

Two 3D Cd^{II} and Zn^{II} Complexes Based on Flexible Dicarboxylate Ligand and Nitrogen-containing Pillar: Synthesis, Structure, and Luminescent Properties

Liu Liu, Yan-hua Fan, Lan-zhi Wu, Huai-min Zhang, and Li-rong Yang*

Henan Key Laboratory of Polyoxometalate, Institute of Molecule and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P.R. China. *E-mail: lirongyang@henu.edu.cn

Received July 24, 2013, Accepted September 24, 2013

Two 3D isomorphous and isostructural complexes, namely, [Zn(BDOA)(bpy)(H₂O)₂]_n (**1**) and [Cd(BDOA)(bpy)(H₂O)₂]_n (**2**); (BDOA = Benzene-1,4-dioxyacetic acid, bpy = 4,4'-bipyridine) were synthesized under hydrothermal conditions and characterized by means of elemental analyses, thermogravimetric (TG), infrared spectrometry, and single crystal X-ray diffraction. Complexes **1** and **2** crystallize in the triclinic system, space group *P*-1 and each metal ion in the complexes are six-coordinated with the same coordination environment. In the as-synthesized complexes, BDOA²⁻ anions link central metal ions to form a 1D zigzag chain [-BDOA²⁻-Zn(Cd)-BDOA²⁻-Zn(Cd)-]_∞, whereas bpy pillars connect metal ions to generate a 1D linear chain [-bpy-Zn(Cd)-bpy-Zn(Cd)-]_∞. Both infinite chains are interweaved into 2D grid-like layers which are further constructed into a 3D open framework, where hydrogen bonds play as the bridges between the adjacent 2D layers. Luminescent properties of complex **1** showed selectivity for Hg²⁺ ion.

Key Words : Benzene-1,4-dioxyacetic acid, Isomorphous, Metal-Organic frameworks, Luminescent properties

Introduction

Metal-organic frameworks (MOFs) have been attracting enormous interests not only the combination of organic ligands and metal ions can construct a large number of intriguing aesthetic and unusual topologies of novel polymers but also they allow the rational design strategies to construct porous materials with high surface areas, predictable structures and tunable pore sizes to target some specific functionalities, which may potentially lead to industrial applications including gas storage and separation, adsorption catalysis, guest exchange, ion exchange, molecular recognition, molecular magnetism, nonlinear optics, and luminescent, *etc.*¹⁻⁹ Naturally, multidentate organic ligands like polycarboxylic acids are recommended as the linkers of metal ions to polymerize into extended open frameworks, because these ligands may potentially provide various coordination modes and favor the construction of multi-dimensional complexes.¹⁰⁻¹⁶ Specifically, flexible linker H₂BDOA exhibits several interesting characteristics: (a) it can be deprotonated to generate HBDOA⁻ and BDOA²⁻ by controlling the pH values carefully, which allows it to display various acidity-dependant coordination modes; (b) chelating and bridging coordination through carboxy oxygen and ether oxygen atoms benefit its versatile bonding fashions; (c) the phenolic oxygen atom may function as electron donor to form hydrogen bonds; (d) it features as a combination of rigidity (benzene ring) and flexibility (pendant carboxylic arms) which is favourable for the construction of multidimensional MOFs.¹⁷⁻²⁰

Herein we wish to report the synthesis, structures, thermal analysis, and luminescent properties of two 3D MOFs obtained from the self-assembly of bridging ligands benzene-1,4-dioxyacetic acid and 4,4'-bipyridine, which are formulated

as [Zn(BDOA)(bpy)(H₂O)₂]_n and [Cd(BDOA)(bpy)(H₂O)₂]_n.

Experimental

Reagents and General Techniques. All starting chemicals are analytical grade and used without further purification. Elemental analysis was performed with a Perkin-Elmer 240C elemental analyzer. Fourier transform infrared (FT-IR) were recorded with an AVATAR 360 FT-IR spectrometer (KBr pellets, in the region of 4000-400 cm⁻¹). The crystal structure was determined with a Bruker Smart CCD X-ray single-crystal diffractometer. Fluorescent data were collected with an F-7000 FL spectrophotometer at room temperature. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were conducted with a Perkin-Elmer TGA7 system under flowing N₂ stream (flow rate 40 mL/min) from room temperature to 1000 °C at a heating rate of 10 K/min.

Synthesis of the Ligand of Benzene-1,4-dioxydiacetic Acid (1,4-H₂BDOA). A mixture of Chloroacetic acid (8 mmol) and 1,4-Benzenediol (2 mmol) in water (20 mL) was stirred at 80 °C for 2 h. The pH value was maintained at 11 by dropwise adding of sodium hydroxide solution (1.0 mol·L⁻¹). Then the reaction mixture was cooled to room temperature and was adjusted to pH ≈ 3 with HCl (1.0 mol·L⁻¹), simultaneously. The brown powder of benzene-1,4-dioxydiacetic acid (1,4-H₂BDOA) formed immediately, which was isolated by filtration and washed twice with distilled water. The product was dried at 50 °C for 24 h. Yield: 85.40%. Anal. Calcd. for C₁₀H₁₀O₆ (226.05): C 53.10, H 4.46; Found: C 53.45, H 4.26%. MS *m/z*: 226.21. IR data (KBr pellet, cm⁻¹): 3415 (br), 1753 (s), 1633 (w), 1508 (m), 1428 (w), 1385 (w), 1322 (w), 1289 (w), 1227 (s), 1091 (s), 992 (w), 993 (w), 889 (w), 824 (w), 799 (w), 665 (m), 555 (w).

Synthesis of the Complex [Zn(BDOA)(bpy)(H₂O)]_n (1). **1** was synthesized from the reaction mixture of benzene-1,4-dioxyacetic acid (0.1 mmol), 4,4'-dipyridyl (0.1 mmol) and zinc acetate (0.2 mmol) in distilled water (10 mL). The resultant mixture was homogenized by stirring for 20 minutes at ambient temperature and then transferred into 25 mL Teflon-lined stainless steel container under autogenous pressure at 160 °C for 4 days. Colourless block-shaped crystals were isolated in 69.7% yield (based on zinc acetate) after cooling to room temperature at a rate of 5 °C/h. After filtration, the product was washed with distilled water and then dried, transparent block crystals suitable for X-ray diffraction analysis were obtained. Anal. Calcd (%) for C₂₀H₂₀N₂O₈Zn: C, 49.86; H, 4.18; N, 5.82. Found: C, 48.82; H, 4.25; N, 5.67. IR data (KBr pellet, cm⁻¹): 3434 (br), 1654 (s), 1586 (s), 1521 (m), 1479 (w), 1438 (s), 1401 (s), 1321 (w), 1266 (w), 1234 (w), 1218 (w), 1146 (w), 1112 (w), 1099 (w), 1037 (w), 1021 (w), 906 (w), 840 (m), 756 (w), 723 (s), 672 (w), 641 (w), 452 (w), 431 (w).

Synthesis of the Complex [Cd(BDOA)(bpy)(H₂O)]_n (2). **2** was synthesized by identical experimental procedures to that of **1** except that zinc acetate was replaced by cadmium acetate at 170 °C for 4 days. After filtration, the product was washed with distilled water and then dried and yellowish transparent crystals suitable for X-ray diffraction analysis were finally isolated. Anal. Calcd (%) for C₂₀H₂₀N₂O₈Cd: C, 45.43; H, 3.81; N, 5.30. Found: C, 45.57; H, 3.95; N, 5.16. IR data (KBr pellet, cm⁻¹): 3437 (br), 1620 (s), 1595 (s), 1510 (m), 1491 (w), 1422 (s), 1385 (s), 1342 (w), 1220 (w), 1231 (w), 1220 (w), 1121 (w), 1075 (w), 1055 (w), 1007 (w), 938 (w), 830 (w), 807 (m), 726 (w), 691 (s), 535 (w), 493 (w).

X-ray Crystallographic Determination. X-ray diffraction measurements of complexes **1** and **2** were carried out on a Bruker Smart CCD X-ray single-crystal diffractometer. Reflection data were measured at 296(2) K using graphite monochromated MoK α -radiation ($\lambda = 0.71073$ Å) and ω -scan technique. All independent reflections were collected in a range of 2.01 to 25.00° and 1.97 to 25.00° for complexes **1** and **2** and determined in the subsequent refinement. SADABS Multi-scan empirical absorption corrections were applied to

Table 1. Crystal data and structure refinement parameters for complexes **1** and **2**

Data	1	2
Empirical formula	C ₂₀ H ₂₀ O ₈ N ₂ Zn	C ₂₀ H ₂₀ O ₈ N ₂ Cd
Formula weight	481.75	528.78
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
a / Å	5.7757(5)	5.8796(4)
b / Å	8.1491(8)	8.2405(6)
c / Å	10.679(1)	10.8904(8)
α / (°)	106.281(1)	105.564(1)
β / (°)	96.793(2)	97.836(1)
γ / (°)	97.056(2)	97.978(1)
Z	1	1
Density(calculated)	1.693 g/cm ³	1.777 g/cm ³
F(000)	248	266
θ (°)	2.01 to 25.00	1.97 to 25.00
R _{int}	0.0155	0.0140
Goodness-of-fit on <i>F</i> ²	1.088	1.073
Volume / Å ³	472.62(8)	494.14(6)
Final R indices	<i>R</i> ₁ = 0.0257, <i>wR</i> ₂ = 0.0664	<i>R</i> ₁ = 0.0181, <i>wR</i> ₂ = 0.0461
[<i>I</i> > 2 σ (<i>I</i>)]		
R indices (all data)	<i>R</i> ₁ = 0.0268, <i>wR</i> ₂ = 0.0671	<i>R</i> ₁ = 0.0181, <i>wR</i> ₂ = 0.0461

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

lengths (Å)			
1			
Zn(1)–O(1WA)	2.150(2)	Zn(1)–N(1)	2.178(2)
Zn(1)–O(2A)	2.096(1)	Zn(1)–O(1W)	2.150(1)
Zn(1)–N(1A)	2.178(2)	Zn(1)–O(2)	2.096(1)
2			
Cd(1)–O(1)	2.277(1)	Cd(1)–N(1)	2.336(2)
Cd(1)–O(1A)	2.277(1)	Cd(1)–O(1WA)	2.339(2)
Cd(1)–N(1A)	2.336(2)	Cd(1)–O(1W)	2.339(2)

the data processing.²¹ The crystal structures were solved by direct methods and Fourier synthesis. Positional and thermal parameters were refined by the full-matrix least-squares

Table 3. Selected bond angles (°) for complexes **1** and **2**

angles (°)					
1					
O(1WA)–Zn(1)–O(2A)	87.45(6)	O(1W)–Zn(1)–O(2A)	92.55(6)	O(2A)–Zn(1)–N(1)	90.30(6)
O(1WA)–Zn(1)–N(1A)	88.09(6)	O(1WA)–Zn(1)–N(1)	91.91(6)	N(1A)–Zn(1)–N(1)	180.00
O(2A)–Zn(1)–N(1A)	89.70(6)	O(2)–Zn(1)–N(1A)	90.30(6)	N(2)–Zn(1)–O(1W)	88.09(6)
O(1WA)–Zn(1)–O(2)	92.55(6)	O(1WA)–Zn(1)–O(1W)	180.00	O(2)–Zn(1)–O(1W)	87.45(6)
O(1W)–Zn(1)–N(1A)	91.91(6)	O(2A)–Zn(1)–O(2)	180.00	O(2)–Zn(1)–N(1)	89.70(6)
2					
O(1)–Cd(1)–O(1A)	180.00(1)	N(1)–Cd(1)–O(1WA)	88.62(6)	N(1)–Cd(1)–N(1A)	180.00(1)
O(1A)–Cd(1)–N(1)	90.70(6)	N(1A)–Cd(1)–O(1WA)	91.38(6)	N(1A)–Cd(1)–O(1W)	88.62(6)
O(1)–Cd(1)–N(1)	89.30(6)	O(1A)–Cd(1)–O(1WA)	88.43(6)	O(1A)–Cd(1)–O(1W)	91.57(6)
O(1A)–Cd(1)–N(1A)	89.30(6)	O(1)–Cd(1)–O(1WA)	91.57(6)	O(1WA)–Cd(1)–O(1W)	180.00
O(1)–Cd(1)–N(1A)	90.70(6)	N(1)–Cd(1)–O(1W)	91.38(6)	O(1)–Cd(1)–O(1W)	88.43(6)

Table 4. Hydrogen bond geometry (Å) for complexes **1** and **2**

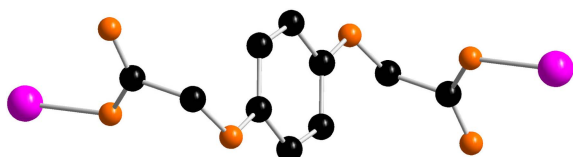
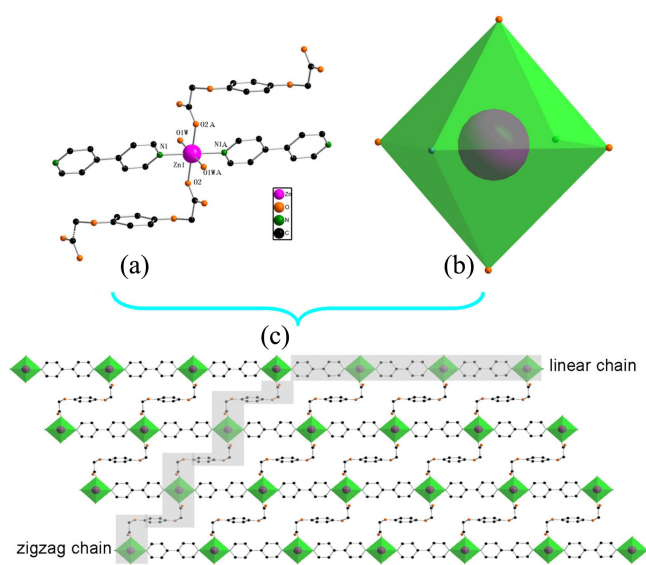
D-H...A	d(D-H)	d(H...A)	d(D...A)	(DHA)
1				
O(1W)-H(1WA)···O(2)	0.85	2.20	2.952(2)	147.3
O(1W)-H(1WB)···O(3)	0.85	1.80	2.613(2)	159.2
2				
O(1W)-H(1WA)···O(1)	0.85	2.05	2.842(2)	154.5
O(1W)-H(1WB)···O(2)	0.85	1.83	2.637(2)	158.8

method on F^2 using the SHELXTL software package.²² Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data, selected bond lengths and angles and hydrogen bonds for complexes **1** and **2** are listed in Tables 1, 2, 3, and 4.

Results and Discussion

The IR Spectra of the Complexes. Complexes **1** and **2** are insoluble in common solvents such as CH₃COCH₃, CH₃CH₂OH, CH₃OH, CH₃CN, and THF, but slight soluble in DMSO or DMF. The structures of **1** and **2** are identified by IR, elemental analysis, and X-ray diffraction. High yield of the products indicates that the title complexes are thermodynamically stable under the reaction conditions. The IR spectra of **1** and **2** are similar. The strong and broad absorption bands in the ranges of 3437 cm⁻¹ in complexes are assigned to the characteristic peaks of water molecules in coordination.^{23,24} The strong vibrations appeared at about 1586 cm⁻¹ and 1595 cm⁻¹ in **1** and **2** are ascribed to the coordinated carboxylates. The absorption bands at 1055 cm⁻¹ is attributed to stretching vibration of the Ar-O-CH₂. The absorption at about 830 cm⁻¹ is related to the *p*-disubstituted benzene stretching vibration.²⁵ The same conclusions are also supported by the results obtained from X-ray diffraction measurements.

Structural Description of 1 and 2. The single-crystal analysis reveal that complexes **1** and **2** are isomorphous and isostructural, crystallizing in monoclinic space group *P*-1. Here, complex **1**, [Zn(BDOA)(bpy)(H₂O)₂]_n is selected as an example to describe the formation of 3D structure in detail. The coordination environment of Zn(II) centers in complex **1** is shown in Figure 2(a). Zn(II) atom situates in the centre of the complex with two oxygen atoms belonging to two

**Figure 1.** Coordination mode of BDOA²⁻ in **1** and **2**.**Figure 2.** (a) Coordination environment of Zn(II) ion. (b) The octahedron for the crystallographically independent of centre Zn(II) ion. (c) The 2D layer constructed by zigzag chains and linear chains in complex **1**.

molecules of BDOA²⁻ and two from water molecules occupying each vertex of the equatorial sites, while two nitrogen atoms deriving from two molecules of bpy locate in the apical positions along the axis, as a result, it makes a slightly distorted octahedron geometry (see Figure 2(b)). Each BDOA²⁻ ligand adopts bidentate bridging mode ($\mu^1-\eta^0:\eta^1+\mu^1-\eta^0:\eta^1$, as illustrated in Figure 1) while bpy adopts μ_2 bridging mode. The Zn-O_{carboxyl} distance is 2.096(1) Å, which is significantly shorter than that of Zn-O_w (Zn-O_w: 2.150(2) Å). The bond lengths in the present work are consistent with those in previous work covering zinc complexes.^{26,27}

In the as-synthesized complexes, two kinds of 1D chains are observed, namely, BDOA²⁻ anions link central metal ions to form a zigzag chain [-BDOA²⁻-Zn(1)-BDOA²⁻-Zn(1)-]_∞, whereas bpy pillars connect metal ions to generate a linear chain [-bpy-Zn(1)-bpy-Zn(1)-]_∞. Both infinite chains are interweaved into 2D grid-like layers which are further constructed a 3D open framework, where hydrogen bonds (O(1W)-H(1WA)···O(2)) play as the bridges between the coordinated water molecules and carboxylate groups of the adjacent 2D layers. Some other hydrogen bonds (e.g. O(1W)-H(1WB)···O(3)) are in favour of maintaining the stability of the architecture of the complexes (see Figure 3(a) and Table 4).

In the 2D grid-like layer, the dihedral angles between carboxylate and benzene are about 86.040° in the flexible BDOA²⁻ anions differing from those in free H₂BDOA, which cause the formation of zigzag chain of [-BDOA²⁻-Zn(1)-BDOA²⁻-Zn(1)-]. It is noteworthy that in the 2D and 3D structures, there exist 46-membered (Zn₄C₃₀O₁₂) with the size of 2 × 11.4740(8) × 4.4144(3) Å², which are comprised of Zn(II) center, BDOA²⁻ and bpy ligands [Zn(1)-BDOA²⁻-Zn(1)-bpy-Zn(1)-BDOA²⁻-Zn(1)-bpy-Zn(1)] (see Figure 2(c) and Figure 3(b)).

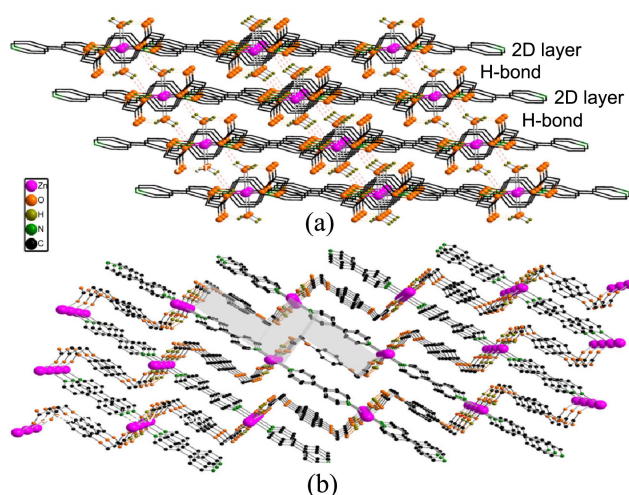


Figure 3. (a) The 3D framework connected through hydrogen bonds in complex **1**. (b) The 46-membered (Zn₄C₃₀O₁₂) cavity in **1**.

Luminescent Properties. Complexes **1** and **2** are a part of d¹⁰ metal complexes, the recent studies reveal that their luminescent behaviors are closely associated with the central metal ions and the ligands coordinated with them.²⁸⁻³¹ The luminescent properties of free benzene-1,4-dioxyacetic acid and complexes **1** and **2** have been investigated at room temperature (see Figure 4(a) and Figure 5).

To examine the possibility of modifying the luminescent properties through cations exchange, the solid sample of complex **1** was immersed in water (10⁻⁴ M) containing metal cations to generate solutions at room temperature. Emission spectra of complex **1** in the presence of Cu²⁺, Zn²⁺, Cd²⁺, Ca²⁺, Pb²⁺, and Hg²⁺ ions with respect to complex **1** are illustrated in Figure 4. It is seen that, as compared with solid state sample **1**, the counterpart in the aqueous solutions exhibits emission bands with unchanged position but changed intensity. The emission intensities of complex **1** are enhanced gradually upon the addition of 1-3 equivalent of Cu²⁺ (Cu(CH₃COO)₂), and its highest peak at 585 nm (excited at 325 nm) is nearly a third times as intense as the corresponding peak of the solution without Cu²⁺ (see Figure 4(b)). When 1-3 equivalent of Zn²⁺ (Zn(CH₃COO)₂) is introduced, the emission intensity of complex **1** decrease to 1/2, 1/4, and 1/8 comparing to the original complex (see Figure 4(c)). It is similar when Ca²⁺ (Ca(CH₃COO)₂) is introduced (see Figure 4(e)). Different from the above-mentioned, the introduction of Cd²⁺ (Cd(CH₃COO)₂) and Pb²⁺ (Pb(CH₃COO)₂) into the water solution of complex **1** causes only minor changes of the emission intensities. Noteworthy, when adding 1-3 equivalent of Hg²⁺ (HgCl₂), the luminescent intensities of complex **1** decrease rapidly (see Figure 4(g) and Figure 4(h)). The fluorescence quenching of complex **1** was perhaps due to the interaction of Hg²⁺ with the original complex. The enhanced luminescent intensities of **1** in aqueous solution may be resulted from more effective intramolecular energy transfer from the BDOA²⁻ ligands to the central Zn(II); and this energy transfer process is accelerated upon the introduction of certain transition metal ions. The mech-

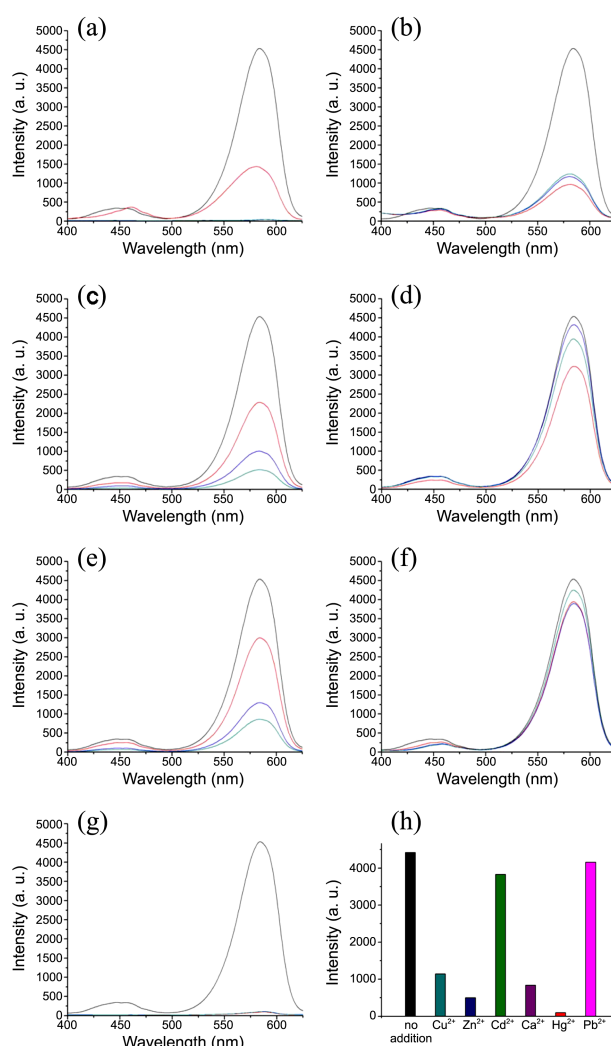


Figure 4. Emission spectra of complex **1** in water (10⁻⁴ M) at room temperature (excited at 325 nm) in the presence of Cu²⁺, Zn²⁺, Cd²⁺, Ca²⁺, Pb²⁺, and Hg²⁺ ions with respect to complex **1**, respectively. (a): black, complex **1** (10⁻⁴ M); green, bpy (10⁻⁴ M); red, H₂BDOA (10⁻⁴ M); blue, Zn(CH₃COO)₂ (10⁻⁴ M). Cu²⁺ (b), Zn²⁺ (c), Cd²⁺ (d), Ca²⁺ (e), Pb²⁺ (f), and Hg²⁺ (g): black, no addition; red, 10⁻⁴ M; blue, 2 × 10⁻⁴ M; green, 3 × 10⁻⁴ M. (h) luminescent intensity of of complex **1** in water (10⁻⁴ M) at room temperature upon the addition of 3 equiv Cu²⁺, Zn²⁺, Cd²⁺, Ca²⁺, Pb²⁺, and Hg²⁺.

anism accounting for the luminescent feature of complex **1** along with its dependence on the co-existing metal ions is still under investigation.

As for complex **2**, under the same conditions, the luminescent properties of complex **2** were also measured, the results showed that it has no luminescent selectivity to the metal ions above mentioned. But we find that the highest peak at 594 nm (excited at 323 nm) of complex **2** is lower than that of H₂BDOA, bpy shows weak peak and Cd²⁺ (Cd(CH₃COO)₂) has no luminescent (see Figure 5). Meanwhile, emission spectra of complex **2** in the presence of Cu²⁺, Zn²⁺, Cd²⁺, Ca²⁺, Pb²⁺, and Hg²⁺ ions are similar, as a result, complex **2** has no selectivity for these metal ions.

Thermal Analysis. Thermogravimetric analyses of complex **1** was performed in the N₂ stream from room temperature to

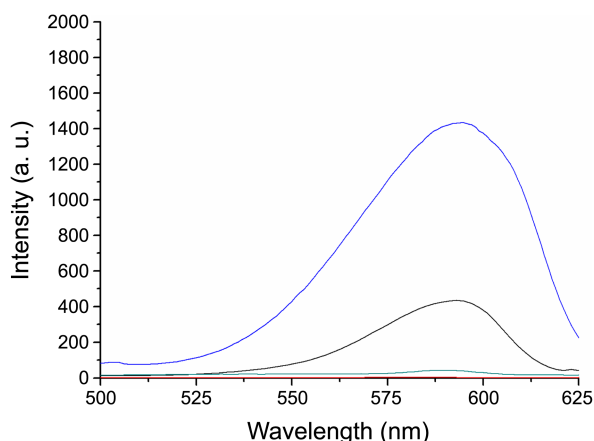


Figure 5. Emission spectra of complex **2** in water (10^{-4} M) at room temperature (excited at 323 nm). black, complex **2** (10^{-4} M); green, bpy (10^{-4} M); red, $\text{Cd}(\text{CH}_3\text{COO})_2$ (10^{-4} M); blue, H_2BDOA (10^{-4} M).

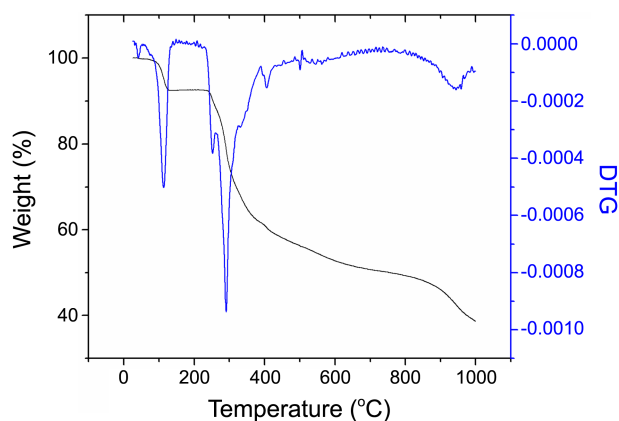


Figure 6. TG and DTG curves of complex **1**.

1000 °C in the Figure 6, which indicates that complex **1** decomposes in three steps. The first stage weight losses of as-synthesized complex **1** (7.44%) taking place covering the temperature ranges of 75–130 °C correspond to the destruction of coordinated water molecules, which is close to relevant calculated weight loss of 7.48% and consistent with the crystal structure analysis. The second stage weight loss (33.68%) of 237–450 °C owing to the ligands decomposition and conforming to the loss of single H_2BDOA without four carboxylic oxygen atoms (Calcd: 33.24%). The third stage weight loss (18.16%) of 843–1000 °C belong to the decomposition of 4,4'-dipyridyl (Calcd: 16.90%), while the remnant (ZnO) of complex **1** is 40.72%. Similarly, complex **2** undergoes three decomposition steps with the corresponding values of 7.37%, 31.09%, 14.77%, and 46.92% (remnant, CdO), respectively, which are inconformity with the theoretical values (6.81%, 30.29%, 38.62%, and 24.28%). As mentioned above, complexes **1** and **2** do not decompose completely under the experimental temperature.

Conclusion

Two 3D isomorphous and isostructural complexes of

$[\text{Zn}(\text{BDOA})(\text{bpy})(\text{H}_2\text{O})_2]_n$ (**1**) and $[\text{Cd}(\text{BDOA})(\text{bpy})(\text{H}_2\text{O})_2]_n$ (**2**) are successfully synthesized by hydrothermal method. Use of 4,4'-bipyridine as pillar leads to the formation of complexes with higher dimensionality. BDOA^{2-} anion exhibits semiflexible behavior and adopts bidentate bridging mode ($\mu^1-\eta^0:\eta^1+\mu^1-\eta^0:\eta^1$) to give rise to zigzag chains in the complexes. 3D supramolecular network of the complexes are assembled through hydrogen bonds between coordinated water molecules and carboxylate groups of the adjacent 2D layers. Luminescent properties of complex **1** showed selectivity toward Hg^{2+} ions.

Acknowledgments. This work was supported by the Natural Science Foundation of Henan Province, P.R. China (No. 13A150056, 12B150005, 122102210174, and 12B150004). And the publication cost of this paper was supported by the Korean Chemical Society.

Supplementary Material. CCDC 918644 (**1**) and 946275 (**2**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac>.

References

- Shi, F.; Cunha-Silva, L.; Ferreira, R. A. S.; Mafra, L.; Trindade, T.; Carlos, L.; Paz, F. A. A.; Rocha, J. *J. Am. Chem. Soc.* **2008**, *130*, 150.
- Yang, Y.; Jiang, G. Q.; Li, Y. Z.; Bai, J. F.; Pan, Y.; You, X. Z. *Inorg. Chim. Acta* **2006**, *359*, 3257.
- Wang, F.; Jing, X. M.; Zheng, B.; Li, G. H.; Zeng, G.; Huo, Q. S.; Liu, Y. L. *Cryst. Growth Des.* **2013**, *13*, 3522.
- Li, X.; Li, Y. Q.; Zheng, X. J.; Sun, H. L. *Inorg. Chem. Commun.* **2008**, *11*, 779.
- Baghel, G. S.; Chinta, J. P.; Kaiba, A.; Guionneau, P.; Rao, C. P. *Cryst. Growth Des.* **2012**, *12*, 914.
- Sahu, J.; Ahmad, M.; Bharadwaj, P. K. *Cryst. Growth Des.* **2013**, *13*, 2618.
- Xiong, S. S.; He, Y. B.; Krishna, R.; Chen, B. L.; Wang, Z. Y. *Cryst. Growth Des.* **2013**, *13*, 2670.
- Chandrasekhar, V.; Hossain, S.; Das, S.; Biswas, S.; Sutter, J. P. *Inorg. Chem.* **2013**, *52*, 6346.
- Haldoupis, E.; Nair, S.; Sholl, D. S. *J. Am. Chem. Soc.* **2012**, *134*, 4313.
- Sun, L. X.; Qi, Y.; Wang, Y. M.; Che, Y. X.; Zheng, J. M. *CrystEngComm* **2010**, *12*, 1540.
- Katie, C.; Christopher, J. K.; Michael, J. F.; Peter, J. S.; Rik, R. T. *J. Am. Chem. Soc.* **2002**, *124*, 7266.
- Li, S. L.; Lan, Y. Q.; Ma, J. F.; Yang, J.; Wei, G. H.; Zhang, L. P.; Su, Z. M. *Cryst. Growth Des.* **2008**, *8*, 675.
- Li, S. L.; Lan, Y. Q.; Ma, J. C.; Ma, J. F.; Su, Z. M. *Cryst. Growth Des.* **2010**, *10*, 1161.
- Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
- Shinpei, H.; Satoshi, H.; Ryotaro, M.; Shuhei, F.; Katsunori, M.; Yoshinori, K.; Susumu, K. *J. Am. Chem. Soc.* **2007**, *129*, 2607.
- Chen, B. L.; Zhao, X. B.; Putkham, A.; Hong, K. L.; Lobkovsky, E. B.; Hurtado, E. J.; Fletcher, A. J.; Thomas, K. M. *J. Am. Chem. Soc.* **2008**, *130*, 6411.
- Georgeta Grosu, I.; Lönnecke, P.; Silaghi-Dumitrescu, L.; Hey-Hawkins, E. *Z. Anorg. Allg. Chem.* **2011**, *637*, 1722.
- Gao, S.; Liu, J. W.; Huo, L. H.; Xu, Y. M.; Zhao, H. *Inorg. Chem.*

- Commun.* **2005**, *8*, 361.
19. Li, L. J.; Hua, X. X.; Wang, G. Y.; Huang, Y. Y.; Wang, L. Z.; Tian, C.; Du, J. L. *Russ. J. Coord. Chem.* **2013**, *39*, 225.
20. Gong, Y. N.; Liu, C. B.; Ding, Y.; Xiong, Z. Q.; Xiong, L. M. *J. Coord. Chem.* **2010**, *63*, 1865.
21. Sheldrick G. M. SADABS software for empirical absorption correction. *University of Göttingen*, 1996.
22. Sheldrick, G. M. SHELXTL V5. 1 software reference manual. Bruker AXS Inc, Madison, 1997.
23. Tang, R. R.; Gu, G. L.; Zhao, Q. *Spectrochim. Acta. A* **2008**, *71*, 371.
24. Vijayalakshmi, R.; Jayachandran, M.; Sanjeeviraja, C. *Curr. Appl. Phys.* **2003**, *3*, 171.
25. Li, X. F.; Han, Z. B.; Cheng, X. N.; Chen, X. M. *Inorg. Chem. Commun.* **2006**, *9*, 1091.
26. Gao, S.; Liu, J. W.; Huo, L. H.; Zhao, H.; Ng, S. W. *Appl. Organomet. Chem.* **2005**, *19*, 169.
27. Li, X. Y.; Liu, C. B.; Che, G. B.; Wang, X. C.; Li, C. X.; Yan, Y. S.; Guan, Q. F. *Inorg. Chim. Acta* **2010**, *363*, 1359.
28. Zheng, S. L.; Yang, J. H.; Yu, X. L.; Chen, X. M.; Wong, W. T. *Inorg. Chem.* **2004**, *43*, 830.
29. Wang, R. H.; Han, L.; Jiang, F. L.; Zhou, Y. F.; Yuan, D. Q.; Hong, M. C. *Cryst. Growth Des.* **2005**, *5*, 129.
30. He, J. H.; Yu, J. H.; Zhang, Y. T.; Pan, Q. H.; Xu, R. R. *Inorg. Chem.* **2005**, *44*, 9279.
31. Li, M.; Xiang, J. F.; Yuan, L. J.; Wu, S. M.; Chen, S. P.; Sun, J. T. *Cryst. Growth Des.* **2006**, *6*, 2036.
-