

## A New 3D Metal-organic Framework Based on the Four-connecting Cobalt(II) Node Showing Unusual dmp Topology with 3-Fold Interpenetration

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The synthesis of polymeric coordination networks or metal-organic frameworks (MOFs) has evoked an enormous amount of recent interest for their intriguing and diverse architectures and for their potential as functional materials with specific properties, such as luminescence, magnetism, absorption, catalysis, ion-exchange, *etc.*<sup>1</sup> From both zeolite chemistry and crystal engineering points of view, the nets built from 4-coordinated (4-c) centers (the tetrahedrally coordinated divalent cations ( $M^{2+} = Zn^{2+}$  or  $Co^{2+}$ ) capture much attention both for their inherent interest (all zeolites are 4-c nets).<sup>2</sup> Recently, Keeffe and Yaghi *et al.*<sup>3</sup> have explored the large majority of 3D MOFs with uninodal net topology involving tetrahedral or square-planar nodes (*e.g.* **dia** or **nob** network). Notably, 4-connected nets with mixed connections of both types of nodes (*e.g.* **pts**, **mog**, **dmp**, **asv**, and **ptf**) have rarely been reported so far.<sup>4</sup> Therefore, new or unusual 4-connected framework topology derived from modulation of the linkages is still of great challenge and focus.

Flexible ligands can bend, rotate around bonds, reorient themselves, and the resulting complexes can often be pleasantly surprising. The viability of using long alkyl spacers in linking benzimidazole fragments and their subsequent use in forming novel coordination polymers has recently been investigated by our and other groups.<sup>5</sup> In this paper, we introduced  $H_2nip$  coligand into Co-bbmi synthesis system and successfully synthesized an unusual 3D 4-connected framework with dmp (6<sup>5</sup>.8) topology, formulated  $[Co(nip)-(bbmi)]_n$  [bbmi = 1,1'-(1,4-butanediyl)bis(2-methylbenzimidazole),  $H_2nip$  = 5-nitroisophthalic acid]. The compound has been characterized by IR spectroscopy, elemental analysis and single crystal X-ray diffraction. Furthermore, the behaviors of the complex as the catalyst in Fenton-like degradation of organic dyes were also investigated.

### Experimental Section

**Materials and Characterization Methods.** All reagents and solvents were commercially available except for bbmi ligand, which was synthesized according to the literature.<sup>6</sup> The FT-IR spectrum was recorded from KBr pellets in the range of 4000-400  $cm^{-1}$  on an Avatar 360 (Nicolet) spectrophotometer. Elemental analyses (C, H, and N) were carried

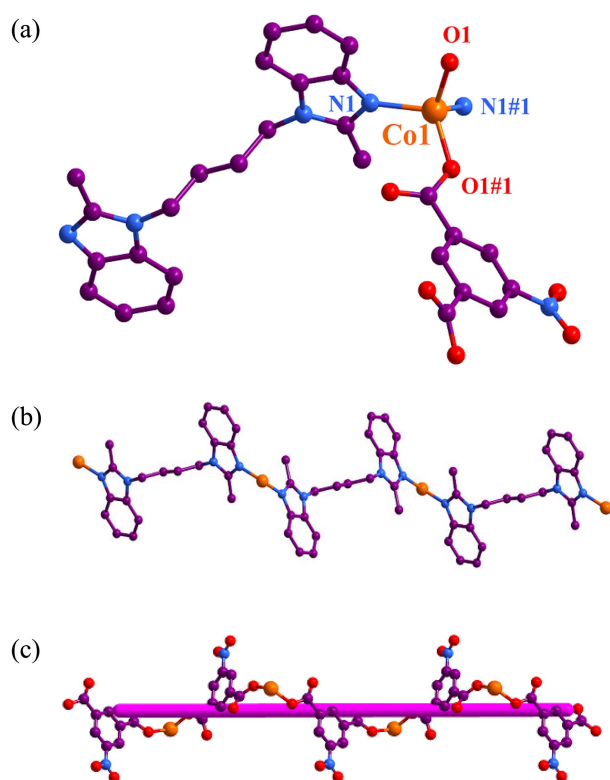
out on a Perkin-Elmer 240C analyzer. Thermal analysis was performed on a Netzsch TG 209 thermal analyzer from room temperature to 1073 K under  $N_2$  at a heating rate of 10  $^{\circ}C/min$ . The luminescence spectra for the powdered solid samples were measured at room temperature on a Hitachi F-7000 fluorescence spectrophotometer. The X-ray powder diffraction (XRPD) pattern was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator.

**Synthesis of  $[Co(nip)(bbmi)]_n$ .** A mixture of  $Co(NO_3)_2 \cdot 6H_2O$  (0.1 mmol, 29.1 mg), bbmi (0.1 mmol, 31.8 mg),  $H_2nip$  (0.1 mmol, 21.1 mg), and NaOH (0.2 mmol, 8.0 mg) in 12 mL of distilled  $H_2O$  was sealed in a 25 mL Teflon-lined autoclave and heated to 413 K for 3 days under autogenous pressure. After the mixture was cooled to room temperature at a rate of 5  $^{\circ}C/h$ , purple block crystals of the complex (yield 55% based on Co) were isolated after washed with distilled water, and dried in air. Anal. Calcd for  $C_{28}H_{25}CoN_5O_6$  (%): C, 57.34; H, 4.30; N, 11.94%. Found: C, 57.21; H, 4.51; N, 11.82%. IR (KBr pellet,  $cm^{-1}$ ): 2927w, 2378m, 2329w, 1634s, 1527w, 1460w, 1332m, 1088m, 747w, 538w, 470w.

**Crystallography.** X-ray single-crystal diffraction data of the complex was collected on a Bruker Smart 1000 CCD diffractometer (Mo  $K\alpha$ ,  $\lambda = 0.71073 \text{ \AA}$ ) at a temperature of 296 K with multi-scan mode. Data absorption corrections were carried out by SADABS software packages.<sup>7</sup> The structures were solved by direct methods and refined with a full-matrix least-squares technique based on  $F^2$  with the SHELXL-97 crystallographic software package.<sup>8</sup> All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of ligands were included in the structure factor calculation at idealized positions by using a riding model and refined isotropically. CCDC-948137 contains the supplementary crystallographic data. The crystallographic data for the complex is summarized in Table S1, the selected bond lengths and angles are listed in Table S2, and positional, thermal and occupancy parameters for the complex are given in Table S3 (Supporting Information).

### Results and Discussion

X-ray crystal structure analysis reveals that the complex

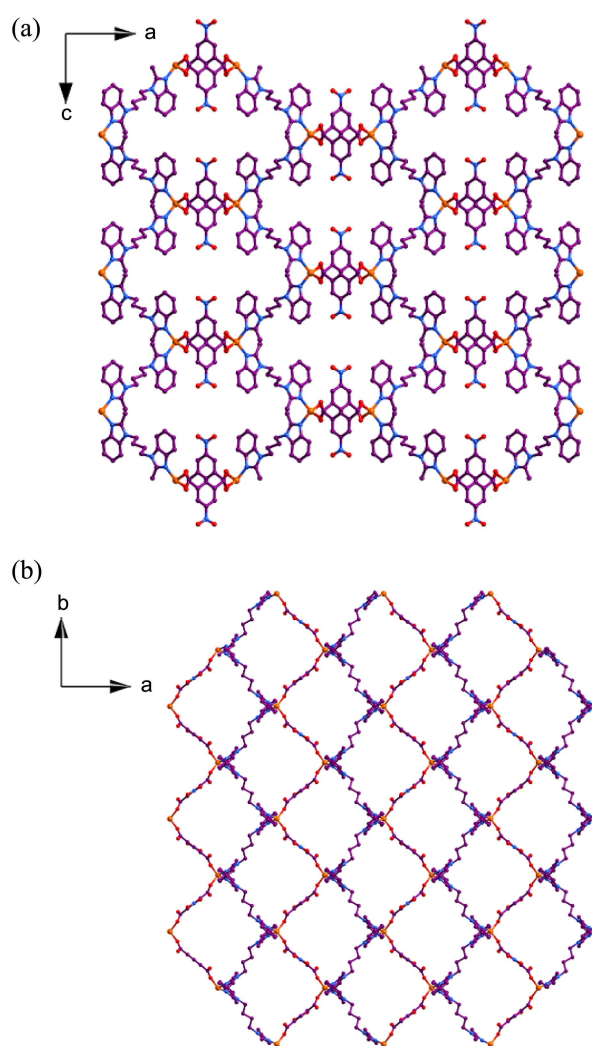


**Figure 1.** (a) Coordination environment around the Co(II) center in the complex. Hydrogen atoms are omitted for clarity. Symmetry code:  $\#1 x, -y+1/2, -z+1/2$ ; (b) the chain constructed by Co atoms and bbmi ligands; (c) the right-handed helical chain constructed by Co(II) ions and  $\text{nip}^{2-}$  ligands.

crystallizes in the orthorhombic space group  $Pnna$ . As exhibited in Figure 1(a), the Co(II) atom is four-coordinated in nearly perfect tetrahedral coordination geometry with  $\tau_4$  value of 0.93,<sup>9</sup> defined by two oxygen atoms from two symmetry-related  $\text{nip}^{2-}$  ligands and two nitrogen atoms from two separated bbmi ligands. The Co1–O1(O1#1) distances are 1.9352(17) Å, the Co1–N1(N1#1) lengths are 2.020(2) Å (symmetry code:  $\#1 x, -y+1/2, -z+1/2$ ), and the bond angles around Co(II) ions range from 104.33(8)° to 112.24(12)°, which drop into the normal scope of the reported Co(II) complexes.<sup>10</sup>

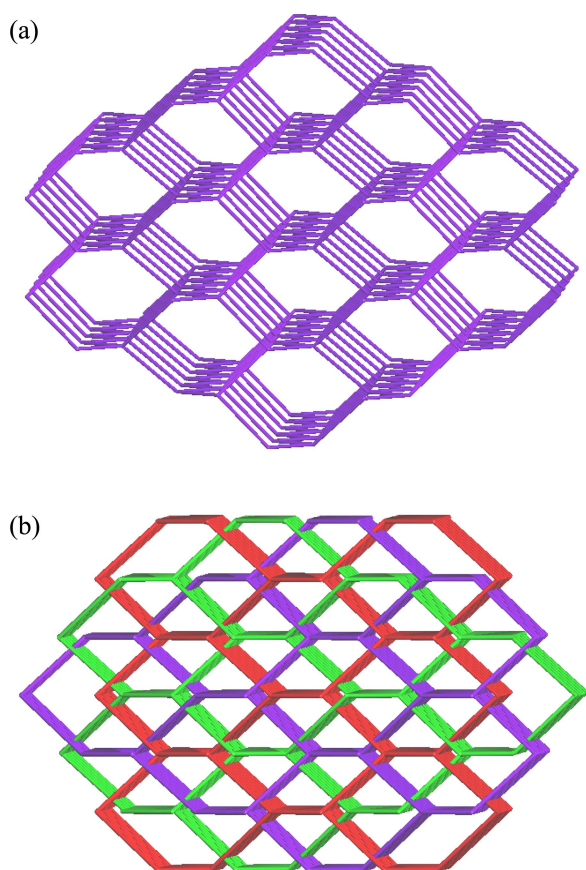
In the complex, bbmi ligand shows the *trans*-conformation with a completely parallel fashion, displaying two flexures with opposite direction. The bbmi ligands bridging neighboring Co atoms produce a 1D zigzag chain, and the Co···Co separation across the bbmi bridge is 14.120 Å (Figure 1(b)). Moreover, the carboxyl groups of  $\text{nip}^{2-}$  ligand adopt a uniform monodentate fashion and link the Co(II) ions to give rise to a 1D right-handed helical chain with non-bonding Co···Co distance of 10.652 Å (Figure 1(c)). The interlaced connection of Co(II)–bbmi and Co(II)/ $\text{nip}^{2-}$  chains along the two directions constructs the 3D framework by sharing Co(II) ions with large rectangular cavities of size *ca.* 18.999 × 25.151 Å<sup>2</sup> and *ca.* 16.246 × 17.246 Å<sup>2</sup> along the *ac* and *ab* plane, respectively, as illustrated in Figure 2(a) and Figure 2(b).

A better insight into the nature of this intricate framework



**Figure 2.** (a) 3D single framework of the complex along the *ac* plane; (b) 3D single framework of the complex along the *ab* plane.

can be acquired by using a topological analysis with TOPOS4.0 professional software.<sup>11</sup> In the complex, each  $\text{nip}^{2-}$  dianion and bbmi ligand can be simplified to be linear connectors; each Co center bridges two bbmi and two  $\text{nip}^{2-}$  moieties, viewed as 4-connected nodes in tetrahedral sphere, therefore, the combination of nodes and connectors suggests an uninodal 4-connected network with an extended Schäfli symbol of 6.6.6.6(2).8(5), assigned to the unusual **dmp** net according to Wells' classification (Figure 3(a)). In literature, the four-connecting **dia**, **PtS**, **CdSO<sub>4</sub>**, **qtz** nets are common. By contrast, the number of MOFs belonging to **dmp** net is still limited, where **dmp** is based on pillared honeycomb-like 6<sup>3</sup> layers, but the different connectivity between the layers leads to such distinct net compared with **dia** net.<sup>12</sup> In comparison with [Co( $\text{nip}$ )(bbbi)]<sub>n</sub> (bbbi = 1,1-(1,4-butanediyl)bis-1H-benzimidazole),<sup>13</sup> their structures are different, generating the CsCl net with the 4<sup>24</sup>6<sup>4</sup> topology. The results suggest that the N-donor ligands play an important role in governing the architectures of the metal–organic frameworks. The large voids formed by a single 3D network allow the incorporation of another two identical networks. Therefore,



**Figure 3.** (a) The 4-connected 3D **dmp** ( $6^5.8$ ) topology with only the 4-connecting Co nodes and connections between them shown; (b) the three interpenetrating **dmp** nets.

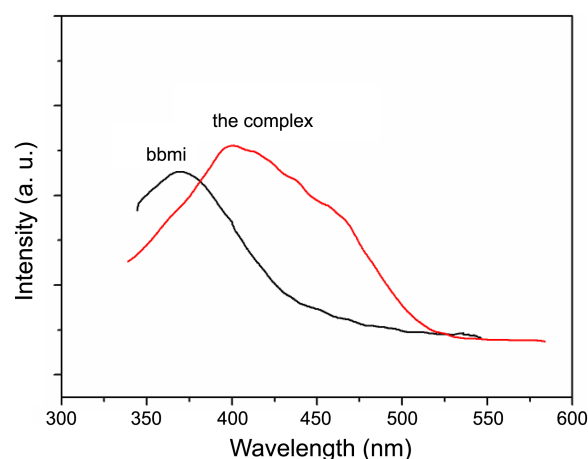
the overall structure of the complex is a 3-fold interpenetrating 3D framework belonging to class Ia (Figure 3(b)).

**IR Spectrum and XRPD Pattern.** The IR spectrum of the complex exhibits the antisymmetric stretching vibration  $\nu_{as}(\text{COO}^-)$  at  $1634\text{ cm}^{-1}$  and the symmetric stretching vibration  $\nu_s(\text{COO}^-)$  at  $1332\text{ cm}^{-1}$ , with a separation  $\nu$  of  $302\text{ cm}^{-1}$ , as expected for the observed monodentate coordination mode of the carboxyl groups. Band around  $2927\text{ cm}^{-1}$  are assigned to the C–H stretches, while band at  $1527\text{ cm}^{-1}$  could be assigned to the  $\nu_{\text{C}=\text{N}}$  absorptions of the benzimidazole rings in the ligand bbmi.

To confirm the phase purity of the complex, the XRPD patterns were recorded, and it is in good agreement with the corresponding simulated one calculated from the single-crystal diffraction data (Figure S1), indicating a pure phase of the bulky sample.

**Thermal Analysis.** The thermal behavior of the complex was also examined by thermogravimetric analysis (TGA) (Figure S2). The complex displays a high thermal stability, which is stable up to 665 K and then keeps losing weight until to 919 K in accord with the losses of the bbmi and  $\text{nip}^{2-}$  ligands. Finally, the CoO residue of 13.4% (calculated 12.8%) is observed.

**Luminescence Property.** The solid state photoluminescence properties of the complex and free bbmi ligand were

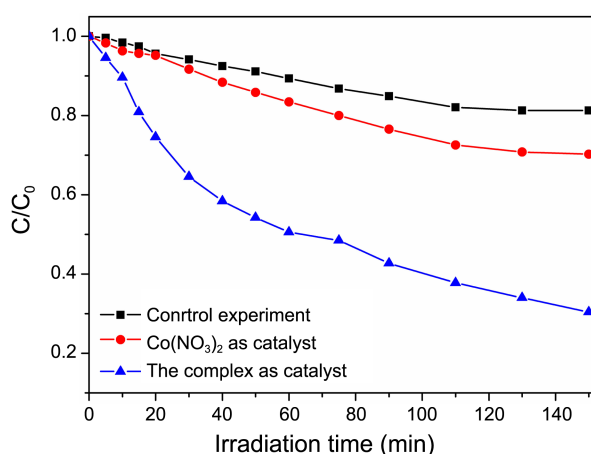


**Figure 4.** Solid-state fluorescence spectra of free bbmi and the complex.

investigated at room temperature. As illustrated in Figure 4, the complex exhibits intense emission bands with a maximum at 401 nm upon excitation at 280 nm. In contrast to the bbmi ligand ( $\lambda_{\text{em}} = 369\text{ nm}$ ,  $\lambda_{\text{ex}} = 300\text{ nm}$ ), the complex with a small red-shifted is probably caused by the coordination of bbmi to the metal centers.

**Catalytic Degradation Experiment.** In recent years, using MOFs as catalysts has becoming an interesting field,<sup>14</sup> which mainly stems from many inherent advantages, such as the controlled oxidation state of the cation, the possibility to tune the electron density on the metal as a contribution of different ligands, as well as multiactive central metal atoms available within the molecule. The oxidative degradation of the azo dye methyl orange has received extremely intensive interest since it is a harmful acidic/anionic dye, and has been widely used in textile, printing, paper, food and pharmaceutical industries and research laboratories.<sup>15</sup> Co(II)-containing complexes were used by our group to effectively activate sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) to induce sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) for oxidation of methyl orange in aqueous solution.<sup>5e</sup>

The catalytic performance of the complex was investigated with degradation of methyl orange through a typical process: 50 mg of the title compound was mixed together with 150 mL of 10.0 mg/L methyl orange solution, magnetically stirred to ensure the equilibrium. At given time intervals 5 mL solution was taken out and centrifuged to remove the residual catalyst. As shown in Figure 5, it can be clearly seen that the concentration of methyl orange decreases obviously for the complex and approximately 58% of methyl orange has been decomposed with 40 min; after which methyl orange oxidation proceeds at a reduced rate, reaching up to 70% after 150 min. In the same time scope, the dissociation of methyl orange is gradually added and finally only 19% has been degraded with merely addition of oxidant. Since Co(II) species may play a key role in these reactions, an equimolar  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with Co(II) containing in the frameworks was investigated. It has been proved that  $\text{Co}^{2+}$  ions have the catalytic effect, but with a lower overall



**Figure 5.** The control experiments of the catalytic degradation of methyl orange.

degradation efficiency being 30%. The results demonstrate that the complex shows high catalytic activity for the degradation of methyl orange, and it may be due to in which unsaturated Co(II) centers is in favor for the methyl orange molecular to enter the metal coordination sphere enhancing the catalytic activity.<sup>16</sup> Four cycles were carried out to evaluate the reusability of the complex powder as catalyst for the removal of methyl orange dye at the same conditions (Figure S3). The catalyst was removed through a centrifugal machine, then washed with distilled water for several times and in vacuum dryer for 10 h after each degradation experiment. The results demonstrate that the degradation efficiencies of methyl orange dye decrease slightly after the each cycle due to enhancement of the Co leaching, but the complex as heterogeneous catalyst still maintains higher catalytic activity.

In summary, a new Co(II)-containing coordination polymer [Co(nip)(bbmi)]<sub>n</sub>, has been synthesized, which shows an unusual 3-fold interpenetrating **dmp** 3D net, indicating that the combination of dicarboxylates with flexible N-donor ligands is a good choice for the construction of MOFs with specific structures and properties. Remarkably, the complex exhibits positive catalytic activity for dye degradation.

**Supplementary Material.** CCDC number: 948137 for the complex. The data can be obtained free of charge via [https://services.ccdc.cam.ac.uk/structure\\_deposit](https://services.ccdc.cam.ac.uk/structure_deposit) (or from the Cambridge Cryst allographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (44)1223-336-033(44); or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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