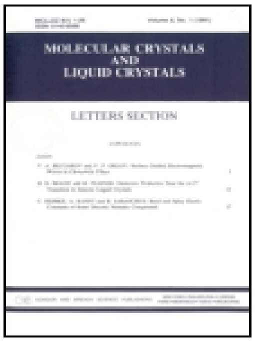

Molecular Crystals and Liquid Crystals

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Synthesis and Characterizations of Two New Coordination Polymers Constructed from 1,1′-Binaphthyl Dicarboxylic Acid Derivatives with Cobalt(II) and Copper(II)

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In this paper, two novel metal-organic frameworks $[Cu(bna\mathbf{1})(DMF)]_n{\cdot}nH_2O{\cdot}nCH_3OH$ *(complex* ***1****)* ($H_2bna\mathbf{1}$ = *2,2′-dihydroxy-1,1′-dinaphthyl-6,6′-dicarboxy acid) and* $[Co(bna\mathbf{2})_2(bpy)(H_2O)_2]_n$ *(complex* ***2****)* ($H_2bna\mathbf{2}$ = *2,2′-dihydroxy-1,1′-Dinaphthyl-4,4′-dicar–boxyacid) have been synthesized under mild conditions and carefully characterized. Crystal structural analysis reveals that complex* ***1*** *adopts a 1D infinite chain structure, which forms 2D sheet by* π–π *weak interactions. Complex* ***2*** *possesses 2D sheet structure, where Cobalt ions are recognized as the nodes. So it generated a regular two-dimensional grid with the size of 1.57 × 1.15 nm. Complex* ***2*** *assembles into a 3D supramolecular network connected by the hydrogen bonds. IR spectra studies indicate that the coordination mode of carboxyl group of complex* ***1*** *and complex* ***2*** *are chelating with the metal ions. X-ray powder diffraction (PXRD) studies of both complexes confirm that there is no impurity phase in both complexes since their diffraction patterns match well with the simulated ones.*

Keywords Cobalt(II); Copper(II); crystal structure; dihydroxy-dinaphthyl-dicarboxylate; metal-organic frameworks

Introduction

Over the past decades, metal-organic frameworks (MOFs) have attracted a great deal of interest owing to their ability of systematically tune their porosity and the functionalities that are incorporated within the framework scaffolds [1–6]. As a result, numerous MOFs have been engineered for potential applications, including nonlinear optics [2], gas storage [7–10], and selective catalysis [11–16]. Although a number of strategies have been developed to achieve extremely large porosity in MOFs in recent years [4], it is still a challenge to obtain MOFs with large open channels about several nanometers in dimensions [17–20]. Such large open channels are essential for asymmetric catalytic reactions because of the need to transport typically very large organic substrates and products [21]. So great progress has been made to the modification of the frameworks.

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The functionalization of binols has been investigated for several years. Such an interest is due to the great diversity of binaphthyl derivatives [22]. Due to the axial chirality with C_2 symmetry and the ability of incorporate functional groups into porous MOFs can lead to larger channels and more stable MOFs, binol derivatives have become important molecules in several fields [22]. The binol core has been conveniently functionalized at both the 3,3′, 4,4′, 5,5′, and 6,6′ positions [23–26]. Furthermore, the access to the 4,4′ carbons has seldom been documented. We are particularly interested in 4,4′-bicarboxyl binol since it provides an ideal platform for catalyst designing because of the identical secondary environments, and bicarboxyl groups suited to bind metal ions to construct coordination polymer [27, 28]. Herein, we report the successful incorporation of carboxyl groups into BINOL and synthesis of two ligands of binol derivatives. Then, the ligands are used to construct two novel MOFs. Crystal structural analysis reveals that complex **1** adopts a 1D infinite chain structure, which forms 2D sheet by π–π weak interactions and complex **2** possesses 2D sheet structure, which further assembles into a 3D supramolecular network connected by the hydrogen bonds.

Experimental

Materials and Methods

All chemicals were purchased commercially and used without further purification. Infrared spectra were obtained with a Nicolet Impact 410 FTIR spectrometer in the range 400–4000 cm^{-1} using the KBr pellets. ^{1}H NMR spectra were obtained with a Bruker 400 (400 MHz) spectrometer. PXRD spectra were recorded with a Bruker D8 ADVANCE.

Synthesis

*Synthesis of 6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthalene (**2**).* 6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthalene was synthesized according to a published procedure [29]. Bromine (1.54 mL, 30.8 mmol) was added slowly to a solution of 2,2′-dihydroxy- 1,1′-binaphthalene (4 g, 14.0 mmol) in CH2Cl2 (20 mL) at 0°C cover a 12 h period. The resulting mixture was warmed to room temperature and a solution of sodium bisulfite in water was added slowly. After then, the organic layer was separated and dried over anhydrous MgSO4 [30]. Pure 6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthalene (2) was obtained by removing the organic volatiles (6.08 g, 98%, mp: 193 ~ 196°C). IR (KBr, cm^{-1}): 3420, 1450 ~ 1600, 1300 ~ 1050. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 5.05 (s, 2H), 6.95 ~ 6.97 (d, $J = 10.7$ Hz, 2H), 7.37 (m, 6H), 8.04 (s, 2H)

*Synthesis of 6,6′-dicyano-2,2′-dihydroxy-1,1′-binaphthalene (**3**).* 6,6′-dicyano-2,2′-dihydroxy-1,1′-binaphthalene was synthesized according to a published procedure [29]. Compound **2** (4.72 g, 10.6 mmol) and CuCN (4.72 g, 42.4 mmol) in DMF (100 mL) were added to a 100 mL three-necked round-bottom flask equipped. The mixture was stirred at 150°C for 72 h, then the solution was added to dilute hydrochloric acid (100 mL), $FeCl_3 \cdot 6H_2O$ (16 g) and concentrated hydrochloric acid (8 mL), the precipitate was collected, dried, and purified from silica-gel column chromatography to afford pure 6,6′-dicyano-2,2′-dihydroxy-1,1′-binaphthalene (**3**) as a brown powder (2.39 g, 67%, mp: 176 ~ 178°C). IR (KBr, cm^{-1}): 3200 ~ 3500, 2923, 2222. ^{1}H NMR (CDCl$_3$, 600 MHz): δ

5.06 (s, 2H), 6.95 ∼ 6.97 (d, $J = 9.0$ Hz, 2H), 7.36 ∼ 7.37 (dd, $J = 10.8$ Hz 2H), 7.38 ∼ 7.40 (d, $J = 9.0$ Hz, 2H), 7.88 ∼ 7.89 (d, $J = 9.0$ Hz, 2H), 8.04 ∼ 8.05 (d, $J = 1.8$ Hz, 2H).

*Synthesis of 2,2′-dihydroxy-1,1′-dinaphthyl-6,6′-dicarboxy acid (**4**).* A mixture of Compound **3** (2.3 g, 6.8 mmol) and NaOH (6 mol/L, 10 mL) was refluxed for 24 h. After that, the reaction was cooled to room temperature and the solution was acidified with concentrated hydrochloric acid (20 mL). The precipitate was collected, dried, and purified from silica-gel column chromatography to afford pure compound **4** (H_2**bna1**) as a yellow powder (2.4 g, 98%, Mp >300°C).IR (KBr, cm^{-1}): 2900 ∼ 3420, 1682, 1478. ^{1}H NMR (DMSO-*d6*, 600 MHz): δ 5.02(s, 2H), 6.98 ∼ 8.50 (m, 10H), 9.84 (s, 2H).

*3-Nitro-1,8-naphthalic anhydride (**6**).* 3-Nitro-1,8-naphthalic anhydride was synthesized according to a published procedure [30]. The reaction above use 1,8-Naphthalic anhydride (5.0 g, 25.2 mmol) to afford a yellow powder compound **6** (4.04 g, 74.5%, mp: 248 ∼ 252°C). IR (KBr, cm^{-1}): 3072, 1780, 1749, 1628, 1594, 1532, 1343, 788, 754, ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.075 ∼ 8.049 (t, $J = 7.2$ Hz, 1H), 9.384 (s, 1H), 8.586 ∼ 8.573 (d, $J = 7.8$ Hz, 1H), 8.868 ∼ 8.854 (dd, $J = 7.8, 7.2$ Hz, 1H), 9.268 (s, 1H).

*Anhydro-3-nitro-8-hydroxymercuri-1-naphthoic acid (**7**).* Anhydro-3-nitro-8-hydroxymercuri-1-naphthoic acid was synthesized according to a published procedure [30]. A mixture of compound **6** (4.04 g, 17 mmol) and sodium hydroxide (2.26 g, 56 mmol) in water (81 mL) was added to a solution of mercury oxide (3.92 g, 18 mmol) in acetic acid (8 mL) and water (11 mL). The mixture was then stirred and heated under reflux for 48 h. The suspension was then hot-filtered and dried to give a creamy white powder compound **7** (6.66 g, 96.0%). IR (KBr, cm^{-1}): 3074, 1608, 1557, 1526, 1489, 1382, 1327, 775.

*3-Nitro-1-naphthoic acid (**8**).* 3-Nitro-1-naphthoic acid was synthesized according to a published procedure [30]. Compound **7** (6.66 g, 16 mmol) was added into hydrochloric acid (19.5 mL) and water (39 mL) to afford a white powder **8** (1.51 g, 43.0%, mp: 258 ∼ 262°C). IR (KBr, cm^{-1}): 3300 ∼ 2500, 3066, 1699, 1595, 1529, 1451, 1338, 917, 795, 759, 686. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.809 (td, 1H, $J = 6{,}3, 0.6$, 1H), 7.937 ∼ 7.909 (td, 1H, $J = 7.2, 1.2$, 1H), 8.415 ∼ 8.401 (d, $J = 8.40$, 1H), 8.749 ∼ 8.744 (d, $J = 3.00$ Hz, 1H), 8.971 ∼ 8.957 (d, $J = 8.40$ Hz, 1H), 9.232 (s, 1H).

*3-Amino-1-naphthalenecarboxylic acid, sodium salt. (**9**).* 3-Amino-1-naphthalenecarboxylic acid, sodium salt was synthesized according to a published procedure [30]. Compound **8** (0.81 g, 4 mmol) was dissolved in 15% ammonia (15 mL), and ferrous sulfate (12.6 g, 45 mmol) in water (15 mL) was added. The mixture was brought to a boil and then filtered. The clear, light yellow filtrate on acidification with sulfuric acid yielded the sulfate which was collected in almost theoretical yield (0.19 g, 75%, mp: 212 ∼ 214°C). IR (KBr, cm^{-1}): 3300 ∼ 2500, 2902, 1695, 1628, 1553, 1513, 1459, 894, 794. ^{1}H NMR (DMSO-*d6,* 600 MHz): δ 7.357 ∼ 7.330 (m, 2H), 7.445 ∼ 7.421 (t, $J = 7.2$, 1H), 7.760 (s, 1H), 8.664 ∼ 8.605 (d, $J = 8.4$, 1H).

*3-Hydroxy-naphthalene-1-carboxylic acid (**10**).* 3-Hydroxy-naphthalene-1-carboxylic acid was synthesized according to a published procedure [30]. A solution of compound **9** (0.15 g, 0.79 mmol) in 1M aqueous sodium hydroxide (1 mL) was treated with 1M aqueous sulfuric acid (1 mL) to give a yellow crystals. (0.06 g, 63.8%, mp: 244 ∼ 246°C). IR (KBr, cm^{-1}): 3366, 3300 ∼ 2500, 2959, 1690, 1624, 1577, 1514, 1464, 1414, 1223, 909, 872, 792, 650. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.341 ~ 7.337 (d, $J = 2.4$, 1H), 7.374 ~ 7,346 (td, $J = 6.9$, 1.2, 1H), 7.443 ~ 7.416 (td, $J = 6.6$, 1.2, 1H),. 7.704 ~ 7.699 (d, $J = 3.0$, 1H), 7.767 ~ 7.753 (d, $J = 8.4$, 1H), 8.686 ~ 8.672 (d, $J = 8.4$, 1H), 9.973 (s, 1H),13.109 (s, 1H).

*2,2′-Dihydroxy-1,1′-dinaphthyl-4,4′-dicarboxy acid (**11**).* A mixture of compound **10** (0.61 g, 3.2 mmol) and $FeCl_3 \cdot 6H_2O$ (2 g, 7.4 mmol) was added to water (20 mL) to afford the compound **11** (H_2**bna2**) (0.41g, 66.6%, mp:>300°C). IR (KBr, cm^{-1}): 3256, 3071, 1691, 1585, 1511, 1287, 1248, 890, 790. ^{1}H NMR (DMSO-*d6,* 600 MHz): δ 7.613 ~ 7.600 (d, $J = 7.8$, 2H), 7.781 ~ 7.753 (td, $J = 6.9$, 1.2, 2H), 7.898 ~ 7.871 (td, $J = 6.6$, 1.2, 2H), 8.566 (s, 2H), 9.437 ~ 9.423 (d, $J = 8.4$ Hz, 2H).

*Synthesis of [Cu(**bna1**)(DMF)]$_n$·nH_2O·nCH_3OH (Complex **1**).* A mixture of compound **4** (H_2**bna1**, 7.5 mg, 0.02 mmol) and NaOH (1.6 mg, 0.04 mmol) was warmed to dissolved in ethanol (5 mL). The solvent was evaporated and the residue was dissolved in DMF (1mL) and H_2O (1 mL) (V:V = 1:1) as the under layer in a tube. DMF (1 mL) was carefully layered as the middle layer in the tube. $CuSO_4 \cdot 5H_2O$ (19.9 mg 0.08 mmol) was dissolved in CH_3OH (2 mL) as the up layer. The tube was then sealed. Diffusion between the three phases over a period produced transparent block pale yellow crystals of complex **1**. Anal. Calcd for $C_{26}H_{25}CuNO_9$: C, 55.86; H, 4.51; N, 2.51%.

*Synthesis of [Co(**bna2**)$_2$(bpy)(H_2O)$_2$]$_n$ (Complex **2**).* $Co(NO)_3 \cdot 6H_2O$ (19 mg, 0.2 mmol) was dissolved in a mixture of DMSO (1 mL) and H_2O (2 mL) (V/V = 1:2) as the under layer in a tube. A mixture of DMF (1 mL) and H_2O (1 mL) (V/V = 1:1) was carefully layered as the middle layer in the tube. A mixture of compound **11** (H_2**bna2**, 7.5 mg, 0.02 mmol) and 4,4′-bipyridine (8 mg, 0.04 mmol) was dissolved in DMF (2 mL) as the up layer. The tube was then sealed. Diffusion between the three phases over a period of 3 months produced transparent rhombic block crystals of complex **2**. Anal. Calcd for $C_{21}H_{17}CoN_2O_6$: C, 55.76; H, 3.79; N, 6.19%.

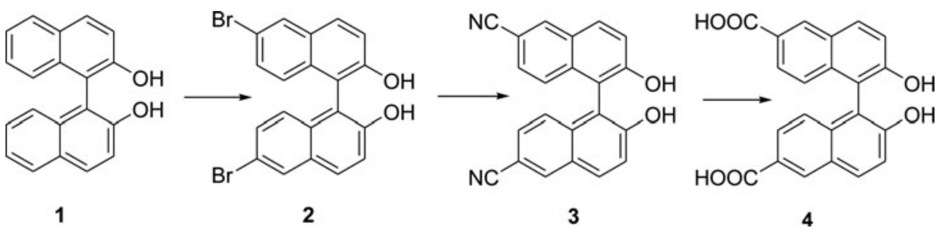
Results and Discussion

Synthesis and Characterizations

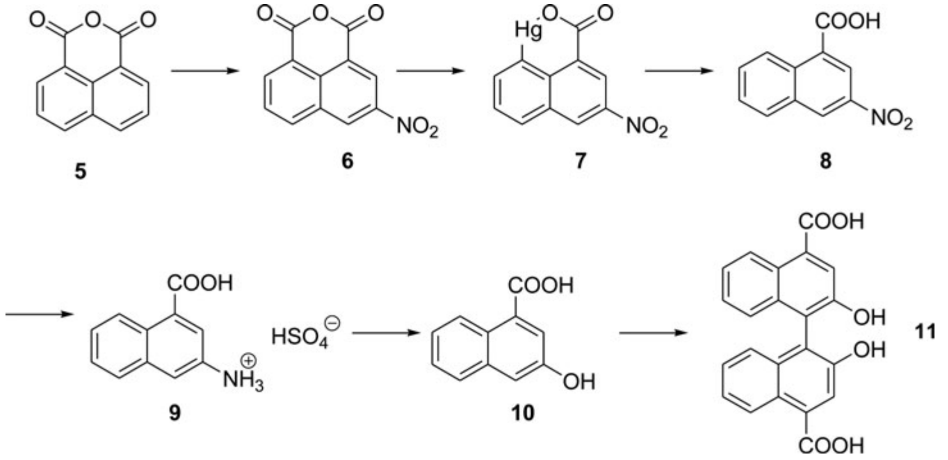
The ligand of 2,2′-dihydroxy-1,1′-dinaphthyl-6,6′-dicarboxy acid (H_2**bna1**) was synthesized from binol through bromination, cyanation, and hydrolysis (Scheme 1). The ligand of 2,2′-dihydroxy-1,1′-dinaphthyl-4,4′- dicarboxy acid (H_2**bna2**) was synthesized from 1,8-naphthalic anhydride through decarboxylation, diazotization, hydrolysis, and microwave coupling of the substrate (Scheme 2). Then the complex **1** and complex **2** were obtained through the method of solvent diffusion.

IR Study

Infrared spectra are recorded in the region from 4000 cm^{-1} to 400 cm^{-1}. IR signal at 2922 and 2850 cm^{-1} belonged to carboxylic O—H groups can be clearly seen in compound 4, yet they cannot be observed in complex **1** due to the ligands coordination with Cu^{2+} ion. However, the typical bonds of the asymmetrical and symmetrical vibrations of COO^- give at 1618 and 1406 cm^{-1} could be observed in both materials. The absorption bond of



Scheme 1. Synthesis of 2,2′-dihydroxy-1,1′-dinaphthyl-6,6′-dicarboxy acid.



Scheme 2. Synthesis of 2,2′-dihydroxy-1,1′-dinaphthyl-4,4′-dicarboxy acid.

phenolic hydroxyl 2500-3600 cm^{-1} has no change, which assured the freedom of the active centers (Fig. 1).

As shown in Fig. 2 characteristic absorption bonds of 4,4′-bipyridine (bpy) emerge at 1591, 1410, 808, 607 cm^{-1}, while they are shifted to 1581, 1399, 816, 598 cm^{-1} in the complex **2.** This implies that the N atoms of the bpy have coordinated with the metal ions which impacted the stretching vibrations of the C=N and C—N bonds. Moreover, IR shows that the characteristic absorption bond of C=O located around 1691 cm^{-1}, C—O bond locates at 1287 cm^{-1} in compound **7** especially moves to 1658 cm^{-1} and 1219 cm^{-1} in the complex **2**. The characteristic absorption bond of OH which belongs to carboxyl at 3071 cm^{-1} disappeared in complex **2** which can be explained that the OH of carboxyl have coordinated with the metal ions. And from IR studies, we observe that the characteristic absorption bond of phenolic hydroxyl at 1248 cm^{-1} has no change, which indicates that the phenolic hydroxyl was not bonded with the metal ions, further confirming the freedom of the active centers.

Structural Determination

Single crystal X-ray diffraction studies reveal that complex **1** crystallizes in the orthorhombic space group *P*nma. There are two [Cu(**bna1**)(DMF)], one noncoordinated CH_3OH and two noncoordinated H_2O guest molecules in the asymmetric unit of complex **1.** As shown in Fig. 3a, the Cu(II) atom is coordinated by another Cu(II) atom with the Cu-Cu distance of 2.6248(13) Å, four carboxyl oxygen atoms from different ligands with the Cu-O distances of 1.961(3) Å and 1.981(3) Å, one oxygen atom from one DMF molecule with the Cu-O distance of 2.135(5) Å, where the latter one O atom occupies the apical positions to fulfill the tetragonal pyramid coordination motif. The last two H_2O and one CH_3OH are freely filled in the space of the unit. The O-Cu-O angles are between 87.35(17)° and 168.21(12)°, and the O-Cu-Cu angles varies from 79.22(9)° to 172.33(14)°. The dihedral angle between the pair of naphthyl rings is 81.75°. In complex **1**, **bna1** act as the bridging molecules, which link the Cu^{2+} into an 1D lattice fence running along the *b*-axis (Fig. 3b), and the adjacent chains are arranged into 2D network by the π–π weak interactions (Fig. 3c). The selected bond distances and angles are listed in Table 1.

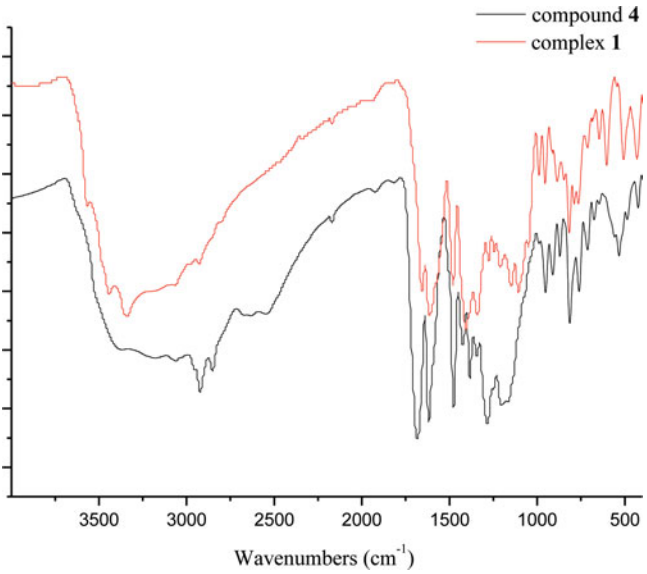


Figure 1. IR spectra of compound **4** and complex **1**.

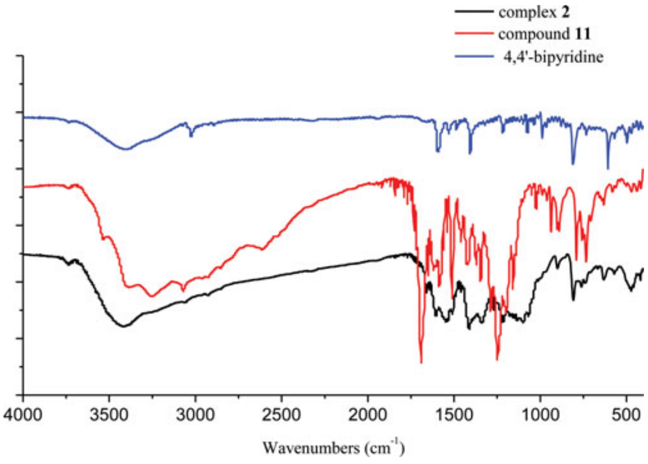


Figure 2. IR spectra of 4,4′-bipyridine, compound 9 and complex 2.

Table 1. Selected bond lengths (Å) and angles (°) for complex 1

Distances			
Cu(1)-O(1)	1.961(3)	C(1)-O(1)	1.255(5)
Cu(1)-O(1)$^{\#1}$	1.961(3)	C(1)-O(2)	1.260(5)
Cu(1)-O(2)$^{\#2}$	1.981(3)	C(1)-C(2)	1.492(5)
C(7)-O(3)	1.345(5)		
Angles			
O(1)-Cu(1)-O(1)$^{\#1}$	87.35(17)	O(1)#1-Cu(1)-O(4)	95.28(13)
O(1)-Cu(1)-O(2)$^{\#2}$	168.21(12)	O(2)#2-Cu(1)-O(4)	96.36(13)
O(1)-Cu(1)-Cu(1)$^{\#2}$	79.22(9)	O(2)#2-Cu(1)-Cu(1)$^{\#2}$	89.01(9)
O(1)-Cu(1)-O(4)	95.29(13)	O(4)-Cu(1)-Cu(1)$^{\#2}$	172.33(14)
O(1)-C(1)-O(2)	124.4(4)	O(2)-C(1)-C(2)	120.2(4)
O(1)-C(1)-C(2)	115.4(4)	O(3)-C(7)-C(6)	121.0(4)

Symmetry code for complex **1**: #1 $x - 1, y, z$, #2 $x + 1, y, z$.

Complex **2** crystallizes in the monoclinic space group P2/c. There were [Co(**bna2**)(bpy)$_2$(H$_2$O)$_2$] in the asymmetric unit of complex **2**. As shown in Fig. 4a, the Co(II) ions in complex **2** was coordinated by two oxygen atoms from two carboxylic groups

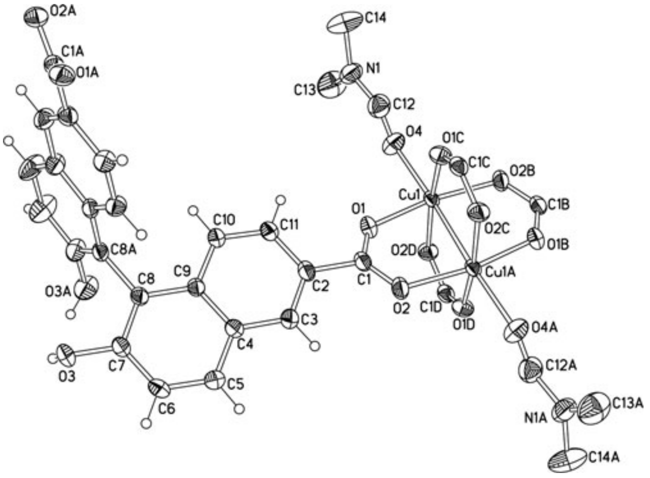


Figure 3a. The coordination environments around Cu(II) wiht 30% thermal ellipsoids of complex 1.

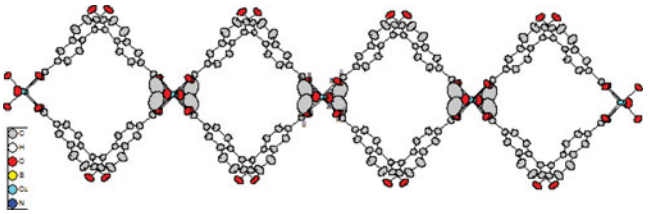


Figure 3b. The 1D spiral structure of complex **1**.

of two independent **bna** ligands [Co-O1 = 2.088(3) Å], two oxygen atoms from two H_2O [Co1-O4 = 2.129(4) Å] and two nitrogen atoms from two bpy [Co1-N1 = 2.180(6) Å and Co1-N2 = 2.182(5) Å], the dihedral angle O1-Co1-N1 and O1-Co1-O4 was 90.3° and 91°, where the latter and the two nitrogen atoms occupy the apical positions to fulfill the octahedron coordination motif .The selected bond distances and angles are listed in Table 2.

The Co(II) ions connects the adjacent ligands to form an infinite 1-Dzigzag line, and then coordinated with bpy molecules at apical positions to extend a 2D network (Fig. 4b). The resulting 2D complex **2**, possesses large channels of 1.56 nm running through the *a* axis and 1.15 nm running through the *c* axis (Fig. 4c). The oxygen of carbonyl and the proton of bpy interact to form a hydrogen bond. Through the interchain C=O . . . O hydrogen bonds, these 2D chains are further assembled into a 3D supramolecular network. What's more, the 3D supramolecular network posses a large open channels which can transfer the substrates and products which is essential for the catalytic applications (Fig. 4d).

And the phenolic hydroxyl of **bna1** and **bna2** which are the active catalytic sites are uncoordinated with any metal ions and locate the same sides which form the uniform modality to improve the effect of active catalytic sites.

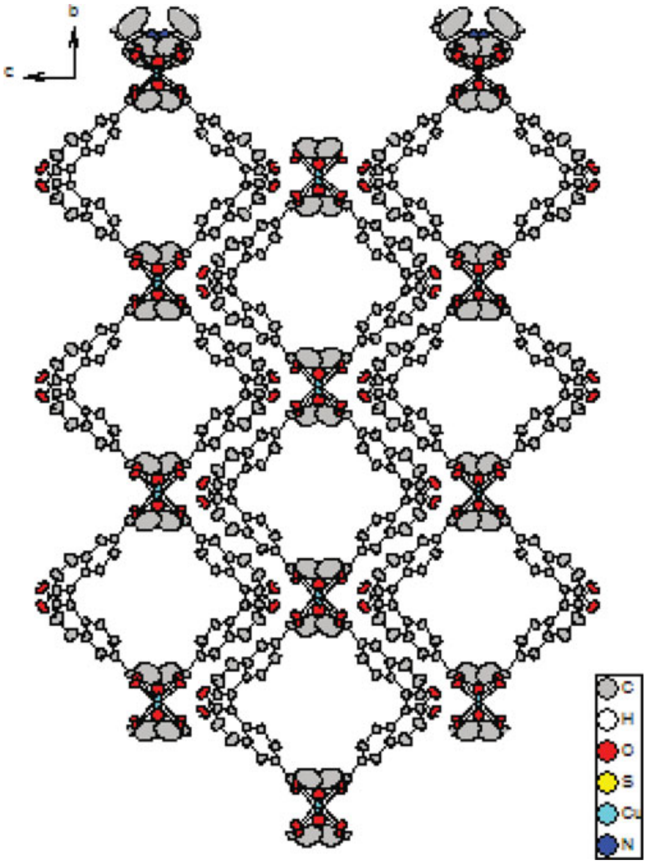


Figure 3c. The 2D layer structure of complex **1** formed by O–H···O interactions.

Table 2. Selected bond lengths (Å) and angles (°) for complex 2

Distances			
N(2)-Co(1)$^{\#2}$	2.182(5)	Co(1)-O(4)	2.129(4)
Co(1)-O(1)	2.088(3)	Co(1)-N(1)	2.180(6)
Co(1)-O(1)$^{\#1}$	2.088(3)	Co(1)-N(2)$^{\#3}$	2.182(5)
Co(1)-O(4)$^{\#1}$	2.129(4)		
Angles			
N(1)-Co(1)-N(2)$^{\#3}$	180.00(2)	O(1)-Co(1)-O(1)$^{\#1}$	179.67(17)
O(1)-Co(1)-O(4)	90.97(14)	C(1)-O(1)-Co(1)	129.10(3)
O(1)$^{\#1}$-Co(1)-O(4)$^{\#1}$	90.97(14)	Co(1)-O(4)-H(4A)	109.50(19)
O(1)-Co(1)-O(4)$^{\#1}$	89.03(14)	Co(1)-O(4)-H(4B)	120.00(3)
O(4)$^{\#1}$-Co(1)-O(4)	179.53(18)	H(4A)-O(4)-H(4B)	112.10
O(1)-Co(1)-N(1)	90.17(8)	C(17)-N(2)-Co(1)$^{\#1}$	122.10(3)
O(4)$^{\#1}$-Co(1)-N(1)	90.24(9)	O(1)-Co(1)-N(2)$^{\#3}$	89.83(8)

Symmetry code for complex **2**: #1 $-x+1, -y+1, -z+1$ #2 $x+1, y, -z+1$ #3 $-x+1, -y+1, z$.

X-Ray Powder Diffraction

In order to confirm the phase purity of the bulk materials, the simulation and experimental measurements of the X-ray powder diffraction pattern of the complex **1** and complex **2** are compared as showed in Figs. 5 and 6. The simulated pattern of complex **1** matches very well with the experimental data, which clearly supports our result that the bulk synthesized material and the as-grown crystals are homogeneous for complex **1.** However, the experimental data of complex **2** looks quite different from the simulated one especially for the intensities of the peaks in the larger angle range. Yet, detailed analysis shows

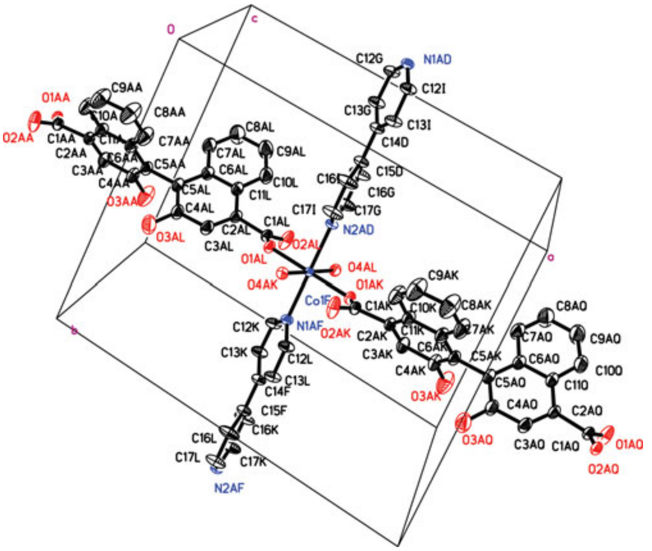


Figure 4a. The coordination environments around Co(II) wiht 30% thermal ellipsoids of complex 2.

that the positions of the peaks in both the simulated and experimental patterns matches well bot not their intensities. It is supposed that our synthesized material has relatively low crystallniity and some solvent molecules in the channels might lower the diffraction intensity. So we can fairly consider that the bulk synthesized material and the as-grown crystals are homogeneous for complex **1** and complex **2**.

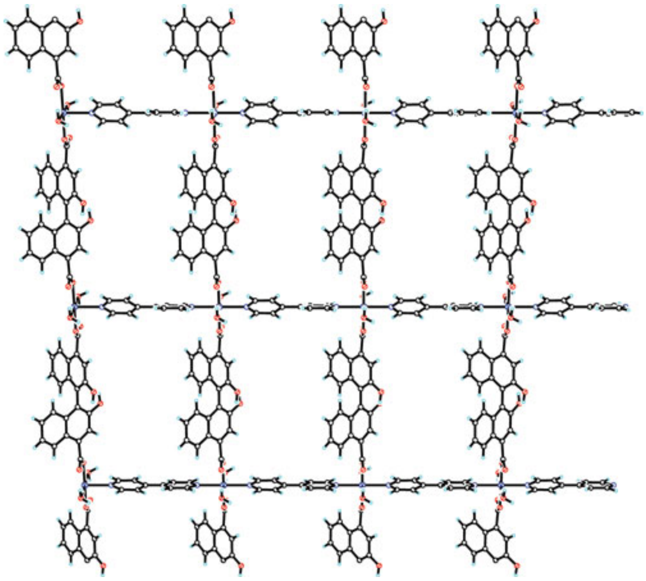


Figure 4b. The 2D chiral sheet structure of complex 2◦.

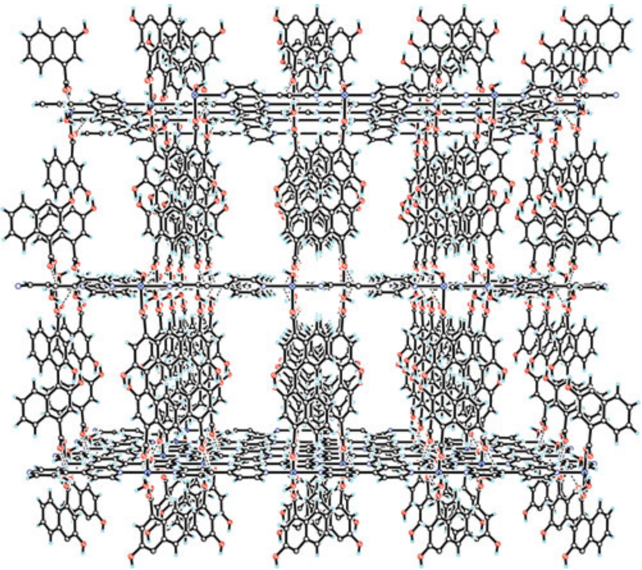


Figure 4c. The packing arrangement of complex 2, viewed along the a-axis.

X-Ray Crystal-Structure Analysis of Complex 1 and 2

The single crystal data of the complexes were collected on a Bruker Smart Apex II CCD diffractometer using the graphite monochromated Mo K radiation ($\lambda = 0.71073$ Å). The data of complex **1** and complex **2** were collected at 296(2) K and 173(2) K. The structure was

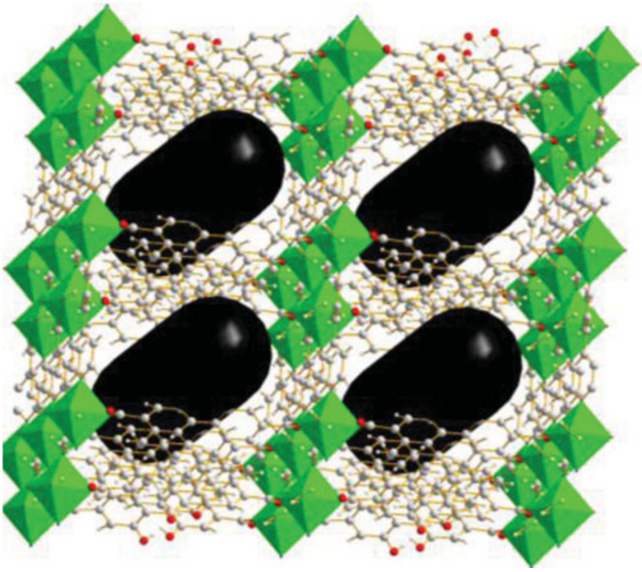


Figure 4d. Channels of complex **2**.

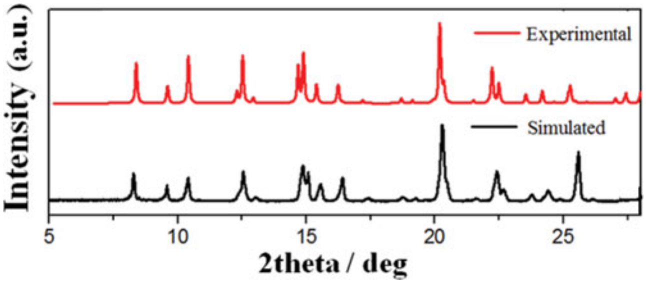


Figure 5. Experimental and simulated PXRD patterns for complex **1.**

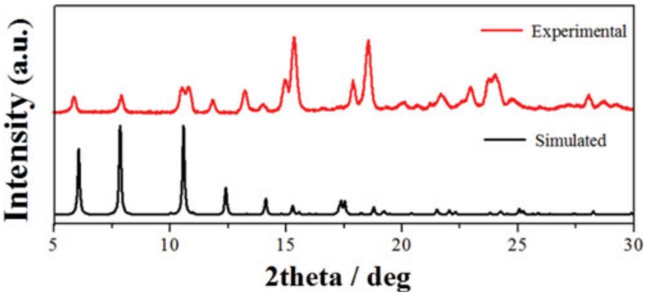


Figure 6. Experimental and simulated PXRD patterns for complex **2**.

Table 3. Crystal data and structure refinement of complex **1**, **2**

Identification code	Complex **1**	Complex **2**
Empirical formula	$C_{26}H_{25}CuNO_9$	$C_{21}H_{17}CoN_2O_6$
Formula weight	559.01	452.3
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	*P*nnm (No. 58)	P2(1)/c
a(Å)	11.4457(14)	a = 15.6515(9)
b(Å)	13.2062(16)	b = 11.4518(7)
c(Å)	20.389(3)	c = 13.7867(8)
α/deg	90	90
β/deg	90	110.2430(10)
γ/deg	90	90
Volume (Åá^3)	3081.9(7)	2318.5(2)
Z	4	4
Calculated density (Mg/m^3)	1.205	1.250
Absorption coefficient (mm^{-1})	0.754	0.774
F(000)	1156	864
Crystal size (mm^3)	0.49 × 0.27 × 0.06	0.75 × 0.28 × 0.27
Range for data collection	1.84 to 28.28°	2.26 to 27.73°
Reflections collected	21303	15958
Independent reflections	3910 ($R_{\text{int}} = 0.1092$)	5431 ($R_{\text{int}} = 0.0248$)
Completeness to theta = 22.02	99.4%	99.70%
Data/restraints/parameters	3910/1/196	5431/0/204
Limiting indices	$-15 < h < 13, -17 < k < 17, -24 < l < 27$	$-20 \leq h \leq 19, -14 \leq k \leq 14, -18 \leq l \leq 13$
Goodness-of-fit on *F*2	1.022	1.751
Final *R* indices [*I*>2sigma(*I*)]	$R^1 = 0.0589$ w$R^2 = 0.1543$	$R^1 = 0.1235$, w$R^2 = 0.3790$
R indices (all data)	$R^1 = 0.1334$ w$R^2 = 0.1992$	$R^1 = 0.1358$, w$R^2 = 0.3960$
Largest diff. peak and hole (eA^{-3})	0.823 and −0.416	3.817 and −0.627

solved with direct method and refined by full-matrix least-square methods using SHELXTL-97 program. All H atoms were added geometrically. The selected bond lengths and bond angles are listed in Tables 1 and 2, and crystallographic data and structure experimental details of both complexes are given in Table 3.

Conclusions

In summary, two novel metal-organic frameworks based on H$_2$**bna1**, H$_2$**bna2**, and 4,4′-bipyridine have been synthesized and structurally characterized. Crystal structural analysis reveals that complex **1** forms an infinite chain structure, which is linked to form 2D sheet by

π–π weak interactions. Complex **2** adopts a two-dimensional pillared layered structure by connecting of infinite one-dimensional chains via 4,4′-bipyridine and is further assembled into a 3D supramolecular network through the hydrogen bonds. In addition, X-ray powder diffraction (PXRD) of complex **1** and complex **2** shows that individual single crystalline structure was the same as the huge mass small crystalline structure. It is believed that new coordination polymers will be synthesized with the same approach. The following catalytic properties studies are currently under investigation in our lab.

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