



Structural diversity of a series of terpyridyl carboxylate coordination polymers: Luminescent sensor and magnetic properties



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ABSTRACT

Eleven new coordination polymers, $[\text{Zn}_2(\text{ctpy})_2(\text{HCOO})_2]_n \cdot 3n\text{H}_2\text{O}$ (**1**), $[\text{Zn}_2(\text{ctpy})_2(\text{HCOO})_2(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (**2**), $[\text{Zn}_2(\text{ctpy})_2(\text{H}_2\text{O})_4]_n \cdot 2n(\text{CH}_3\text{COO}) \cdot n\text{H}_2\text{O}$ (**3**), $[\text{Zn}_2(\text{ctpy})_2(\text{CH}_3\text{COO})_2]_n \cdot n\text{H}_2\text{O}$ (**4**), $[\text{Zn}(\text{ctpy})_2]_n \cdot n\text{H}_2\text{O}$ (**5**), $[\text{Zn}_2(\text{ctpy})_2(\text{Hidc})(\text{H}_2\text{O})_2]_n$ (**6**), $[\text{Cd}_2(\text{ctpy})_4]_n$ (**7**), $[\text{Cd}_2(\text{ctpy})_2(\text{Hidc})]_n$ (**8**), $[\text{Co}_2(\text{ctpy})_2(\text{HCOO})_2(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (**9**), $[\text{Co}(\text{ctpy})(\text{DMF})(\text{ox})_{0.5}]_n$ (**10**), $[\text{Co}(\text{ctpy})(\text{ox})_{0.5}]_n$ (**11**) and the closely related compound $[\text{Zn}(\text{ctpy})(\text{ox})_{0.5}]_n \cdot 0.5n\text{H}_2\text{O}$ (**12**) ($\text{Hctpy} = 4'$ -carboxy- $4,2':6',4''$ -terpyridine, $\text{H}_2\text{ox} =$ oxalic acid and $\text{H}_3\text{idc} =$ imidazole-4,5-dicarboxylic acid) have been synthesized by hydro(solvo)thermal reaction of $4'$ -carboxy- $4,2':6',4''$ -terpyridine with divalent metal salts and characterized by elemental analysis, IR spectra, single crystal X-ray diffraction. Compounds **1** and **4** have similar structure which demonstrate a two-fold interpenetrating 3D framework with a 3-connected **utp** topological net, which contains the same number of left and right-handed 2_1 helical chains. Compounds **2** and **9** are isostructural 2D layer with a 3-connected **hcb** topological net. Similar to **2**, compound **3** also displays a 3-connected 2D **hcb** topological net. Compounds **5** and **10** are a 2D layer with a 4-connected **sql** topological net. Compound **6** shows a chiral 2D layer based on a 1D left- or right-handed helical chains, which are further extended into an achiral 2D + 2D → 3D supramolecular network by hydrogen bonds with alternately arrangement. Compound **7** features an unusual 2-fold interpenetrating 3D coordination network which exhibits a new intriguing (3,5)-connected binodal topological net with the Schläfli symbol of $(5^2 \cdot 6)(5^3 \cdot 6^3 \cdot 7^3 \cdot 8)$. Compound **8** shows a 2D → 3D supramolecular structure based on (3,4)-connected 2D bilayers with the Schläfli symbol of $(4^4 \cdot 6^2)$. Compound **11** displays an unusual three-dimensional coordination network which exhibits an intriguing (3,8)-connected binodal new topological net with Schläfli symbol $(4^2 \cdot 6^2)_2(4^2 \cdot 6^{23} \cdot 8^3)$. Compound **12** features a two-fold interpenetrating (3,4)-connected 3D framework with the **fsc** topological net. Compounds **1–12** were obtained under similar reaction conditions. The diverse structures indicate that rational selection of the second ligand, metal salt, counter anion and solvent are good methods to further design metal-organic compounds with new structures and properties. Moreover, their thermal stabilities, photo-luminescent and magnetic properties were also investigated. More importantly, compound **12** has been successfully applied in the detection of Fe^{3+} ion in DMF solutions and nitrobenzene and the possible detecting mechanism was also discussed.

1. Introduction

Increasing interest has been evoked by multifunctional coordination polymers (CPs) or metal-organic frameworks (MOFs), this is due to their specific solid-state properties of enhancing stability, gas-sorption, magnetism, luminescence, sensing and so forth [1–5]. Currently, a variety of coordination frameworks with fascinating topologies (such as diamond, rutile, cube, ice and brick wall net) and

helical structures have been synthesized [6]. But the rational design and synthesis of novel functioned polymeric metal-organic compounds remains a great challenge in crystal engineering [7]. As far as we know, the diversity in the framework architectures of such coordination polymers depends on many factors, such as the coordination geometry of metal centers, the coordination ability of organic ligands, the choice of the auxiliary ligand, counter anion and the reaction conditions (pH, temperature, solvent and so on) [8,9]. Among these factors, the

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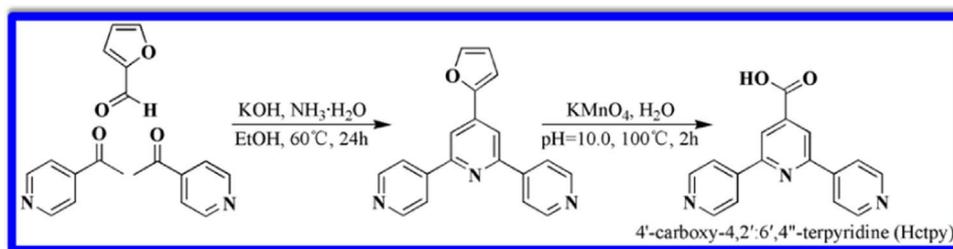
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Scheme 1. Synthetic route of Hctpy.

selection of organic ligand with suitable binding groups is especially crucial [10–12]. In contrast to much research on bridging carboxylic acid or pyridyl ligands, the investigation of polypyridyl ligands with additional carboxylic functional binding sites has remained largely unexplored in the assembly of metal-organic frameworks (MOFs). We have been interested in MOFs constructed from the rigid N-donor and O-donor bifunctionalized ligands and metal ions [13].

We chose a bridging trigonal bifunctionalized ligand, 4'-carboxy-4,2':6',4''-terpyridine (Hctpy, Scheme 1), as a primary ligand for our synthetic strategy. Hctpy contains a rigid pyridylcarboxylate moiety and two freely rotating pyridine groups. Firstly, its rigidity and trigonal geometry would afford a directional control at three dimensional extensions and may lead to the formation of nanosized cages, porous frameworks enclosing cavities, and channels [14]. Secondly, this trigonal ligand may cause the planes of the two terminal pyridyl groups to rotate with respect to the plane of the central pyridyl ring, and so it is a good candidate to form unique structural motifs with fascinating topological network. As a typical example, Li and co-workers have obtained and structurally characterized the 3,5-bis(4-pyridylmethoxy) benzoate coordination polymers previously [15]. Another feature of Hctpy ligand is that it has a large π -conjugated nonlinear structure with N, O donors that can offer additional hydrogen bonding and π - π interactions to consolidate the whole MOFs. And metal ions prefer binding carboxylate O atoms and N atoms of two terminal pyridine rather than the N atom of the central pyridine in Hctpy because of steric effect resulting from two terminal pyridine, so this N atom as a functional site is predicted to recognize small Lewis acidic molecules and metal ions. Finally, polycarboxylic acid, such as oxalic acid [16], imidazole-4,5-dicarboxylic acid [17], have been widely employed to construct MOFs. So we introduce these two polycarboxylates as secondary ligands to promote structural diversity in constructing kinds of MOFs. We notice that the deprotonated process of carboxylic acid can be more easily completed by solvothermal reaction in DMF and water mixed solvent than that of hydrothermal reaction [18]. In this work, we prepare eleven new coordination polymers, $[\text{Zn}_2(\text{ctpy})_2(\text{HCOO})_2]_n \cdot 3n\text{H}_2\text{O}$ (**1**), $[\text{Zn}_2(\text{ctpy})_2(\text{HCOO})_2(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (**2**), $[\text{Zn}_2(\text{ctpy})_2(\text{H}_2\text{O})_4]_n \cdot 2n(\text{CH}_3\text{COO}) \cdot n\text{H}_2\text{O}$ (**3**), $[\text{Zn}_2(\text{ctpy})_2(\text{CH}_3\text{COO})_2]_n \cdot n\text{H}_2\text{O}$ (**4**), $[\text{Zn}(\text{ctpy})_2]_n \cdot n\text{H}_2\text{O}$ (**5**), $[\text{Zn}_2(\text{ctpy})_2(\text{Hidc})(\text{H}_2\text{O})_2]_n$ (**6**), $[\text{Cd}_2(\text{ctpy})_4]_n$ (**7**), $[\text{Cd}_2(\text{ctpy})_2(\text{Hidc})]_n$ (**8**), $[\text{Co}_2(\text{ctpy})_2(\text{HCOO})_2(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (**9**), $[\text{Co}(\text{ctpy})(\text{DMF})(\text{ox})_{0.5}]_n$ (**10**), $[\text{Co}(\text{ctpy})(\text{ox})_{0.5}]_n$ (**11**) and the closely related compound $[\text{Zn}(\text{ctpy})(\text{ox})_{0.5}]_n \cdot 0.5n\text{H}_2\text{O}$ (**12**) (Hctpy = 4'-carboxy-4,2':6',4''-terpyridine, H_2ox = oxalic acid, H_3idc = imidazole-4,5-dicarboxylic acid) by solvothermal reaction in DMF or DMA and water mixed solvents. This work reports their crystal structures, luminescent properties, magnetic properties and the unique application of **12** in detecting of Fe(III) ion in DMF solutions and nitrobenzene. Furthermore, the possible detecting mechanism has been discussed.

2. Experimental section

2.1. Materials and physical measurements

Ligand Hctpy was synthesized according to the reported procedure

with some modification [19a-c]. Other commercially available chemicals and solvents are of reagent grade and were used as received without further purification. All metal salts and solvents were obtained from Xi'an chemical reagent company in China. Oxalic acid, imidazole-4,5-dicarboxylic acid, 4-acetylpyridine, 2-furaldehyde were obtained from J & K Scientific Ltd. in China. Infrared spectra were obtained from KBr pellets on a Bruker EQUINOX 55 Fourier transform Infrared spectrometer in the 400–4000 cm^{-1} region. Elemental analyses (C, H and N) were performed on an elemental Vario EL elemental analyzer. Fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer at room temperature. Variable-temperature magnetic susceptibility data for polycrystalline **9**, **10** and **11** were obtained on a SQUID XL-7 magnetometer under an applied field of 1000 Oe over the temperature range of 1.8–300 K. Thermal gravimetry analyses (TGA) were carried out with a Universal V2.6 DTA system at a rate of 10 $^\circ\text{C}/\text{min}$ in a nitrogen atmosphere. Powder X-ray diffraction (PXRD) measurements were measured on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu- K_α , 1.5418 Å). Simulations of the PXRD spectra were carried out by the single-crystal data and diffraction-crystal module of the Mercury program [20].

2.2. Synthesis

2.2.1. Synthesis of Hctpy

To a mixture of 4-acetylpyridine (9.68 g, 40 mmol) and 2-furaldehyde (3.84 g, 20 mmol) was added in 200 mL of ethanol. After the mixture was stirred at room temperature for 10 min, KOH (3.08 g, 55 mmol) and 120 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ (30%) was added and the resulting mixture was stirred under reflux for 24 h. After the mixture was cooled to room temperature, the solvent was removed under vacuum, and washed several times with water and ethanol, dried in vacuo to give a white powder. Yield: 3.94 g (66%). The product was used in the following reaction without further purification. The above white solid (2.00 g) was added to a mixture of KMnO_4 (4.20 g, 26.7 mmol) and water (100 mL) and stirred at room temperature. In this period, the solution was adjusted to pH = 10.0 with the addition of KOH. After stirring for 2 h at 100 $^\circ\text{C}$, the mixture was filtered and washed with hot water, then the filtrate was made slightly acidic (pH = 5.0) by addition of HCl (aq., conc.), the resulting white precipitate was filtered off, recrystallized with methanol, and dried in a vacuum to give Hctpy (confirmed by single-crystal X-ray analysis) as colorless block crystals. Yield: 1.65 g (63%). Anal. Calc. for $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_3$ (Mr = 277.28) (%): C, 69.31; H, 4.00; N, 15.15. Found (%): C, 69.23; H, 3.92; N, 15.09. IR data (KBr pellet, cm^{-1}): 3431 (w), 2389 (w), 3069 (m), 1713 (s), 1599 (vs), 1546 (s), 1431 (s), 1403 (vs), 1350 (s), 1030 (m), 829 (w), 775 (m). ESI-MS: $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{16}\text{H}_{11}\text{O}_2\text{N}_3$: 298.0930; found: 298.0924. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ = 8.78 (d, J = 5.0, 4H), 8.52 (s, 2H), 8.26 (d, J = 6.0, 4H) (Fig. S1).

2.2.2. Synthesis of $[\text{Zn}_2(\text{ctpy})_2(\text{HCOO})_2]_n \cdot 3n\text{H}_2\text{O}$ (**1**)

A mixture of Hctpy (27.7 mg, 0.1 mmol) and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (21.9 mg, 0.1 mmol) were added to 10 mL of a $\text{H}_2\text{O}/\text{DMF}$ mixture (4/1, v/v), being stirred for 30 min and the pH value was then adjusted to 4.0 with 0.5 mol L^{-1} NaOH aqueous solution, then sealed in a

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