

Three New Coordination Compounds Based on 2-Phenyl-4-quinolinecarboxylic Acid and Nitrogenous Neutral Ligands: Syntheses, Structural Features, and Properties

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Abstract. Solvothermal reactions of 2-phenyl-4-quinolinecarboxylic acid (Hpqba) with Cd^{II}, Co^{II}, Zn^{II} and/or 4,4'-bipyridyl (4,4'-bipy), 1,4-bis(imidazol-1-ylmethyl)benzene (biyb), 2,2'-bipyridyl (2,2'-bipy) afford three new coordination compounds of stoichiometries [Cd(pqba)₂(4,4'-bipy)] (**1**), [Zn(pqba)₂biyb] (**2**), and [Co₃(pqba)₆(2,2'-bipy)₂] (**3**). Compounds **1–3** were characterized by elements analysis, IR spectroscopy, thermogravimetry, and single-crystal X-ray diffraction study. Compound **1** has a two-dimensional structure, whereas compound **2** consists of a one-dimensional (1D) network,

which is further expanded by $\pi\cdots\pi$ stacking interactions to form a 3D supramolecular structure. Complex **3** also exhibits a 3D supramolecular structure completely based on $\pi\cdots\pi$ stacking interactions. The pqba ligands adopt μ_1-k^1, k^1 , μ_1-k^1 , μ_2-k^1, k^1 , and μ_2-k^1, k^2 coordination modes for compounds **1**, **2**, and **3**. The fluorescence properties were examined on compounds **1** and **2** in the solid state at room temperature. Magnetic susceptibility measurements indicate that in complex **3** anti-ferromagnetic coupling between adjacent Co^{II} ions exist.

Introduction

The search for complexes with intriguing architectures^[1] and desired properties assembled by coordination bonds and/or weak supramolecular interactions such as $\pi\cdots\pi$ stacking is of current interest and great importance because these materials can exhibit a variety of physical properties such as magnetism, fluorescence properties, and gas adsorption, etc.^[2] Studies in this field have been focused on the rational design and synthesis of novel frameworks and the relationships between their structures and properties, however, remains a great challenge. The observation of coordination complexes constructed from organic ligands and metal ions through a self-assembly route has been explored, and many efforts have been devoted to use of organic ligands as co-ligands to bridge metal ions to form infinite network structures. Among various organic ligands, multicarboxylate organic ligands are often selected as linkers because of their abundant coordination modes to metal ions, allowing for various architectures and supramolecular structures. Recently, rigid ligands are usually the typical building elements in the multidimensional networks (such as 4-quinolinecarboxylate acid, 9-acridinecarboxylic acid, anthracene-9-carboxylic acid, adamantane-1-carboxylic acid, quinoline-

based carboxylic acid) and have been well used in the preparation of various complexes owing to their rich coordination modes.^[3] In contrast, the use of 2-phenyl-4-quinolinecarboxylic acid ligands with huge skeleton to construct functional coordination polymers or supramolecular structure has been less investigated to date.^[4] This ligand has four obvious characteristics: first, Hpqba adopts various coordination modes when it coordinates to metals, although its only carboxylate arm; secondly, it has larger conjugated π systems (three benzene rings), $\pi\cdots\pi$ stacking, and/or C–H $\cdots\pi$ interactions, which may play important roles in the formation of their complexes, especially in the aspect of linking the dinuclear or multinuclear discrete subunits or low-dimensional entities into higher-dimensional supramolecular frameworks; third, the carboxylic groups can propagate magnetic super exchange between central metal atoms; fourth, rigid ligands containing multi benzene rings and suitable metal ion form complexes having fluorescence properties.

Considering all the aspects stated above, to design complexes showing interesting architectures, magnetic behavior, and fluorescence properties, we have chosen the Co^{II}, Zn^{II}, Cd^{II} ions and the Hpqba ligand. And the introduction of 2,2'-bipyridyl-like bidentate chelating or 1,4-bis(imidazol-1-ylmethyl)benzene and 4,4'-bipyridyl-like linear bridging molecules into the reaction systems, as auxiliary ligands, may generate interesting coordination architectures. Herein, we report the synthesis and characterization of compounds **1–3**, namely, [Cd(pqba)₂(4,4'-bipy)] (**1**), [Zn(pqba)₂biyb] (**2**), and [Co₃(pqba)₆(2,2'-bipy)₂] (**3**). The crystal structures, fluorescence properties, and magnetic properties of these new compounds are studied in detail.

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Experimental Section

Materials and Methods: All available solvents and starting materials of analytical grade in the experiments were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) measurements were performed with a Bruker D8 Advance X-ray diffractometer using Cu- K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$), in which the X-ray tube was operated at 40 kV and 40 mA. Elemental analysis (C, H, N) was determined with a Perkin-Elmer 2400 type elemental analyzer. Infrared spectra were recorded with a Bruker EQUINOX-55 spectrophotometer in the range 400–4000 cm^{-1} using KBr disks. Thermogravimetric analyses were recorded with a NETZSCH STA 449C thermal analyzer. Photoluminescence analyses of the solid samples were performed with an Edinburgh Instrument F920 fluorescence spectrometer at ambient temperature.

Syntheses of [Cd(pqba)₂(4,4'-bipy)] (1): A mixture of Hpqb (0.2 mmol, 0.0496 g), 4,4'-bipy (0.2 mmol, 0.0312 g), and CdCO₃ (0.2 mmol, 0.0345 g) in 15 mL mixed solution of methanol/dimethyl fumarate (1:1, v/v) was sealed into a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure, heated at 130 °C for 3 d, and cooled to 20 °C at 4 °C·h⁻¹. Colorless prismatic single crystals suitable for X-ray analyses were obtained. The crystals were collected by filtration, washed with distilled water and methanol, and dried at room temperature. Yield 60% (based on Cd). C₄₂H₂₈O₄N₄Cd (765.12): calcd: C 65.93, H 3.69, N 7.32%; found: C 65.87, H 3.72, N 7.21%. IR (KBr): $\tilde{\nu} = 3060$ (m), 1649 (s), 1630 (s), 1622 (s), 1535 (s), 1383 (s), 1335 (s), 1281 (w), 1177 (m), 1095 (w), 866 (w), 807 (w), 776 (w) cm^{-1} (Figure S1a, Supporting Information).

Syntheses of [Zn(pqba)₂biyb] (2): A mixture of Hpqb (0.2 mmol, 0.0496 g), biyb (0.2 mmol, 0.0477 g), and zinc acetate (0.3 mmol, 0.0659 g) was added to 15 mL of methanol/dimethyl fumarate (1:2, v/v). The final mixture was placed in a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure, heated at 110 °C for 3 d, and cooled to 20 °C at 5 °C·h⁻¹. Colorless crystals suitable for X-ray analyses were obtained. Yield 56% (based on Zn).

C₄₆H₃₄O₄N₆Zn (800.16): calcd: C 69.05, H 4.28, N 10.50%; found: C 68.87, H 4.36, N 10.41%. IR (KBr): $\tilde{\nu} = 3045$ (m), 1678 (s), 1630 (s), 1630 (s), 1567 (s), 1365 (s), 1326 (s), 1276 (w), 1107 (m), 1065 (w), 874 (w), 787 (w) cm^{-1} (Figure S1b).

Syntheses of [Co₃(pqba)₆(2,2'-bipy)₂] (3): A mixture of Hpqb (0.2 mmol, 0.0496 g), (2,2'-bipy)₂ (0.2 mmol, 0.0312 g), and cobalt acetate (0.3 mmol, 0.0747 g) was added to 15 mL of methanol/dimethyl fumarate (1:1, v/v). The final mixture was placed in a 25 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure, heated at 100 °C for 4 d, and cooled to 20 °C at 3 °C·h⁻¹. A large quantity of red crystals was obtained. Yield 76% (based on Co). C₁₁₆H₇₆Co₃N₁₀O₁₂ (1978.66): calcd: C 70.41, H 3.87, N 7.08%; found: C 69.57, H 3.84, N 7.22%. IR (KBr): $\tilde{\nu} = 3112$ (m), 1716 (s), 1674 (s), 1643 (s), 1506 (s), 1403 (s), 1323 (s), 1276 (w), 1147 (m), 1083 (w), 872 (w), 798 (w), 760 (w) cm^{-1} (Figure S1c).

Crystal Structure Determination: X-ray crystallographic data for the compounds 1–3 were collected at room temperature with a Bruker Smart-1000CCD diffractometer. Graphite monochromated Mo- K_{α} ($\lambda = 0.71073 \text{ \AA}$) radiation was used. All absorption corrections were applied using the multiscan program SADABS. The structures of compounds 1–3 was solved by direct methods using the SHELXS-97^[5] and refined on F^2 by the full-matrix least-squares methods using the SHELXL-97 program package.^[6] Atoms were located from iterative examination of difference F -maps following least-squares refinements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2 times U_{eq} of the attached carbon atoms. The crystal data and refinement details of the compounds are summarized in Table 1, and selected bond lengths and angles are listed in Table 2.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-919473, CCDC-919476, and CCDC-919475

Table 1. Crystal data for compounds 1–3.

	1	2	3
Measurement temperature	293(2)	296(2)	293(2)
Empirical formula	C ₄₂ H ₂₈ CdN ₄ O ₄	C ₄₆ H ₃₄ N ₆ O ₄ Zn	C ₁₁₆ H ₇₆ Co ₃ N ₁₀ O ₁₂
Formula weight	765.08	800.16	1978.66
Crystal system	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
$a / \text{\AA}$	9.895(2)	25.862(5)	12.8796(6)
$b / \text{\AA}$	12.243(2)	11.243(2)	13.8874(6)
$c / \text{\AA}$	15.499(3)	14.830(3)	15.2458(7)
$\alpha / ^\circ$	108.61(3)	90	108.0540(10)
$\beta / ^\circ$	99.89(3)	114.620(4)	107.0250(10)
$\gamma / ^\circ$	106.24(3)	90	101.6760(10)
$V / \text{\AA}^3$	1636.5(6)	3920.1(13)	2346.65(18)
$D_c / \text{Mg}\cdot\text{m}^{-3}$	1.553	1.356	1.400
θ range for data collection / °	3.11 to 25.05	1.73 to 25.09	1.75 to 25.50
Indices range (h, k, l)	$-12 \leq h \leq 12$ $-15 \leq k \leq 13$ $-15 \leq l \leq 20$	$-30 \leq h \leq 30$ $-13 \leq k \leq 10$ $-17 \leq l \leq 17$	$-11 \leq h \leq 15$ $-16 \leq k \leq 16$ $-17 \leq l \leq 18$
λ (Mo- K_{α}) / \AA	0.71073	0.71073	0.71073
Reflections collected	14505	9731	24914
Data / restraints / parameters	7354 / 0 / 460	3495 / 0 / 258	8666 / 0 / 599
$F(000)$	776	1656	1019
Final R	$R_1 = 0.0585, wR_2 = 0.1635$	$R_1 = 0.0485, wR_2 = 0.1231$	$R_1 = 0.0539, wR_2 = 0.1370$
R indices (all data)	$R_1 = 0.0789, wR_2 = 0.1706$	$R_1 = 0.0748, wR_2 = 0.1557$	$R_1 = 0.0746, wR_2 = 0.1552$
Z	2	4	1

Table 2. Selected bond lengths /Å and angles /° of compounds **1–3**.

1					
Cd1–O1	2.241(4)	Cd1–O2#1	2.314(4)	Cd1–O3	2.318(4)
Cd1–O4#2	2.247(4)	Cd1–N4	2.365(5)	Cd1–N3	2.386(5)
O1–Cd1–O3	84.26(15)	O3–Cd1–N4	95.42(17)	O4#2–Cd1–N4	99.75(16)
O4#2–Cd1–N3	79.81(16)	O3–Cd1–N3	85.25(17)	O1–Cd1–N3	95.41(16)
Symmetry codes: #1: 2–x, 2–y, 1–z; #2: 1–x, 2–y, 1–z					
2					
Zn1–O1	1.942(3)	Zn1–N2	2.000(3)	O1–Zn1–O1#1	93.73(17)
O1–Zn1–N2#1	111.40(12)	O1#1–Zn1–N2#1	117.27(13)	N2–Zn1–N2#1	106.00(17)
Symmetry codes: #1: –x, y, 1.5–z.					
3					
Co1–O3	2.012(2)	Co1–O2	2.062(3)	Co1–O5	2.157(2)
Co1–O6	2.214(3)	Co1–N5	2.094(3)	Co1–N4	2.146(3)
Co2–O1	2.063(2)	Co2–O5	2.121(2)	Co2–O4	2.066(2)
O3–Co1–O2	95.09(11)	N5–Co1–N4	76.34(13)	O5–Co1–O6	59.66(9)
O1–Co2–O4#1	86.61(10)	O1–Co2–O5	90.35(10)	O4#1–Co2–O5	90.25(9)
Symmetry codes: #1: 1–x, 1–y, 1–z.					

for complexes **1**, **2**, and **3** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>)

Supporting Information (see footnote on the first page of this article): IR spectra, additional figures of the $\pi\cdots\pi$ stacking interactions; experimental and simulated PXRD patterns, and TGA curves for complexes **1–3**.

Results and Discussion

Structural Description of Compounds **1–3**

Crystal Structure of $[Cd(pqba)_2(4,4'-bipy)]$ (**1**)

X-ray crystallographic analysis revealed that **1** crystallizes in the triclinic $P\bar{1}$ space group, and its structure features a 2D coordination network. As shown in Figure 1a, the asymmetric unit of compound **1** contains one Cd^{II} cation, two pqba anions, and one 4,4'-bipy molecule. The coordination environment around the Cd1 adopts slightly distorted octahedral coordination arrangement with four carboxylate oxygen atoms (O1, O3, O2#1, O4#2) from four pqba ligands, and two nitrogen atoms (N3, N4) from two 4,4'-bipy molecules, whereas the O1 and O4#2 atoms exist in the equatorial positions. The Cd1–O lengths are in the range of 2.241(4)–2.318(4) Å and the Cd1–N lengths are in the range of 2.365(5) Å and 2.386(5) Å. The selected bond lengths and angles are listed in Table 2. All bond lengths and angles in **1** are within normal ranges and comparable with those observed in other reported Cd²⁺-carboxylates.^[7]

It is obvious that the angles of O–C–O for two pqba ligands around each Cd1 cation are not the same, 126.47°, 125.74° for each O–C–O. The angles between the two planes are 24.4° and 29.8° (Figure S2a, Supporting Information). One plane is formed by a single benzene ring and the other is formed by a quinol.

In compound **1**, the pqba anions adopts a μ_2-k^1,k^1 coordination mode to bridge two central Cd1 atoms (Scheme 1c). If the 4,4'-bipy ligand is omitted, each of the Cd^{II} atoms are bridged by carboxylate oxygen atoms (O1, O2, O3, O4) to form one-

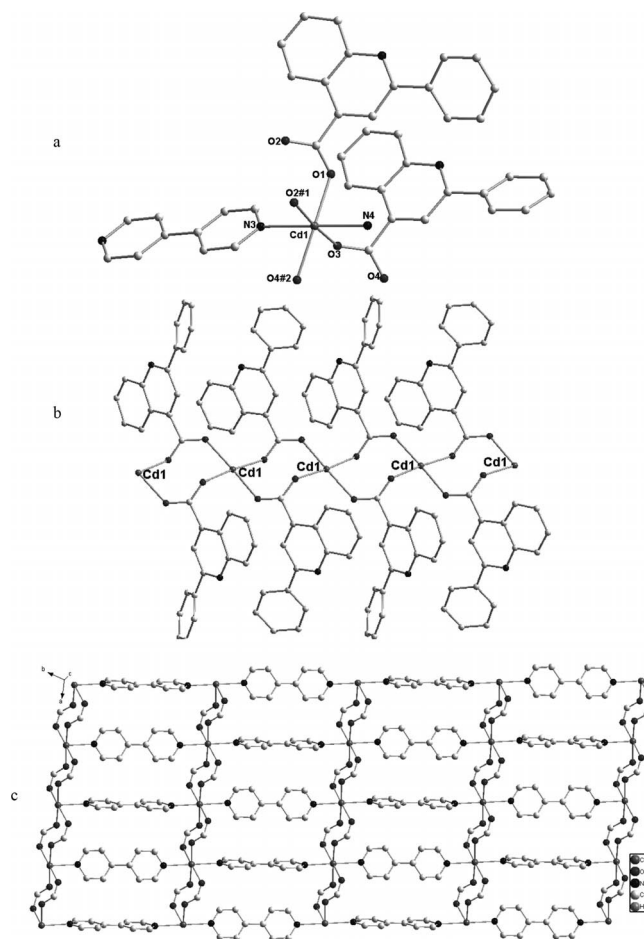
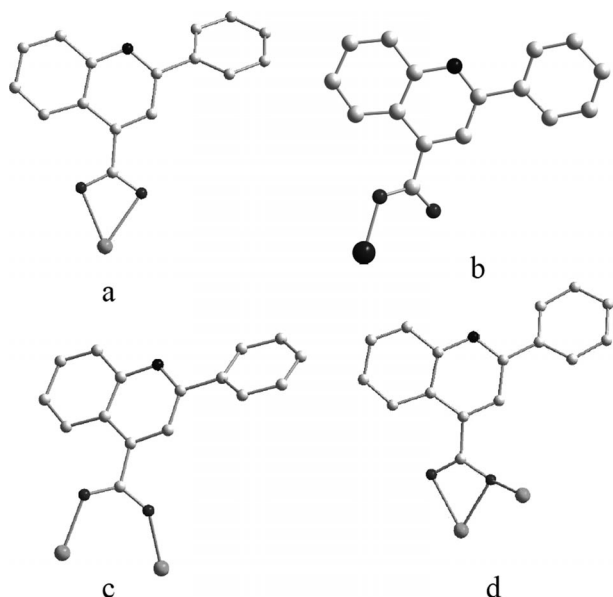


Figure 1. (a) Coordination environment of the Cd^{II} ion in **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1: 2–x, 2–y, 1–z; #2: 1–x, 2–y, 1–z. (b) View of 1D chain constructed by carboxylate along the *a* axis of **1**. (c) View of 2D framework by 4,4'-bipy along the *b* axis of **1**. The pqba anions are omitted for clarity.

dimensional infinite chains along the *a* axis with a Cd1 \cdots Cd1 separation of 4.917(4) and 4.982 Å (Figure 1b). The eight-



Scheme 1. The coordination mode of the pqba ligand.

membered ring, $[\text{Cd}_2(\mu_2\text{-CO}_2)_2]$ with the angles of two O–C–O are 125.74° and 126.47° , is formed between in the one-dimensional chain. These one-dimensional chains and the lin-

ear 4,4'-bipy ligand form the 2D coordination network, as shown in Figure 1c. The 4,4'-bipy molecule adopts a bis(monodentate) coordination mode to bridge two central cadmium atoms. This is particularly mentioned that two 4,4'-bipy molecules of linking metal cadmium are not in the same plane, and the angle between the two planes is 63.2° (Figure S2b, Supporting Information).

Crystal Structure of $[\text{Zn}(\text{pqba})_2\text{biyb}]$ (**2**)

X-ray single-crystal diffraction reveals that complex **2** has a 1D coordination polymer, which expand 3D supramolecules via strong $\pi\cdots\pi$ stacking interactions. Complex **2** crystallized in the monoclinic $C2/c$ space group. As shown in Figure 2a, each asymmetric unit contains of one Zn^{2+} ions, two pqba anionic ligands, and one biyb ligand. Zn1 is four-coordinated by two carboxylate oxygen atoms (O1, O1#1) from two pqba ligands and two nitrogen atoms (N2, N2#1) from two biyb ligands to form a slight distorted tetrahedral arrangement. The bond lengths of Zn–N/O are in the range from 1.942(3) to 2.000(3) Å, and the O–Zn–O(N) angles around the central ions vary from $93.73(17)^\circ$ to $117.27(13)^\circ$. The selected interatomic distances and angles are listed in Table 2, which are closely similar to those observed in four-coordinate zinc complexes with oxygen donor and nitrogen donor ligands.^[8]

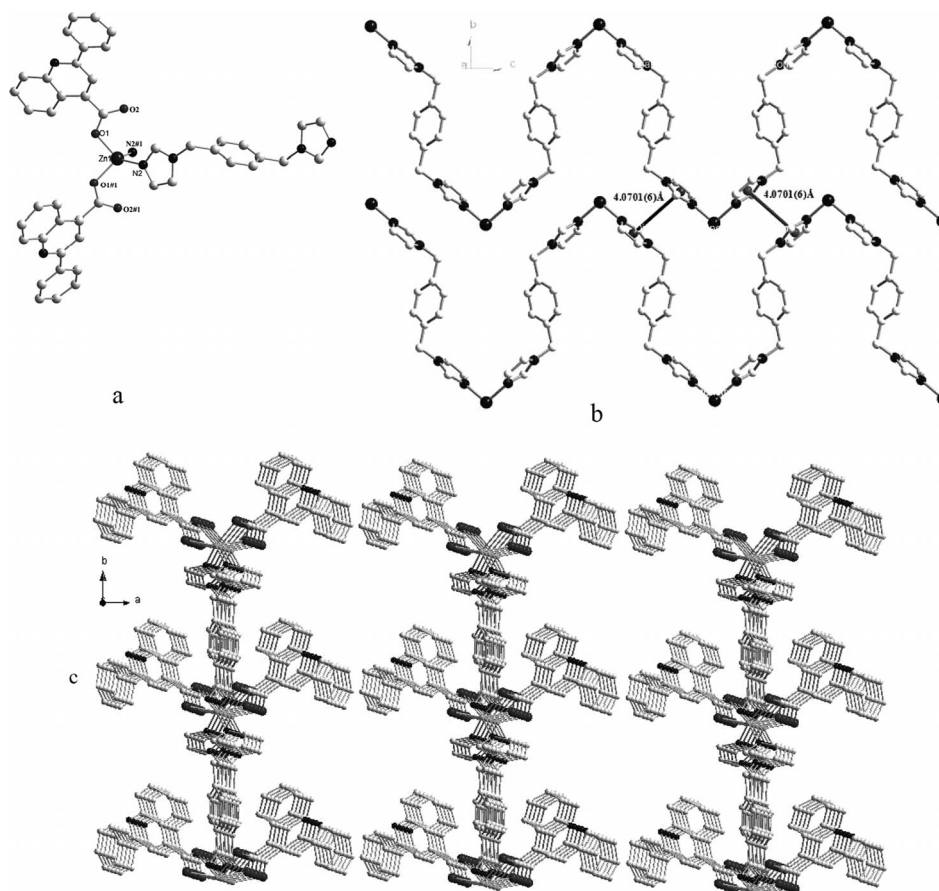


Figure 2. (a) Coordination environment of the Zn^{II} ion in **2**. Hydrogen atoms are omitted for clarity. Symmetry codes: #1: $-x, y, 1.5-z$. (b) View of 1D chain constructed by biyb ligand along the c axis and 2D supramolecular structure by π - π stacking interactions along the b axis of **2**. (c) View of 3D supramolecular structure by π - π stacking interactions along the a axis.

There is only one unique kind of coordination mode of the pqba ligand in compound **2**, the carboxylic oxygen atom of the pqba ligand is coordinated with Zn^{II} by μ_1-k^1 mode (Scheme 1b). The pqba ligand contributes to coordination number around each metal ion. If the pqba ligand is omitted, as shown in Figure 2b, compound **2** forms a one-dimensional zigzag chains structure along the c axis through biyb ligand coordinated zinc(II) ions with a $\text{Zn}\cdots\text{Zn}$ distance of 14.630 Å. In one-dimensional chains, the pqba ligands seem to act as “wings”, whereas the biyb and Zn^{II} acts as “trunk”, thus, they compose a butterfly-like structure (Figure S3a, Supporting Information). In **2**, there are $\pi\cdots\pi$ stacking interactions (centroid \cdots centroid distances: 4.071 Å, centroid \cdots plane distances: 3.490 Å) between two adjacent 1D zigzag chains, whose interaction changes the framework from 1D zigzag chains to 2D structure in the bc plane (Figure 2c). Further, strong $\pi\cdots\pi$ stacking interaction (centroid \cdots centroid distances: 3.639 Å, centroid \cdots plane distances: 3.365 Å) (Figure S3b, Supporting Information) exists between adjacent 2D structure, and it plays important roles in the assembly process of the 3D supramolecular architecture (Figure 2c).

Crystal Structure of $[\text{Co}_3(\text{pqba})_6(2,2'\text{-bipy})_2]$ (**3**)

Compound **3** is engaged in the formation of π - π stacking interaction between the mononuclear units leading to the construction of the three-dimensional supramolecules. X-ray analysis reveals that compound **3** crystallizes in the triclinic $P\bar{1}$ space group. As shown in Figure 3a, compound **3** consists of one and a half Co^{II} ions, three pqba anionic ligands, and a 2,2'-bipy ligand. The six-coordinate Co1(II) adopts distorted $[\text{CoO}_4\text{N}_2]$ octahedron arrangement, where four oxygen atoms come from three different pqba anionic ligands [Co1–O3: 2.012(2) Å, Co1–O2: 2.062(3) Å, Co1–O5: 2.157(2) Å, and Co1–O6: 2.214(3) Å], two nitrogen atoms are from one 2,2'-bipy molecule [Co1–N5: 2.094(3) Å, Co1–N4: 2.146(3) Å], which O5 and N5 atoms are in the equatorial positions. The Co2 is also distorted $[\text{CoO}_6]$ octahedrally coordinated, bound to six oxygen atoms from six pqba anions, where the O1 and O1#1 atoms are in the equatorial positions. The bond lengths of Co2–O are 2.063(2), 2.063(2), 2.121(2), 2.121(2), 2.065(2), 2.065(2) Å, respectively. The selected interatomic distances and angles for **3** are listed in Table 2. All bond lengths and angles are comparable to those observed in other Co^{II} complexes.^[9]

The pqba anionic ligands adopt two coordination modes: one is μ_2-k^1, k^1 coordination mode to bridge two central cobalt atoms, another is μ_2-k^1, k^2 mode connecting with two cations (Scheme 1a and d). The linear trinuclear cobalt cluster unit $[\text{Co}_3(\text{pqba})_6\text{bipy}_2]$ is formed, which is centrosymmetric through the connection of two $\mu_2\text{-CO}_2$ and two $\mu_2\text{-CO}_2$. The angle of Co1–Co2–Co1#1 is 180.00° and a Co \cdots Co separation is 3.459 Å in the trinuclear basic unit. Each trinuclear basic unit is connected by $\pi\cdots\pi$ stacking interaction (Figure S4a–c, Supporting Information) to form a 3D supramolecular architecture (Figure 3b). The interplanar and centroid \cdots centroid distances are 3.9159 Å and 3.9772 Å along the c axis, 3.4062

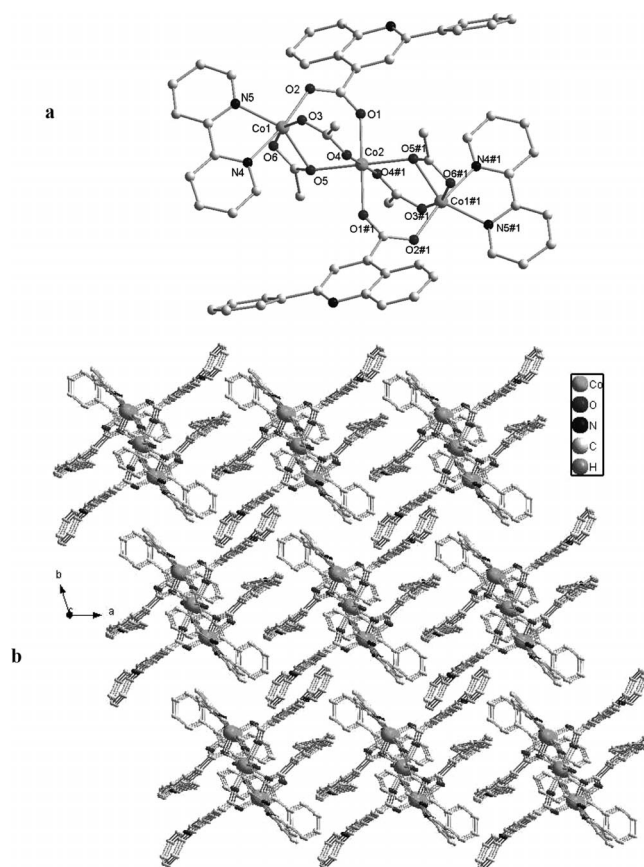


Figure 3. (a) Schematic description of the Co_3 unit and its coordination environment in **3**. The hydrogen and part of the carbon atoms are omitted for clarity. Symmetry codes: #1: 1– x , 1– y , 1– z . (b) The 3D supramolecular structure by π - π stacking interactions of **3**.

and 3.5176 Å along the a axis, and 3.9159 Å, 3.7322 Å, and 3.9771 Å, 4.3737 Å along the b axis, respectively. $\pi\cdots\pi$ Stacking interactions can be viewed as medium to strong if they exhibit rather short centroid \cdots centroid distances (<3.8 Å) together with large slip angles (β , $\gamma < 25^\circ$) and vertical displacements ($d < 1.5$ Å). In comparison, weak $\pi\cdots\pi$ stackings show rather short centroid \cdots centroid contacts (>4.0 Å), small slip angles (β , $\gamma > 30^\circ$) and vertical displacements ($d > 2.0$ Å), which translate into a sizeable overlap of the aromatic planes.^[10] Obviously, these $\pi\cdots\pi$ stacking interactions increase the stability of the whole crystal structure of **3**.

PXRD and TG Results

The purity of compounds **1–3** is confirmed by powder PXRD analyses. The PXRD experimental and computer-simulated patterns of the corresponding complexes are shown in the Supporting Information (Figures S5), in which the main peaks of the experimental spectra of **1–3** are almost consistent with its simulated spectra.

In order to estimate the stability of the frameworks, thermal gravimetric analysis (TG) of **1–3** was carried out from 30 °C to 900 °C in a nitrogen atmosphere (Figure S6, Supporting Information). Complexes **1–3** show similar thermal behaviors.

For compound **1**, it reveals that a continuous weight loss of 64.7% occurs from 255 to 420 °C, which can be attributed to the release of pqba anion (calcd. 64.9%). Further, the second weight loss from 430 to 700 °C is attributed to the release of 4,4'-bipy molecule. The remaining residue corresponds to the formation of CdO (obsd. 16.5%; calcd. 16.8%). For **2**, the first weight loss in the temperature range of 275–470 °C is consistent with the removal of pqba anion (obsd 61.6%; calcd. 62.1%). The second weight loss from 510 to 720 °C is attributed to the collapse of the bipy molecule. The remaining residue corresponds to the formation of ZnO (obsd 10.7%; calcd. 10.2%). For **3**, the first weight loss in the temperature range of 180–380 °C is consistent with the removal of the pqba anion (obsd 75.4%; calcd. 75.3%). The second weight loss from 380 to 620 °C is attributed to the collapse of the 2,2'-bipy molecule. The remaining residue corresponds to the formation of CoO (obsd 11.7%; calcd. 11.4%).

Luminescence Properties of **1** and **2**

The luminescence properties of the free ligand Hpqba, and complexes **1** and **2**, are investigated in the solid state at room temperature, as shown in Figure 4. These compounds exhibit strong emission with a broad band. Emission bands are observed at 410 nm ($\lambda_{\text{ex}} = 380$ nm) for **1**, 440 nm ($\lambda_{\text{ex}} = 380$ nm) for **2**, and 505 nm (the intense emission at 415 nm, which is

attributed to the $\pi^* \rightarrow \pi$ transition) for the Hpqba ligand, respectively. Compared with the emission spectra of the Hpqba ligand, compounds **1** and **2** are all blue-shifted, and the emission peaks of complexes **1** and **2** are blue-shifted 95 and 65 nm, respectively. It is well-known that both zinc and cadmium ions are difficult to be oxidized or reduced, owing to their stable d^{10} configurations. As a result, the observed emissions of **1** and **2** can probably be attributed to the intraligand fluorescent emission of Hpqba, which is modified by metal coordination.^[11] Both **1** and **2** may be suitable as excellent candidates of fluorescent materials.

Magnetic Properties of **3**

Complex **3** containing 3d magnetic metal ions (Co), so their magnetic properties should be interesting to be investigated. The magnetic measurements were performed on polycrystalline samples of **3** using a MPMS-XL-7 magnetometer under an applied field of 1000 Oe in the temperature range of 1.8–300 K. At room temperature, magnetic susceptibility data per Co³⁺ unit for **1** shows a $\chi_M T$ value of $8.51 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ (Figure 5), which is much higher than the spin only value of three high-spin Co^{II} ion ($5.63 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, $S = 3/2$, $g = 2.0$), due to significant orbital contribution.^[12] The $\chi_M T$ value of polymer **3** decreases with decreasing temperature down to a minimum value of $2.77 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2 K, which indicates an intracul-

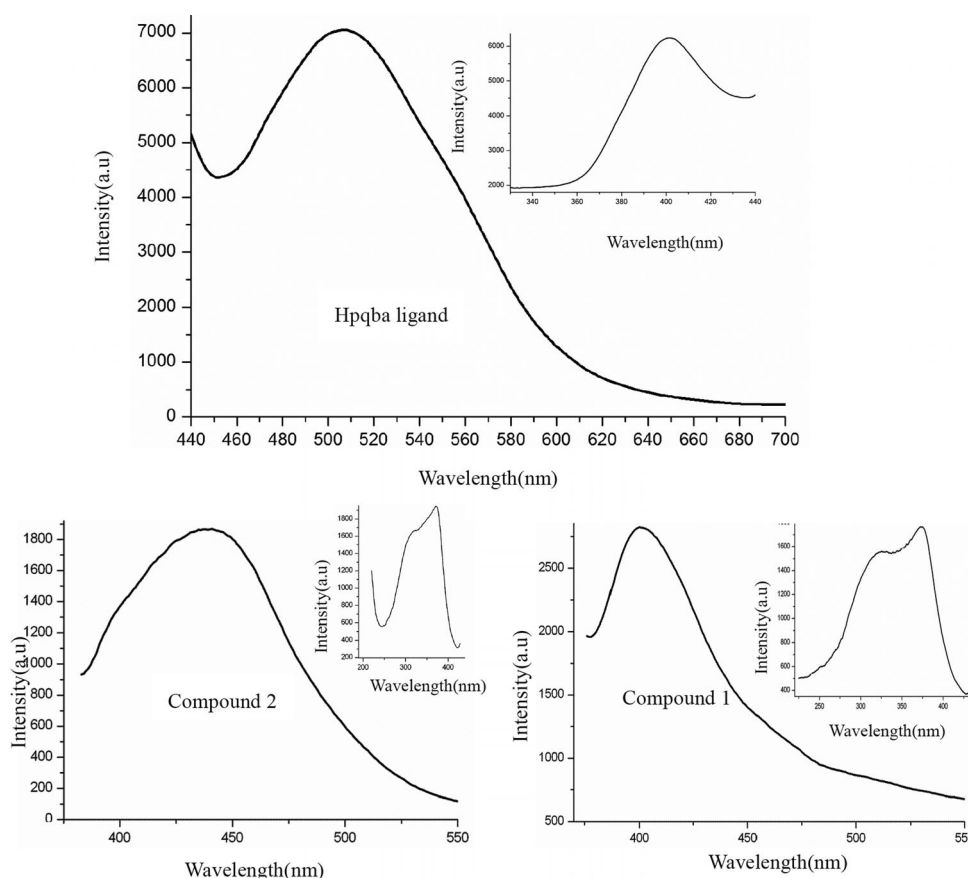


Figure 4. Fluorescence properties of Hpqba ligand and complexes **1** and **2** in solid state at room temperature.

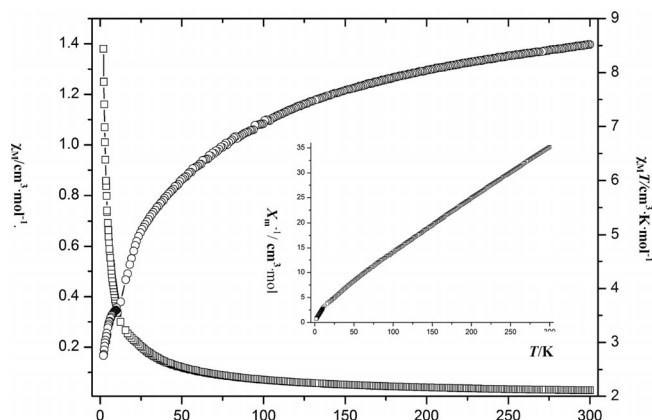


Figure 5. Temperature dependence of magnetic susceptibility in the form $\chi_M T$, χ_M and $1/\chi_M T$ (inset) for complex **3**.

ter antiferromagnetic interaction between the Co^{II} ions through the carboxyl oxygen bridges.^[13] The data of $1/\chi_M$ vs. T give straight lines over 30 K, and can be fitted by the Curie-Weiss law [$\chi_M = C/(T-\theta)$] in the range of 30–300 K giving the parameters $C = 9.28 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and $\theta = -29.78 \text{ K}$. The negative value of θ further confirmed the presence of dominant antiferromagnetic behavior at experiment temperature region.^[14] Co^{II} ions were bridged through carboxylic oxygen bridge, therefore, the overall antiferromagnetic interaction should be mainly attributed to the $\mu_2\text{-CO}_2$ bridge in trinuclear cobalt unit for **3**.

Conclusions

Three new complexes [$\text{Cd}(\text{pqba})_2(4,4'\text{-bipy})$] (**1**), [$\text{Zn}(\text{pqba})_2(\text{biyb})$] (**2**), and [$\text{Co}_3(\text{pqba})_6(2,2'\text{-bipy})_2$] (**3**) were synthesized by self-assembly reactions of pqba anion ligands, 4,4'-bipy, 2,2'-bipy, or biyb neutral ligands, and Cd^{II} , Co^{II} , Zn^{II} system. The pqba ligand with unusual coordination modes, neutral ligands, and metal ions common control the dimensional architectures and properties of complexes **1–3**. Especially, photoluminescence measurements indicate that the compounds **1** and **2** show strong luminescence. The temperature dependence of magnetic susceptibilities was studied, and antiferromagnetic was observed for compound **3**. It is believed that the presented results of complexes **1–3** provide new information regarding synthetic strategy, luminescence, and magnetic chemistry.

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