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Two fluorescent coordination polymers constructed from mixed rigid and flexible carboxylate ligands: Formation of cross-linking helical and zigzag chains

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Abstract

Two 3D coordination polymers with different structure motifs, $[Zn_2(PCPA)_2(IN)_2]_n$ (**1**) and $[Co(PCPA)(IN)]_n$ (**2**) (PCPA = *p*-chlorophenoxyacetate, IN = isonicotinate), first constructed from mixed rigid and flexible carboxylate ligands, have been obtained under hydrothermal condition and characterized by elemental analyses, IR spectra, thermogravimetric analysis, fluorescent spectra and single crystal X-ray diffraction analysis. The most intriguing structural feature is that each complex exhibits both infinite helical Zn(μ_2-carboxylate) or Co(μ_3-carboxylates) chain units with 2_1 helices and zigzag $M_2(IN)_2$ (M = zinc and cobalt) chain units by reason of two different carboxylate ligands coordinating to metal centers. Additionally, compounds **1** and **2** show similar blue fluorescence in the solid state at room temperature.

Keywords: Zinc; Cobalt; Coordination polymer; Fluorescent emission; Crystal structure; Mixed carboxylate ligands

1. Introduction

There has been intense research effort on the design, synthesis and characterization of metal-organic coordination polymers (MOCP) with novel topologies in recent years [1]. Among the most extensively studied metal-organic frameworks are those based on carboxylate ligands due to their interesting molecular topologies and diverse structural properties along with potential applications as functional materials [2]. Most of the recent studies on the preparation of MOCP reveal that the use of well-designed or selected bridging ligands in combination with metal centers of diverse geometries has led to the construction of numerous coordination networks with a variety of topologies such as ladders, brick walls, honeycombs, helices, and diamondoid networks. In a sense, the formation of molecular racks and grids results from the rigidity of the ligands, while that of helices results from the flexibility of the ligands [3]. Therefore, of great interest is the rational design of MOCP via appropriate selection or combination of flexible and rigid ligands such as pyridine- or carboxylate-based ligands. However, comparatively few efforts have been made to the investigation of MOCP based upon two or more kinds of carboxylate ligands coordinated to one metal center by hydrothermal synthesis mainly due to more difficult control in view of inherent coordinating properties of reactants. Hence, attempts are made by us to construct MOCP from mixed carboxylate ligands, flexible *p*-chlorophenoxyacetate (PCPA) and rigid isonicotinate, in order to obtain new architectures with useful properties and more detailed understanding of the formation of the helices and other interesting frameworks. The coordination chemistry of PCPA—a widely used herbicide, has been extensively studied and well understood

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for mono-, dinuclear complexes but few polymers and the coordination modes show a rich variety of structure motifs [4]. Additionally, it possesses flexibility owing to the presence of a –OCH$_2$– spacer between the phenyl ring and carboxylate moiety. IN, a rigid ligand frequently employed, in which both neutral and anionic donor groups are present, can be expected to coordinate to metal centers potentially to result in neutral polymeric structures [5]. Furthermore, it was expected that the combination of d^{10} metal with carboxylic acid would exhibit intriguing structural and photoluminescent properties. Zheng and his coworkers have recently summarized the recent advances on the luminescence studies of Zn(II)/Cd(II) coordination complexes [6]. Herein, based on these considerations, we now report the synthesis, crystal structure and photoluminecent property of $[Zn_2(PCPA)_2(IN)_2]_n$(**1**) and $[Co(PCPA)(IN)]_n$(**2**).

2. Experimental

2.1. General

All reagents were used as purchased without further purification. Elemental analyses of C, H, and N were performed with an Elementar Vario EL III elemental analyzer. The IR spectra were recorded with a Perkin–Elmer Spectrum 2000 FT-IR spectrometer in the range of 400–4000 cm^{-1} using the KBr pellet technique. Thermogravimetric (TG) analyses were conducted on a NETZSCH STA 449C Thermal Analyzer in an argon atmosphere with a heating rate of 10 °C/min from room temperature to 1000 °C. Fluorescent spectra were measured with an Edinburgh F920 analytical instrument at Fuzhou University.

2.2. Synthesis of the complex **1**

An aqueous-glycol (4:2) solution containing $ZnSO_4 \cdot 7H_2O$(574 mg, 2.0 mmol), *p*-chlorophenoxyacetic acid (186.5 mg, 1.0 mmol) and isonicotinic acid (123 mg, 1.0 mmol) was stirred for 20 min at room temperature, then the pH of the mixture was adjusted to 4.3 by adding drops of 10% sodium hydroxide solution. Finally, the mixture was heated at 120 °C for 3 days under autogeneous pressure in a sealed 15 mL teflon-lined stainless steel vessel. The colorless crystals of **1** were obtained after the reaction solution was cooled down gradually, and washed with water and ethanol. Yield: 0.26 g (69.7% based on isonicotinate) $C_{28}H_{20}C_{12}N_2O_{10}Zn_2$ (746.10): calcd. C 45.08, N 3.76, H 2.70; found C 44.91, N 3.82, H 2.79.

2.3. Synthesis of the complex **2**

An aqueous-glycol (4:2) solution containing $Co(NO_3)_2 \cdot 6H_2O$ (582 mg, 2.0 mmol), *p*-chlorophenoxyacetic acid (186.5 mg, 1.0 mmol) and isonicotinic acid (123 mg, 1.0 mmol) was stirred for 20 min at room temperature, then 0.1 mL 35% ammonia was slowly added, and the pH of the mixture was adjusted to 4.6 by adding drops of 10% hydrochloric acid solution. Finally, the mixture was heated at 120 °C for 3 days under autogeneous pressure in a sealed 15 mL teflon-lined stainless steel vessel. The purple-red crystals of **2** and pink red crystals of $[Co(iso)_2(H_2O)_4]$ (iso = isonicotinate) [7] were obtained after the reaction solution was cooled down gradually, and washed with water and ethanol. Yield: 0.12 g (42.8% based on isonicotinate) $C_{14}H_{10}ClNO_5Co$ (366.61): calcd. C 45.87, N 3.82, H 2.75; found C 45.76, N 3.88, H 2.86.

2.4. X-ray crystallography

The reflection intensities of **1** were collected on Bruker SMART CCD diffractometer with Mo*K*α radiation ($\lambda = 0.71073$ Å) at 298 ± 2 K. A total of 24,249 reflections (6836 independent, *R*(int) = 0.0568), were collected, of which 5303 reflections with $I > 2\sigma(I)$ were considered observed. An empirical absorption correction was applied to the data using the Multi-Scan program. As for **2**, the data collection was performed on a Rigaku Weissenburg IP diffractimeter with Mo*K*α radiation ($\lambda = 0.71069$ Å) at 298 ± 2 K. A total of 1829 independent reflections were collected, of which 1469 reflections with $I > 2\sigma(I)$ were considered observed. Lp correction and a ψ empirical absorption correction were made for the intensity data. The structures of **1** and **2** were solved by the direct methods and successive Fourier difference syntheses, and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-hydrogen atoms (SHELXTL-97). The remaining hydrogen atoms were generated geometrically and not refined. Crystallography data are given in Table 1. Selected bond lengths and angles

Table 1
Crystallographic data and structure refinement for **1** and **2**

Complex	**1**	**2**
Empirical formula	$C_{28}H_{20}Cl_2N_2O_{10}Zn_2$	$C_{14}H_{10}ClNO_5Co$
Formula mass	746.10	366.61
Space group	$P2_1/n$	$Pna2_1$
a [Å]	11.6336(7)	20.4254(10)
b [Å]	6.9889(4)	11.7365(8)
c [Å]	35.670(2)	6.0910(3)
α [deg.]	90.00	90.00
β [deg.]	99.3710(10)	90.00
γ [deg.]	90.00	90.00
V [Å^3]	2861.5(3)	1460.15(14)
D_c [g/cm^3]	1.732	1.668
Z	4	4
F(000)	1504	740
λ(Mo*K*α) [Å]	0.71073	0.71069
θ range [deg.]	1.16–28.34	1.99–27.48
Flack parameter		0.0534
Final *R* indices	R_1[a], 0.0611; wR_2[b], 0.1525	R_1[a], 0.0292; wR_2[b], 0.0688,

[a] $R_1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

are listed in Table 2. All calculations were performed on a computer with SHELEXTL-PC program package [8].

3. Results and discussion

3.1. Structural description of $[Zn_2(PCPA)_2(IN)_2]_n$ (1)

The immediate coordination environment around the zinc centers in compound **1** is shown in Fig. 1. The Zn(II) ions lie in pentacoordinate environments, consisting of two oxygen atoms of two independent PCPA ligands, one nitrogen atom from one isonicotinate, as well as one oxygen atom and a semi-chelating carboxylate oxygen atom from another isonicotinate leading to a highly distorted square pyramidal geometry (the semi-chelating fashion, is similarly adopted by $[Cd(isonicotinate)_2(EtOH)][EtOH]$, $[Cd(isonicotinate)_2(H_2O)][pyrazine]$ [9], and $[\{Cd_2(dpa)(pya)_6\}(pya)_6(dpe)_3]_n$ [10]). The bond lengths of Zn–O ranging from 1.967(3) to 2.021(4) Å are consistent with those of the reported polymers except that one oxygen atom from isonicotinate (IN) weakly interacts with the metal center as the Zn⋯O distances (Zn1⋯O10, 2.344(4) Å; Zn2⋯O6, 2.440(4) Å), are too long to be considered as true coordinated bonds, and therefore are best described as semi-chelating interactions; while the Zn–N distances, 2.020(3) and 2.059(4) Å, are slightly shorter than those of reported Zn(II) coordination polymers, which indicates the existence of strong interactions between Zn and N atoms, for example $[Zn(4,4'\text{-bipy})(H_2O)_3(ClO_4)](ClO_4)\cdot(4,4'\text{-bipy})_{1.5}\cdot H_2O$ (Zn–N: 2.104(2)–2.117(2) Å) [11a], $[Zn(tp)(4,4'\text{-bipy})]$ (tp = terephthalate) (Zn–N: 2.154(2)–2.186(3) Å) [11b], and $[Zn(fca)_2(bpe)]_n\cdot 2nH_2O$ ($fca = C_5H_5FeC_5H_4C(OH)CHCOCH_3$) (Zn–N: 2.196(8)–2.205(8) Å) [11c], but close to those of the related bibenzimidazolyl Zn(II) coordination polymer $\{[Zn(FcCOO)_2(bbbm)]\cdot 2H_2O\}_n$ (Zn–N: 2.028(4)–2.071(3) Å) [11d]. However, a slight difference result in two crystallographically independent Zn(II) centers {Zn(1) and Zn(2)}: As for Zn(1), both the two PCPA groups bridge in *syn, skew* mode five-coordinate Zn(1) atoms, forming a puckered eight-membered $Zn_2O_4C_2$ ring (Fig. 2). The metal centers exhibit no metal–metal bonding as separated by 3.659(5) Å, slightly longer than those of reported dinuclear Zn(II) complexes [12]. While for Zn(2), as shown in Fig. 2, each PCPA acting as bidentate bridging ligands in *syn, anti* mode connects two zinc atoms to form an infinite helical chain Zn(μ_2-carboxylate) with 2_1 helices along *b*-axis with the intrachain distance Zn2⋯Zn2 of 4.9536(2) Å (Figs. 2 and 3). Each dinuclear unit, links to four helical Zn(μ_2-carboxylate) chain units through four IN bridges as illustrated in Fig. 3. While the rigid isonicotinate, acting as a tridentate bridging ligand centers links two adjacent Zn(II) {Zn(1) and Zn(2)} centers to form an infinite zigzag chain as shown in Fig. 3, and the carboxylate groups from PCPA connect two adjacent counter chains to form an infinite double-edged sawlike chain, two sides of which crosslink with numerous helical

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

Complex **1**[a]			
Zn1–O7	1.972(3)	Zn1–O3	2.016(3)
Zn1–N2	2.020(3)	Zn1–O9	2.021(3)
Zn1–O10	2.344(4)	Zn2–O6	2.440(4)
Zn2–O5	1.967(3)	Zn2–O1	1.982(3)
Zn2–O2	1.998(3)	Zn2–N1	2.059(4)
Complex **2**[a]			
Co1–O3	1.995(3)	Co1–O5#1	2.041(4)
Co1–O2	2.091(4)	Co1–N1	2.094(4)
Co1–O4	2.272(4)	Co1–O1	2.279(3)

[a] Symmetry codes: #1 $-x+1$, $-y$, $z+1/2$; #2 $-x+1$, $-y$, $z-1/2$; #3 $-x+1/2$, $y-1/2$, $z-1/2$; #4 $-x+1/2$, y+1/2, z+1/2.

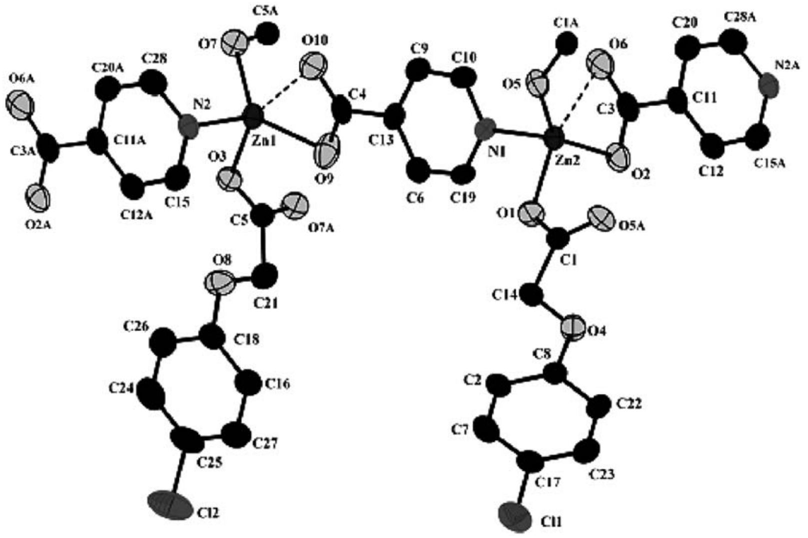

Fig. 1. Perspective view of the coordination environment of the Zn(II) ion in **1**. Hydrogen atoms were removed for clarity.

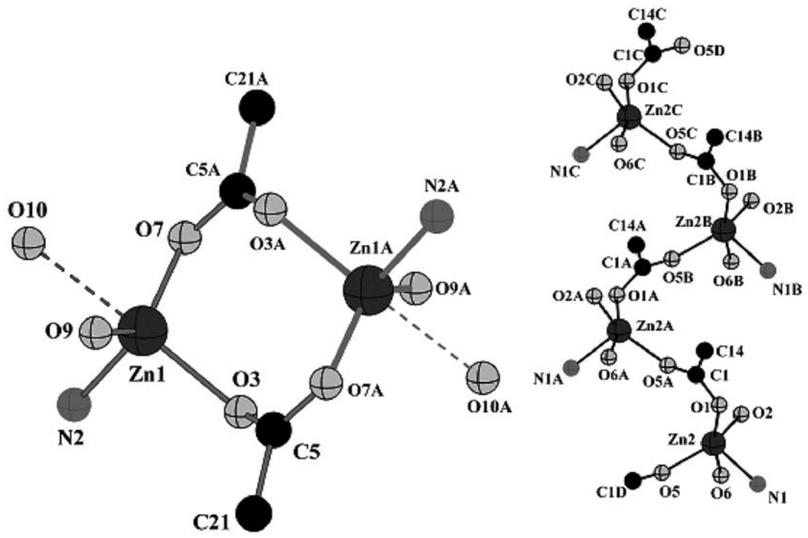

Fig. 2. View of the dinuclear unit eight-membered $Zn_2O_4C_2$ ring (left) and the helical Zn(μ_2-carboxylate) chain unit (right). Other atoms were removed for clarity.

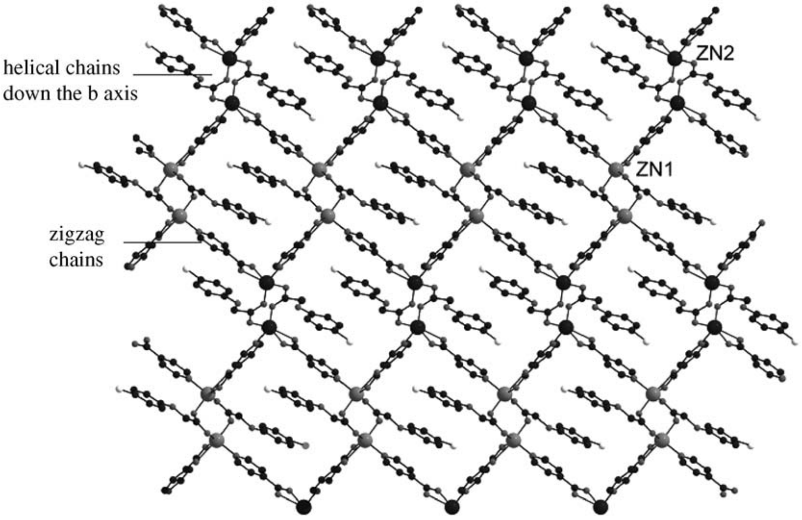

Fig. 3. View of structure of complex **1** down the *b*-axis, showing the cross-linking helical and zigzag chain units. Hydrogen atoms were removed for clarity.

chain units. And numerous cross-linking helical chains along *b*-axis and zigzag chains along *a*-axis further result in an unprecedented complicated 3D framework structures as shown in Fig. 3.

3.2. Structural description of $[Co(PCPA)(IN)]_n$ (**2**)

Compared to **1**, a different coordination environment is found for the cobalt center in compound **2**, although the same ligands are used. As shown in Fig. 4, the Co(II) centers lie in an octahedral environment with the axial positions occupied by one phenoxyl oxygen and pyridyl nitrogen donors from the two ligands and the equatorial positions occupied by two carboxylate oxygen atoms of two different phenoxyacetic ligands and two carboxylate oxygen atoms from isonicotinate. Bond distances around the Co center are typical of other cobalt-based coordination polymers containing nitrogen donor ligands: N(1)–Co(1), 2.094(4) Å with Co–O bond distances in the range 1.995(3)–2.279(3) Å, consistent with corresponding bond lengths found in $[Co(Pht)(bpy)(H_2O)_3]\cdot 3H_2O$ [13a], $[Co(1,4\text{-bis(4-pyridyl)-butadiyne})(NO_3)_2(H_2O)_2\cdot 2H_2O]_n$ [13b]. Similar to **2**, each PCPA in **2** acting as tridentate bridging ligands in *syn, anti* mode connects two cobalt atoms to form an infinite helical chain unit Co(μ_3-carboxylates) with 2_1 helices along *c*-axis with the intrachain distance Co⋯Co of 5.3891(11) Å (Fig. 5). While the rigid isonicotinate, acting as a tridentate bridging ligand centers links two adjacent Co(II) centers to form an infinite zigzag chain as shown in Fig. 6, and numerous cross-linking helical chains and zigzag chains further result in an unprecedented complicated 3D framework structures (Fig. 6).

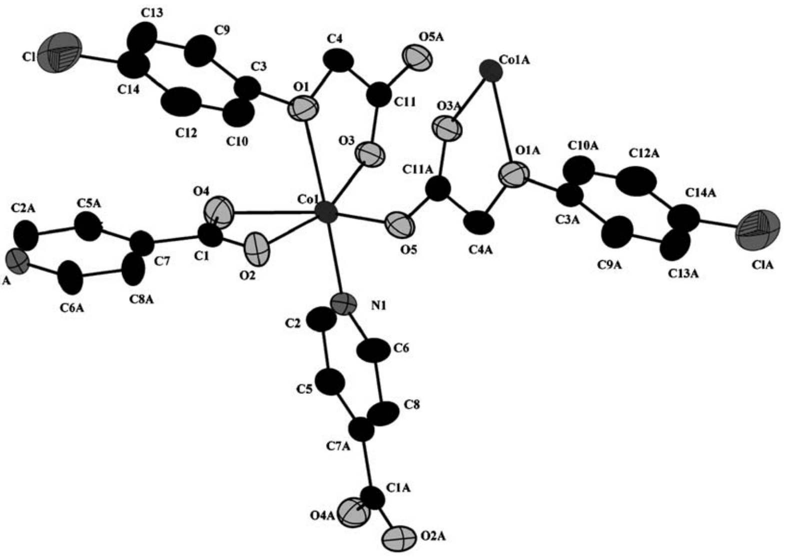

Fig. 4. Perspective view of the coordination environment of the Co(II) ion in **2**. Hydrogen atoms were removed for clarity.

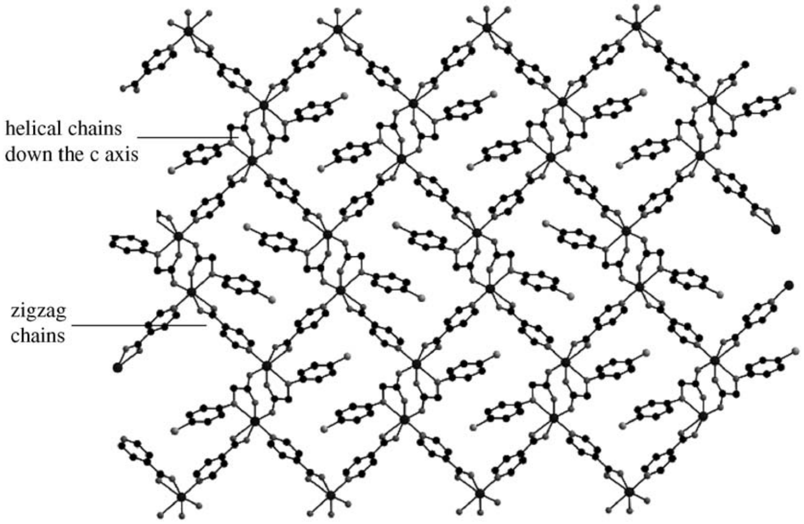

Fig. 5. View of structure of complex **2** down the *c*-axis. Hydrogen atoms were removed for clarity.

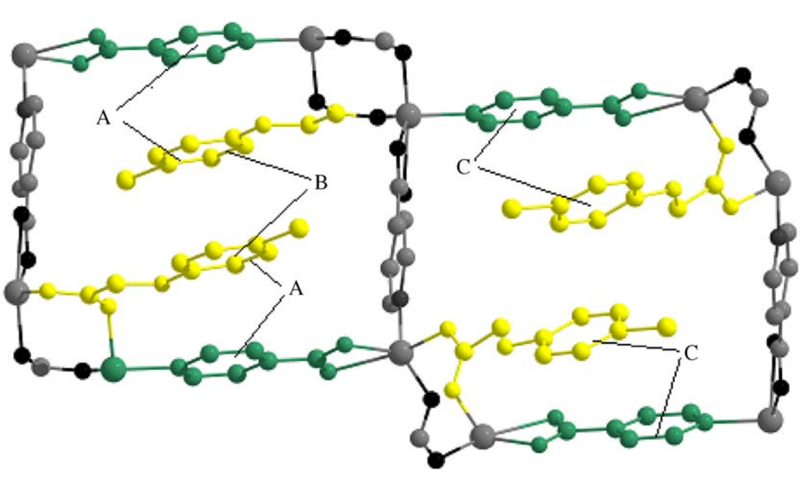

Fig. 6. Three types of aromatic stacking interactions in **1**. Color code: ligands PCPA, yellow; IN, green.

3.3. Similarities and contrasts

It is evident from the above discussion of individual structures of complexes **1** and **2** that they are closely related to each other with cross-linking infinite helical and zigzag chain units constructed by the interaction between the metals and the same two ligands, but a close look at the structures in an individual manner indicates several differences along with common features. First, only complex **1** has dinuclear unit eight-membered $Zn_2O_4C_2$ ring. Further, different coordination modes of PCPA lead to different helical chain units Zn(μ_2-carboxylate) and Co(μ_3-carboxylate), which of course result in creation of different topologies. The most salient feature is the formation of the different types of chain units in **1** and **2**. The accepted model for helication requires a long multidentate ligand as a molecular thread, containing a number of discrete metal-binding sites separated by spacer units. Such a molecular thread can twist around several metal ions controlled by their coordination behavior [14]. Most previous metal helicates, such as $[Ln_2(\text{pdc})_3\cdot 3H_2O]_n$ ($Ln = $ La, Ce, Nd) [14], have been synthesized using multidentate ligands partitioned into a number of discrete metal-binding sites suitable for the formation of helical complexes. In **1** and **2,** the ligand PCPA twists around several metal ions owing to the presence of a $–OCH_2–$ spacer between the phenyl ring and carboxylate moiety as mentioned earlier. Therefore its unique stereochemistry, result in helical chain units along 2_1 helices due to its flexibility (Figs. 2 and 5). While the rigid isonicotinate, acting as a tri-connector links two adjacent Zn(II) {Zn(1) and Zn(2)} or Co(II) centers to form an infinite zigzag chain due to the rigidity of the ligands as shown in Figs. 3 and 5, which agrees with $[\text{Zn(ini)I(iniH)}]_n$ (ini = isonicotinate) containing infinite zigzag chains generated by bridging isonicotinate units [15]. Interestingly, previous studies show that 4-pyridylacetic acid, which possesses flexibility owing to the presence of a $–CH_2–$ spacer between the pyridyl ring and carboxylate moiety, can lead to helical chains structure by coordinating to metal ions, such as $[trans\text{-}M(C_7H_6NO_2)_2(H_2O)_2]_n$ ($M =$ Zn, Cd, Mn) [16].

Another interesting and useful point is that only **1** exhibit attractive aromatic stacking interaction. Overlapped arrangements of parallel pyridine and benzene rings of complex **1** are observed in the crystal as shown in Fig. 6, which also indicates three types of π–π interactions. The angles are: 5.033° between the benzene ring and pyridine ring (for A), 0.115° between the two benzene rings (for B) and 13.413° between the benzene ring and pyridine ring(for C). And the interplanar distances between them are approximately 3.47–3.63 Å strongly suggesting the presence of the intermolecular stacking interaction [17]. Interestingly, as Fig. 6 shows, A and C stacks occur in a roughly "face-to-face" manner while B stacks in an almost strict "face-to-face manner" (a strict "face-to-face" stack is very unusual and is not possible between rings of different sizes [17a]). In complex **2**, however, such interactions are not observed, since both types of aromatic rings do not overlapped and are far apart from each other in the crystal.

3.4. Infrared spectral studies

The IR spectra of **1** and **2** clearly show both the presence of the PCPA and IN ions. The absence of the expected absorption at 1690–1730 cm^{-1} for the protonated carboxylate groups illustrates the complete deprotonation of the ligands in the reaction with zinc or cobalt. The strong absorptions at 1602,1630 and 1466,1397 cm^{-1} for **1**, 1590,1647 and 1418,1387 cm^{-1} for **2** correspond to asymmetric and symmetrical stretching vibrations, v_{as}(COO) and v_s(COO), of the coordinated carboxylate groups of PCPA and IN, respectively. The strong C–O stretching vibrations at about 1240 cm^{-1} in the spectra of both **1** and the ligand PCPA suggest that the oxygen atom from phenoxyl may not coordinate to Zn centers, while the absence of that in the spectra of **2** indicates that the oxygen atom from phenoxyl may take part in coordination. This is in accordance with the result of X-ray diffraction (XRD) analysis. In conclusion, the IR spectra indicate the versatile carboxylate-bridging coordination modes of **1** and **2** constructed by mixed carboxylate ligands.

3.5. TG analysis

To characterize the thermal stability of the different self-assemblies constructed by the same ligands and different metals, the complexes **1** and **2** were investigated by the TG techniques. The TG analysis curve recorded at 20–1000 °C reveals that the structure of **1** remains thermally stable up to 295.5 °C. On further heating, compound **1** began to decompose rapidly with a weight loss of 51.28% (calculated 49.73%) corresponding to the removal of the coordinate PCPA ligands (Fig. 7). Subsequent slow decomposition from 425 °C may correspond to the release of IN groups. The reason why PCPA is first lost during thermal decomposition may be attribute to the stronger interaction between the metal center and IN as IN is a linear three-connector while PCPA has only one terminal carboxylate linked to metal centers. The thermal decomposition behavior of compound **2** is similar to that of **1**. It began to decompose at 332.5 °C followed immediately by a sharp decrease in weight of 47.00% terminating at 432.7 °C, corresponding to the loss of the coordinate PCPA ligands (calculated 50.60%). Above this temperature a gradual weight loss accompanying decomposition of the IN ligands is observed. The high thermal stability of **1** and **2** is mainly attributed to the absence of the guest molecular (i.e., water and ethanol) and hydrogen bond in **1** and **2** as well as the formation of infinite chains that solidifies the flexible organic ligands.

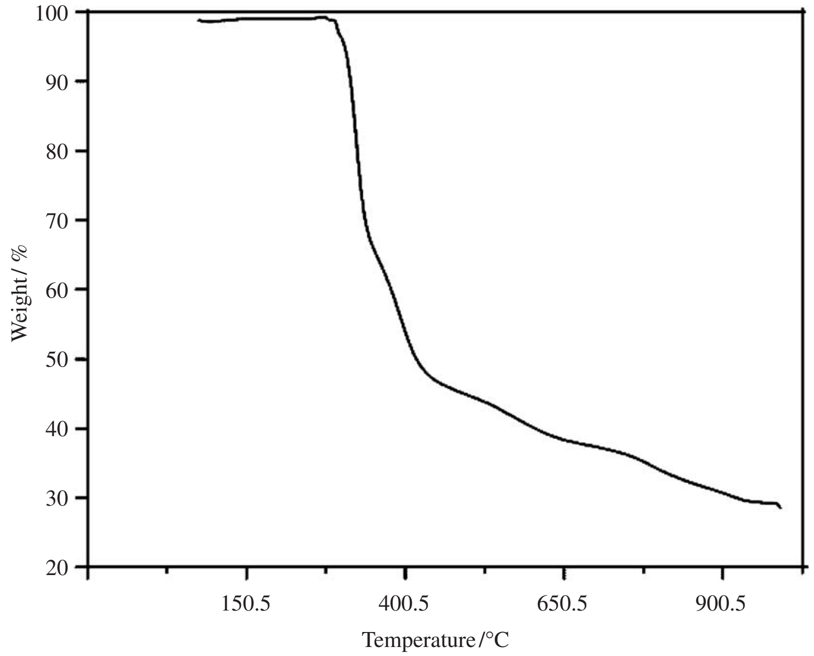

Fig. 7. TGA diagram for complex **1**.

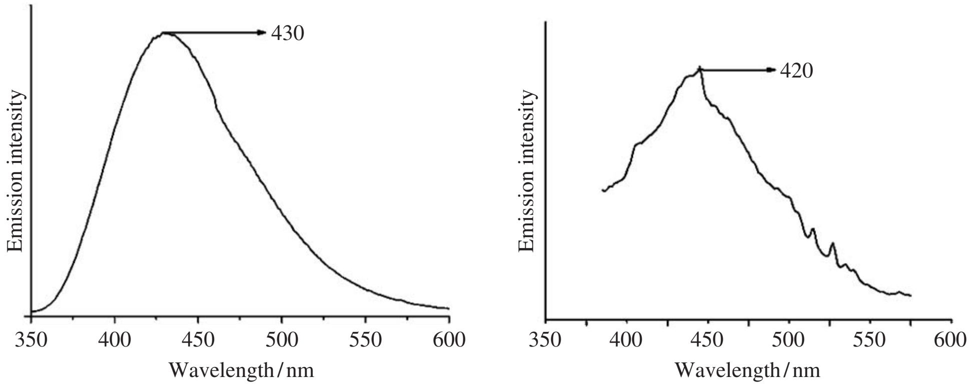

Fig. 8. Solid-state emission spectra of **1** (left) and **2** (right) at room temperature.

3.6. Fluorescent properties

Fig. 8 shows the emission spectra of the complex **1** and **2** in the solid state at room temperature. Upon photoexcitation at 330 nm ($\lambda_{ex} = 330$ nm), complex **1** exhibits an intense fluorescent emission band with a maximum at 430 nm, while **2** shows analogous, but obviously weak fluorescence signals at 420 nm ($\lambda_{ex} = 350$ nm). In contrast, free IN ligand shows no photoemission while PCPA ligand exhibits photoemission at 311 nm upon photoexcitation at 270 nm, which is attributable to the $\pi-\pi^*$ transition. Therefore, the emissions at 430 nm for complex **1** and 420 nm for complex **2** may not be related to $\pi-\pi^*$ transition of the ligands. In addition, a similar emission band at about 430 nm has been observed previously for other zinc–organic polymer compounds with either photoluminescent or non-photoluminescent ligands, such as $[\text{Zn(mpa)(phen)}]_n$ [18a], $[\text{Zn(PDB)}]_n$ [18b]. Hence, the two emissions may be assigned to the ligand-to-metal-charge-transfer bands (LMCT) [19]. Additionally, it is notable that the complex **1** exhibits a quenching of the fluorescence with $\tau = 6.80$ ns ($\tau =$ lifetime, the short lifetime suggests that luminescence should be assigned to fluorescence). These observations suggest that **1** may be used as an advanced material for blue-light emitting diode device [20], and may be an excellent candidate for highly thermally stable and solvent-resistant blue fluorescent material since it is almost insoluble in common polar and non-polar solvents.

4. Conclusion

In summary, we have successfully synthesized two new 3D coordination polymers under hydrothermal conditions. Compounds **1** and **2** not only show fascinating structural feature that two building chain units, M(PCPA) and $M_2(\text{IN})_2$ ($M =$ zinc and cobalt), cross-link into new

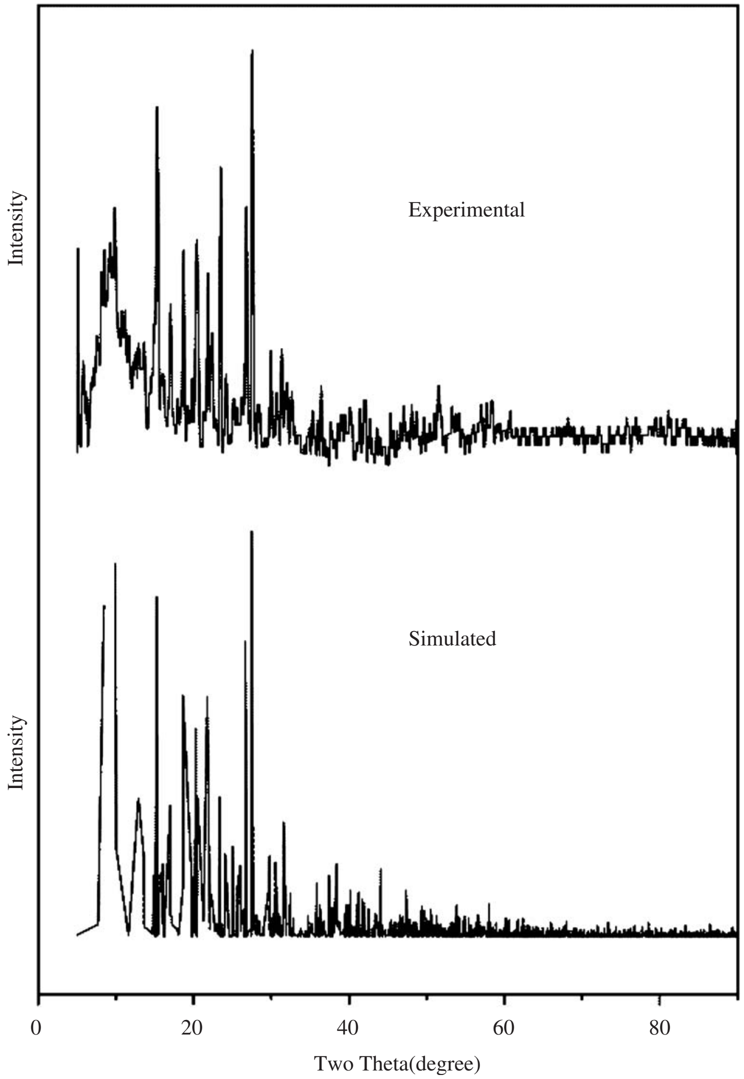

Fig. 9. Experimental and theoretically simulated XRD patterns for complex **1**.

complicated 3D framework structure, but also exhibit good stability and blue fluorescent emission in the solid state. Of particular interest is the fact that the two polymers were first constructed by mixed flexible and rigid carboxylate ligands, which play an important role in the formation of helical chain units and zigzag chain units. Further study of this kind of reaction is underway in order to get more useful information about the construction of MOCP through mixed rigid and flexible carboxylate ligands.

5. Supplementary materials

Crystallographic data for **1** and **2** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC-274481(**1**), -276264(**2**)). These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

Powder XRD was performed by Philips X'Pert MPD diffractometer for phase identification. Fig. 9 shows experimental and theoretically simulated XRD patterns for complex **1**. The generally good agreement between the two patterns shows a very pure phase.

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