



# Assembly of novel phenanthroline-based cobalt(II) coordination polymers by selecting dicarboxylate ligands with different spacer length: From 1-D chain to 3-D interpenetrated framework

Xiu-Li Wang\*, Yong-Qiang Chen, Guo-Cheng Liu, Hong-Yan Lin, Wen-Yan Zheng, Jin-Xia Zhang

Faculty of Chemistry and Chemical Engineering, Bohai University, Liaoning, Jinzhou 121000, PR China

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## ABSTRACT

Three novel Co<sup>II</sup> coordination polymers [Co(Dpq)<sub>2</sub>(1,4-NDC)<sub>0.5</sub>] · (1,4-HNDC) (**1**), [Co(Dpq)(2,6-NDC)] (**2**), and [Co<sub>2</sub>(Dpq)<sub>2</sub>(BPEA)<sub>4</sub>(H<sub>2</sub>O)] · H<sub>2</sub>O (**3**) have been obtained from hydrothermal reaction of cobalt nitrate with the mixed ligands dipyrido[3,2-d:2',3'-f]quinoxaline (Dpq) and three dicarboxylate ligands with different spacer length [1,4-naphthalene-dicarboxylic acid (1,4-H<sub>2</sub>NDC), 2,6-naphthalene-dicarboxylic acid (2,6-H<sub>2</sub>NDC) and biphenylethene-4,4'-dicarboxylic acid (BPEA)]. All these complexes are fully structurally characterized by elemental analysis, IR, and single-crystal X-ray diffraction analysis. Single-crystal X-ray analysis reveal that complex **1** is infinite one-dimensional (1-D) chains bridged by 1,4-NDC ligands, which are extended into a two-dimensional (2-D) supramolecular network by π–π interactions between the Dpq molecules. Complex **2** is a distorted three-dimensional (3-D) PtS network constructed from infinite Co–O–C rod units. Complex **3** has a 5-fold interpenetrated 3-D structure with diamondoid topology based on dinuclear [Co<sub>2</sub>(CO<sub>2</sub>)<sub>2</sub>(μ<sub>2</sub>-OH<sub>2</sub>)N<sub>4</sub>O<sub>2</sub>] units and BPEA molecules. The different structures of complexes **1–3** illustrate the influence of the length of dicarboxylate ligands on the self-assembly of polymeric coordination architectures. In addition, the thermal properties of complexes **1–3** and fluorescent properties of complexes **2** and **3** have been investigated in the solid state.

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## 1. Introduction

Over the past few decades, the rational design and synthesis of metal–organic hybrid coordination polymers have undergone tremendous development [1,2], and particularly the chemistry of transition metal carboxylate system has been a rapidly expanding research field due to their fascinating structural diversities as well as their potential in diverse applications such as small molecular shape-selective adsorption and separation, catalysis, luminescence, and nonlinear optics [3–5]. Among the reported works of metal carboxylate hybrids, various carboxylic acids have been used, for example, aliphatic, aromatic, and heterocyclic acids [6–11]. On the other hand, 1,10-phenanthroline and their analogues have been used as a kind of good N-donor chelate ligands to construct metal–organic frameworks (MOFs) [12,13]. As far as we know, the studies of coordination polymers based on dipyrido[3,2-d:2',3'-f]quinoxaline (Dpq) are limited [14–16], especially in the presence of naphthalene-dicarboxylic acid as the coligand.

Recently, we focus our attention on the study of the inorganic–organic hybrids constructed from 1,10-phenanthroline-

based analogues and carboxylate mixed ligands and have obtained various hybrids with interesting structures and properties [17–20]. In the present study, we chose three O-donor aromatic dicarboxylate ligands, 1,4-naphthalene-dicarboxylic acid (1,4-H<sub>2</sub>NDC), 2,6-naphthalene-dicarboxylic acid (2,6-H<sub>2</sub>NDC), biphenylethene-4,4'-dicarboxylic acid (BPEA) and Dpq as the mixed ligands based on the following considerations: (a) the carboxylate oxygen can bridge metal centers to construct multidimensional systems [21,3,22–24]; (b) the spacer length of ligands has influence on the structure of complexes. As a kind of long O-donor aromatic dicarboxylate ligand, biphenylethene-4,4'-dicarboxylic acid has been regarded as a good candidate to construct interpenetrated MOFs [25]; (c) compared with 1,10-phenanthroline, Dpq has the larger aromatic-ring system and may provide potential supramolecular recognition sites for π–π interactions [17].

In this article, we report the syntheses, structures and properties of three novel Co<sup>II</sup> coordination polymers, namely, [Co(Dpq)<sub>2</sub>(1,4-NDC)<sub>0.5</sub>] · (1,4-HNDC) (**1**), [Co(Dpq)(2,6-NDC)] (**2**) and [Co<sub>2</sub>(Dpq)<sub>2</sub>(BPEA)<sub>4</sub>(H<sub>2</sub>O)] · H<sub>2</sub>O (**3**). Complex **1** is infinite one-dimensional (1-D) chains bridged by 1,4-NDC ligand, which are extended into a two-dimensional (2-D) supramolecular layer by π–π interactions. Complexes **2** and **3** have a distorted three-dimensional (3-D) PtS network and a 5-fold interpenetrated 3-D framework with diamondoid topology, respectively. Moreover, the

\* Corresponding author. Tel.: +86 416 3400158.

E-mail address: [wangxiuli@bhu.edu.cn](mailto:wangxiuli@bhu.edu.cn) (X.-L. Wang).

thermal properties of complexes **1–3** and fluorescent properties of complexes **2** and **3** have been investigated in the solid state.

## 2. Results and discussion

### 2.1. Description of the structures

#### 2.1.1. $[\text{Co}(\text{Dpq})_2(1,4\text{-NDC})_{0.5}] \cdot (1,4\text{-HNDC})$ (**1**)

Single-crystal X-ray analysis shows that complex **1** exhibits a 1-D linear chain. The coordination environment of  $\text{Co}^{\text{II}}$  ion is shown in Fig. 1. The repeating unit of complex **1** consists of two  $\text{Co}^{\text{II}}$  ions [Co(1), Co(1A)], four Dpq molecules and one 1,4-NDC ion. Each  $\text{Co}^{\text{II}}$  ion is coordinated in a distorted octahedral geometry by four nitrogen atoms of two Dpq molecules with normal Co–N distances from 2.132(4) to 2.180(4) Å, and two oxygen atoms from different 1,4-NDC with Co–O distances are 2.064(3) and 2.078(3) Å, respectively. Two such  $\text{Co}^{\text{II}}$  ions are connected by two carboxylate groups of different 1,4-NDC to form dinuclear units  $[\text{Co}_2(\text{CO}_2)_2\text{N}_8]^{2+}$  with the Co(1)··Co(1A) distance of 4.607 Å (the distance between the cores of adjacent dinuclear units is 9.637 Å). The dinuclear units are linked by 1,4-NDC of which the two carboxyl groups all adopt bidentate coordination model to form 1-D chains, which are further extended into a 2-D supramolecular architecture by intermolecular  $\pi$ – $\pi$  interactions (Fig. 2). The face-to-face distance between Dpq ligands is 3.726 Å (the dihedral angle is 3.79°).

Interestingly, there exist non-coordinated 1,4-HNDC guest molecules in complex **1**, which form a 1-D supramolecular chain by hydrogen bonding interactions  $[\text{O}(3)\text{---H}\cdots\text{O}(6)]$ , 2.476 Å, 166.66°, as shown in Fig. 3.

#### 2.1.2. $[\text{Co}(\text{Dpq})(2,6\text{-NDC})]$ (**2**)

Single-crystal X-ray analysis shows that complex **2** is a 3-D coordination polymer with a PtS topology structure. The  $\text{Co}^{\text{II}}$  ion is six-coordinated by four oxygen atoms of carboxyl groups from four different 2,6-NDC ligands (Co–O bond distances are ranging from 2.051(2) to 2.137(2) Å) and two nitrogen atoms from a chelating Dpq ligand (Co–N 2.166(2) Å) exhibiting a slightly distorted octahedral geometry [the bond angles are from 76.31(1) to 167.25(1)°] (Fig. 4). Two carboxyl groups of 2,6-NDC ligand adopt bridging bis-bidentate coordination modes, which results in infinite Co–O–C rods second building units (SBUs) running along the (001) direction, with Co··Co distance of 4.550 Å (Fig. 5a). The rods are linked to four neighboring rods by the 2,6-NDC arms and extended into 3-D structure (Fig. 5b). Moreover, there exist 1-D supramolecular Dpq arrays through offset face-to-face  $\pi$ – $\pi$  interactions, which may prohibit the interpenetration of 3-D framework by steric hindrance. Considering each six-coordinated  $\text{Co}^{\text{II}}$  ion as a

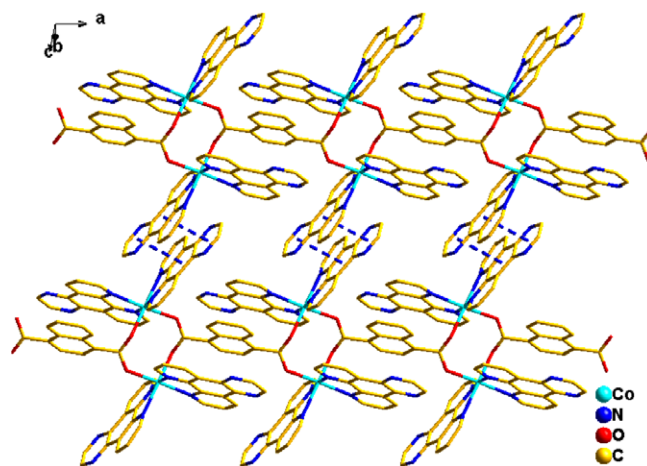


Fig. 2. 2-D supramolecular layer of **1** formed by  $\pi$ – $\pi$  stacking interactions (H atoms are omitted for clarity).

tetrahedral node, and every 2,6-NDC ligand as square planar node, the whole structure of complex **2** can be considered to be a PtS network (Fig. 6). There are some examples of the interpenetrated PtS nets [25–27], whereas complex **2** is the first example of  $\text{Co}^{\text{II}}$  complex with distorted PtS topology constructed from bpy-like chelating ligands and naphthalene-dicarboxylate ligands.

#### 2.1.3. $[\text{Co}_2(\text{Dpq})_2(\text{BPEA})_4(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**3**)

Single-crystal X-ray structural analysis reveals that complex **3** contains two crystallographically independent cobalt ions [Co(1) and Co(2)]. Each  $\text{Co}^{\text{II}}$  ion in the dinuclear motif is coordinated by two nitrogen atoms of Dpq with normal Co–N distances [from 2.157(2) to 2.177(3) Å], three oxygen atoms from three different BPEA ligands with the Co–O distances of 2.049(2)–2.098(2) Å, and one oxygen atom of water molecule with Co–O distances of 2.157(2) Å [Co(1)–O(9)] and 2.089(2) Å [Co(2)–O(9)], respectively (Fig. 7). The dinuclear cobalt clusters bridged by two  $\mu$ -carboxylic groups and a  $\mu_2$ -water molecule constitute a SBU  $[\text{Co}_2(\text{CO}_2)_2(\mu_2\text{-OH}_2)\text{N}_4\text{O}_2]$ , with Co1··O1··Co2 angle of 113.72(1)° and non-bonding Co1··Co2 distance of 3.555 Å. Moreover, the adjacent SBUs are connected by BPEA ligands with two different kinds of coordination modes [bridging bis(bidentate) and bridging bis(monodentate)] to generate a single cage delimited by four cyclohexane-like windows in chair conformation (Fig. 8a), and the distance is 17.480 Å between two cores of SBUs linked by bridging bis(bidentate) BPEA, and 19.754 Å between two cores of SBUs connected by bridging bis(monodentate) BPEA, respectively. The topological analysis of complex **3** reveals that it is a typically diamondoid framework containing large adamantanoid cages (Fig. 8b).

The large amount of empty space within a single diamondoid lattice allows for the mutual interpenetration of five identical frameworks within the crystal structure (Fig. 8c), which were analyzed by TOPOS software [28,29]. The interpenetration within the structure of complex **3** belongs to Class Ia (translation only) with Full Interpenetration Vectors [30].

In this work, we select three dicarboxylate ligands with different spacer length, (1,4-H<sub>2</sub>NDC, 2,6-H<sub>2</sub>NDC, BPEA) intending to observe the spacer effect on the assembly of the MOFs. The effects of the dicarboxylate ligands on the structures of complexes **1–3** have been clearly demonstrated. In complex **1**, the short spacer length between the two carboxylate groups (about 5.846 Å for the C··C distance) makes it possible for the 1,4-NDC ligand to bridge two  $\text{Co}^{\text{II}}$  ions to form a very stable dinuclear units  $[\text{Co}_2(\text{CO}_2)_2\text{N}_8]^{2+}$ . Clearly, the short spacer length between the two carboxylate

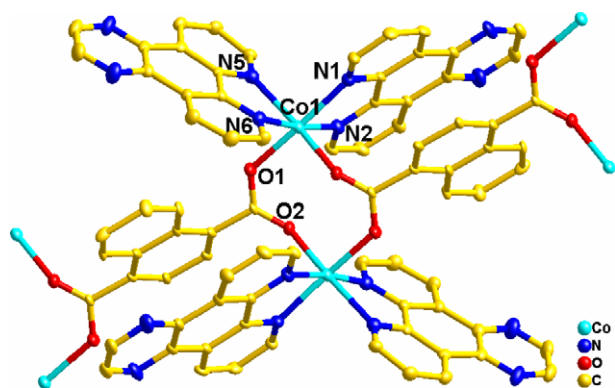
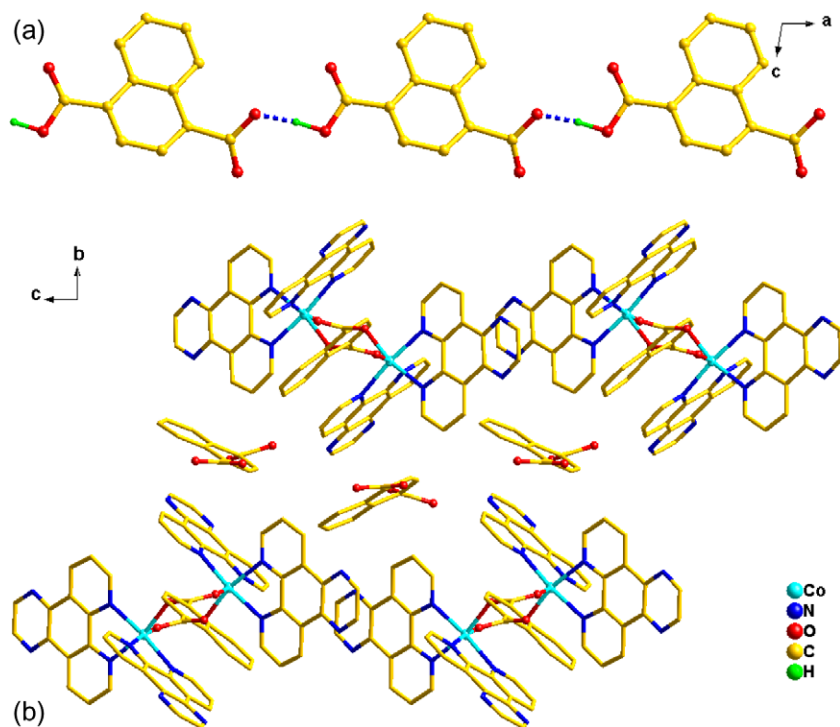
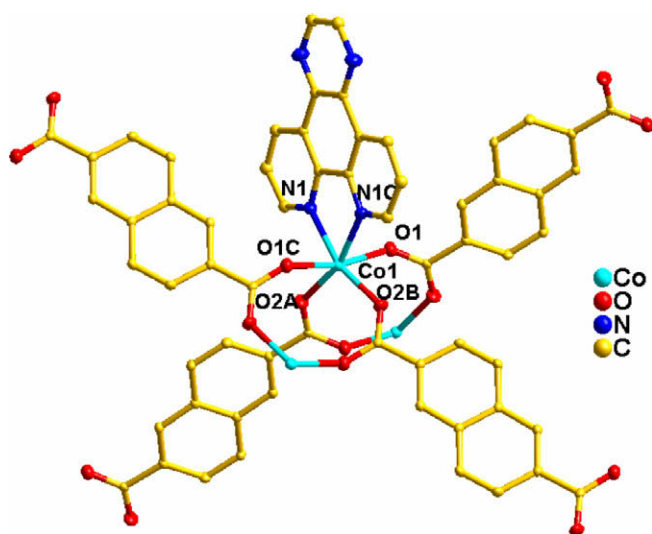


Fig. 1. View of the coordination environment in **1** of ORTEP drawing with 30% probability thermal ellipsoids (H atoms are omitted for clarity).



**Fig. 3.** (a) 1-D 1,4-HNDC chain formed by hydrogen bonding interactions in **1**; (b) a perspective view of the packing along the *a*-axis in complex **1**, showing the free 1,4-HNDC chain lying in the interlayer regions.



**Fig. 4.** View of the coordination environment in complex **2** of ORTEP drawing with 30% probability thermal ellipsoids (H atoms are omitted for clarity).

groups of 1,4-NDC ligand helps the formation of 1-D chains. As an isomer, 2,6-H<sub>2</sub>NDC possesses the longer spacer than 1,4-H<sub>2</sub>NDC ligand (about 8.071 Å for the C...C distance between the two carboxylate groups). In complex **2**, two carboxyl groups of 2,6-NDC ligand adopt bridging bis-bidentate coordination modes, leading to a 3-D PtS net structure. In contrast with naphthalene-dicarboxylic acid ligands, the BPEA ligand shows relatively flexible coordination properties due to the presence of a  $-(CH=CH)-$  spacer. Generally, longer ligands will lead to larger voids. It therefore has more flexibility and conformational freedom. This feature allows that the BPEA molecules may have two different kinds of coordination modes to connect [Co<sub>2</sub>(CO<sub>2</sub>)<sub>2</sub>(μ<sub>2</sub>-OH<sub>2</sub>)N<sub>4</sub>O<sub>2</sub>] SBUs, leading to a 5-fold interpenetrating diamondoid topology in complex **3**.

## 2.2. Infrared spectra

The IR spectra of complexes **1–3** are shown in Figs. S1–S3 (Supplementary material), respectively. The bands at about 786 and 742 cm<sup>-1</sup> may be attributed to the ν<sub>C–N</sub> stretching of the pyrazinyl ring or pyridyl ring [17]. For complex **1**, the asymmetric and symmetric vibrations of carboxylate groups appeared at 1543, 1473 and 1396 cm<sup>-1</sup>, respectively. The expected characteristic band at 1689 cm<sup>-1</sup> for the protonated carboxylate groups also appeared in the complex **1** [25]. For complex **2**, its characteristic bands of the carboxylate groups are shown at 1635 cm<sup>-1</sup> for asymmetric vibrations and at 1381 cm<sup>-1</sup> for symmetric vibrations. The Δ value is 241 cm<sup>-1</sup>, which indicates that the carboxylate groups adopt bridging bis-bidentate coordination modes [31,32]. In complex **3**, the characteristic bands of the carboxylate groups are shown at 1597 cm<sup>-1</sup> for the asymmetric vibrations and at 1419 cm<sup>-1</sup> for the symmetric vibrations. The Δ value is 177 cm<sup>-1</sup>. The separation of Δ value indicates that the carboxylate groups adopt chelating bis-bidentate coordination modes [25].

## 2.3. Thermogravimetric analysis

The decomposition behaviors of complexes **1–3** were examined by thermogravimetric analysis (TGA) with a heating rate of 10 °C/min in the temperature 25–600 °C, as shown in Fig. 9. For complex **1**, TGA shows that chemical decomposition starts at 310 °C and ends at 446 °C with the weight loss of 91.38%, equivalent to the loss of organic ligands (calcd. 91.11%); the remaining weight corresponds to CoO. The decomposition of complex **2** was similar to that of complex **1**, but showed higher thermal stability. Here mass decrease began at 420 °C; a rapid mass loss was complete by 506 °C, which corresponds to the loss of 85.70% (calcd. 85.21%). The TGA trace of complex **3** exhibits two main steps of weight losses. The first step started at 272 °C and completed at 304 °C, which corresponds to the release of lattice water molecules. The observed



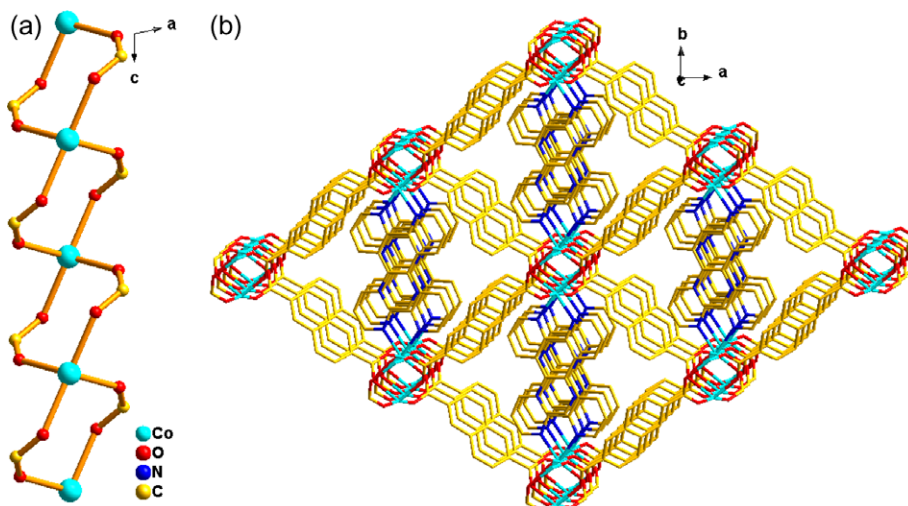


Fig. 5. (a) Infinite Co–O–C rod-like SBUs in **2**; (b) view of the 3-D network in **2**.

weight loss of 0.76% is close to the calculated values 0.79%. The second step covers from 353 to 471 °C, during which the organic ligands are burned, the weight loss of 85.92% (calcd. 86.03%), the remaining weight corresponds to CoO.

#### 2.4. Photoluminescence properties

In order to investigate the photoluminescence properties of the bulk materials, fluorescence spectra were performed for complexes **2** and **3** on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer at room temperature, as shown in Fig. 10. Complex **1** does not exhibit obvious emission peak. Free Dpq ligand fluoresces in solid state with two main emission peaks at 436 nm and 562 nm upon excitation at 360 nm [17]. The main emission band was located at 467 nm ( $\lambda_{\text{ex}} = 298$  nm) for **2**. Comparing with

the emission of the free ligand Dpq, red-shift of ca. 31 nm has been observed in **2**. As previously reported [33,34], solid state aromatic dicarboxylate ligands can also exhibit fluorescence at room temperature and the emission bands of these ligands can be assigned to the  $\pi^* \rightarrow n$  transition, which is very weak compared with that of the  $\pi^* \rightarrow \pi$  transition of the Dpq ligand [35,36], so the main emission band of **2** would be assigned to  $\pi^* \rightarrow \pi$  transition of coordinated Dpq ligand. The red-shift emission peak may be related to the intraligand fluorescent emission [37,38]. Complex **3** shows an emission with a maximum at ca. 465 nm upon excitation at 300 nm. The emission peak position of **3** is similar to that of complex **2** that also can be attributed to intraligand fluorescent emission. The different emission intensity of complexes **2** and **3** may be caused by the coordination model of aromatic dicarboxylate ligands and the coordination environment of metal center [34,39].

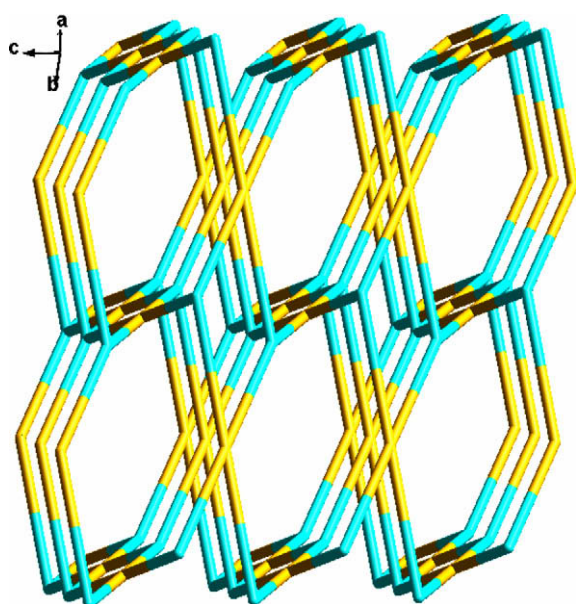


Fig. 6. 3-D PtS topology of complex **2** (every Co atom as tetrahedral node in blue and every 2,6-NDC as square planar node in yellow). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

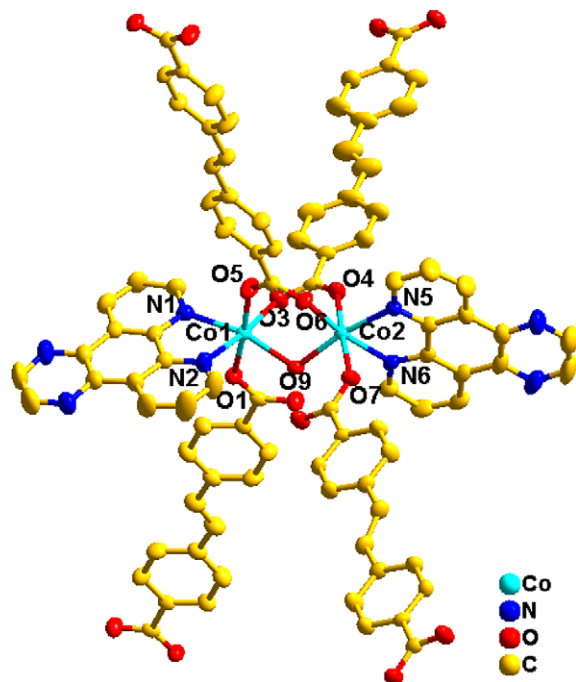
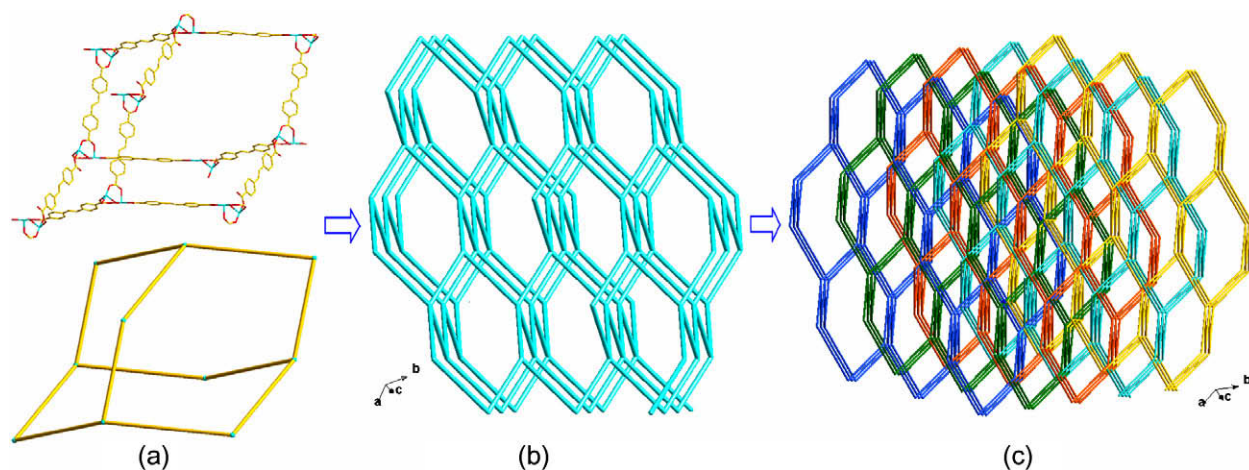
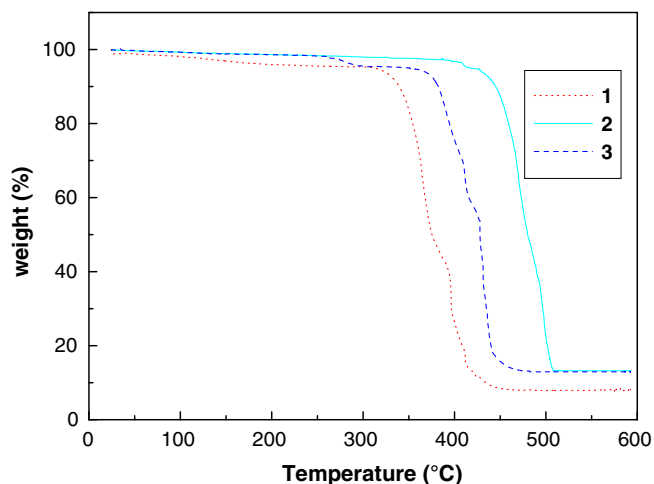


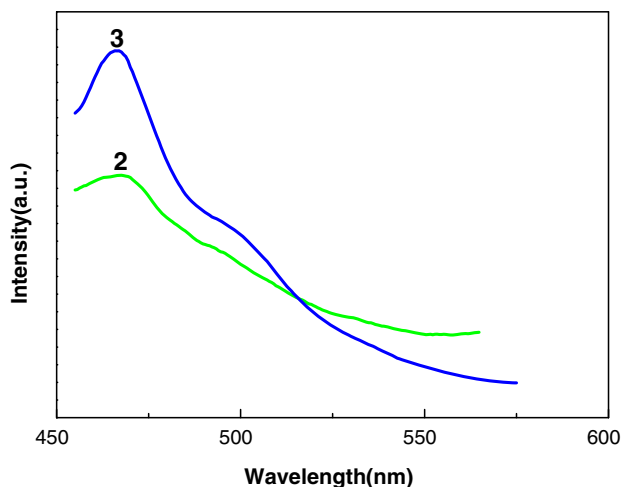
Fig. 7. View of the coordination environment in **3** of ORTEP drawing with 30% probability thermal ellipsoids (H atoms are omitted for clarity).



**Fig. 8.** (a) Single adamantanoid cage in **3**; (b) the schematic view of a single diamond-like framework in **3**; (c) view of the full 5-fold interpenetrated framework in complex **3**. Individual networks are displayed in different colors, and ligands are represented by straight lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 9.** Thermogravimetric curves for complexes **1–3**.



**Fig. 10.** Fluorescence spectra for complexes **2** and **3** in the solid state at room temperature.

### 3. Conclusion

In summary, using three dicarboxylate ligands with different spacer length, we successfully obtained three novel metal–organic complexes under hydrothermal conditions. The structural analysis show that the longer the spacer length of the ligands, the higher is the dimensionality for complexes **1–3**, that is, the 1-D linear chain structure for complex **1**, the 3-D PtS network structure for complex **2**, and 5-fold interpenetrated diamondoid lattices for complex **3**. The successful isolation of the three species demonstrates that the use of different length of dicarboxylate ligands and large aromatic ligands opens a promising route for the construction of novel complex structures, a goal we are actively pursuing.

### 4. Experimental

#### 4.1. Materials and instrumentation

All chemicals purchased were of reagent grade and used without further purification. Dpq was synthesized by the methods of the literature [40] and characterized by FT-IR spectra and  $^1\text{H}$  NMR. FT-IR spectra (KBr pellets) were taken on a Magna FT-IR 560 spectrometer. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 240C analyzer. Thermogravimetric data for the title compounds were collected on a Pyris Diamond thermal analyzer. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer at room temperature.

#### 4.2. Synthesis the complexes

##### 4.2.1. Synthesis of $[\text{Co}(\text{Dpq})_2(1,4\text{-NDC})_{0.5}] \cdot (1,4\text{-HNDC})$ (**1**)

A mixture of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (29.1 mg, 0.1 mmol), Dpq (23.4 mg, 0.1 mmol), 1,4- $\text{H}_2\text{NDC}$  (21.6 mg, 0.1 mmol), NaOH (2 mL, 0.1 mol/L), and  $\text{H}_2\text{O}$  (9 mL), stirred for 20 min, was sealed to a Teflon-lined stainless steel autoclave (25 mL) and kept at 170 °C for 3 days. After the mixture was slowly cooled to room temperature, orange block crystals suitable for X-ray diffraction of complex **1** were obtained in 28% yield (based on Co). Anal. Calc. for  $\text{C}_{46}\text{H}_{25}\text{CoN}_8\text{O}_6$ : C, 65.40; H, 2.96; N, 13.27. Found: C, 65.55; H, 2.78; N, 13.22%. IR (KBr,  $\text{cm}^{-1}$ ): 3440(s), 2354(s), 1912(w),

1698(m), 1541(s), 1392(s), 1235(s), 1193(s), 1143(m), 1079(w), 787(m), 730(m), 652(w).

#### 4.2.2. Synthesis of [Co(Dpq)(2,6-NDC)] (2)

The orange block crystals of complex **2** was obtained by adopting the same procedure as that for **1** only with the use of 2, 6-H<sub>2</sub>NDC instead of 1,4-H<sub>2</sub>NDC. Yield: 26% (based on Co). Anal. Calc. for C<sub>26</sub>H<sub>16</sub>CoN<sub>4</sub>O<sub>4</sub>: C, 61.54; H, 3.16; N, 11.05. Found: C, 61.35; H, 3.29; N, 11.17%. IR (KBr, cm<sup>-1</sup>): 3442(w), 3072(w), 2353(m), 1641(s), 1606(m), 1570(m), 1371(s), 1350(m), 1086(w), 773(m), 730(m).

#### 4.2.3. Synthesis of [Co<sub>2</sub>(Dpq)<sub>2</sub>(BPEA)<sub>4</sub>(H<sub>2</sub>O)] · H<sub>2</sub>O (3)

A mixture of Co(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O (29.1 mg, 0.1 mmol), Dpq (23.4 mg, 0.1 mmol), BPEA (26.8 mg, 0.1 mmol), NaOH (2 mL, 0.1 mol/L), and H<sub>2</sub>O (9 mL), stirred for 20 min, was sealed to a Teflon-lined stainless steel autoclave (25 mL) and kept at 160 °C for 5 days. After the mixture was slowly cooled to room temperature, orange block crystals suitable for X-ray diffraction of complex **3** were obtained in 31% yield (based on Co). Anal. Calc. for C<sub>120</sub>H<sub>78</sub>Co<sub>4</sub>N<sub>16</sub>O<sub>19</sub>: C, 63.10; H, 3.42; N, 9.82. Found: C, 63.01; H, 3.32; N, 9.98%. IR (KBr, cm<sup>-1</sup>): 3456(w), 2360(m), 1620(s), 1527(m), 1478(w), 1385(s), 1079(w), 851(w), 787(m), 695(w), 630(w).

#### 4.3. X-ray crystallography

All diffraction data were collected using a Bruker P4 diffractometer (Mo K $\alpha$  radiation, graphite monochromator,  $\lambda = 0.71073$  Å). The structures were solved by direct methods with SHELXS-97 and Fourier techniques and refined by the full-matrix least-squares method on F<sup>2</sup> with SHELXL-97 [41,42]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors, and the H atoms of water molecules were located in different Fourier synthesis maps. In the complex **1**, part of the 1,4-HNDC ligands are disordered and the C33, C34, C35, C36 positions were refined with half-occupancy atoms. All the crystal data and structure refinement details for the

three complexes are given in Table 1. Selected bond lengths and angles for complexes **1–3** are presented in Tables S1–S3.

#### Acknowledgements

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#### Appendix A. Supplementary data

CCDC 701512, 701513 and 701514 contains the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.03.008.

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**Table 1**  
Crystal data and structure refinement for complexes **1–3**.

Complex	1	2	3
Formula	C <sub>46</sub> H <sub>25</sub> CoN <sub>8</sub> O <sub>6</sub>	C <sub>26</sub> H <sub>16</sub> CoN <sub>4</sub> O <sub>4</sub>	C <sub>120</sub> H <sub>78</sub> Co <sub>4</sub> N <sub>16</sub> O <sub>19</sub>
Formula weight	844.67	507.36	2283.70
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2 <sub>1</sub> /c	C2/c	P1
a (Å)	9.637(5)	20.254(1)	13.847(5)
b (Å)	25.462(5)	13.519(1)	14.452(5)
c (Å)	15.168(5)	7.452(6)	15.643(5)
$\alpha$ (°)	90	90	93.08(5)
$\beta$ (°)	99.61(5)	101.53(1)	111.93(5)
$\gamma$ (°)	90	90	113.93(5)
V (Å <sup>3</sup> )	3670(2)	1999.2(3)	2575.2(1)
Density (g/cm <sup>3</sup> )	1.529	1.686	1.473
Z	4	4	1
F(000)	1728	1036	1170
$\theta_{\max}$ (°)	25.00	25.02	25.96
Total data	18553	5005	14229
Unique data	6442	1765	9880
[R <sub>int</sub> ]	0.0594	0.0247	0.0307
R <sub>1</sub> <sup>a</sup> [I > 2 $\sigma$ (I)]	0.0677	0.0367	0.0503
wR <sub>2</sub> <sup>b</sup> (all data)	0.2093	0.0934	0.1062
GOF	1.020	1.070	1.010
$\Delta\rho_{\max}$ (e Å <sup>-3</sup> )	1.408	0.433	0.888
$\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	-0.319	-0.778	-0.341

<sup>a</sup>  $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$ .

<sup>b</sup>  $wR_2 = [\sum(w(|F_o|^2 - |F_c|^2)^2) / \sum(w|F_o|^2)]^{1/2}$ .

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