

Hydrothermal synthesis, crystal structures and fluorescence properties of three novel frameworks constructed with mixed ligands of isophthalic acid (1,3-BDC) and 2,3-di-2-pyridylquinoxaline (Dpdq): $[M(1,3-BDC)(Dpdq)(H_2O)_m] \cdot nH_2O$ ($M = Co^{II}$, Cd^{II} or Zn^{II})

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Abstract

Three novel metal–organic frameworks $[M(1,3-BDC)(Dpdq)(H_2O)_m] \cdot nH_2O$ ($M = Co^{II}$ (**1**), Cd^{II} (**2**) or Zn^{II} (**3**); $m = 0, 1$; $n = 0, 1, 2$, respectively) have been obtained from hydrothermal reactions of three different metal(II) nitrates with the same mixed ligands [isophthalic acid (1,3-BDC) and 2,3-di-2-pyridylquinoxaline (Dpdq)], and structurally characterized by elemental analyses, IR spectroscopy, and single-crystal X-ray diffraction analyses. Single-crystal X-ray analyses show that each pair of metal ions are bridged by various coordination modes of 1,3-BDC ligands to form left- and right-handed helical chains in **1**, linear chains in **2**, and double chains in **3**, respectively. N-containing flexible ligand Dpdq takes a chelating coordination mode acting as terminal ligand. In the compound **1**, adjacent left- and right-handed helical chains are packed through hydrogen bonds to form a two-dimensional (2-D) structure. In the compounds **2** and **3**, adjacent chains are further linked by hydrogen bonds and/or π – π stacking interactions to form a three-dimensional (3-D) distorted hexagon meshes supramolecular framework for **2** and a ZnS-related three-dimensional (3-D) topology for **3**, respectively. The different structures of compounds **1**–**3** illustrate that the influence of the metal ions in the self-assembly of polymeric coordination architectures. In addition, compounds **2** and **3** exhibit blue emission in the solid state at room temperature.

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1. Introduction

In the recent years, the design and synthesis of metal–organic frameworks (MOFs) have attracted much more attention not only for their interesting molecular topologies but also for the fact that they may be designed with specific functionalities [1–3]. Although the formation of MOFs is greatly affected by the organic ligands, the nature of the metal ions, counterions, and other factors [4,5], it is possible to get a targeted architecture and predictable properties by choosing versatile organic ligands and functional metal ions [6–8]. Multidentate aromatic dicarboxylic

acid, 2,2'-bipyridyl-like chelating ligands, and their analogues have been extensively utilized to bridge the metal centers, leading to interesting MOF structures and properties [9–11]. MOFs formed with metal ions and *exo*-bidentate organic bridges in a 1:1 stoichiometry are usually based on either rigid linear or zigzag chain structures [11a]. It has been noted that employment of flexible or V-shaped *exo*-bidentate organic bridges can improve the helicity of the polymeric chains [11a,7b,12]. The aromatic chelate ligands are important in maintaining the one dimensionality and may provide potential supramolecular recognition sites for π – π aromatic stacking interactions to form multistranded helices [11a,13].

3-Di-2-pyridylquinoxaline (Dpdq) is a multifunctional aromatic chelate ligand containing both benzpyrazinyl

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group and two pyridyl groups, which can potentially afford various coordination modes and diverse MOFs architecture. Meanwhile, since the aromatic rings of Dpdq can be twisted at different degrees across the C–C single bond, it possesses both rigidity and flexibility, which makes it a wonderful candidate for the construction of interesting supramolecular networks. However, there are only a few reports on the interesting networks constructed with the Dpdq ligand [14]. We assumed that the V-shaped dicarboxylic acid 1,3-BDC could be useful in the formation of helical chains or other novel networks in the presence of Dpdq. Herein we report three novel compounds: $[\text{Co}(1,3\text{-BDC})(\text{Dpdq})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**1**), $[\text{Cd}(1,3\text{-BDC})(\text{Dpdq})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**2**), and $[\text{Zn}(1,3\text{-BDC})(\text{Dpdq})] \cdot \text{H}_2\text{O}$ (**3**), with Dpdq and 1,3-BDC as mixed ligands. Meanwhile, compounds **2** and **3** exhibit blue emission in the solid state at room temperature, and may be used as a potential photoluminescence material candidates.

2. Results and discussion

2.1. Description of the structure

$[\text{Co}(1,3\text{-BDC})(\text{Dpdq})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ (**1**). Single-crystal X-ray analysis reveals that compound **1** is a unique 1-D coordination polymeric helical chain. The coordination environment of Co^{II} is shown in Fig. 1. In the building unit of **1**, Co^{II} ion is coordinated by three oxygen atoms from two different 1,3-BDC ligands with Co–O bond distances ranging from 2.005(1) to 2.257(2) Å, an oxygen atom of coordinated H_2O molecule (Co–O bond distance is 2.088(2) Å), and two nitrogen atoms from one Dpdq ligand (Co–N bond distances are 2.082(2) and 2.190(2) Å), showing distorted octahedral coordination geometry. Two such asymmetric units are connected by bridging ligands 1,3-BDC to form 1-D helical chain, in which 1,3-BDC ligand

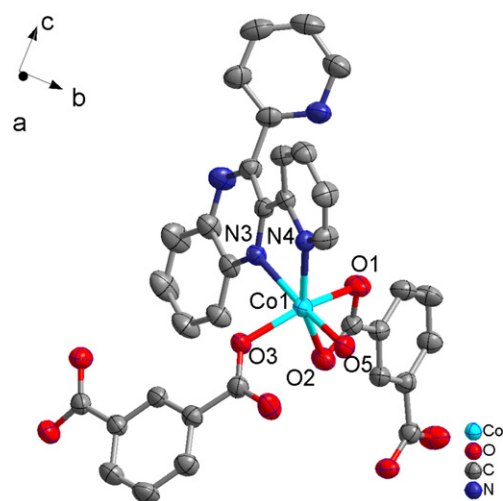
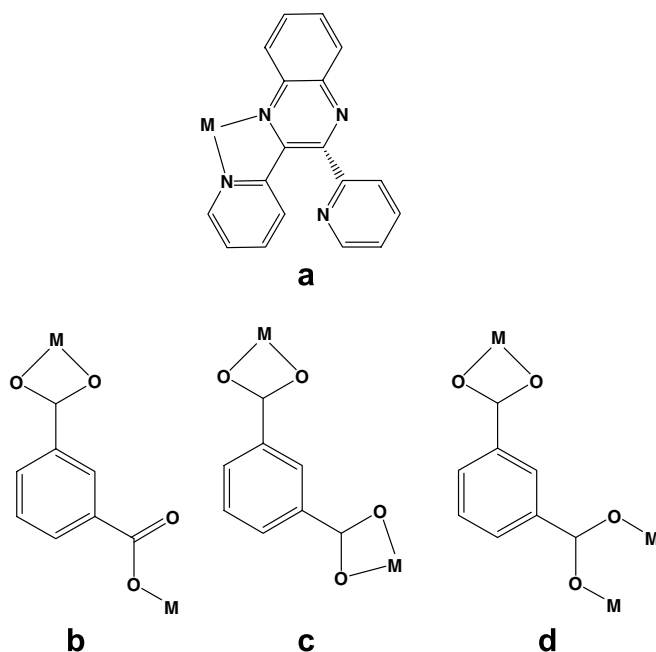


Fig. 1. View of the coordination environment in **1** of ORTEP drawing with 50% probability thermal ellipsoids (H atoms omitted for clarity).

adopts a chelating-monodentate coordination mode (see Scheme 1b).

The peculiar feature of compound **1** is that adjacent chains can be attributed to left- and right-handed helical structure as shown in Fig. 2a and c, respectively. The central axis of each helical chain is a twofold screw axis. Moreover, the adjacent helical chains are packed through hydrogen bonds between lattice water molecules and coordinated water molecules/carboxylate oxygen atoms with O···O distances of 2.704(2) Å [O(W1)···O(5)]/2.732(2) Å [O(W1)···O(1)] into two-dimensional supramolecular networks as shown in Fig. 2b. Additionally, the hydrogen bond interactions between lattice water molecules and nitrogen atoms of non-coordinated pyridyl rings from Dpdq ligands with O(W1)···N(1) distance of 2.877(3) Å consolidate the 2-D supramolecular networks in compound **1**.

$[\text{Cd}(1,3\text{-BDC})(\text{Dpdq})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**2**). Single-crystal X-ray analysis reveals that **2** is a 1-D linear polymeric coordination chain. The Cd^{II} ion center is seven coordinated by two nitrogen atoms [N(1), N(2)] of a chelating Dpdq ligand with the Cd–N distances 2.343(3) and 2.448(2) Å, four carboxylate oxygen atoms [O(1), O(2), O(3), O(4)] from two 1,3-BDC ligands with the Cd–O distances (2.251(2)–2.584(2) Å), and one oxygen atom [O(5)] of coordinated H_2O molecule with the Cd–O distance 2.278(2) Å (as shown in Fig. 3). The bond lengths and angles of Cd–Ocar and Cd–N are similar to those in other cadmium coordination polymers, respectively [15]. Adjacent two Cd^{II} ion centers are connected by bridging ligands 1,3-BDC to form 1-D infinite linear chain. V-shaped 1,3-



Scheme 1. The coordination modes of Dpdq and 1,3-BDC observed in compounds **1**–**3**.

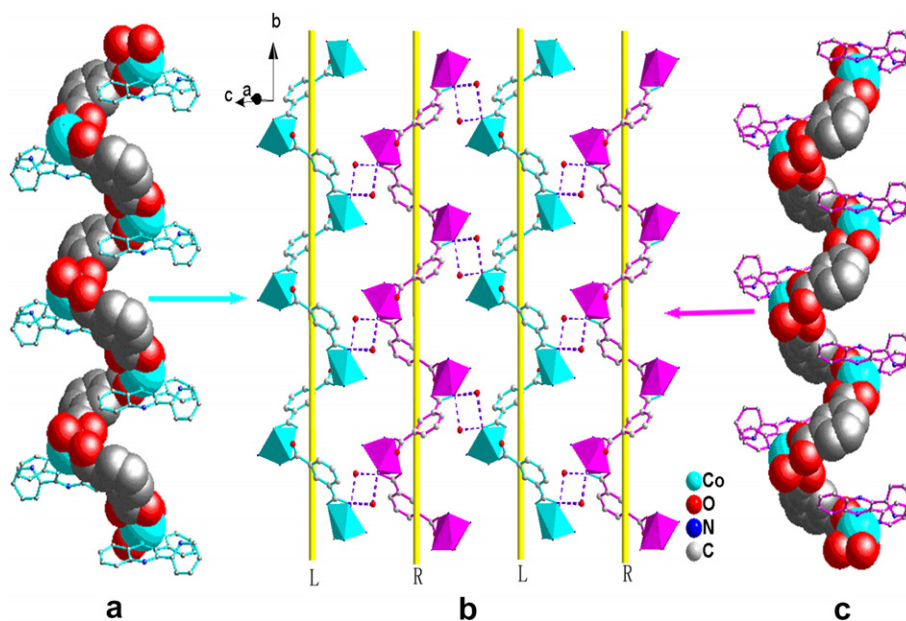


Fig. 2. (a) or (c) 1-D polymeric coordination helical chain of **1** (H atoms omitted for clarity); (b) 2-D supramolecular network of **1** formed by hydrogen bond interactions (H atoms and part of terminal groups of ligands omitted for clarity).

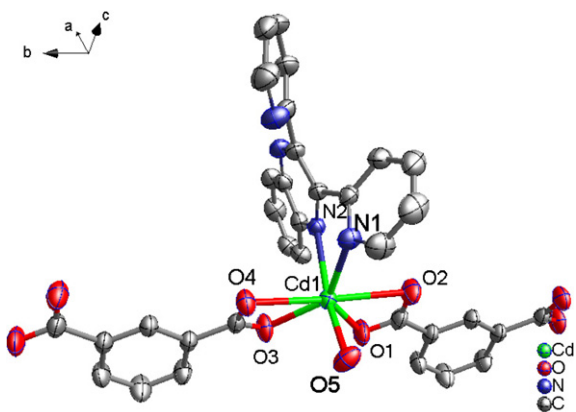


Fig. 3. View of the coordination environment in **2** of ORTEP drawing with 50% probability thermal ellipsoids (H atoms omitted for clarity).

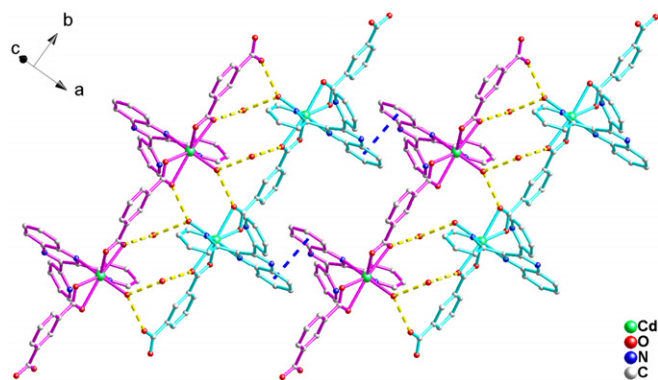


Fig. 4. 2-D network of **2** formed by π - π stacking and hydrogen bond interactions (H atoms omitted for clarity).

BDC ligand adopts chelating-bis(bidentate) coordination fashion which is different from that in **1** (see Scheme 1c).

Strong O-H \cdots O hydrogen bonds [O(W1) \cdots O(5), 2.717(3) Å; O(W1) \cdots O(2), 2.858(3) Å; O(5) \cdots O(4), 2.843(3) Å] connect adjacent two chains to form double chain structure. Moreover, the double chains are extended to 2-D networks by π - π stacking interactions among aromatic rings of Dpdq ligands with face-to-face distance ca. 3.35 Å, as shown in Fig. 4. Additionally, the 2-D networks are ultimately packed into a 3-D supramolecular structure through interlayer C-H \cdots π interactions [15b] between the carbon atoms [C(2)] with H(2A) from non-coordinated pyridyl group of Dpdq ligands and Dpdq rings from adjacent chains [C(2)-H(2A) \cdots π , 3.44 Å, 131°], as shown in Fig. 5.

To best understand the framework topology, it is necessary to simplify the building blocks from which the 3-D

supramolecular net of **2** is built. Considering the Cd atoms as a nodes and keeping the 1,3-BDC ligands and supramolecular interactions (represented by *a*, *b*, *c*, and *d*, respectively) as spacers, the total topology of **2** can be considered to be distorted hexagon meshes, as can be seen in Fig. 6. The distorted hexagon meshes are elongated significantly in one direction, and exhibit maximum dimensions of 23.04 Å \times 17.30 Å \times 13.54 Å (corresponding to the longest intracage Cd \cdots Cd distances).

[Zn(1,3-BDC)(Dpdq)] \cdot H₂O (**3**). Single-crystal X-ray analysis reveals that the asymmetric unit contains one Zn^{II} ion. Zn^{II} ion is coordinated by four oxygen atoms from three carboxylate groups [Zn(1)-Ocar, 1.963(1)–2.528(2) Å], and two nitrogen atom from a chelating Dpdq ligand [Zn(1)-N(1) = 2.391(2), and Zn(1)-N(2) = 2.065(2) Å] to furnish a distorted octahedral geometry. Two such asymmetric units connect to form an 8-membered ring, which contains two

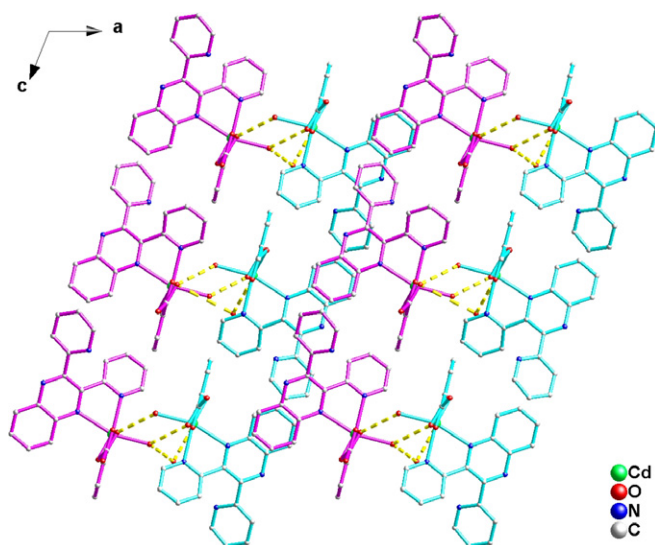


Fig. 5. 3-D network structure of **2** formed by supramolecular interactions (H atoms and part of the aromatic rings omitted for clarity).

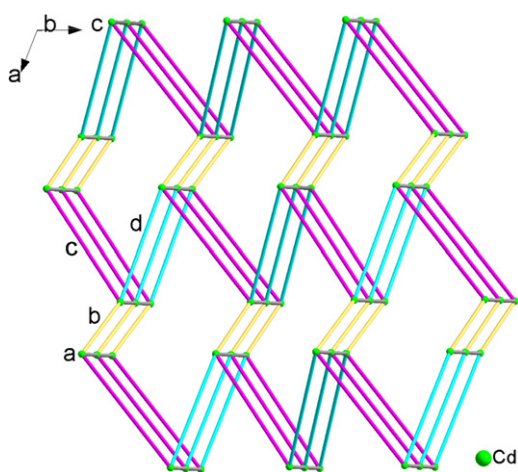


Fig. 6. Schematic of 3-D supramolecular network formed by hydrogen bond and π - π stacking interactions in **2** (*a*: 1-D polymeric coordination chains of **2**; *b*: hydrogen bond formed by coordinated water and carboxylate oxygen atom; *c*: interlayer C-H \cdots π interactions; *d*: π - π stacking interactions formed by benzpyrazinyl rings).

Zn^{II} ions, four 1,3-BDC ligands, and two Dpdq ligands, as shown in Fig. 7. Such a binuclear unit (with Zn \cdots Zn distance ca. 4.64 Å) connected with each other by 1,3-BDC to form a 1-D polymeric double chain (*a* as shown in Fig. 8). In compound **3**, 1,3-BDC ligands assume a chelating-bidentate coordination mode (see Scheme 1d), which is different from that in **1** and **2**. Interestingly, each asymmetric unit contains one lattice water leading to forming intra-chain hydrogen bonds between lattice water and the same lattice water/carboxylate oxygen atoms [O(1W) \cdots O(1W), 2.927(6) Å; O(1W) \cdots O(1), 2.736(3) Å], which just consolidate the 1-D double chain structure of **3**.

It is interesting that each double chain connects with surrounding six chains through two kinds of supramolecu-

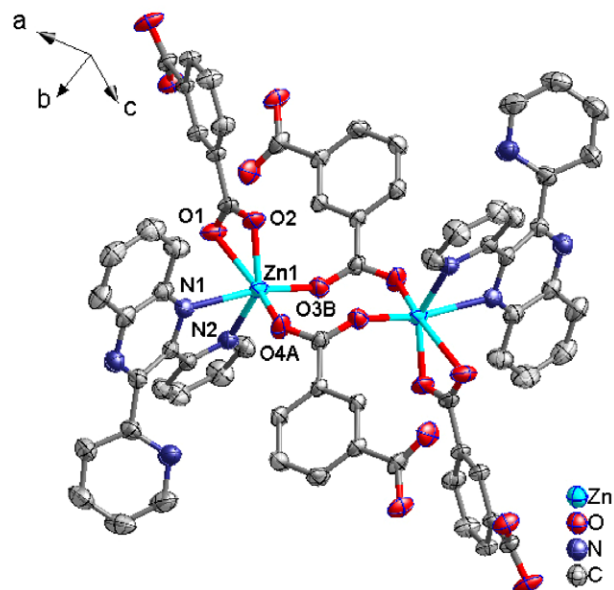


Fig. 7. View of the coordination environment in **3** of ORTEP drawing with 50% probability thermal ellipsoids (H atoms omitted for clarity).

lar interactions: one is π - π stacking interactions between coordination pyridyl rings of Dpdq ligands with face-to-face distance ca. 3.37 Å and hydrogen bonds [C(3)-H(3A) \cdots O(2), 3.332(2) Å, 148°] represented as *b* in Fig. 8; the other is π - π stacking interactions among benzpyrazinyl rings of different Dpdq ligands from adjacent double chains with face-to-face average distance ca. 3.47 Å (*c* in Fig. 8). Taking all these interactions (*a*, *b*, and *c*) into account, a 3-D supramolecular frameworks formed as shown in Fig. 8. Considering the binuclear Zn ions as nodes and keeping the 1,3-BDC ligands and supramolecular interactions as spacers, the overall structure of the 3-D framework of **3** can be best described as a ZnS-related topology as shown in Fig. 9.

As shown above, V-shaped benzene-dicarboxylate ligands (1,3-BDC), adopting three distinctly different coordination modes, were introduced to the three different metal-to-ligand coordination systems, furnishing one-dimensional helical chain in **1**, linear chain in **2**, and linear double chain in **3**, respectively. Comparing the structures of the three compounds, we found that N-containing chelating ligands Dpdq had adopted the same chelating coordination mode (see Scheme 1a), but the distorted extent between benzpyrazinyl ring and coordinated pyridyl ring (or non-coordinated pyridyl ring) is different. Such as, in compounds **1–3**, the dihedral angle between benzpyrazinyl ring and coordinated pyridyl ring is 21.63°, 41.72° and 30.49°, while the dihedral angle between benzpyrazinyl ring and non-coordinated pyridyl ring is 46.82°, 32.98° and 42.96°, respectively. Dihedral angles in compound **2** remarkably differ from that in **1** and **3**, which may be due to the effect of C-H \cdots π interactions in **2**. All of these may be attributed to the coordination environment and geometry around the different metal

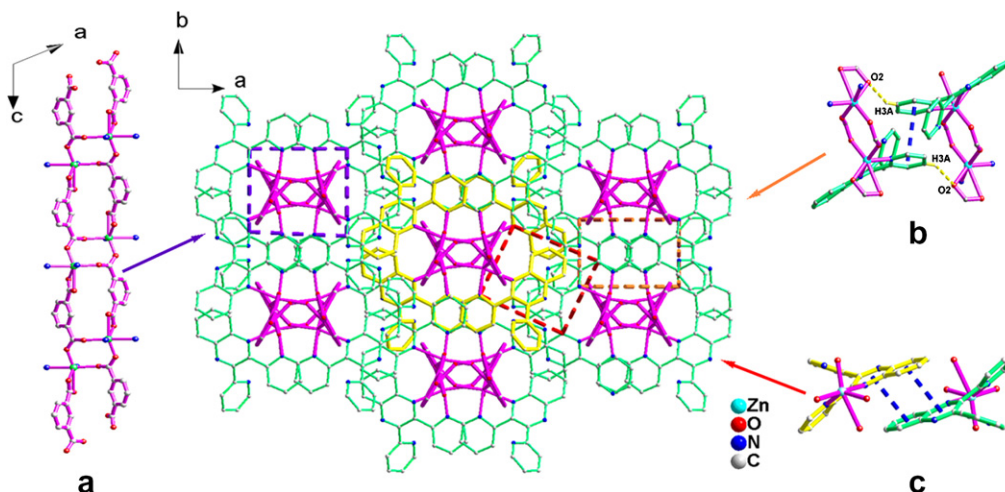


Fig. 8. The schematic of 3-D supramolecular network of compound **3** formed by O–H···O bonding and two kinds of π – π stacking interactions. [*a*: 1-D polymeric coordination double chains of **3**; *b*: π – π stacking interactions formed by coordination pyridyl rings of Dpdq and hydrogen bond interactions; *c*: π – π stacking interactions formed by benzpyrazinyl rings of Dpdq] (H atoms and part of terminal groups of ligands omitted for clarity).

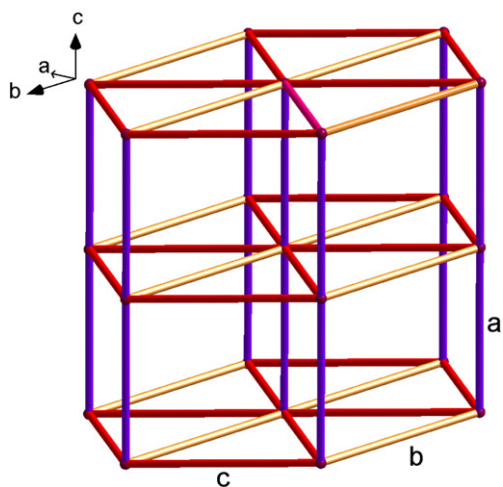


Fig. 9. Three-dimension topology structure of compound **3** formed by two kinds of supramolecular interactions. [*a*: 1-D polymeric coordination double chains of **3**; *b*: π – π stacking interactions formed by coordination pyridyl rings and hydrogen bond; *c*: π – π stacking interactions formed by benzpyrazinyl rings].

atoms. Additionally, the presence of coordinated and lattice water molecules plays some role on constructing such different MOFs.

2.2. Infrared spectra

The main features in the IR spectra of **1–3** mainly concern the carboxylate groups and the ligand Dpdq. (Figures S1–3, Supporting Information). The IR spectra display the typical stretching bands of carboxylate groups between 1400 and 1622 cm^{-1} , a very strong band appears at around 1600 cm^{-1} due to the asymmetric stretching (ν_{as}) of the carboxylate group; the symmetrical stretching (ν_{s}) band of this group appears at 1475–1620 and 1384–1480 cm^{-1} ,

respectively. The bands at about 1560, 1480, 1076, and 752 cm^{-1} may be attributed to the $\nu_{\text{C-N}}$ stretching of the pyridyl ring or pyrazinyl ring. No strong absorption peaks around 1700 cm^{-1} for –COOH are observed, indicating that all carboxyl groups of organic moieties in **1–3** are deprotonated [10c,16]. Weak absorptions observed at 2844–3065 cm^{-1} for **1–3** can be attributed to the $\nu_{\text{C-H}}$ of the pyridyl group. The strong broad band at around 3440 cm^{-1} is assigned to the vibrations of coordinating or non-coordinating water molecules in these compounds.

2.3. Photoluminescence properties

The d^{10} metal compounds have been shown to exhibit interesting photoluminescent properties [17]. In the present work, we have examined the photoluminescent properties of **2**, **3** in the solid state at room temperature due to the excellent luminescent properties of Cd^{II} or Zn^{II} ions, as shown in Fig. 10. Compounds **2** and **3** both

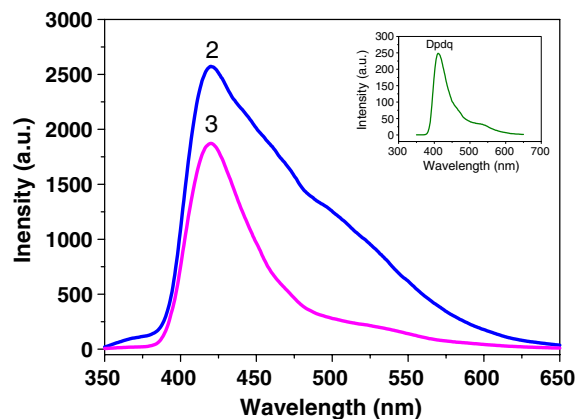


Fig. 10. Fluorescence spectra for compounds **2** and **3** in the solid state at room temperature. Inset: Emission spectra of Dpdq in the solid state.

exhibit blue photoluminescence with an emission maximum at ca. 419 and 420 nm upon excitation at 319 and 329 nm, respectively. Free Dpdq displays a photoluminescent emission at 410 nm upon excitation at 334 nm (Fig. 10, inset). The emission peak positions of compounds **2** and **3** are similar to those of free Dpdq, but the emission intensities of the two compounds increase comparing with those of Dpdq ligand, respectively. The slight red-shift of emission bands and intensity increases would be assigned to chelating of the Dpdq ligand to the metal ion (LMCT), which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay of the intraligand emission excited state [9d,18]. This is consistent with the fact that the Cd^{II} or Zn^{II} coordination compounds with 2,2'-bipyridyl-like chelating ligands may possess an LMCT photoluminescent property [15b,19]. The slight difference of emission spectra may be due to the differences of metal ions in **2** and **3**, because the fluorescence behavior is closely associated with the metal ions and the ligands coordinated around them [20]. These compounds may be used as a potential material for blue-light emitting diode devices and may be a candidate for thermally stable and solvent-resistant blue fluorescent material [21].

2.4. Conclusions

In this paper, we have hydrothermally synthesized three novel 1-D coordination polymers chain structures based on mixed O- and N-donor ligands. Different combinations of V-shaped dicarboxylate with chelating Dpdq ligands in the presence of different metal ions (Co, Cd and Zn), can furnish different one-dimensional polymeric structures: helical chain, linear single chain and double chain. So the appropriate selection of metal ions has significant effects on the formation and dimension of the resulting structures. The successful preparation of compounds **1–3** provides a valuable approach for the construction of other coordination polymers with different structures via the introduction of metal ions. Furthermore, the fluorescent properties of compounds **2** and **3** may make them excellent candidates for potential photoactive materials.

3. Experimental

3.1. General remarks

All reagents employed were commercially available and used as received without further purification. Dpdq were synthesized by the methods of the literature [22]. FT-IR spectra (KBr pellets) were taken on a Scimitar 2000 Near FT-IR Spectrometer and the elemental analyses (C, H, and N) were carried out on a Perkin–Elmer 240C elemental analyzer. Fluorescence spectra were performed on a HITACHI F-4500 fluorescence/phosphorescence spectrophotometer at room temperature.

3.2. Preparation of the compounds

$[Co(1,3-BDC)(Dpdq)(H_2O)] \cdot H_2O$ (**1**). Compound **1** was prepared by simple hydrothermal reaction of Co(N-O₃)₂ · 6H₂O (0.024 g, 0.1 mmol), 1,3-H₂BDC (0.016 g, 0.1 mmol), Dpdq (0.032 g, 0.1 mmol), H₂O (10 mL) and NaOH (0.012 g, 0.3 mmol), the mixture was stirred for 30 min in air, then transferred and sealed in a 25-ml Teflon reactor, which was heated at 160 °C for 72 h leads to the formation of red block crystals **1**. (16% yield based on Co). Anal. Calc. for C₂₆H₂₀N₄O₇Co: C, 57.46; H, 3.71; N, 10.31. Found: C, 57.31; H, 3.53; N, 10.59%. IR (KBr, cm⁻¹): 3439s, 3048w, 2924w, 2362m, 1617s, 1531m, 1475m, 1388s, 1283w, 1073m, 998s, 826w, 788m, 702w, 578m, 549m.

$[Cd(1,3-BDC)(Dpdq)(H_2O)] \cdot 2H_2O$ (**2**). A mixture of Cd(NO₃)₂ · 4H₂O (0.036 g, 0.12 mmol), 1,3-H₂BDC (0.032 g, 0.2 mmol), Dpdq (0.032 g, 0.1 mmol), H₂O (12 mL) and NaOH (0.016 g, 0.4 mmol) was stirred for 30 min in air, then transferred and sealed in a 25-ml Teflon reactor, which was heated at 160 °C for 72 h leads to the formation of yellow block crystals, and washed by water, ethanol, dried in air. Yield: ~39% (based on Cd). Anal. Calc. for C₂₆H₂₂N₄O₇Cd: C, 50.78; H, 3.61; N, 9.11. Found: C, 50.67; H, 3.88; N, 9.30%. IR (KBr, cm⁻¹): 3394s, 3058w, 2364m, 1598s, 1541s, 1480w, 1437m, 1386s, 1150w, 1076m, 1003w, 752s, 721m, 551w.

$[Zn(1,3-BDC)(Dpdq)(H_2O)]$ (**3**). A mixture of Zn(NO₃)₂ · 6H₂O (0.036 g, 0.12 mmol), 1,3-H₂BDC (0.032 g, 0.2 mmol), Dpdq (0.032 g, 0.1 mmol), H₂O (10 mL) and NaOH (0.016, 0.4 mmol) was stirred for 30 min in air, then transferred and sealed in a 25-ml Teflon reactor, which was heated at 160 °C for 72 h leads to the formation of yellow block crystals **3**. Yield: ~47% (based on Zn). Anal. Calc. for C₂₆H₁₈N₄O₅Zn: C, 58.71; H, 3.41; N, 10.54. Found: C, 58.58; H, 3.69; N, 10.38%. IR (KBr, cm⁻¹): 3431s, 3058w, 2364m, 1620s, 1560s, 1480m, 1437w, 1384s, 1260w, 1156w, 1080m, 991m, 820w, 783m, 748s, 715m, 545m.

3.3. X-ray crystallography

Crystallographic data for **1–3** were collected at 293(2) K on a Bruker Smart 1000 CCD diffractometer with Mo K α ($\lambda = 0.71073$ Å) by ω scan mode. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [23]. Metal atoms in each complex were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on *F*². The hydrogen atoms of the ligand were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The crystallographic data for **1–3** are listed in Table 1. Selected bond lengths and angles for **1–3** are presented in Tables S1–S3, and hydrogen-bonding geometries are summarized in Table 2, respectively.

Table 1
Crystal data and structure refinement for compounds **1–3**

	1	2	3
Formula	C ₂₆ H ₂₀ CoN ₄ O ₆	C ₂₆ H ₂₂ CdN ₄ O ₇	C ₂₆ H ₁₈ ZnN ₄ O ₅
Formula weight	543.39	614.89	531.83
<i>T</i> (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	12.065(3)	14.3494(7)	26.8904(15)
<i>b</i> (Å)	11.748(3)	10.1560(5)	9.1994(4)
<i>c</i> (Å)	17.431(4)	18.8827(9)	20.5075(11)
β (°)	100.486(3)	111.9170(10)	116.381(2)
<i>V</i> (Å ³)	2429.4(10)	2552.9(2)	4544.7(4)
<i>Z</i>	4	4	8
Density (Mg m ⁻³)	1.486	1.600	1.555
Absorption coefficient (mm ⁻¹)	0.757	0.909	1.129
<i>F</i> (000)	1116	1240	2176
θ_{\max} (°)	29.16	28.310	28.270
Total number of data	14882	15436	13546
Number of unique data	6554	6117	5390
Number of parameters	350	367	325
<i>R</i> _{int}	0.0248	0.0235	0.0239
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0348	0.0268	0.0311
<i>wR</i> ₂ ^b (all data)	0.1082	0.0726	0.0905
Goodness-of-fit on <i>F</i> ²	1.008	1.001	1.058
$\Delta\rho_{\max}$ (e Å ⁻³)	0.260	0.399	0.321
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.440	-0.286	-0.427

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

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

Table 2
Hydrogen-bonding geometry (Å, °) for compounds **1–3**

D–H···A	D–H	H···A	D···A	∠D–H···A
1				
O(W1)–H(W1)···O(1) ⁱ	0.89	1.84	2.732(2)	177
O(W1)–H(W2)···N(1) ⁱ	0.86	2.02	2.877(3)	173
O(5)–H(5B)···O(W1) ⁱⁱ	0.85	1.89	2.704(2)	160
2				
O(W2)–H(W2B)···O(4) ⁱ	0.85	2.06	2.885(3)	163
O(W2)–H(W2A)···N(3) ⁱ	0.85	2.15	2.978(3)	163
O(W1)–H(W1A)···O(2) ⁱⁱ	1.06	1.84	2.858(3)	160
O(5)–H(5A)···O(4) ⁱⁱⁱ	0.76	2.09	2.843(3)	170
O(5)–H(5B)···O(W1) ⁱ	0.85	1.88	2.717(3)	167
3				
O(1W)–H(W1B)···O(1W) ⁱ	1.11	2.01	2.927(6)	138
O(1W)–H(W1A)···O(1) ⁱⁱ	1.10	1.65	2.736(3)	170
C(3)–H(3A)···O(2) ⁱⁱⁱ	0.93	2.51	3.332(2)	148

Symmetry code for **1**: (i) 1 - *x*, 2 - *y*, -1 - *z*; (ii) *x*, *y*, *z*; for **2**: (i) *x*, *y*, *z*; (ii) -*x*, 1 - *y*, 1 - *z*; (iii) -*x*, -*y*, 1 - *z*; for **3**: (i) -*x*, *y*, 1/2 - *z*, (ii) 1/2 - *x*, 1/2 + *y*, 1/2 - *z*, (iii) *x*, -1 + *y*, *z*.

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Appendix A. Supplementary material

CCDC 629003, 629004 and 629005 contain the supplementary crystallographic data for **1**, **2** and **3**. These data

can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.07.004.

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