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A 2D Metal-Organic Framework with a Flexible Cyclohexane-1,2,5,6-tetracarboxylic Acid Ligand: Synthesis, Characterization and Photoluminescent Property

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Abstract

A novel metal-organic framework, $[\text{Zn}_2(\text{OH})(\text{Hcht})(4,4'\text{-bpy})]_n \cdot 4n\text{H}_2\text{O}$ (**1**) (H_4cht = cyclohexane-1,2,4,5-tetracarboxylic acid and $4,4'\text{-bpy}$ = 4,4'-bipyridine), was synthesized by the hydrothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4,4'-bipyridine, and cyclohexane-1,2,4,5-tetracarboxylic acid in the presence of sodium carbonate. The complex was obtained by controlling the ratio of the starting materials and a reaction temperature at 120°C and was characterized by IR, X-ray powder diffraction, thermogravimetric analysis, fluorescent spectrum, and single crystal X-ray diffraction. Single-crystal X-ray investigation reveals that the structure features a two-dimensional framework with novel coordination mode of Hcht ligand and all Hcht ligands exclusively convert to a sole conformation in the complex. IR spectrum reveals the characteristic absorption peaks of asymmetric stretching vibrations that result from the protonated and deprotonated carboxyl groups,. Thermogravimetric analysis shows four clear courses of weight loss, which corresponds to the decomposition of different ligands. Fluorescent spectrum displays that complex **1** is a potential blue-luminescent material.

Keywords

cyclohexane-1,2,5,6-tetracarboxylic acid; 4,4'-bipyridine; flexible ligand; infrared spectrum; thermogravimetric analysis; photoluminescent property

1. Introduction

Much of recent interest in the rapidly growing field of metal-organic framework (MOF) coordination polymers derives from the applied potential of these materials in catalysis, gas storage, separations, ion exchange, sensors, and photochemistry [1-3]. To conduct a systematic investigation on these varieties of properties, a large number of coordination polymers with versatile organic ligands and functional metal ions have been designed and synthesized [4-5].

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Supporting Information Available: X-ray crystallographic file in CIF format for the structure determination of complex $[\text{Zn}_2(\text{OH})(\text{Hcht})(4,4'\text{-bpy})]_n \cdot 4\text{H}_2\text{O}$ (**1**) (H_4cht = cyclohexane-1,2,5,6-tetracarboxylic acid and $4,4'\text{-bpy}$ = 4,4'-bipyridine) has been deposited to the Cambridge Crystallographic Data Center (CCDC 719952), it is available free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html. The IR spectrum and X-ray powder diffraction diagram of complex **1** are also available free of charge as supplemental information.

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In the past decade, researchers devoted themselves to the prediction and control of MOF structures so that sufficiently stable materials with special and optimized physical and chemical properties could be obtained. For example, Yaghi and coworkers have reported many porous structures with useful gas and liquid adsorption properties, which demonstrates that porous structures constructed by metal-carboxylate clusters and organic links are strong enough to stabilize networks against collapse and amenable to systematic variation in porosity and functionality [6]. Lately, some investigations have been focused on flexible multidentate ligands as they are able to form diversified coordination networks with different metal ions [7]. On the other hand, however, it is difficult to predict and control the final structure of coordination polymers constructed by these flexible ligands and metal ions due to the flexibility of these ligands. Until now, only a few papers concerning the selection of conformation and configuration of flexible ligands in coordination polymers have been published [8]. Our interest in this research field is to investigate how synthetic conditions, metal ions, and cooperative ligands influence the conformation preference of the flexible ligands and the structural construction of the polymers, and ultimately to get products that all ligands exclusively change their conformation to a single form. Meanwhile, we also try to explore the potential applications of these materials in various areas. In this work, a novel two-dimensional metal-organic framework, $[\text{Zn}_2(\text{OH})(\text{Hcht})(4,4'\text{-bpy})]\cdot 4\text{H}_2\text{O}$ (**1**) (H_4cht = cyclohexane-1,2,4,5-tetracarboxylic acid and 4,4'-bpy = 4,4'-bipyridine), was synthesized and characterized by IR, X-ray powder diffraction, thermogravimetric analysis, fluorescent spectrum, and single crystal X-ray diffraction. The flexible ligand H_4cht contains seven kinds of possible conformations in a mixture of cis- and trans- isomers, but all Hcht ligands exclusively adopt the a,e,e,a conformation in the complex **1** when controlling the ratio of the starting materials and hydrothermal temperature.

2. Experimental Section

2.1 Materials and methods

All reagents used in the synthesis of **1** were purchased from Aldrich Chemical Co. and used without further purification. The cyclohexane-1,2,4,5-tetracarboxylic acid is a mixture of cis and trans. The X-ray powder diffraction experiment was performed on a Bruker D8 Advance X-ray powder diffractometer operating at 40kV and 40mA ($\text{CuK}\alpha$ radiation, $\lambda = 1.5418 \text{ \AA}$). The data collection was carried out with a step size 0.03 degree and counting time of 1s per step. The 2-theta angular range is from 5 to 40 degrees. IR spectrum was recorded on a Nicolet AVATAR 370 FTIR infrared spectrophotometer. The fluorescent spectrum was measured on a SPEX fluorolog-3 Tau3 system equipped with a 450w xenon lamp and double monochromators on both excitation and emission sides. The simultaneous DSC-TGA thermalgravimetric analysis was performed on TGA Instruments SDI Q600 under a flowing nitrogen atmosphere. The flow rate of nitrogen gas was controlled at about 100 milliliters per minute. A total of 6.5812mg of complex **1** was heated between room temperature and 790°C at a heating rate of 10°C/min.

2.2 X-ray analysis

The crystallographic data and structure refinements parameters of complex **1** are summarized in Table 1. The diffraction data of complex **1** were collected on a SMART CCD diffractometer with a graphite-monochromated Mo $\text{K}\alpha$ sealed tube ($\lambda = 0.71073 \text{ \AA}$) at 273 K, using a ω scan mode with an increment of 0.3°. Preliminary unit cell parameters were obtained from 45 frames. Final unit cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The empirical absorption correction was based on equivalent reflections and other possible effects such as absorption by the glass fiber were simultaneously corrected. The structure was solved by direct methods followed by successive difference

Fourier methods. All non-hydrogen atoms were refined anisotropically. Computations were performed using SHELXTL and final full-matrix refinements were against F^2 . The SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants; SAINT-PLUS for integration of intensity of reflections and scaling; SADABS for absorption correction; and SHELXL for space group and structure determination, refinements, graphics, and structure reporting [9-11].

2.3 Synthesis of complex 1

Zn(NO₃)₂·6H₂O (0.2258g), cyclohexane-1,2,4,5-tetracarboxylic acid (0.0668g), 4,4'-bipyridine (0.0781g), and sodium carbonate (0.0538g) in a molar ratio of 3:1:2:2 and distilled water (8.0033g) were mixed in a 22.2ml vial and the mixture was shaken in an ultrasonic bath for 10 minutes. The initial PH was 5.12. The vessel was then sealed and heated at 120°C for 65 hours. The autoclave was subsequently allowed to cool to room temperature. The plate-shaped transparent colorless crystals, suitable for X-ray crystallography, were obtained by filtration and washed with distilled water, methanol, and ethanol. The solid was dried under vacuum for several hours. Yield: 154 mg (94.6% based on H₄cht). FT-IR $\nu_{\text{as}}(\text{COO}^-)$: 1706, 1599 cm⁻¹.

3. Results and Discussion

3.1 Description of crystal structure

Selected bond lengths and bond angles for complex **1** are listed in Table 2. Single-crystal X-ray structural analysis shows that complex **1** is a 2D MOF structure crystallized in triclinic *P*-1 space group and the asymmetric unit consists of two zinc atoms, one not fully deprotonated Hcht ligand, one 4,4'-bipyridine, and four crystallization water molecules (Figure 1). Two types of Zn²⁺ ions are all five-coordinated with distorted square-pyramidal geometry (Figure 2b). Zn1 is connected to one oxygen from the e-carboxylate [Zn1-O3 1.979(4) Å], two oxygens from the a-carboxylate groups [Zn1-O5, O6 2.450(4), 1.984(4) Å], one hydroxyl-oxygen [Zn1-O9 1.945(4) Å], and one nitrogen [Zn1-N1 2.097(5) Å]. Interestingly, the bond length of Zn1-O5 is obviously longer than all others even though O5 and O6 come from the same carboxylate group. Zn2 is bonded with one oxygen from the e-carboxylate [Zn2-O4 2.085(4) Å], one oxygen from the a-carboxylate groups [Zn2-O7 2.002(4) Å], two hydroxyl-oxygens [Zn2-O9, O9A 2.041(4), 2.140(4) Å], and one nitrogen [Zn2-N2 2.059(5) Å]. As shown in Figure 2a, each ligand is bridged to five Zn atoms through three different carboxylate groups in complex **1**. Noticeably, one of carboxyl groups of the ligand does not bond with metal ions despite the molecule contains coordinated hydroxyl groups. This is in agreement with the FT-IR spectrum (Figure S1, Supporting Information), where the characteristic absorption peaks of asymmetric stretching vibration $\nu_{\text{as}}(\text{COO}^-)$ were observed at 1706 cm⁻¹ for the protonated carboxyl group and at 1599 cm⁻¹ for the deprotonated carboxyl group. The peaks were shifted to lower values compared with the carbonyl frequencies (1736 cm⁻¹) of the free H₄cht ligand. However, it is slightly different from our other investigations that all carboxyls are deprotonated when using different metal ions but without cooperative ligand [13]. As shown in Figure 3, the 2D MOF structure is formed by the cross of two 1D chains (Figure 3a). The unique [Zn₄(μ_3 -O)₂] units are bridged with Hcht to produce a 1D zigzag chain (Figure 3b), whereas [Zn₄(μ_3 -O)₂] units are connected by 4,4'-bipyridine to gain another 1D ladder-shaped chain (Figure 3c). The final 3D supramolecular networks in the polymer are obtained by the hydrogen bonding interactions between lattice water molecules and carboxylate groups in the 2D layers.

3.2 The investigation of synthetic conditions

As the structure of coordination networks in MOFs has been found to be greatly influenced by the physical and chemical factors of reactions such as solvent systems, concentration, the ratio of starting materials, and reaction temperatures [12], we performed a series of reactions by

using different synthetic conditions such as initial ratios, reaction temperatures, and solvents. When controlling the ratio of initial materials at 3:1:2:2 and the hydrothermal temperature at 120°C, complex **1** was obtained. The phase purity was confirmed by comparison of its powder diffraction pattern with the one calculated from the single crystal analyses (Figure S2, Supporting Information). Colorless plate-shaped crystals consisted of only 4,4'-bipyridine and H₄cht through H-bond interaction were obtained when the reaction was conducted without sodium carbonate; Colorless needle-shaped solids were obtained while using lower ratio of 4,4'-bipyridine and reaction temperature at 80-100°C; and ball-shaped solids were obtained while using DMF and methanol as the solvent. However, the effort trying to obtain the single-crystal structures of needle-shaped and ball-shaped solids fails. It is interesting to note that all Hcht ligands in complex **1** only adopt one type of coordination mode and exclusively change their chair conformations to the a,e,e,a form. Moreover, our other investigations display that all cht ligands were also converted exclusively to the sole a,e,e,a chair conformation when using different metal ions but without cooperative ligand [13]. These results demonstrate that the ratios of initial materials, reaction temperatures, and solvent systems have potential influence on the formation of the desired complexes and the conformation choice of flexible ligands in coordination polymers, however, the cooperative ligand has a great influence on the coordination mode of metal ions but no influence on the conformation preference of flexible ligand.

3.3 Thermogravimetric analysis

Thermogravimetric analysis was carried out to explore the thermal stabilities of complex **1**. The sample was heated up to 790°C under a flow of nitrogen atmosphere. As shown in Figure 4, a slow weight loss of 8.8% between 40°C and 175°C is in accordance with the release of three crystallization water molecules per formula (calcd, 8.5%). The compound is stable until 260°C. Subsequently, a slight weight loss of 5.2% from 260°C to 350°C is related to the removal of one crystallization water molecule and a hydroxyl group (calcd 5.5%). After that, a rapid weight loss of 40.9% up to 500°C results from the decomposition of organic ligands Hcht (40.6%). The residual framework keeps relatively stable up to 600°C, then the final structure slowly collapses with the loss of 4,4'-bipyridine. Notably, no obvious plateau is observed between 260°C and 500°C, which means that the μ_3 -hydroxyls have important effect on the stability of the coordination structure.

3.4 Photoluminescent property

Photoluminescent properties of complexes **1** was investigated in the solid state at room temperature (Figure 5). Upon the excitation of ultraviolet light at 370 nm, a strong fluorescent emission was observed with the maximum at 439 nm for complex **1**. Because Zn²⁺ ion is difficult to oxidize or to reduce owing to their d¹⁰ electronic configuration, the emission is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal (LMCT) in nature. It is tentatively attributed to the intraligand transition of Hcht and 4,4'-bipyridine that are modified by the metal coordination in comparison with the emission spectra of free ligands H₄cht and 4,4'-bipyridine [14], which showed weak peak at 450 and 415 nm, respectively. The emission in the blue region suggests that the complex may have potential to be used as a blue-fluorescent material.

4. Conclusions

In conclusion, a novel complex [Zn₂(OH)(Hcht)(4,4'-bpy)]·4H₂O, where all Hcht ligands exclusively adopt the a,e,e,a conformation, was obtained by changing the synthetic conditions. The complex has been characterized by IR, X-ray powder diffraction, thermogravimetric analysis, fluorescent spectrum, and single crystal X-ray diffraction. The results suggest that the ratios of the starting materials, reaction temperatures, and solvent systems have an

important influence on the conformation choice of the flexible ligand, whereas the cooperative ligand has a great influence on the coordination mode of metal ions but no influence on the conformation preference of the flexible ligand. Thermogravimetric analysis shows four courses of weight loss corresponding to the decomposition of different ligands. Fluorescent spectrum displays that complex **1** is a potential blue-luminescent material.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1. ORTEP drawing of X-ray crystal structure of **1**, showing the asymmetric unit with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Figure 2.
(a) Coordination mode of the ligand; and (b) coordination environment of the metal ions in the molecular structure of complex **1**.

Figure 3.

(a) 2-D framework; (b) 1-D zigzag chain consisted of Zn1, Zn2, O9, and Hcht; and (c) 1-D chain consisted of Zn1, Zn2, O9, and 4,4'-bpy viewed along the b-axis in the molecular structure of **1**.

Figure 4.
Thermogravimetric analysis curve of complex **1**.

Figure 5. Solid-state fluorescent spectra of complex **1** (strong) and free ligand H₄cht (weak) at the room temperature.

Table 1Crystallographic data collection and refinement parameters for **1**

formula	C20 H26 N2 O13 Zn2
M_r	633.17
size (mm ³)	0.18 × 0.14 × 0.08
T (K)	293(2)
λ (Å)	0.71073
crystal system	Triclinic
space group	P-1
a (Å)	8.8754(7)
b (Å)	10.0779(8)
c (Å)	13.4952(12)
α (°)	96.491(6)
β (°)	99.845(6)
γ (°)	93.894(6)
V (Å ³)	1176.98(17)
Z	2
$F(000)$	648
d (g cm ⁻³)	1.787
μ (mm ⁻¹)	2.112
range (°)	2.04 to 25.19
Reflec. collected	13163
Indep. reflec.	4171 ($R_{int}=0.0811$)
$R1$ [$I > 2\sigma(I)$]	0.0529
$wR2$ [$I > 2\sigma(I)$]	0.1229
$R1$ (all data)	0.0966
$wR2$ (all data)	0.1498
goodness of fit	0.985

Table 2Selected bond lengths (Å) and bond angles (°) for **1**

Zn1-O3	1.979(4)	O6-Zn1-N1	102.7(2)
Zn1-O5	2.450(4)	O9-Zn1-O5	84.90(16)
Zn1-O6	1.984(4)	O3-Zn1-O5	96.10(17)
Zn1-O9	1.945(4)	O6-Zn1-O5	58.67(16)
Zn1-N1	2.097(5)	N1-Zn1-O5	160.60(19)
Zn2-O4	2.085(4)	O7-Zn2-O9	101.18(16)
Zn2-O7	2.002(4)	O7-Zn2-N2	107.03(19)
Zn2-O9	2.041(4)	O9-Zn2-N2	150.57(18)
Zn2-O9A	2.140(4)	O7-Zn2-O4	100.42(17)
Zn2-N2	2.059(5)	O9-Zn2-O4	98.23(16)
O9-Zn1-O3	111.45(17)	N2-Zn2-O4	84.93(19)
O9-Zn1-O6	118.42(17)	O7-Zn2-O9A	98.61(16)
O3-Zn1-O6	119.57(19)	O9-Zn2-O9A	80.23(15)
O9-Zn1-N1	101.52(19)	N2-Zn2-O9A	87.35(18)
O3-Zn1-N1	98.43(19)	O4-Zn2-O9A	160.83(16)