

A Novel 3D Polypseudo-rotaxane Metal-organic Framework Based on a Flexible Bis-pyridyl-bis-amide Ligand

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A novel 3D compound $\{[\text{Cu}(\text{L})(\text{H}_2\text{O})_4][\text{Cu}_2(\text{SIP})_2(\text{L})_2]\} \cdot 2\text{H}_2\text{O}$ (**1**) (L = *N,N*-bis(4-pyridinecarboxamide)-1,4-butane, SIP = 5-sulfoisophthalate) is hydrothermally synthesized. X-ray diffraction analysis reveals that compound **1** is composed of 2D anionic $[\text{Cu}_2(\text{SIP})_2(\text{L})_2]_n^{2n-}$ double-layers and discrete 1D cationic $[\text{Cu}(\text{L})(\text{H}_2\text{O})_4]_n^{2n+}$ polymeric chains, which represents a rare 3D polypseudo-rotaxane MOF from intercalation of 1D and 2D framework. In addition, the luminescent property and electrochemical behavior of compound **1** have been investigated.

Key Words : Flexible bis-pyridyl-bis-amide ligand, Polypseudo-rotaxane network, Hydrothermal synthesis, Luminescent property, Cyclic voltammetry

Introduction

Metal-organic frameworks (MOFs) have attracted much attention during the last decades, not only for their fascinating architectures and novel topologies, such as polycatenation, polythreading, and polyknotting,¹ but also for their desired physical and chemical properties in photoluminescence, catalysis, magnetic materials and gas storage *etc.*²⁻⁵ To date a large number of MOFs based upon bipyridine-based ligands have been reported.⁶ However, MOFs constructed by bis-pyridyl-bis-amide ligands are less documented.⁷ Our group and others have been studying the coordination chemistry of bis-pyridyl-bis-amide ligands, and have obtained several interesting MOFs. For example, using the rigid *N,N*-bis(4-pyridinecarboxamide)-1,4-benzene (4-bpcb) ligand, we have recently reported a novel three-fold interpenetrating 3D MOF $[\text{Cu}_3(4\text{-bpcb})_3(\text{BTC})_2]_3 \cdot \sim 12\text{H}_2\text{O}$ (BTC = 1,3,5-benzenetricarboxylate anion) containing discrete cage-like $(\text{H}_2\text{O})_{12}$ water cluster guests.⁸ Cao's group has reported several 2D and 3D coordination polymers based on the isomers of 4-bpcb ligand and aromatic bicarboxylate ligands.⁹ In comparison, the reports on the flexible bis-pyridyl-bis-amide ligands are limited.¹⁰

In this work, a flexible bis-pyridyl-bis-amide ligand *N,N*-bis(4-pyridinecarboxamide)-1,4-butane (L) (Scheme S1) is chosen as the main ligand based on the following considerations: (a) The ligand L, equipped with amide and pyridyl groups, can donate more N atoms, which can offer multiple coordination sites; (b) The flexible $-(\text{CH}_2)_4-$ backbones may bend larger twist-degree and endows the ligand more molecular isomerism, so novel structures should be expected; (c) The amide groups with both the N-H hydrogen donor and C=O hydrogen acceptor may result in interesting hydrogen bonding interactions in the final crystal structure.¹¹ As a result, a novel 3D MOF $\{[\text{Cu}(\text{L})(\text{H}_2\text{O})_4][\text{Cu}_2(\text{SIP})_2(\text{L})_2]\} \cdot 2\text{H}_2\text{O}$ (**1**) with the flexible bis(4-pyridinecarboxamide)-1,4-butane (L) and 5-sulfoisophthalate (SIP) mixed ligands has

been obtained, which exhibits a rare 3D polypseudo-rotaxane structure. Among those reported coordination complexes based on the bis-pyridyl-bis-amide ligands, the entangled and interpenetrated structures are limited,¹² and there are no 3D polypseudo-rotaxane MOFs to the best of our knowledge. The fluorescence and electrochemical properties of the title compound are reported.

Experimental

Materials and Methods. All of the reactions were performed under air condition and the chemicals we used are purchased from commercial sources without any purification. The ligand L was prepared according to the literature method.¹³ The elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were recorded in the range from 4000 to 500 cm^{-1} on a VARIAN Scimitar 2000 using KBr pellets. Thermogravimetric analyses (TGA) were performed on a PYRIS/N5350030 instrument with a heating rate of 10 $^\circ\text{C} \cdot \text{min}^{-1}$. Fluorescence spectra were recorded on a F-4500 FL. Spectrophotometer. A CHI 440 Electrochemical Quartz Crystal Microbalance was used for the electrochemical experiments. A conventional three-electrode cell was used at room temperature.

Preparation of $\{[\text{Cu}(\text{L})(\text{H}_2\text{O})_4][\text{Cu}_2(\text{SIP})_2(\text{L})_2]\} \cdot 2\text{H}_2\text{O}$ (1**).** A mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.06 g, 0.24 mmol), L (0.03 g, 0.10 mmol), NaH_2SIP (0.025 g, 0.093 mmol), H_2O (12 mL) and NaOH (0.016 g, 0.40 mmol) was stirred at room temperature. The suspension was put into a Teflon-lined autoclave and kept under autogenous pressure at 120 $^\circ\text{C}$ for 4 days. When the autoclave was cooled to room temperature, blue block crystals of **1** were obtained. Anal. Calcd. for $\text{C}_{64}\text{H}_{72}\text{Cu}_3\text{N}_{12}\text{O}_{26}\text{S}_2$ (1680.13): C 45.71, H 4.29, N 10.00. Found: C 45.78, H 4.40, N 10.11.

Crystallography. The diffraction data for compound **1** was collected on a Bruker SMART APEX II diffractometer equipped with a monochromator in the Mo K α ($\lambda = 0.71073$

Å) incident beam. The structure was solved by direct methods and refined on F^2 by full-matrix least squares methods using SHELXTL97. The crystallographic data for compound **1** is listed in Table S1, and the selected bond distances and angles are listed in Table S2. Structural information was deposited at the Cambridge Crystallographic Data Center (CCDC reference numbers: CCDC 884185 for **1**).

Results and Discussion

Description of the Structure. Single crystal X-ray diffraction reveals that compound **1** is a 3D MOF constructed from 1D cationic $[\text{CuL}(\text{H}_2\text{O})_4]_n^{2n+}$ chain and 2D anionic $[\text{Cu}_2(\text{SIP})_2(\text{L})_2]_n^{2n-}$ layer network.

There are two crystallographically independent Cu(II) ions in the asymmetric unit of compound **1**. As depicted in Figure 1(a), the Cu2 ion is coordinated by two pyridyl nitrogen atoms from L ligands and four oxygen atoms from coordinated water molecules with the bond distances of 2.055(2) Å for Cu–N and 2.027(2) – 2.341(3) Å for Cu–O, showing an octahedral geometry. In Figure 1(b), Cu1 ion adopts a distorted octahedral geometry, which is coordinated by two pyridyl nitrogen atoms from two L ligands and four carboxyl oxygen atoms from two SIP ligands. The Cu–N bond distances are 2.021(2) Å [Cu1–N2] and 2.031(2) Å [Cu1–N4], the Cu–O bond distances range from 1.958(2) to 2.578(2) Å.

In compound **1**, the L ligand adopts two different conformations due to the flexible $-(\text{CH}_2)_4-$ spacers (L^1 and L^2 , Fig S1): (i) The L^1 ligand shows the AAAAAA *trans* conformation. L^1 connects two Cu^{II} ions [Cu2...Cu2A] to form the discrete 1D cationic $[\text{CuL}(\text{H}_2\text{O})_4]_n^{2n+}$ chain (Fig. 2(a)) with the non-bonding distances of 20.36 Å, and the corresponding dihedral angle between the pyridyl rings is 0° ; (ii) The L^2 ligand shows the AGAGA *trans* conformation. L^2 connects two Cu^{II} ions [Cu1 and Cu1A] to form a 1D $[\text{CuL}]_n$

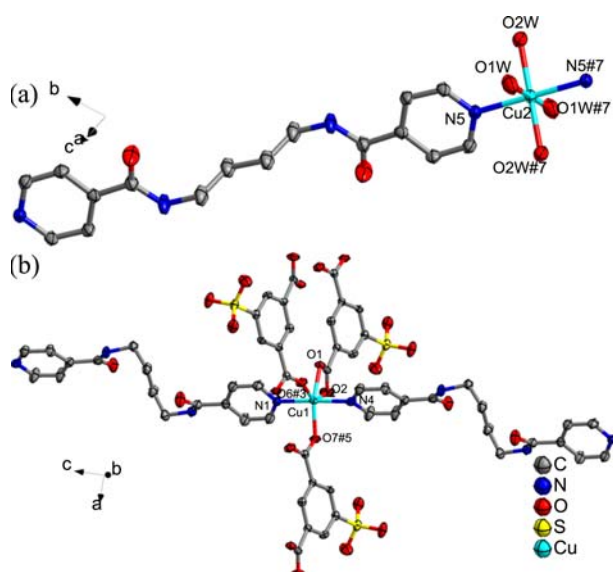


Figure 1. Coordination environment of the Cu(II) ions in **1**.

(Fig S2a) with the non-bonding distance of 18.74 Å, the dihedral angle of the two pyridyl rings is 15.44° .

Then the Cu1 ions belonging to the 1D $[\text{CuL}]_n$ chains are linked by SIP anions with chelating-bidentate coordination mode to build a 2D anionic $[\text{Cu}_2(\text{SIP})_2(\text{L})_2]_n^{2n-}$ double-layer (Fig. 2(b) and S3), in which two carboxyl groups of SIP connect the Cu1 to build a 1D $[\text{Cu}_2(\text{SIP})_2]_n$ double-chain structure (Fig. S2b), and the sulfonate group does not participate in the coordination. The similar Cu-carboxylate double-chain motif can be found in the isophthalate-containing phases $[\text{Cu}(\text{isophthalate})(4,4'\text{-dipyridylamine})]_n$ and $[\text{Cu}(\text{isophthalate})(4,4'\text{-bpy})]_n$.¹⁴

In compound **1**, the Cu1 ions are surrounded by five organic ligands (two L and three SIP ligands) and can simply be regarded as the 5-connected nodes. Each SIP is further linked to three Cu1 ions, therefore, defined as a 3-connected node, while the L ligating with two 5-connected Cu1 ions only serves as a linear linker. Considering Cu1 ions and the SIP ligands as nodes and keeping the L ligands as spacers, the schematic of the 2D double-layer is best described as a unique binodal (3,5)-connected network with the Schläfli symbol of $\{4^2.6^7.8\}\{4^2.6\}$ analyzed by TOPOS40 (Fig. S3 (bottom)). The 2D $[\text{Cu}_2(\text{SIP})_2(\text{L})_2]_n^{2n-}$ polymeric double-layer exhibits rectangle window shape motif with the size of $18.7 \text{ \AA} \times 10.2 \text{ \AA}$.

The rectangle windows of the adjacent sheets are staggered along the *a*-axis, and each window is occupied by two discrete 1D cationic $[\text{CuL}(\text{H}_2\text{O})_4]_n^{2n+}$ chains (Fig S4). The discrete 1D chains interpenetrate into the 2D double-layers, which achieved the transition from 1D chain and 2D layer to 3D framework for compound **1** (Fig. 3 and S5). The compound **1** is the first example of *polypseudo*-rotaxane MOF based on the flexible bis-pyridyl-bis-amide ligands.

IR spectrum and XRPD pattern. The main feature of IR spectrum for compound **1** concerns the L ligand and the carboxyl groups of SIP. The strong absorption at 3330 and 3126 cm^{-1} corresponds to the N–H group of L ligand and the band around 1635 cm^{-1} suggests the presence of C=O group of L ligand. The bands centered at 775, 730 and 582 cm^{-1} are attributed to the ring of pyridine, and the moderate band at 1434 cm^{-1} may be attributed to $-\text{CH}_2-$ of the L ligand. The

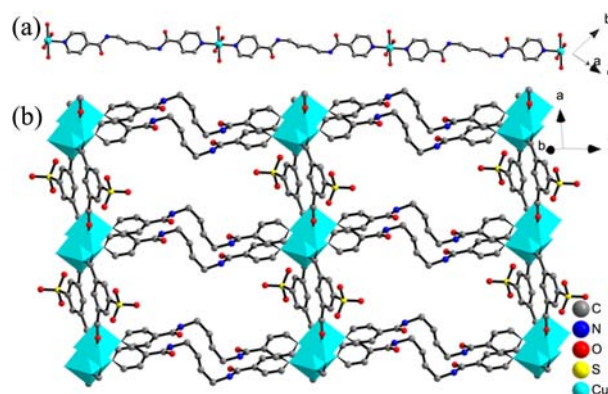


Figure 2. (a) The discrete 1D cationic $[\text{CuL}(\text{H}_2\text{O})_4]_n^{2n+}$ chain of **1**. (b) A view of a 2D anionic $[\text{Cu}_2(\text{SIP})_2(\text{L})_2]_n^{2n-}$ double-layer in **1**.

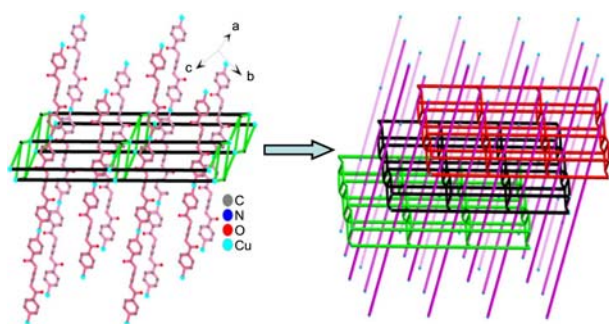


Figure 3. The polypseudo-rotaxane network of compound **1** formed by discrete 1D chains penetrating the stagger-peaked 2D sheets.

bands at 1548, 1434 and 1317(s) cm^{-1} may be assigned to the COO^- groups of the ligand SIP. The IR spectrum also shows a band around 1041 cm^{-1} for the sulfonate group. The crystalline phase purity of compound **1** was evidenced by the similarity of the simulated and experimental XRPD patterns, as shown in Fig. S7. Their peak positions are in good consistency with each other, indicating the phase purity of the as-synthesized samples.

Thermal Analysis. Compound **1** is air-stable, which can retain its crystalline integrity at room temperature. To characterize the thermal stability of compound **1**, thermal gravimetric analysis (TGA) has been carried out in the temperature range of 20–800 $^{\circ}\text{C}$ under nitrogen atmosphere (Fig. S8). The TGA of compound **1** shows the first weight loss of 7.21% from 70 $^{\circ}\text{C}$ to 213 $^{\circ}\text{C}$ corresponding to the loss of the lattice and coordinated water molecules (calcd.: 6.42%). The second weight loss is observed from 263 $^{\circ}\text{C}$ to 556 $^{\circ}\text{C}$, which is attributed to the decomposition of the organic ligands. The residue holds a weight of 14.38% of the total sample (the calculated CuO weight is 14.28%), indicating that the final product is CuO.

Fluorescence Spectroscopy of Complex 1. It has been found that the transition metal coordination compounds usually show diverse photoluminescence properties.¹⁵ The emission spectra of compound **1** and ligand L were investigated in the solid state at room temperature and shown in

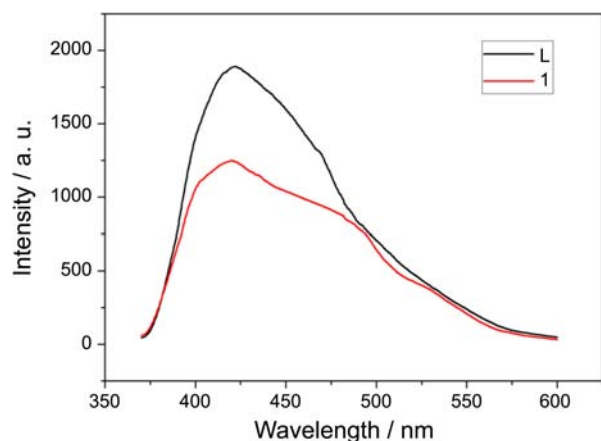


Figure 4. Fluorescent emission spectra of compound **1** and **L** in the solid state at room temperature.

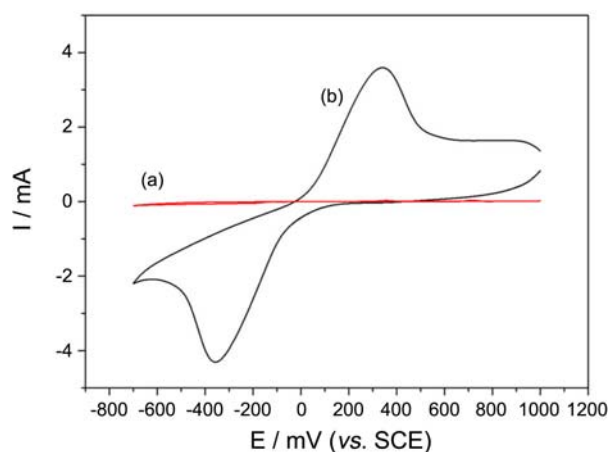


Figure 5. Cyclic voltammograms of (a) the bare CPE and (b) **1**-CPE in 1 M H_2SO_4 aqueous solution in the potential range of 1000 to -700 mV.

Figure 4. Upon excitation at 350 nm, similar emission peaks are observed at 420 nm for ligand L and 422 nm for compound **1**. The fluorescent emissions of **1** may be attributed to the intraligand π - π^* transitions.¹⁶

Electrochemical Behavior of Compound 1. In order to investigate the redox property of the title compound, cyclic voltammetry measurements of the compound **1** bulk-modified carbon paste electrode (**1**-CPE) were carried out in 1 M H_2SO_4 aqueous solution. The cyclic voltammograms of bare CPE and **1**-CPE have been shown in Figure 5. No redox peak can be found for the bare CPE, while a quasi-reversible redox peak has been observed for the **1**-CPE in the potential range of 1000 to -700 mV, and the mean peak potential is -9 mV $E_{1/2} = (E_{pa} + E_{pc})/2$, which should be attributed to the redox of $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$.¹⁷

Conclusion

In summary, a novel copper compound formulated as $\{[\text{Cu}(\text{L})(\text{H}_2\text{O})_4][\text{Cu}_2(\text{SIP})_2(\text{L})_2]\} \cdot 2\text{H}_2\text{O}$ (**1**) has been synthesized hydrothermally. Compound **1** represents the first 3D polypseudo-rotaxane metal-organic framework based on the flexible bis-pyridyl-bis-amide ligands. Moreover, compound **1** shows good luminescent and electrochemical property. This work provides a reasonable route to design and synthesize novel MOFs by selecting appropriate flexible bis-pyridyl-bis-amide ligands and aromatic polycarboxylate ligands.

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