-Cl1ii	95.78(5)	Cl1ii-Cd1-Cl1	85.462(17)	N4i-Cd1-Cl1ii	92.50(5)

Symmetry code: ^{i} x, y+1, z+1 for **1**; ^{i} x−1, y−1, z+1; ^{ii} x+1, −y+1, −z+1 for **2**

2 Results and discussion

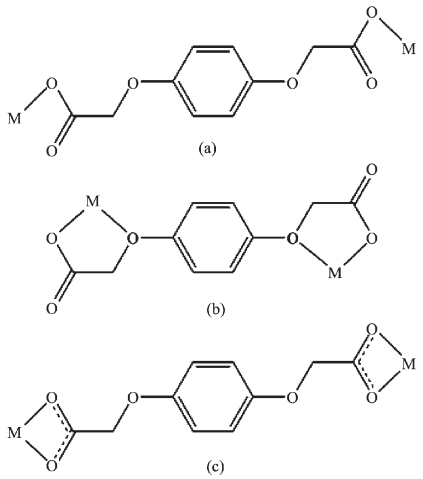
2.1 Crystal structure

The crystallographic analysis reveals that **1** is a two-dimensional corrugated layer structure. As shown in Fig.1, the asymmetric unit contains one Ni(Ⅱ) ion, one BDOA anion, one BIDPE ligand and one coordinated water molecule. Each Ni(Ⅱ) ion is six-coordinated by three oxygen atoms from two different $BDOA^{2-}$ anions, two nitrogen atoms from two BIDPE ligands and one coordinated water molecule to form a distorted octahedral geometry. Its basal plane is occupied by three oxygen atoms, O4, O6 and O1W, and one nitrogen atom, $N3^{i}$, while the apical position is occupied by the other nitrogen atom (N1) and one oxygen atom (O2). The Ni-O bond lengths are in the range of 0.202 58(19)~0.226 44(18) nm. The Ni-N bond lengths are in the range of 0.205 8 (2)~0.207 2(2) nm and the coordination angles around Ni ion are in the range of 75.04(7)°~172.00(8)°.



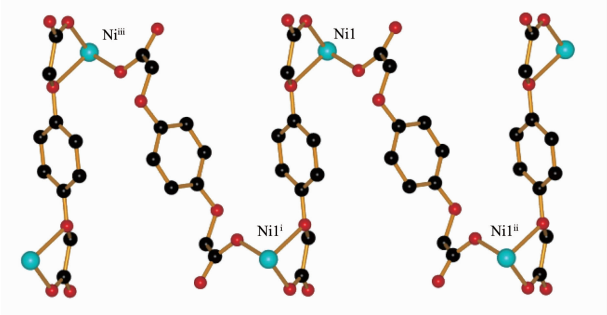
Hydrogen atoms are omitted for clarity; Symmetry code: [i] x, $1+y$, $1+z$; [ii] $1-x$, $2-y$, $2-z$; [iii] $1-x$, $1-y$, $2-z$

Fig.1　Coordination environment of Ni(Ⅱ) in complex **1** with thermal ellipsoids at 30% probability



Scheme 1　Coordination modes of the $BDOA^{2-}$ ligand

All the Ni(Ⅱ) ions are joined by the $BDOA^{2-}$ ligands in two different coordination modes (Scheme 1a and 1b) to produce a 1D infinite chain (Fig.2), with the Ni ⋯ Ni distances of 1.226 and 0.865 nm, respectively. Two crystallographically independent "half" $BDOA^{2-}$ ligands occupy different inversions in the middle of the benzene rings, respectively. It is noted that the C1-C2-O3-C4 torsion angle is 80.18(3)° in Scheme 1a, whereas in Scheme 1b, the oxyacetate groups and benzene ring are almost perpendicular, with the torsion angle being 164.05(2)°. This demonstrates that the $BDOA^{2-}$ ligand has remarkable flexibility corresponding to the rigid aromatic carboxylic acid ligand such as terephthalate. It is



Symmetry code: [i] $1-x$, $1-y$, $2-z$; [ii] $1-x$, $2-y$, $2-z$; [iii] x, $-1+y$, z

Fig.2　View of 1D infinite $[Ni(BDOA)]_n$ chain in **1**

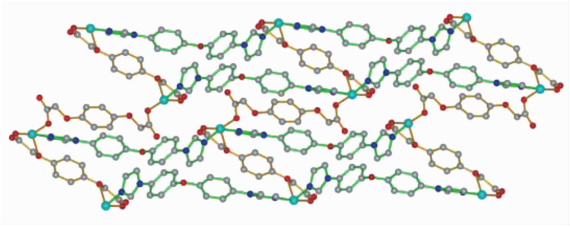


Fig.3 Corrugated 2D (4,4) layer bridged the BDOA and BIDPE ligands in **1**

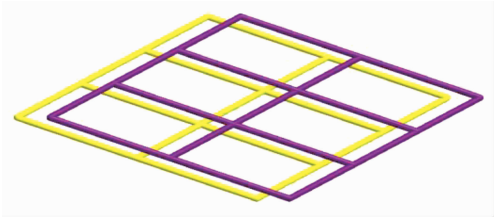
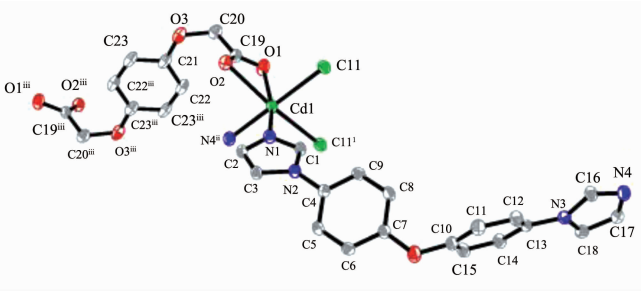


Fig.4 Schematic description of stacking sequence of the layers in **1**

obviously observed from the reported complex, [Cd(bipy)(terephthalate)(H_2O)]$_n$[38], in which the dihedral angles of the two carboxyl groups and the phenyl are 5.63° and 12.58°, respectively. The 1D infinite chains are further bridged by BIDPE ligands to give a two-dimensional corrugated layer structure. The separation of neighboring Ni(Ⅱ) ions is about 1.607 7(1) nm as illustrated in Fig.3. In the crystal, adjacent 2D layers stacked in a parallel mode, leading to a three-dimensional supramolecular network (Fig.4). Based on distance calculations, there are intermolecular C-H⋯O hydrogen bonds and strong $\pi \cdots \pi$ stacking interactions (the centroid-to-centroid distance between the two adjacent benzene rings of BIDPE ligands is 0.356 1 nm), which might contribute to stabilization of the whole MOF structure.

When $CdCl_2$ was reacted with BIDPE and H_2BDOA using a preparation procedure similar to that of **1**, complex **2** was isolated. As shown in Fig.5, the asymmetric unit consists of one crystallographically unique Cd(Ⅱ) ions, one individual BIDPE ligand, half of BDOA anion and one chlorine ion. Each Cd(Ⅱ) ion is six-coordinated by two oxygen atoms from a carboxylate group of the $BDOA^{2-}$ anion, two nitrogen atoms from two different BIDPE ligands and two chlorine ions to form a distorted octahedral geometry. Its basal plane is occupied by one oxygen atom (O2), one nitrogen atom (N4^{ii}) and two chlorine ions (Cl1, Cl1^{i}), while the apical position is occupied by the other nitrogen atom (N1) and oxygen atom (O1). The Cd-O bond lengths are in the range of 0.233 93(17)~0.244 32(16) nm, and the Cd-N bond lengths are in the range of 0.229 54(17)~0.229 62(18) nm and the coordination angles around Cd ion are in the range of 54.93(5)°~163.06(6)°. Two Cd(Ⅱ) ions are double bridged by two chlorine ions with Cd⋯Cd separations of 0.358 2 nm to from a binuclear Cd_2 unit, which is further linked by the BIDPE and $BDOA^{2-}$ ligands to



Hydrogen atoms were omitted for clarity; Symmetry code: $^{i}1-x, 1-y, 1-z$; $^{ii}x-1, y-1, 1+z$; $^{iii}-x, -y, 2-z$

Fig.5 Coordination environments of the Cd(Ⅱ) atoms in **2** with the ellipsoids drawn at the 30% probability level

generate a one-dimensional chain structure (Fig.6). The fully deprotonated $BDOA^{2-}$ anion coordinates to two Cd ions with two carboxylate groups adopting monodentate mode (Scheme 1c). In the crystal, adjacent 1D chains are stacked into a three-dimensional supramolecular network through intermolecular C-H ⋯ Cl hydrogen bonding and weak $\pi \cdots \pi$ stacking interactions (the centroid-to-centroid distance between the two adjacent benzene rings of BIDPE ligands is 0.412 3 nm, and the dihedral angle is 3.785 (2)°).

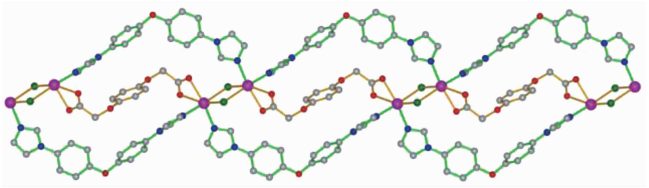


Fig.6　View of the 1D infinite chain formed by the BIDPE ligands and $BDOA^{2-}$ anions

As to the synthesis of **1** and **2**, the reaction conditions are the same except for the difference of the metal ions. As a result, complex **1** is a 2D supramolecular structure, while complex **2** is a 1D infinite chain. The differences between **1** and **2** reveal that metal ions play an extreme role in the generation of crystal structure, due to the size of metal ions and the versatility of the metal coordination geometry. In other words, it is found that suitable metal ions may be a good candidate for the target coordination polymeric frameworks.

2.2　FTIR spectra

FTIR spectra revealed valuable information about the coordination modes of H_2BDOA. The absence of the characteristic bands at around 1 700 cm^{-1} attributed to the protonated carboxylate group indicates that the complete deprotonation of H_2BDOA upon reaction with metal ion. The difference between asymmetric and symmetric carbonyl stretching frequencies ($\Delta\nu=\nu_{asym}-\nu_{sym}$) was used to fetch information on the metal-carboxylate binding modes. Complex **1** showed two pairs of ν_{asym} and ν_{sym} frequencies at 1 609, 1 422 cm^{-1} ($\Delta\nu$=187 cm^{-1}) and 1 559, 1 371 cm^{-1} ($\Delta\nu$=188 cm^{-1}) for the carbonyl functionality indicating two coordination modes as observed in the crystal structure. Complex **2** showed a pairs of ν_{asym} and ν_{sym} frequencies at 1 695, 1 362 cm^{-1} ($\Delta\nu$=233 cm^{-1}) corresponding to the carbonyl functionality of dicarboxylate ligand indicating a symmetric monodentate coordination mode. OH stretching broad bands at 3 445 cm^{-1} for **1** are attributable to the coordinated lattice water. The bands in the region of 640~1 250 cm^{-1} are attributed to the -CH- in-plane or out-of-plane bend, ring breathing, and ring deformation absorptions of benzene ring. The IR spectra exhibit the characteristic peaks of imidazole groups at ca.1 520 cm^{-1}[39].

2.3　Photoluminescence study

Coordination polymers and conjugated organic linkers are promising candidates for photoactive materials with potential applications such as chemical sensors and photochemistry[40-41]. Solid state photoluminescence behavior of **1** and **2** at ambient temperature was examined. Absorption maxima for ligands BIDPE and H_2BDOA were observed at 272 and 287 nm respectively, however complex **1** and **2** showed major absorption bands at *ca.* 369 and 291 nm, respectively. As illustrated in Fig.7, the intense emission band at 417 nm (λ_{ex}=369 nm) for **1** is observed. Upon excitation with 291 nm, strong emission at 454 nm with an overall luminescence quantum yield ($\Phi_{overall}$) of 5.02%

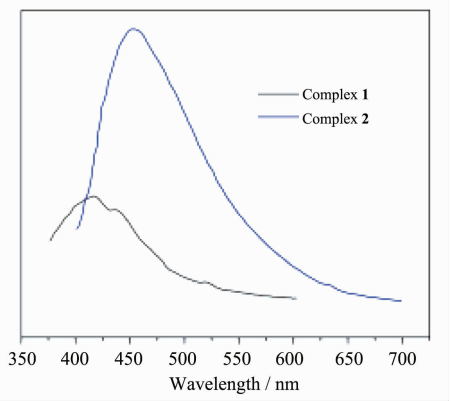


Fig.7　Solid-state photoluminescent spectra of complexes **1** and **2**

for **2** was recorded at room temperature. The red shift in the emission bands of **2** could be ascribed to the metal-perturbed intraligand emission and ligand field transitions. The good photoluminescence of **2** may also be attributed to the closed shell metal configuration of Cd(Ⅱ). Furthermore, the higher quantum yield of **2** may also be attributed to the triple helical motif as such rigid structural features substantially cease the radiationless vibrational energy loss[42-44].

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