COORDINATION COMPOUNDS =

Self-Assembly of Two 1D Tube-Like Metal-Organic Networks Based on Flexible Bis(Benzimidazole) Ligand and 5-Nitroisophthalate¹

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Abstract—Two new polymeric networks, $[Co(pbbm)(nip)] \cdot H_2O(1)$ and $[Ni(pbbm)(nip) \cdot (H_2O)]$ (2) (pbbm = 1,1-(1,3-propanediyl)bis-1H-benzimidazole, $H_2nip = 5$ -nitroisophthalic acid) have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Complex 1 is an interesting one-dimensional (1D) tube-like chain utilizing $[Co_2(pbbm)_2]$ metallocycle as subunit. Complex 2 is also an interesting 1D tube-like chain based on $[Ni_2(pbbm)_2]$ loop subunit. In the title complexes, the π - π stacking and H-bonding interactions extend the 1D tube into 3D supramolecular framework, respectively. The structural differences between the title complexes indicate the importance of metal ions for the creation of molecular architectures. Furthermore, the luminescent properties of 1 and 2 were investigated.

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Metal-organic complexes have been experiencing great growth in the field of crystal engineering and inorganic chemistry due to their versatile structures and numerous potential applications as new solid materials [1-5]. Self-assembly of metal-organic networks from organic ligands and metal ions is an important aspect in this field [6]. An effective strategy is that the metal ions are linked by a kind of organic ligand to generate discrete moieties (cluster or quadrate unit) first as the subunits, then the subunits are connected by the second organic ligand to form polymeric structures [7-11]. As is known, the self-assembly and structures of metal-organic complexes is highly determined by the coordination geometry of the ligands and metal ions [12, 13]. Thus, selection of a suitable organic ligand with certain flexibility is crucial to the construction of coordination polymers.

As is known, the bis(benzimidazole)-based ligand has been widely used to construct metal-organic complexes [14–17]. However, the flexible bis(benzimidazole)-based ligands can bend or rotate to adopt the appropriate conformations in the assembly process, which have been less investigated [18, 19]. Recently, Lang's group has reported two 1D chain structures [(Cu(SCN)₂(prbbm)]_n and [{(CuSCN)₂(prbbm)₂} · 2MeCN]_n [20], and Hou's group has also reported two 1D chain structures [Cd(pbbm)₂(ClO₄)₂]_n and {[Cd(pbbm)SO₄(H₂O)₂] · CH₃OH}_n (prbbm = pbbm = 1,1-(1,3-propanediyl)bis-1H-benzimidazole) [21], which all utilized the small inorganic anions, such as,

 SCN^- , ClO_4^- and SO_4^{2-} as the secondary ligands. To our knowledge, however, combination of the flexible ligand pbbm (Scheme 1) with organic aromatic carboxylate anions for construction of metal-organic complexes is less investigated.



Here, we select the flexible ligand pbbm as main ligand and 5-nitroisophthalic acid (H_2 nip) as the secondary organic ligand, and two new coordination polymers [Co(pbbm)(nip)] \cdot H_2O (1) and [Ni(pbbm)(nip) \cdot (H_2O)] (2) have been successfully synthesized under hydrothermal conditions, which contain quadrate metallocycle as the subunits and the subunits are ultimately extended into one dimensional (1D) tube-like chains. In addition, the luminescent property of the complexes have also been investigated in the solid state.

EXPERIMENTAL

Solvents and starting materials for synthesis were commercially available and used as received. Ligand

¹ The article is published in the original.

pbbm was prepared according to the literature [22] and characterized by Fourier transform infrared (FT-IR) spectra. 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 240°C analyzer. Fluorescence spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer.

Synthesis of [Co(pbbm)(nip)] \cdot H₂O (1). The mixture of CoCl₂ \cdot 6H₂O (0.024 g, 0.1 mmol), H₂nip (0.021 g, 0.1 mmol) and pbbm (0.014 g, 0.05 mmol) was dissolved in 8 mL of distilled water and stirred for 0.5 h. Then the pH was adjusted to 6.0 by 0.1 M NaOH solution. Consequently, the resulting mixture was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel, which was heated at 150°C for 50 h, and then, the reaction system was cooled to room temperature at a rate of 5°C h⁻¹. Purple-red block crystals of 1 suitable for X-ray diffraction were isolated by mechanical separation from amorphous solid in 37% yield (based on Co(II) salt).

For $C_{25}H_{21}CoN_5O_7$ anal. calcd. (%): C, 53.34; H, 3.73; N, 12.45.

Found (%): C, 53.12; H, 3.78; N, 12.56.

IR (KBr) (v, cm⁻¹): 3364 (m), 3109 (w), 3091 (w), 2360 (s), 1629 (s), 1560 (m), 1515 (s), 1458 (s), 1398 (m), 1348 (s), 1240 (s), 1080 (s), 736 (s), 704 (s), 684 (w).

Synthesis of [Ni(pbbm)(nip) \cdot (H₂O)] (2). The synthetic procedure for 2 is the same as that for 1 except that Ni(NO₃)₂ \cdot 6H₂O (0.029 g, 0.1 mmol) was used instead of CoCl₂ \cdot 6H₂O. Green crystals of 2 suitable for X-ray diffraction were isolated by mechanical separation from amorphous solid in 43% yield (based on Ni(II) salt).

For $C_{25}H_{21}NiN_5O_7$ anal. calcd. (%): C, 53.56; H, 3.39; N, 12.50.

Found (%): C, 53.83; H, 3.41; N, 12.44.

IR (KBr) (v, cm⁻¹): 3325 (m), 3107 (w), 3078 (w), 2935 (w), 2360 (s), 1624 (s), 1556 (m), 1519 (s), 1461 (s), 1390 (m), 1344 (s), 1257 (m), 1072 (m), 738 (s), 725 (s), 669 (m).

X-ray crystallography. A Bruker Apex CCD diffractometer (Mo K_{α} radiation, graphite monochromator, $\lambda = 0.71073$ Å) was used to collect data. The structures were solved by direct methods with SHELXS-97 and Fourier techniques and refined by the full-matrix least-squares method on F^2 with SHELXL-97 [23, 24]. All non-hydrogen atoms were refined anisotropically, hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The H-atoms of water molecules have not been localized. All the crystal data and structure refinement details for the two complexes are given in Table 1. The data of relevant

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

Formula FW Crystal system Space group <i>a</i> (Å) <i>b</i> (Å)	$C_{25}H_{21}CoN_5O_7$ 562.40 Triclinic <i>P</i> -1 9.882(5) 11.505(5) 11.625(5) 64.261(5) 80.824(5)	$C_{25}H_{21}NiN_5O_7$ 562.18 Triclinic <i>P</i> -1 9.566(5) 10.073(5) 13.450(5) 72.470(5)		
FW Crystal system Space group <i>a</i> (Å) <i>b</i> (Å)	562.40 Triclinic <i>P</i> -1 9.882(5) 11.505(5) 11.625(5) 64.261(5)	562.18 Triclinic <i>P</i> -1 9.566(5) 10.073(5) 13.450(5) 72.470(5)		
Crystal system Space group <i>a</i> (Å) <i>b</i> (Å)	Triclinic <i>P</i> -1 9.882(5) 11.505(5) 11.625(5) 64.261(5) 80.834(5)	Triclinic <i>P</i> -1 9.566(5) 10.073(5) 13.450(5) 72.470(5)		
Space group <i>a</i> (Å) <i>b</i> (Å) <i>c</i> (Å)	<i>P</i> -1 9.882(5) 11.505(5) 11.625(5) 64.261(5)	<i>P</i> -1 9.566(5) 10.073(5) 13.450(5) 72.470(5)		
a (Å) b (Å)	9.882(5) 11.505(5) 11.625(5) 64.261(5)	9.566(5) 10.073(5) 13.450(5) 72.470(5)		
$b(\text{\AA})$	11.505(5) 11.625(5) 64.261(5)	10.073(5) 13.450(5) 72.470(5)		
- (Å)	11.625(5) 64.261(5)	13.450(5) 72.470(5)		
<i>c</i> (A)	64.261(5)	72 470(5)		
α (°)	20 224(5)	72.470(5)		
β (°)	89.834(J)	84.166(5)		
γ (°)	77.205(5)	74.869(5)		
$V(Å^3)$	1154.4(9)	1192.6(10)		
Ζ	2	2		
$D ({\rm g}{\rm cm}^{-3})$	1.618	1.566		
μ (mm ⁻¹)	0.803	0.871		
<i>F</i> (000)	578	580		
θ _{max} (°)	2.73 - 25.00	2.69-25.00		
Index ranges	$-11 \le h \le 11$	$-11 \le h \le 9$		
	$-13 \le k \le 13$	$-11 \le k \le 11$		
	$-13 \le l \le 13$	$-14 \le l \le 15$		
Reflections collected	8240	8478		
Unique reflections	4019	4149		
<i>R</i> _{int}	0.0166	0.0136		
R_1^{a}, wR_2^{b}	0.0413	0.0273		
$[I > 2\sigma(I)]$	0.1134	0.0701		
R_1^{a}, wR_2^{b}	0.0467	0.0286		
(all data)	0.1174	0.0710		
GOF on F^2	1.092	1.056		
$\Delta \rho_{\text{max}} (e A^{-3})$	0.703	0.552		
$\Delta \rho_{\min} (e A^{-3})$	-0.641	-0.461		
${}^{a}R_{1} = \sum F_{o} - F_{c} / \sum F_{o} . \qquad b wR_{2} = \{\sum w(F_{o}^{2} - F_{o}^{2}) ^{1/2} + \sum w(F_{o}^{2} - F_{$				

bond distances and angles are listed in Table 2. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 798759–798760 for complexes 1 and 2, respectively.

RESULTS AND DISCUSSION

 $[Co(pbbm)(nip)] \cdot H_2O(1)$: Compound 1 crystallizes in the space group *P*-1. The asymmetric unit con-

-	Comp	pound 1	
Co(1)–O(3A)	2.005(2)	Co(1)–N(1)	2.054(2)
Co(1)–O(1)	2.081(3)	Co(1)-N(3B)	2.146(2)
Co(1)–O(2)	2.391(4)	O(3A)Co(1)N(1)	113.48(10)
O(3A)Co(1)O(1)	144.62(12)	N(1)Co(1)O(1)	95.63(11)
O(3A)Co(1)N(3B)	101.27(9)	N(1)Co(1)N(3B)	94.96(10)
O(1)Co(1)N(3B)	95.48(10)	O(3A)Co(1)O(2)	89.86(10)
N(1)Co(1)O(2)	152.76(10)	O(1)Co(1)O(2)	57.86(11)
N(3B)Co(1)O(2)	93.90(10)		
Symmetry code: A: $x - 1$, y , z ; B	x - x, -y, -z.	1	
	Comp	pound 2	
Ni(1)–O(1)	2.0054(14)	Ni(1)–N(1)	2.0726(18)
Ni(1)–O(7A)	2.0880(14)	Ni(1)–O(2)	2.0845(15)
Ni(1)–N(3)	2.1033(17)	Ni(1)–O(6A)	2.2563(16)
O(1)Ni(1)N(1)	91.70(6)	O(1)Ni(1)O(7A)	94.48(6)
N(1)Ni(1)O(7A)	91.25(6)	O(1)Ni(1)O(2)	100.14(6)
N(1)Ni(1)O(2)	83.00(6)	O(7A)Ni(1)O(2)	164.42(5)
O(1)Ni(1)N(3)	93.65(6)	N(1)Ni(1)N(3)	170.38(6)
O(7A)Ni(1)N(3)	96.30(6)	O(2)Ni(1)N(3)	88.19(7)
O(1)Ni(1)O(6A)	154.87(5)	N(1)Ni(1)O(6A)	86.53(5)
O(7A)Ni(1)O(6A)	60.55(5)	O(2)Ni(1)O(6A)	104.50(6)
N(3)Ni(1)O(6A)	91.97(5)		
Symmetry code: A: $x, y - 1, z$.			

Table 2. Selected bond lengths (d, A) and angles (ω, deg) for 1 and 2

sists of one independent Co(II) atom, one pbbm ligand and one nip anion, as shown in Fig. 1. The Co(II) atom is five-coordinated by three oxygen atoms



Fig. 1. Coordination environment of the Co(II) atom in **1** (thermal ellipsoids are at the 30% probability level).

from two different nip ligands, and two nitrogen atoms from two pbbm ligands, showing a distorted square pyramidal coordination geometry $[CoN_2O_3]$. The basal plane of Co(II) atom is defined by N1, O1, O2, and O3A atoms. The apical site is occupied by N3B atom. The Co–N bond length is 2.054(2) and 2.146(2) Å, and the Co–O bond lengths range from 2.005(2) to 2.391(4) Å. All the bond lengths are in agreement with those reported in other Co(II) complexes of N,Omixed ligands [25].

In complex 1, two pbbm molecules act as bridging linkers to connect with two cobalt ions, resulting in the generation of a rectangular loop $[Co_2(pbbm)_2]$ (Fig. 2a). The completely deprotonated nip anions act as the secondary bridging linkers to connect two cobalt ions of the $[Co_2(pbbm)_2]$ loops, giving rise to a 1D tubelike chain (Figs. 2b and 2c).

There are evident face-to-face $\pi-\pi$ stacking interactions between the interdigitated ligands, with the overlapping mainly occurring between the benzimidazole rings moieties. The $\pi-\pi$ stacking interactions link adjacent 1D tubes to produce a 2D supramolecular layers. The center-to-center distance for the $\pi-\pi$ stacking interactions is 3.978 Å. The adjacent 2D supramolecular architectures are further connected by



Fig. 2. (a) Rectangular metallocycle. (b and c) View of a 1D tube of 1.



Fig. 3. The 3D supramolecular structure of 1 formed through hydrogen bonding and $\pi - \pi$ interactions between different 1D tubes.

a kind of hydrogen bonding interaction between the carbon atom of benzimidazole group and the oxygen atom from carboxylate $[C(1)-H(1A)\cdots O(2) 3.168 \text{ Å}, 161^{\circ}]$ to form a 3D supramolecular network (Fig. 3).

[Ni(pbbm)(nip) \cdot (H₂O)] (2): When Ni(NO₃)₂ \cdot $6H_2O$, instead of $CoCl_2 \cdot 6H_2O$, was selected to assemble with the pbbm and nip under the same reaction condition, a new coordination polymer 2, similar to that of complex 1, was isolated. Single-crystal X-ray diffraction reveals that complex 2 is also a 1D tube based on the rectangular metallocycle $[Ni_2(pbbm)_2]$, which is composed of two pbbm ligands and two nickel ions. As shown in Fig. 4, the asymmetric unit of 2 consists of one nickel ion, one nip ligand, one pbbm molecule, and one coordinated water molecule. The central nickel ion is six-coordinated by two nitrogen atoms from two pbbm ligands, three oxygen atoms from two nip ligands, and one oxygen atom from the coordinated water molecule, which is different from that of complex 1. The Ni–O bond lengths are in the range of 2.0054(14) - 2.2563(16) Å, and the Ni-N



Fig. 4. Coordination environment of the Ni(II) atom in **2** (thermal ellipsoids are at the 30% probability level).

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Fig. 5. (a) rectangular metallocycle. (*b* and *c*) View of a 1D tube of 2.



Fig. 6. The 3D supramolecular structure of 2 formed through hydrogen bonding and $\pi - \pi$ interactions between different 1D tubes.

bond lengths are 2.0726(18) and 2.1033(17) Å, respectively.

Similar to that of complex 1, two nickel ions are connected by two pbbm ligands to generate a rectangular metallocycle in 2 (Fig. 5a). The remaining coordination sites of the nickel ion are occupied by the oxygen atoms of nip ligands and coordinated water molecule. Thus, the rectangular metallocycle are infinitely connected by nip ligands to give rise to a 1D tube (Figs. 5b and 5c).

Indeed, there are multiple supramolecular interactions in complex **2**. The intermolecular hydrogenbonding interactions between the carbon atom of benzimidazole group and the oxygen atom of carboxylate $[C(4)-H(4A)\cdots O(7) 3.476 \text{ Å}, 161^{\circ}]$ link the 1D tube to generate 2D supramolecular layer. The $\pi-\pi$ stacking interactions (3.816 Å) between benzimidazole rings further connect the 2D supramolecular architecture to give rise to a 3D supramolecular network (Fig. 6).

In this work, we selected the flexible bis(benzimidazole) pbbm as the main ligand and H_2 nip as the secondary ligand to assemble with different metal ions Co(II) and Ni(II), and obtained two related com-

plexes. Both compound 1 and 2 showed 1D tube-like chain structure. Although the same ligands were used under similar synthetic conditions, the compound 1 based on Co(II) center is slightly different from compound 2 based on the Ni(II) center. The coordination environments of the metal ions is different: complex 1 is five-coordinated, while complex 2 is six-coordinated, which indicate that the metal centers play an important role in the assembly process. In addition, it can be seen that the pbbm ligand can rotate and bend around the $-CH_2$ group freely when coordinating to the central metals and the conformation of pbbm can change correspondingly, leading to the subtle distinction of the metallocycle subunits and the resultant structures. Several metal complexes based on pbbm ligand have been reported. However, Co(II) and Ni(II) complexes constructed from pbbm ligand are limited. In the previously reported related complexes, two new 1D chain structures $[(Cu(SCN)_2(prbbm)]_n]$ with channel, and $[{(CuSCN)_2(prbbm)_2} \cdot 2MeCN]_n$ with double chain have been reported by Lang et al. [20], two new 1D chain structures $[Cd(pbbm)_2(ClO_4)_2]_n$ (1) with double-stranded ribbons and



Fig. 7. The emission spectra of 1, 2 and pbbm ligand in the solid state at room temperature.

 $\{[Cd(pbbm)SO_4(H_2O)_2] \cdot CH_3OH\}_n$ (2) with 1D looped chains based on two kinds of rings have been reported by Hou et al. [21]. However, complexes 1 and 2 are 1D tube-like chains constructed by metallocycle subunits and nip anions and ultimately extended to 3D supramolecular networks by hydrogen bonding and $\pi-\pi$ stacking interactions, which is different from the above reported complexes.

The photoluminescent behaviors of polymers 1, 2 and free ligand pbbm were studied in the solid state at room temperature (Fig. 7). The free ligand pbbm display luminescence with emission maxima at 445 nm ($\lambda_{ex} = 320$ nm). The emission for the complexes 1 and 2 can be observed, with the maximum emission wavelength at 421 nm ($\lambda_{ex} = 250$ nm) for 1 and 470 nm ($\lambda_{ex} = 250$ nm) for 2. Compared with the emission spectrum of pbbm, complexes 1 and 2 are 14 nm blueshifted, and 35 nm red-shifted, respectively, which is considered to mainly arise from ligand-to-metal charge transfer (LMCT) as discussed previously [26–29].

In this paper, the self-assembly reactions of the flexible main ligand pbbm and rigid auxiliary ligand nip with cobalt(II) or nickel(II) salts produce two coordination polymers under hydrothermal condition. Both complexes 1 and 2 are 1D tubes constructed by metallocycle subunits and nip anions, and extended into 3D supramolecular structures by weak interactions. The flexibility of pbbm and the different coordination preferences of the Co(II) and Ni(II) metal ions lead cooperatively to the different architectures of 1D tube. Further studies will focus on producing other metal-organic complexes with novel structures by using a wide range of bridging flexible bis(benzimidazole)-based ligands and polycarboxylates. Therefore, the prospect of tuning the size of metallocycle through bridging bis(benzimidazole)-based ligands provides an impetus for further design and synthesis of nanotubular metal-organic frameworks.

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