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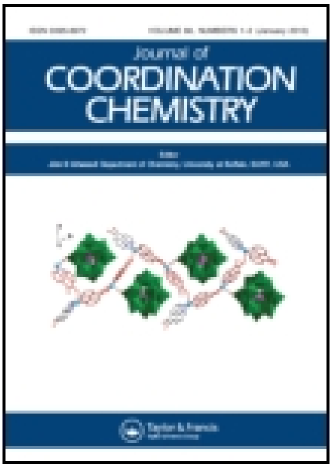

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Two new entangled complexes based on 4,4′-bis(1-imidazolyl)biphenyl: syntheses, structures, thermal and photoluminescent properties

Yue Wang[a], Yan Qi[a], Qun Li[a], Zhou Lu[a] & Yanwei Wang[a]
[a] College of Chemical Science and Engineering, Qingdao University, Qingdao, China

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Two new entangled complexes based on 4,4′-bis(1-imidazolyl) biphenyl: syntheses, structures, thermal and photoluminescent properties

YUE WANG*, YAN QI, QUN LI, ZHOU LU and YANWEI WANG

College of Chemical Science and Engineering, Qingdao University, Qingdao, China

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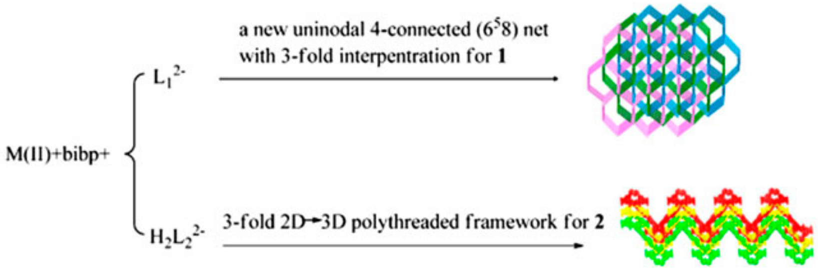

Two new entangled complexes, $[Zn(bibp)(L^1)]\cdot 0.25H_2O$ (**1**) and $[Co(bibp)(H_2L^2)]$ (**2**) (bib*p* = 4,4′-bis(1-imidazolyl)biphenyl, H_2L^1 = 4,4′-(2,2′-oxybis(ethane-2,1-diyl)bis(oxy))dibenzoic acid, and H_4L^2 = 5,5′-(2,2′-oxybis(ethane-2,1-diyl)bis(oxy))diisophthalic acid), have been synthesized hydrothermally. Complex **1** features a new uninodal four-connected ($6^5\cdot 8$) net with vertex symbol $6\cdot 6\cdot 6\cdot 6\cdot 6_2\cdot 8_2$, which is different from all that exhibit uninodal four-connected ($6^5\cdot 8$) nets found in the literature, including **cds**, **dmp**, **ict**, **mok**, **unl** and **unm**. Three of these nets interpenetrate. Complex **2** shows an unusual threefold 2-D → 3-D polythreaded framework, in which each 2-D wave-like net is formed by the intersection, at the shared Co nodes, of the 1-D left- and right-handed single-helical $(H_2L^2)^{2-}$ chains and the 1-D bibp *meso*-helices. Furthermore, the thermal and photoluminescent properties of **1** have also been studied.

Keywords: Coordination polymer; Rigid bis(imidazole) ligand; Interpenetration; Polythreading

1. Introduction

Entanglements, such as polycatenanes, polyrotaxanes, and molecular knots, have emerged as a class of supramolecular architectures attracting interest due to their esthetic attributes and promising applications as functional materials [1, 2]. One common phenomenon related to the entanglement is interpenetration, in which two or more identical nets pass through each other either in parallel or inclined mode. There are some comprehensive reviews by

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*Corresponding author. Email: wangyue@qdu.edu.cn

Robson, Batten, and Ciani's groups of many fascinating entangled structures [3–5]. Conceptually, interpenetrating networks can be described as the number of individual nets participating in interpenetration with each other. However, polythreaded systems are characterized by the presence of closed loops, as well as of elements that can thread through the loops, and can be considered as extended periodic analogs of molecular rotaxanes and pseudorotaxanes. Higher dimensional polyrotaxane-like and polythreading networks are still quite rare [6–10]. On the other hand, a large number of mixed-ligand coordination complexes have been successfully obtained by our group and others [11], which suggests that the introduction of N-containing auxiliary ligands into a metal–polycarboxylate system often leads to structural changes and affords new frameworks. Hence, mixed-ligands are a good choice for the construction of new polymeric structures.

Network topology is a useful approach for crystal engineering of MOFs, in which the metal centers and ligands can be considered as nodes with certain connectivity to simplify the coordination frameworks [12]. Four-connected topological coordination polymers have been intensively investigated. Generally, square-planar nodes prefer to assemble into a 2-D (4,4) square net rather than the less common 3-D **NbO** ($6^4 8^2$–a), **CdSO$_4$** ($6^5 8$), and **lvt** ($4^2 8^4$) nets, while tetrahedral nodes usually give 3-D **diamondoid** (6^6), **SrAl$_2$** ($4^2 6^3 8$), **quartz** ($6^4 8^2$–b), and zeolite-related nets. Moreover, there are a number of nets containing more than one type of node, such as the **PtS** ($4^2 8^4$) net which contains equal numbers of tetrahedral and square-planar nodes [4(d), 13]. Other four-connected nodal nets have been reported less. In our previous work, we reported the first successful isolation and characterization of a cobalt coordination complex, [Co(bimb)(4,4′-bpy)(SCN)$_2$] (4,4′-bpy = 4,4′-bipyridine and bimb = 1,4-bis(imidazol-1-yl)butane), which displays a twofold interpenetrated 3-D four-connected $(6^4 8^2)(6^3 8^3)_2(6^5 8)$ net based on three kinds of planar Co nodes, one of which is square planar and the other two have "fork"-shaped planar geometries [14]. Professor Blatov *et al.* have performed a computer-aided systematic investigation of interpenetrated metal–organic frameworks in Cambridge Structural Database [4(c), 15], which shows that only six types of four-connected uninodal ($6^5 \cdot 8$) networks are included, namely, **cds**, **dmp**, **ict**, **mok**, **unl,** and **unm**. Inspired by the aforementioned considerations and as a continuation of our research, our strategy is to select a rigid bis(imidazole) ligand, 4,4′-bis(1-imidazolyl)biphenyl (bibp), and a good candidate to construct a 3-D porous framework with large voids [16] as organic linkers, and the long polycarboxylic acid, 4,4′-(2,2′-oxybis(ethane-2,1-diyl)bis(oxy))dibenzoic acid (H_2L^1) and 5,5′-(2,2′-oxybis(ethane-2,1-diyl)bis(oxy))diisophthalic acid (H_4L^2) as coligands. Fortunately, two entangled complexes, [Zn(bibp)(L^1)]·0.25H_2O (**1**) and [Co(bibp)(H_2L^2)] (**2**), were isolated and characterized by single-crystal X-ray diffraction, elemental analysis, IR spectra, and thermogravimetric analysis (TG). The photoluminescence of **1** has also been studied.

2. Experimental

2.1. *Materials and methods*

Solvents and starting materials for synthesis were purchased commercially and used as received. Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240 analyzer. IR spectra were recorded as KBr pellets on a Nicolet Magna-FT-IR 560 spectrometer from 4000 to 400 cm^{-1}. The photoluminescence measurements were carried out on crystalline samples at room temperature, and the spectra were collected with a Hitachi F-2500FL spectrophotometer. Thermogravimetric analyses were investigated on a standard TG analyzer under nitrogen flow at a heating rate of 5 °C min^{-1} for all the measurements.

2.2. *Synthesis of [Zn(bibp)(L)]·0.25H_2O (1)*

A mixture of $Zn(NO_3)_2·6H_2O$ (297 mg, 1.0 mM), H_2L (346 mg, 1.0 mM), bibp (286 mg, 1.0 mM), and water (8 mL) was placed in a 25 mL Teflon-lined stainless steel vessel. The pH was then adjusted to 6.0 with 1 M NaOH solution, the mixture was heated at 160 °C for 3 days, and then the reaction system was cooled to room temperature. Colorless block crystals were obtained in 65% yield (based on Zn). Elemental analysis (%): Calcd for **1**: C, 60.55; H, 4.52; and N, 7.85. Found: C, 60.51; H, 4.50; N, 7.88. Selected IR (KBr): $\nu(cm^{-1})$ = 3116 (m), 1621 (s), 1586 (s), 1531 (s), 1428 (s), 1301 (s), 1108 (s), 987 (s), 824 (s), and 654 (m).

2.3. *Synthesis of [Co(bibp)(H_2L^2)] (2)*

A mixture of $CoCl_2·6H_2O$ (238 mg, 1.0 mM), H_4L^2 (217 mg, 0.5 mM), bibp (286 mg, 1.0 mM), and water (8 mL) was placed in a 25 mL Teflon-lined stainless steel vessel. The pH was then adjusted to 6.0 with 1 M NaOH solution, the mixture was heated at 160 °C for 3 days, and then the reaction system was cooled to room temperature. Red crystals were obtained in 45% yield (based on Co). Elemental analysis (%): Calcd for **2**: C, 58.69; H, 3.89; and N, 7.21. Found: C, 58.71; H, 3.84; and N, 7.25. Selected IR (KBr): $\nu(cm^{-1})$ = 1596 (s), 1560 (s), 1522 (s), 1425 (s), 1239 (s), 1105 (s), 1086 (s), 724 (s), 684 (s), and 655 (m).

2.4. *Crystal structure determination*

Accurate unit cell parameters of **1** and **2** were determined by a least-squares fit of 2θ values, and intensity data were measured on a Rigaku *r*-axis rapid IP area detector with Mo-Kα radiation (λ = 0.71073 Å) at 293 K. The intensity was corrected for Lorentz and polarization effects as well as for empirical absorption based on multi-scan technique. The structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97. All non-hydrogen atoms were refined anisotropically; hydrogens bound to carbons were calculated theoretically and those of hydroxyl and water molecules were determined by difference Fourier maps. The crystal data and refinement details of the compounds are summarized in table 1 and selected bond lengths (Å) and angles (°) for **1** and **2** are listed in table S1 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.975219).

3. Results and discussion

3.1. *Structure description of 1*

Crystallographic analysis revealed that **1** crystallizes in the orthorhombic group *Fddd*. The coordination environment around Zn(II) centers of **1** is represented in figure 1(a). Each Zn is four-coordinate by two carboxylic oxygens from two L^1 anions and two nitrogens from two bibp. The Zn–O/N bond lengths are 1.989(4) and 2.028(3) Å, respectively, which are similar to those found in other related Zn complexes [17]. The Zn(II) ions are connected by

Table 1. Crystal data and structure refinements for **1** and **2**.

Compound	**1**	**2**
Formula	$C_{144}H_{120}N_{16}O_{29}Zn_4$	$C_{38}H_{30}CoN_4O_{11}$
Fw	2800.2	777.59
T (K)	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*Fddd*	*P2/c*
a (Å)	18.457(4)	13.156(3)
b (Å)	21.777(4)	5.4704(11)
c (Å)	32.693(7)	25.535(7)
β (°)	90	117.24(2)
V (Å^3)	13140(5)	1633.9(7)
Z	4	2
Calcd D (g cm^{-3})	1.415	1.581
F(0 0 0)	5792	802
Reflns. collected/unique	29943/3777 R(int) = 0.1412	14802/3728 R(int) = 0.1936
GOF	0.975	0.966
Final R [$I > 2\sigma(I)$]	$R_1 = 0.0702$, $wR_2 = 0.2080$	$R_1 = 0.0783$ $wR_2 = 0.1315$

L^1 anions and bibp ligands to give the complicated 3-D framework with the void space occupied by free waters. Better insight into such elegant frameworks can be accessed by the topology method. An analysis using TOPOS [18] indicates that the coordination framework of **1** represents a uninodal four-connected net with Schläfli symbol: $(6^5\cdot8)$ and vertex symbol: $6\cdot6\cdot6\cdot6\cdot6_2\cdot8_2$, if the Zn ions are considered as four-connected nodes, and the organic ligands are regarded as linkers [figure 1(b)]. This topology is completely different from **cds**, which is a usual uninodal four-connected $(6^5\cdot8)$ net with vertex symbol $6\cdot6\cdot6\cdot6\cdot6_5\cdot8$. In fact, the topology of **1** is distinguished from any other reported uninodal four-connected $(6^5\cdot8)$ net, including **cds**, **dmp** (vertex symbol: $6\cdot6\cdot6\cdot6\cdot6_2\cdot8_3$), **ict** (vertex symbol: $6\cdot6_2\cdot6\cdot6_2\cdot6\cdot8_4$), **mok** (vertex symbol: $6\cdot6\cdot6\cdot6\cdot6_2\cdot8_4$), **unl** (vertex symbol: $6\cdot6_2\cdot6\cdot6_2\cdot6\cdot8_4$), and **unm** (vertex symbol: $6\cdot6\cdot6\cdot6_2\cdot6\cdot8_5$). Thus, it is a new example of uninodal four-connected $(6^5\cdot8)$ net. Of particular interest, three of these networks interpenetrate, as shown in figure 1(c).

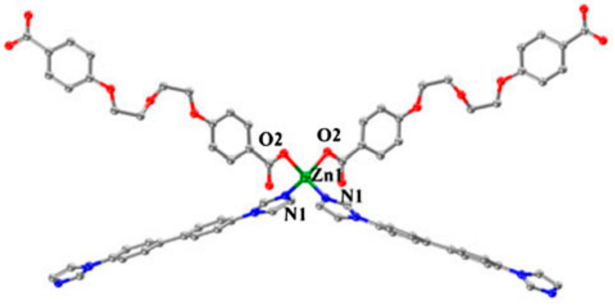

Figure 1a. The immediate coordination environment around Zn(II) in **1**. All hydrogens and free waters are omitted for clarity.

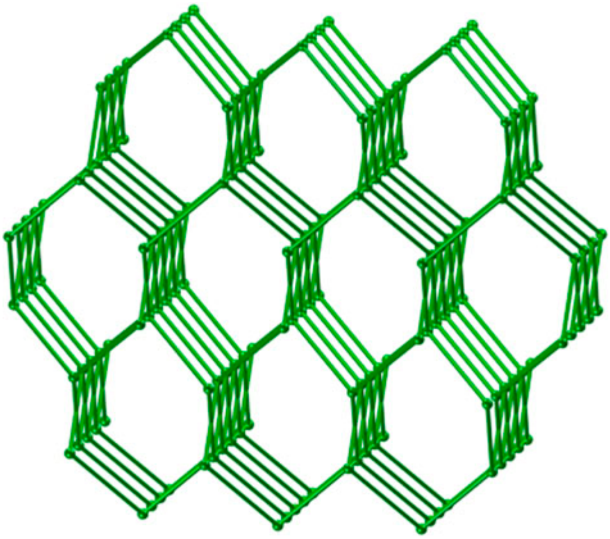

Figure 1b. The schematic view of the 3-D uninodal four-connected ($6^5 \cdot 8$) net in **1**.

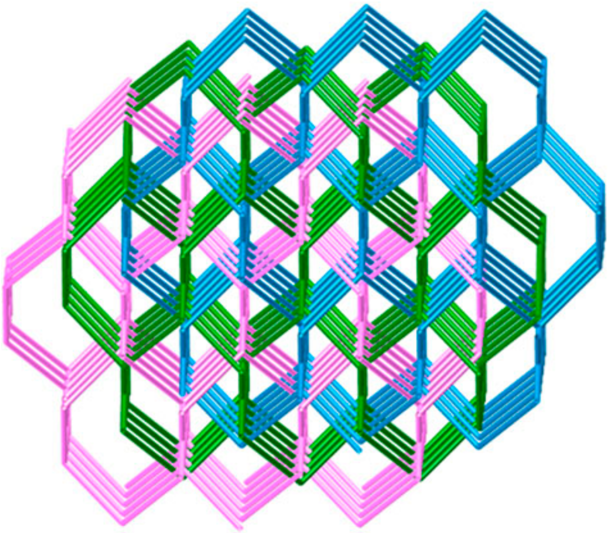

Figure 1c. The three interpenetrating networks present in **1**.

3.2. *Structure description of 2*

Single-crystal X-ray analysis reveals that **2** crystallizes in the monoclinic space group *P2/c*. The asymmetric unit consists of one independent Co(II) ion, one $(H_2L^2)^{2-}$, and one bibp ligand. As shown in figure 2(a), each Co is coordinated by two $(H_2L^1)^{2-}$ oxygens and two bibp nitrogens to give a distorted CoO_2N_2 tetrahedral geometry. The Co–O bond length is 1.967(3) Å and the Co–N bond length is 2.001(4) Å, which are similar to those found in other related Co complexes [11].

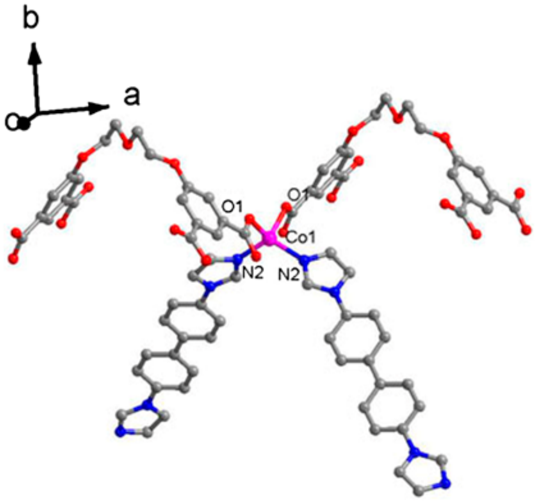

Figure 2a. The immediate coordination environment around Co(II) in **2**. All hydrogens are omitted for clarity.

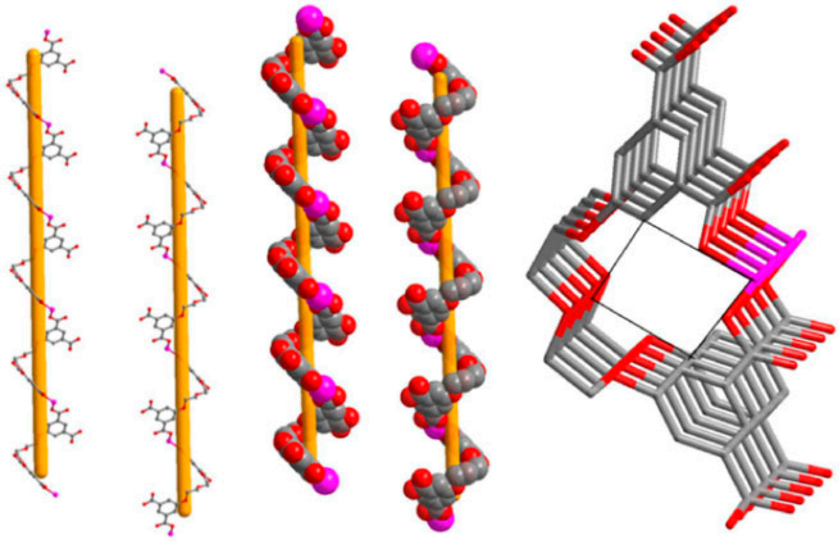

Figure 2b. Perspective (left) and space-filling (middle) views of the 1-D $[Co(H_2L^2)]_n$ helical chain and the tubular motif shown by the helices, with the width being *ca.* 4.89 × 5.32 Å (right).

The incompletely deprotonated $(H_2L^2)^{2-}$ favor *cis* conformation and are monodentate connecting the adjacent Co(II) ions to form 1-D left- and right-handed single-helical chains of $[Co(H_2L^2)]_n$ along the *a* direction with the pitch of the helices being 13.156 Å. A helical tube is formed with the width of *ca.* 4.89 × 5.32 Å [figure 2(b)]. Each bibp links two Co centers to afford an extraordinary *meso*-helical chain with Co···Co distances of 17.849 Å, which contains both left- and right-handed helical loops and displays a "∞" shape [figure 2(c)]. The pitch is 27.005 Å. The overall 2-D net is wave-like, formed by the

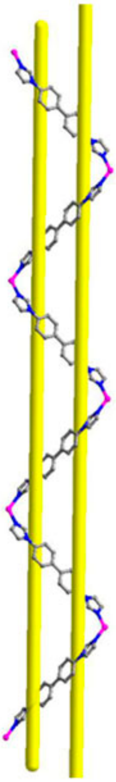

Figure 2c. View of a 1-D [Co(bibp)]$_n$ *meso*-helical chain.

intersection, at the shared Co nodes, of the 1-D left- and right-handed single-helical $(H_2L^2)^{2-}$ chains and the 1-D bibp *meso*-helices [figure 2(d)]. The most striking feature of **2** is the presence of the polythreading array. The C-O–C bond skeletons of $(H_2L^2)^{2-}$ ligands are disposed in an alternate anti-orientation with respect to the layer plane of Co ions due to the orientation of C-O–C bond with a distance of 8.391 Å (the nearest distance between H_2L^2 and the layer plane of Co), which can be considered as "rods." As a result, such "rods" of each layer are threaded into the voids of the two adjacent layers above and below, thus, every window of each layer is threaded by only two "rods" that come from opposite directions. Finally, this unique simultaneous threading of adjacent polymeric motifs gives a threefold 2-D → 3-D polythreading array [figure 2(e)]. So far, only a few examples of polythreading structures have been characterized, including polythreading 0-D rings with side arms that give 1-D or 2-D arrays [6], 1-D chains of alternating rings and rods (1-D → 1-D) [7], molecular ladders with dangling arms that result in (1-D → 2-D) or (1-D → 3-D) polythreading arrays [8], and the 2-D → 3-D polythreaded networks assembled from 2-D motifs [9] as well as 1-D chains and 2-D sheets (1-D + 2-D → 2-D) or (1-D + 2-D → 3-D) polythreaded systems [10]. Compound **2** is distinct from other previously known 2-D → 3-D polythreaded networks [9]. In the latter, the dangling ligands act as "rods" and are not disposed in an alternate but a mutual anti-orientation with respect to the layer plane. That is to say each metal ion connects two "rods" up and down, while in **2** each Co ion only connects one "rod" up or down.

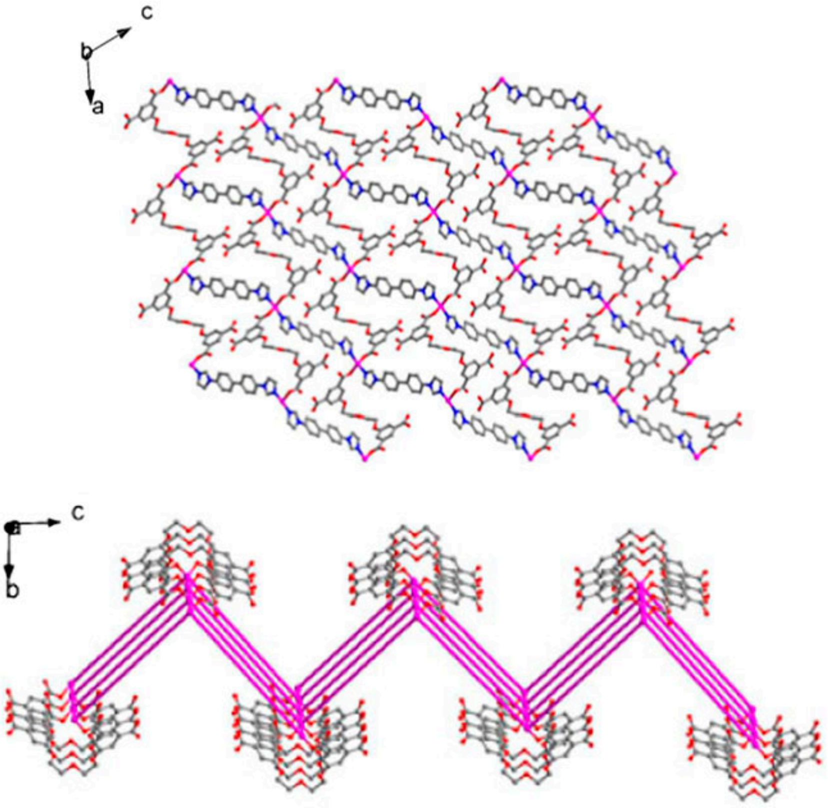

Figure 2d. The front (up) and side (down) views of the 2-D wave-like network with dangling "rod" in **2**.

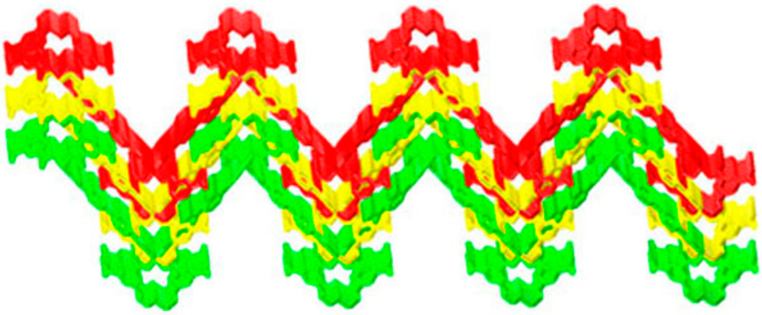

Figure 2e. The threefold 2-D → 3-D polythreading net of **2**.

Careful inspection of other related coordination polymers of these metals and ligands reported in the literature [19, 20] shows different structures in **1** and **2** such as high-dimensional structural features, threefold interpenetration, and *meso*-helical chain, mainly attributed to the rigidity and the appropriate length of bibp ligand.

3.3. *Thermogravimetric analyses*

To study the thermal stability of **1** and **2**, TG was performed on single-crystal samples of **1** and **2** under N_2 with a heating rate of 5 °C min^{-1}. As shown in figure S1, **1** gradually released the free waters from room temperature to about 80 °C (obsd. 0.85%, Calcd 0.64%) and began to decompose at 320 °C. However, it did not decompose completely until 700 °C. Complex **2** began to decompose at 240 °C.

3.4. *Photoluminescence property*

Photoluminescence experiments for **1** were performed at room temperature in the solid state. The emission bands for the free rigid bibp are at 355 and 373 nm (λ_{ex} = 280 nm), which can be assigned to the ligand centered π–π^* transitions of the benzene–imidazole rings [21]. Excitation of **1** at 340 nm produces one broad emission peak at 448 nm (figure S2), probably attributed to intraligand charge transfer of the bibp, because the Zn(II) is difficult to oxidize or to reduce due to its d^{10} configuration [22].

4. Conclusion

Two new 3-D entangled coordination complexes have been isolated. Complex **1** is a new uninodal four-connected ($6^5 \cdot 8$) net with vertex symbol $6 \cdot 6 \cdot 6 \cdot 6 \cdot 6_2 \cdot 8_2$, which is different from all exhibiting uninodal four-connected ($6^5 \cdot 8$) nets found in the literature. Three of these nets interpenetrate. Complex **2** shows an unusual threefold 2-D → 3-D polythreaded framework. In **2,** the Co ions are connected by the rigid bis(imidazole) ligands to generate 1-D helical chains, which suggests that rigid ligands can also construct helical motifs when they exhibit suitable conformation. As expected, **1** displays photoluminescence.

Acknowledgements

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