

Post-Synthetic Modification to Access Two New Cobalt-Based Coordination Polymers

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Abstract

Two new compounds were successfully obtained through the post-synthetic modification of the 2D precursor $[\text{Co}_3(\text{L})_2(\text{H}_2\text{O})_4]_n \cdot 2n\text{DMF}$ (**1a**). Compound **1** $\{[\text{Co}_3(\text{L})_2(4,4'\text{-bipy})_3(\text{H}_2\text{O})_8] \cdot 8\text{H}_2\text{O}\}$ exhibits a 2D structure characterized by high inherent porosity. In contrast, Compound **2** $\{[\text{Co}_3(\text{L})_2(\text{bpe})_3] \cdot 4\text{H}_2\text{O} \cdot \text{DMF}\}_n$ demonstrates an increased dimensionality, forming a 3D architecture with a two-fold interpenetrating network. Their phase purity was confirmed by powder X-ray diffraction (PXRD), while thermogravimetric analysis (TGA) demonstrated compound **2** have good thermal stability. This work demonstrates that post-synthetic transformation provides a new avenue for a deeper understanding of coordination bond cleavage and formation at the molecular level. These findings offer constructive information for the future rational design and targeted synthesis of related crystalline materials.

1. Introduction

Over the past two decades, coordination polymers (CPs) have attracted broad interdisciplinary interest owing to their versatile application potential in energy storage [1, 2], chemical sensing [3, 4], and catalysis [5–10]. The rational selection of metal nodes and organic ligands enables the construction of functional networks with tunable porosity [11–14]. However, the self-assembly process is inherently sensitive to external parameters—such as reaction temperature, solvent systems, light exposure, stoichiometric ratios, and mechanical forces, which ultimately govern the configuration of the final products [15–17]. Consequently, direct one-pot synthesis poses significant challenges in isolating target crystalline materials with specific dimensions, unique topologies, or desired final state [18–20]. In addition, direct synthesis is often constrained by the conformations and coordination modes of the starting materials, as well as specific thermodynamic or kinetic crystallization pathways. For instance, under the high-temperature, high-pressure, or harsh solvent conditions of direct synthesis, certain auxiliary ligands (such as long-chain flexible nitrogen-heterocyclic ligands) may undergo competitive precipitation with the primary ligand or fail to co-crystallize due to significant differences in solubility [19, 21, 22]. In contrast, post-synthetic transformations enable the precise replacement and insertion of ligands under relatively mild conditions, thereby bypassing these energetic barriers to yield novel compounds [23–25]. Furthermore, post-synthetic processes are routinely accompanied by significant alterations in the coordination geometries of metal centers, space groups, and ligand coordination modes, thereby effectively modulating the physicochemical properties of the materials [26–28].

In this work, by employing the as-synthesized 2D precursor **1a**, we successfully obtained two novel compounds via post-synthetic strategies. Among them, compound $\{[\text{Co}_3(\text{L})_2(4,4'\text{-bipy})_3(\text{H}_2\text{O})_8] \cdot 8\text{H}_2\text{O}\}$ (**1**) features a 2D network with substantial intrinsic porosity that is inaccessible via direct synthesis, while compound $\{[\text{Co}_3(\text{L})_2(\text{bpe})_3] \cdot 4\text{H}_2\text{O} \cdot \text{DMF}\}_n$ (**2**) exhibits a 2-fold interpenetrated 3D framework. The successful isolation of these two compounds demonstrates the efficacy of post-synthetic approaches and provides valuable insights for the future targeted synthesis of crystalline materials.

2. Experimental section

2.1 Materials and methods

The ligand 5-[3-(carboxy)benzyloxy]isophthalic acid (H_3L) was synthesized according to a reported procedure [29]. All other chemicals were of analytical grade and used as purchased without further purification. Elemental analyses (EA) of C, H, N were performed on a Vario EL III analyzer. Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet Avatar-370 spectrometer in the range 400–4000 cm^{-1} using KBr pellets. Single-crystal X-ray diffraction data were obtained on a Bruker Smart Apex II CCD diffractometer. Powder X-ray diffraction data (PXRD) were recorded on a Rigaku DLMAX-2550 diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) over the 2θ range 5–50°. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 449C thermal analyzer under nitrogen atmosphere from room temperature to 800°C with a heating rate of 10°C min^{-1} . UV–vis spectrophotometer was used on a TU-1900 from Puxi in the range of 200–800 nm. A portable UV lamp (WFH-204B, 10 W) was used for visual inspection.

2.2 Syntheses

2.2.1 Synthesis of **1** $\{[Co_3(L)_2(4,4\text{-bipy})_3(H_2O)_8] \cdot 8H_2O\}_n$

A mixture of $[Co_3(L)_2(H_2O)_4]_n$ 2nDMF (**1a**) (15.0 mg) and 4,4'-bipy (15.6 mg, 0.10 mmol) in 7.5 mL H_2O and DMF (v: v = 2:1) were stirred for 10 minutes. The resulting mixture was transferred to a 20 mL reaction vial, which was subsequently sealed and heated at 100°C for 3 days. Subsequently, the mixture was allowed to stand at room temperature for an additional week, yielding orange plate-like crystals with the yield of 86% (based on 4,4'-bipy). Anal. Calcd for $C_{62}H_{74}O_{30}N_6Co_3$: 47.73%; H, 4.78%; N, 5.39%.

Found: C, 47.68%; H, 5.13%; N, 5.68%. IR (KBr pellet, cm^{-1}): 3420 w, 3385 w, 1660 s, 1609 s, 1549 s, 1413 m, 1365 s, 1258 s, 1216 s, 1039 s, 811 m, 776 m, 703 m, 627 m.

2.2.2 Synthesis of **2** $\{[Co_3(L)_2(bpe)_3] \cdot 4H_2O \cdot DMF\}_n$

$[Co_3(L)_2(H_2O)_4]_n$ 2nDMF (**1a**) (15.0 mg) and bpe (18.0 mg, 0.10 mmol) were added into a 7.5 mL mixture of H_2O and DMF (v: v = 2:1). The mixture were stirred for 10 minutes and poured into a hydrothermal reactor (15 mL) at 100°C for three days and then cooled to room temperature at a programmed rate, affording pink block crystals compound **2** with the yield of 68% (based on bpe). Anal. Calcd for $C_{71}H_{63}O_{19}N_7Co_3$: C, 57.03%; H, 4.25%; N, 6.56%. Found: C, 57.58%; H, 4.35%; N, 6.78%. IR (KBr pellet, cm^{-1}): 3370 w, 3060 w, 1670 s, 1600 s, 1550 s, 1380 m, 1250 s, 1100 s, 1030 s, 835 m, 768 m, 548 m.

2.3. X-ray crystallography

The single-crystal structure data for compounds **1–2** were collected on a Bruker Smart Apex-II CCD diffractometer with graphite-monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293K. Data were collected in ω -scan mode, corrected for Lorentz and polarization effects, integrated and reduced with

SAINT-5.0 program, and empirical absorption corrections were applied using SADABS program [30]. The structures were solved by direct method with SHELXL-2013 program and refined by full-matrix least squares on F^2 with SHELXL software [31]. As highly disordered solvent molecules were present in the crystal lattice, the SQUEEZE routine was employed by PLATON [32]. All non-hydrogen atoms were solved by direct methods and refined anisotropically with full-matrix least-squares methods. Hydrogen atom positions were located via Fourier difference maps or generated by theoretical geometric hydrogenation. The crystal parameters, data collection and refinements for **1–2** were summarized in Table 1. Selected bond lengths and angles for **1–2** were collected in Table S1.

Table 1
Crystallographic data for compounds **1–2**

Compound	1	2
Formula	C ₆₂ H ₇₄ O ₃₀ N ₆ Co ₃	C ₆₈ H ₄₈ Co ₃ N ₆ O ₁₄
Formula weight	1560.06	1349.91
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	10.839(15)	25.183(3)
<i>b</i> (Å)	14.17(2)	13.6482(19)
<i>c</i> (Å)	17.66(2)	20.025(3)
α (°)	73.47(2)	90
β (°)	74.146(15)	98.094(5)
γ (°)	68.146(15)	90
<i>V</i> (Å ³)	2369(6)	6814.2(16)
<i>Z</i>	1	4
<i>D</i> _c (mg/m ³)	1.093	1.316
<i>F</i> (000)	809	2764
μ (mm ⁻¹)	0.586	0.787
<i>R</i> _{int}	0.0458	0.1397
GOF on <i>F</i> ²	0.853	1.071
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0748, 0.1912	0.1246, 0.2753
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1379, 0.2275	0.1452, 0.2865
$R_1 = \sum(F_o - F_c) / \sum F_o $, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$		
GOF = $[\sum w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{params})]^{1/2}$, based on the data <i>I</i> > 2 σ (<i>I</i>)		

3. Results and discussion

3.1 Descriptions of X-ray crystal structures

3.1.1 Structural description of $\{[\text{Co}_3(\text{L})_2(4,4'\text{-bipy})_3(\text{H}_2\text{O})_8]\cdot 8\text{H}_2\text{O}\}_n$ (1)

Compound **1** belongs to the $P\bar{1}$ space group of the triclinic crystal system, exhibiting a novel two-dimensional structure. The asymmetric unit contains one and a half crystallographically independent Co(II) ions, one fully deprotonated L^{3-} ligand, four coordinating water molecules, one and half 4,4'-bipy molecules, and four lattice water molecules (Fig. 1a). As illustrated in Fig. 1a, both Co(II) centers display six-coordinated, distorted octahedral geometries. The Co1 center is bound to one monodentate carboxylate oxygen donor from an L^{3-} ligand, three oxygen atoms from coordinated water molecules, and two nitrogen donors from two 4,4'-bipy ligands. Similarly, the Co2 sphere is completed by two monodentate carboxylate oxygen atoms from two distinct L^{3-} ligands, two aqua oxygen atoms, and two 4,4'-bipy nitrogen donors. The Co–O and Co–N bond lengths fall within normal ranges of 2.032(4)–2.164(5) Å and 2.149(5)–2.197(5) Å, respectively, with the O–Co–O and N–Co–N bond angles varying between 88.9(2)°–180.0° and 178.01(2)° – 180.00(2)°. Alternating Co1 and Co2 sites are linked by 4,4'-bipy into a one-dimensional chain (Fig. 1b). These 1D chains are further connected via the fully deprotonated, partially coordinated carboxylate ligands, yielding a defective 2D layer endowed with rectangular channels (Fig. 1c). The carboxylic acid ligand adopts a $(k^1)-(k^1)-\mu_2$ coordination pattern, with a dihedral angle of 82.066(19)° between the isophthalic acid ring and the benzoic acid ring (Scheme 2). As shown in Fig. 1c, the benzoic acid rings of the ligands are inserted into the adjacent rectangular grids, exhibiting an AA repeat packing pattern of the layers. These layers are further interconnected into the final three-dimensional structure via inter-layer π - π interactions between benzene rings (~ 3.759 Å). Platon program shows 45% pore is formed in compound **1**. Finally, these isolated 2D layers interpenetrate and interleave with each other to form a 3D supramolecular framework (Fig. S1). Topological analysis reveals that by treating the dinuclear cobalt units as 4-connected nodes and the L^{3-} ligands as 3-connected nodes, compound **1** can be regarded as a (3,4)-connected 2-nodal net topology. The Schläfli notation is $\{4.6^2\}_2\{4^2.6^2.8^2\}$ for this net as indicated by the TOPOS software [33] (Fig. 1d).

3.1.2 Structural description of $\{[\text{Co}_3(\text{L})_2(\text{bpe})_3]\cdot 4\text{H}_2\text{O}\cdot \text{DMF}\}_n$ (2)

Compound **2** exhibits a 2-fold interpenetrating three-dimensional (3D) framework that crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit contains three independent Co(II) ions, two L^{3-} ligand and three semi-rigid bpe molecules (Fig. 2a). The Co1 center is six-coordinated by two bidentate chelating carboxylate oxygen donors from one H_3L ligand, two bidentate bridging carboxylate oxygen atoms from two separate H_3L ligands, and two nitrogen donors from two bpe ligands. Co2 exhibits an identical coordination environment to Co1. Co3 is hexa-coordinated by four bidentate chelating carboxylate oxygen atoms from two L^{3-} ligands, along with two nitrogen donors from two bpe ligands. All three Co centers (Co1, Co2 and Co3) feature a distorted octahedral coordination geometry. As

illustrated in Fig. 2b, Co1 and Co2 are bridged by carboxylate groups to form a dinuclear unit with a Co1...Co2 separation of 4.065 Å. The Co–O and Co–N bond lengths fall in the range of 2.034(8) ~ 2.329(12) Å and 2.065 ~ 2.185(10) Å, respectively, while the O–Co–O and N–Co–N bond angles are in the range of 59.13(4) ~ 151.7(3) and 100.8(5) ~ 177.1(4)° respectively, all falling within the normal ranges. The L³⁻ ligand adopts a $\eta(k^1-k^1)-(k^2)-(k^2)-\mu_4$ coordination mode (Scheme 2), with a dihedral angle of 80.512° between the isophthalic acid ring and the benzoic acid ring. Adjacent dinuclear cobalt units are linked by L³⁻ ligands to form a chain-like structure, and these chains are further interconnected via Co3 nodes and ligands to construct a 2D layered network (Fig. 2b) [34]. The void in the framework is filled via mutual interpenetration of more independent frameworks, generating a two-fold interpenetrating three-dimensional architecture (Fig. 2c). PLATON program indicates that the porosity of compound **2**, after solvent removal is 20.3%. Topological analysis reveals that by treating the dinuclear cobalt units as 6-connected nodes, Co3 as 4-connected nodes and the L³⁻ ligands as 3-connected nodes, compound **2** can be regarded as a trinodal (3,4,6)-connected net topology. The Schläfli notation is {4.6²}₂{4².6⁸.8⁵}{6⁴.8²} for this net as calculated by the TOPOS software (Fig. 2d).

3.1.3 Structural and synthetic relationships among compounds **1a**, **1**, and **2**

Building upon the aforementioned structural transformation system, a stepwise synthesis via ligand substitution was successfully achieved by leveraging the active coordination sites in the previously reported precursor, [Co₃(L)₂(H₂O)₄]_n·2nDMF (**1a**). Under solvothermal conditions, compound **1** was obtained through a dissolution-recrystallization structural transformation upon introducing 4,4'-bipyridine as the bridging ligand, accompanied by the observation of an intermediate transition state (Fig. 3a-c). The molar amount of 4,4'-bipy exerted a significant influence on the transformation process, with the optimal crystal quality of compound **1** being achieved at a dosage of 0.10 mmol (Fig.S2).

By comparing the crystal structures of precursor **1a** and compound **1**, we proposed a plausible mechanism for bond breaking and formation during the structural transformation. The coordinated oxygen atoms on the trinuclear cobalt units of precursor **1a** are vulnerable to attack by abundant water molecules, resulting in bond cleavage and the subsequent collapse of the original secondary building units (SBUs). Meanwhile, upon the introduction of 4,4'-bipy, Co(II) centers coordinate with 4,4'-bipy ligands, ultimately yielding the two-dimensional compound **1** featuring high porosity. The comparative PXRD patterns of the precursor, intermediate transition phase, and compound **1** are provided in Fig. S3, and a schematic illustration depicting the potential conversion process from **1a** to **1** is presented in Fig. S4.

Further reaction of **1a** with bpe yielded a new compound, **2**. In the structure of **2**, the original trinuclear cobalt cluster was disassembled into a dinuclear cobalt unit and an isolated cobalt ion, which were linked by the ligands. In Compound **1a**, Co1 and two symmetrical Co2 are linked by six bridging carboxyl groups to form a trinuclear unit of [Co₃O₁₂] with Co1...Co2 separation of 3.5108 Å, while in compound **2**,

Co1 and Co2 are bridged by carboxylate groups to form a dinuclear unit with a Co1...Co2 separation of 4.065 Å (Fig.S5). Notably, nucleophilic attack by water molecules along with substitution by bpe served as the primary driving forces for this structural transformation from **1a**. In situ microscopic observation of crystal transformation as shown in Fig. S6.

We also attempted to synthesize Compounds **1** and **2** via the direct one-pot method. For Compound **1**, this approach proved unsuccessful. Although Compound **2** could be obtained through the direct route, it was plagued by a low yield and the presence of concurrent byproducts.

3.2. Infrared spectra

The IR spectra of compounds **1** and **2** are presented in Fig. S7. The absence of absorption bands near 1700 cm⁻¹ confirms the complete deprotonation of all carboxylate ligands. For compound **1**, a broad absorption band spanning 3550–3400 cm⁻¹ is observed is assigned to O–H stretching vibrations, proving the presence of coordinated water molecules. The characteristic asymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of the carboxylate groups appear within the ranges of 1670–1500 cm⁻¹ and 1455–1310 cm⁻¹, respectively. The carboxylate coordination modes were further elucidated by evaluating the frequency separation, $\Delta\nu$ ($\Delta\nu = \nu_{as} - \nu_s$), large $\Delta\nu$ values of 244 cm⁻¹ (with ν_{as}/ν_s at 1609/1365 cm⁻¹) for compound **1** are characteristic of a monodentate coordination mode [35–38]. Additionally, a weak band at 2927 cm⁻¹ in the spectrum of compound **2** is assigned to the C–H stretching vibration of the DMF molecule.

3.3. PXRD pattern and Thermal analysis

To confirm the phase purity of compounds **1–2**, Powder X-ray diffraction (PXDR) experiments have been carried out at room temperature. The experimental PXRD pattern for each compound is in accord with the simulated one, demonstrating the phase purity of compounds **1–2** (Fig. S8).

To estimate the stability of compounds **1–2**, thermogravimetric (TG) analyses are performed in the temperature range of 30–800 °C under N₂ atmosphere. As shown in Fig. S9, for compound **2**, a total weight loss of 9.72% is observed from room temperature to 340°C, in good agreement with the calculated value of 9.71% for the release of four lattice water molecules and one lattice DMF molecule. In contrast, compound **1** exhibits lower thermal stability. It underwent a weight loss of 18.00% between 30 and 150°C, corresponding to the loss of eight water molecules (calcd. 18.43%). Beyond this temperature, the framework of **1** suffered rapid decomposition.

4. Conclusion

We successfully obtained two new Co-based coordination polymers via post-synthetic methods. Compound **1** exhibits a two-dimensional porous framework; however, due to its high porosity, the skeleton suffers from poor thermal stability. Compound **2** features a two-fold interpenetrating three-

dimensional structure. Notably, Compound **1** cannot be synthesized through the direct method. Although Compound **2** can be prepared via the direct method, it suffers from a low yield accompanied by side products. The phase purity of all compounds was confirmed by powder X-ray diffraction. This work demonstrates that post-synthetic transformations serve as an ideal experimental model for investigating the molecular-level mechanisms of crystal phase transitions, as well as the processes of coordination bond cleavage and formation. This contributes to a deeper understanding of crystal engineering and the principles governing crystallization kinetics and thermodynamics.

Declarations

Conflict of Interest

The authors declare no conflict of interest.

Author Contribution

Miao Yu: Writing - original draft, Visualization, Software, Methodology. Jia-Qi Li: Formal analysis, Investigation, Data curation. Xiang He: Writing - review & editing, Supervision, Project administration, Funding acquisition, Conceptualization, Resources.

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Data Availability

The data that support the findings of this study are available within the article and its supplementary materials.

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Schemes

Schemes 1 and 2 are available in the supplementary files section.

Figures

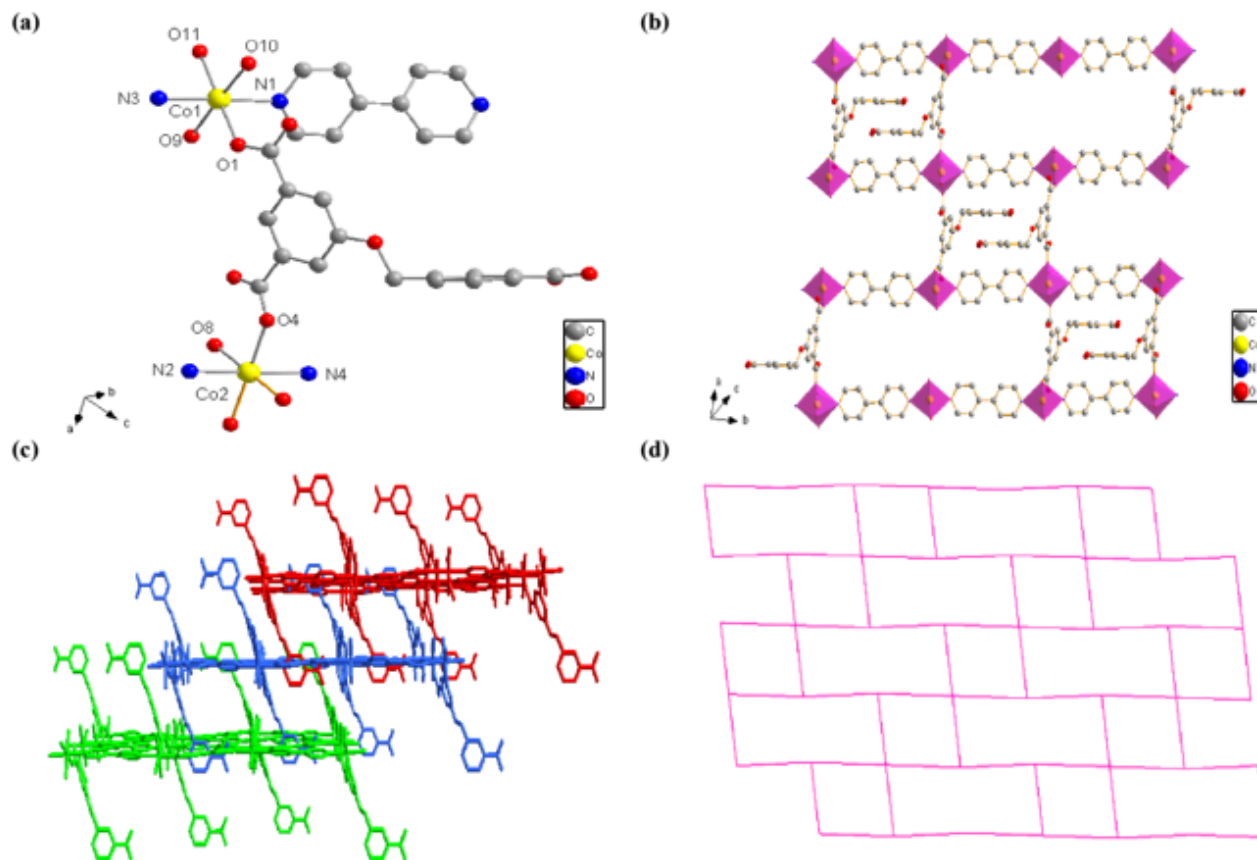


Figure 1

a) Perspective view of the asymmetric unit of **1**.; b) The 2D structure framework of **1**.; c) AA repeat packing pattern of the layers of **1**. d) The topology of compound **1**. (All the hydrogen atoms and solvent molecules have been omitted for clarity.)

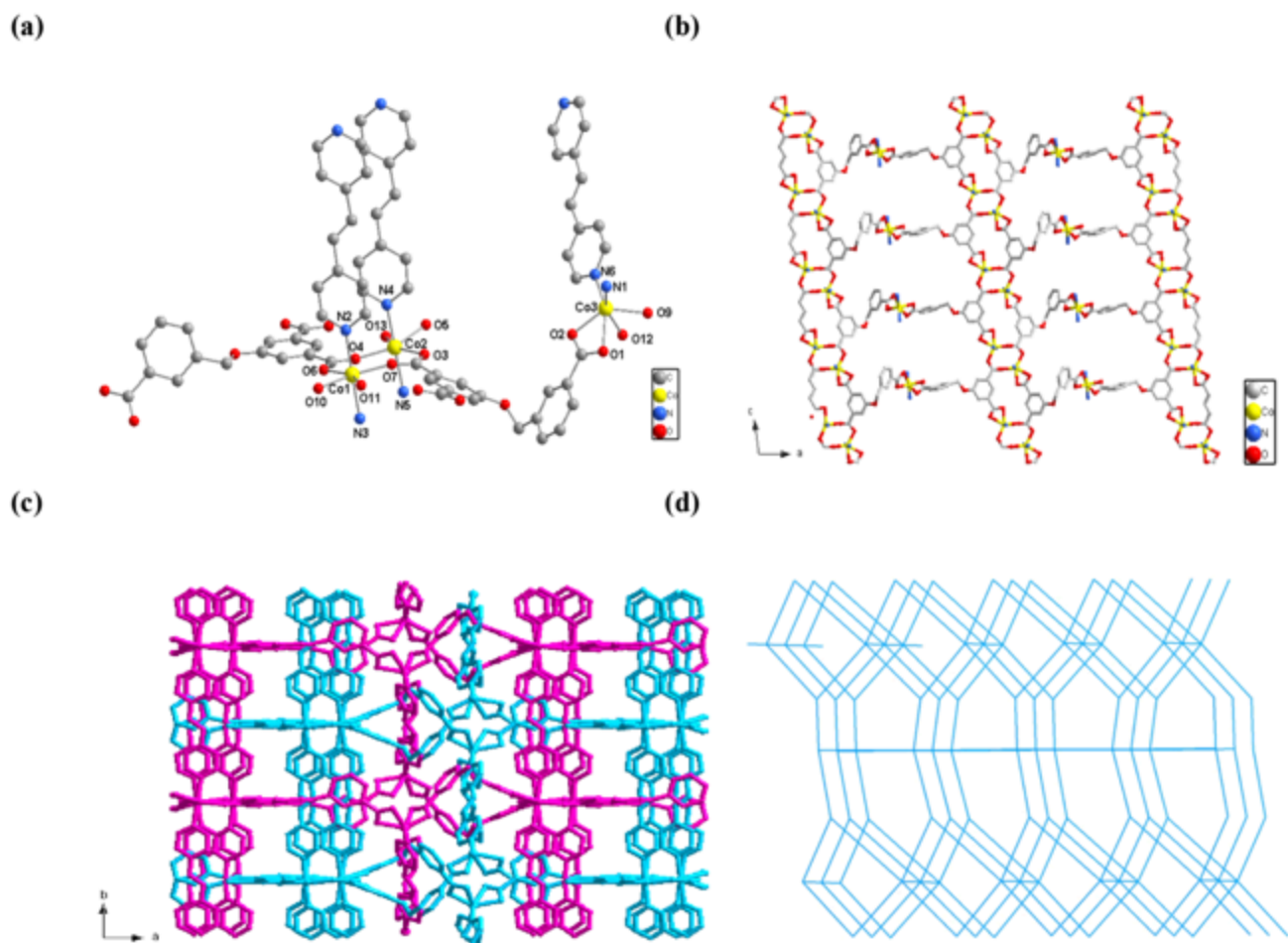


Figure 2

a) Perspective view of the asymmetric unit of **2**; b) The 2D structure framework of **2**, viewed down from the *b*-axis.; c) Two-fold interpenetrating three-dimensional architecture of **2**, viewed down from the *c*-axis.; d) The topology of compound **2**. (All the hydrogen atoms and solvent molecules have been omitted for clarity.)

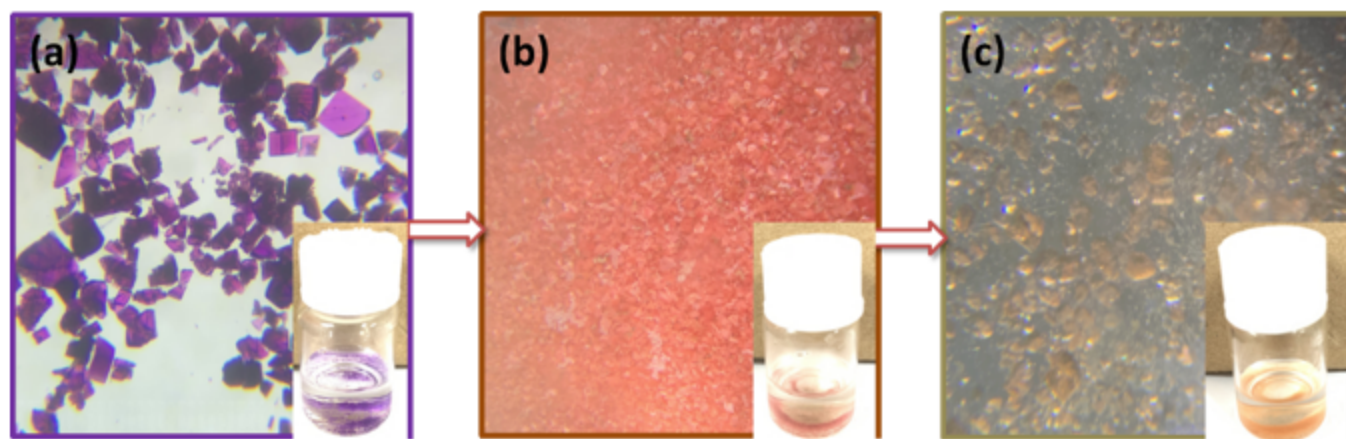


Figure 3

The optical images of the obtained crystals during step-wise synthesis process (a) **1a**; (b) transition state; (c) **1**.

Supplementary Files

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