Synthesis, Structures and Luminescent Properties of Two Coordination Polymers Based on 5-(4-Carboxyphenyl)-2,6-Pyridinedicarboxylic Acid

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Abstract. Two coordination polymers, Zn₇O(cpda)₃(OH)₃ (1) and $[Tb(H_2cpda)(Hcpda)(H_2O)] \cdot (H_2O) (2) (H_3cpda = 5 - (4 - carboxyphenyl) - (4 - carb$ 2,6-pyridinedicarboxylic acid), were synthesized and characterized by elemental analysis, FTIR spectroscopy, TGA, PXRD, and single-crystal X-ray diffraction. Complex 1 has a 3D framework structure with

Introduction

Over the past decades, design and synthesis of metal-organic frameworks (MOFs) or coordination polymers have attracted great interest not only because of their fascinating topological architectures,^[1-3] but also their potential applications in a wide variety of fields, such as gas storage, catalysts, magnetism, light emitting device, and chemical sensing.^[4-11] Compared with traditional inorganic or organic luminescent materials, MOFs assemble by the inorganic and the organic moieties, both of which can provide the platforms to generate luminescence. Meanwhile metal-ligand charge transfer related luminescence within MOFs can add another dimensional luminescent functionalities.^[2,32–35] Furthermore, some guest molecules within MOFs are also able to emit and/or induce luminescence.^[2,33] Thus, MOFs can be used as excellent multifunctional luminescent materials.

However, it is still a challenge for chemists to construct novel metal-organic frameworks that have expected applications and intriguing structures, due to the coordination arrangement affected by many subtle factors, such as the structural characteristic of organic ligands, temperature, molar ratio of the materials, counter anions, pH value, etc.^[12,13] It has been proven that the selection of appropriate ligands is an efcient method for the construction of novel MOF materials, and great efforts have been devoted to the design of suitable organic

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high thermal stability and complex 2 exhibits 1D chain structure. Luminescent measurements indicate that complex 1 shows strong ligandto-metal charge transfer (LMCT) luminescence, while complex 2 exhibits the characteristic emission of Tb³⁺ ions.

ligands.^[14,15] Among previous reports, organic aromatic polycarboxylate ligands are most extensively used because they can adopt a variety of coordination modes and result in diverse multidimensional structures.[16-19]

Compared with organic aromatic polycarboxylate ligands, N-heterocycle polycarboxylate ligands have another nitrogen coordination site, so its coordination modes are more abundant. Using this kind of ligands, such as pyridine-2,6-dicarboxylic acid, pyridine-2,4,6-tricarboxylic acid, pyridine-2,3,5,6-tetracarboxylates,^[20-25] a variety of MOFs have been synthesized. 5-(4-carboxyphenyl)-2,6-pyridinedicarboxylic acid (H₃cpda) contains one nitrogen atom and three carboxyl groups, that make it has potential diverse chelating and bridging modes, so it is a good candidate ligand for constructing MOFs. But to the best of our knowledge, only one MOF based on this ligand was reported so far.^[26] Herein, using this ligand we synthesized two novel coordination polymers, $Zn_7O(cpda)_3(OH)_3$ (1) and $[Tb(H_2cpda)(Hcpda)(H_2O)] \cdot (H_2O) (2)$, by solvothermal reaction. In this paper we describe the synthesis, structure, and luminescence studies of the two novel coordination polymers.

Results and Discussion

Crystal Structures Description

Single-crystal X-ray structural analysis reveals that $Zn_7O(cpda)_3(OH)_3$ (1) crystallizes in the rhombohedral space group $R\bar{3}$ and exhibits a 3D network. As shown in Figure 1a, the H₃cpda ligand has only one coordination mode, in which each H₃cpda ligand connects six Zn²⁺ ions. Three kinds of crystallographically independent Zn²⁺ ions exist in the asymmetry unit: Zn1, Zn2, and Zn3, as shown in Figure 1b-c. Zn1 and Zn2 are five-coordinate and Zn3 is four-coordinate. Zn1 is surrounded by one nitrogen atom of one H₃cpda ligand, three oxygen atoms of two different H₃cpda ligands and one

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Figure 2. (a) 12-Membered ring and Zn_4O SBU; (b) the 2D layer structure simplified by SBU; (c) the 3D framework of 1 viewed along the *a* axis.

oxygen atom of one coordinated hydroxyl group (Figure 1b). Zn2 is surrounded by three oxygen atoms of three different H₃cpda ligands, one oxygen atom of a hydroxyl group and one single oxygen atom (O8) (Figure 1c). Zn3 is surrounded by three oxygen atoms of three different H₃cpda ligands and one single oxygen atom (O8) (Figure 1d). Interestingly, three Zn2 and one Zn3 together with one O8 form a special Zn₄O tetrahedron, while six Zn1 atoms alternatingly connect with six O1 atoms to form a Zn-O 12-membered ring (Figure 2a). Meanwhile, the Zn₄O secondary building unit and the 12-member ring are connected by a bridge oxygen atom O7 and another oxygen atom O3 from another ligand. In this way, both the 12member ring and Zn₄O SBU yield a complete layer (Figure 2b). Furthermore, the layers are connected by the H₃cpda ligands between the layers like pillars to hold a robust 3D framework structure (Figure 2c).



Figure 1. (a) Coordination mode of H_3 cpda; (b–d) three kinds of crystallographically independent Zn^{2+} ions with different coordination modes.

Single-crystal X-ray structural analysis reveals that $[Tb(H_2cpda)(Hcpda)(H_2O)]\cdot(H_2O)$ (2) crystallizes in the monoclinic space group C2/c and shows a 1D structure. The asymmetric unit consists of one Tb^{3+} ion, two H₃cpda ligands, and one coordinated water molecule (Figure 3a). The H₃cpda ligand shows two kinds of coordination modes: one act as bridging ligand, the other act as terminal ligand. And Tb^{3+} ion is eight-coordinate by two nitrogen atoms and six oxygen atoms, in which six from two tridentate cheated ONO atoms of two H₃cpda ligands, one oxygen atom from neighboring H₃cpda ligand, and another one oxygen atom from coordinated

water molecule. The coordination arrangement of Tb³⁺ ion is a distorted dicapped trigonal prismatic (Figure 3b). The neighboring Tb³⁺ ions (distance between them 6.4296 Å) are connected by monodentate carboxyl groups of the H₃cpda ligands, and give rise to a zigzag 1D chain (Figure 3c). From Figure 4, we can see that the neighboring 1D chains are packed together to form a 2D layer structure through the π - π interactions (3.542 Å) and hydrogen bonding interactions (2.477 Å). Further, there are some H₃cpda ligands with uncoordinated carboxyl groups acting as hydrogen bonding acceptor that extend the 2D layer into 3D framework. The π - π interactions and hydrogen bonding interactions play an important role in constructing and stabilizing of the crystal structure of **2**.



Figure 3. (a) Coordination environment of the Tb^{3+} atom; (b) the distorted dicapped trignoal prismatic arrangement; (c) the zigzag 1D chain.

Phase Purity and Thermal Stability

To investigate the phase purity of the as-synthesized samples of **1** and **2**, powder X-ray diffractions and elemental analyses were carried out. Figure S1 (Supporting Information) shows that the powder X-ray diffraction patterns of as-synthesized samples are agreed well with the simulated ones from the single crystal structure analyses. Coupled with the elemental analyses presented in the experimental, the phase purity of the as-synthesized samples is confirmed.

The thermal stability of both coordination polymers were examined by thermogravimetric analysis (TGA) from room temperature to 900 °C (Figure 5). The TGA curve of 1 indicates that 1 can be stable up to 440 °C, and it quickly starts losing weight and collapses above 440 °C. The high thermal



Figure 4. (a) 3D structure of 2 viewed along the *b* axis; (b) the π - π interaction and hydrogen bond of the 2D layer structure; (c) hydrogen bonding interactions in two adjacent layers.

stability of **1** is mainly attributed to the strong metal-carboxylate and nitrogen interactions.^[31] The TGA curve of **2** shows that **2** exhibits three weight loss steps. The first event take place from 110 to 200 °C, that may be related to the release of one coordinated water molecule (found 2.22%; calcd. 2.41%). The other two steps from 215 to 380 °C and from 390 to 850 °C, respectively, which correspond to the removal and decomposition of the H₃cpda ligand. The residue might be Tb₄O₇ (found 24.24%; calcd. 24.38%).



Figure 5. TGA curve for complex 1 and 2 under nitrogen.



Luminescent Properties

Taking into account of the excellent luminescent properties of MOFs with central d¹⁰ metal and Ln^{3+} ions, the solid-state luminescent spectra of compounds **1** and **2** and corresponding ligand were studied at room temperature. The excitation spectra of **1**, **2**, and H₃cpda ligand are shown in Figure S2 (Supporting Information). The free H₃cpda ligand exhibits a broad emission band with the maximum emission at 449 nm under

Figure 6. Luminescence emission spectra of H_3 cpda ligand and 1 excited at 367 nm (a), and 2 excited at 335 nm (b).

367 nm excitation (Figure 6a), which may be attributed to the π - π * transition. Under the same excitation, complex 1 exhibits much enhanced blue emission and the maximum emission shifts to 470 nm (Figure 6a). The enhancement and red-shift of the emission may be attributed to the coordination of the H₃cpda ligand to Zn²⁺ that increases the rigidity of the ligand



and thus reduces the loss of energy via radiationless decay of the intraligand emission excited state.^[32] The emission spectra of **2** consist of four characteristic emission band of Tb³⁺ located at about 489, 546, 582, and 622 nm under 335 nm excitation, which are assigned to the transitions of the Tb³⁺ from ${}^{5}D_{4} \rightarrow {}^{7}F_{J}$ (J = 6, 5, 4, 3), respectively (Figure 6b), However, the main intraligand band disappeares. These phenomena suggest that the H₃cpda ligand absorbs and transfers energy efficiently to the central metal ions of Tb³⁺, which is well knowed by ligand-to-metal charge transfer (LMCT).^[33–35]

Conclusions

Two novel coordination polymers based on 5-(4-carboxyphenyl)-2,6-pyridinedicarboxylic acid were successfully synthesized by solvothermal reaction. Complex **1** has a 3D framework structure and exhibits high thermal stability up to 440 °C. 3D supramolecular structure of complex **2** is structured by connecting 1D chain substructure through π - π interactions and hydrogen bond interactions. Moreover, complexes **1** and **2** exhibit strong LMCT luminescence and characteristic emission of Tb³⁺ ions, respectively, under UV light excitation, which makes them excellent candidates in light-emitting devices applications.

Experimental Section

Materials and Methods: All the chemicals were commercially available and used without further purication. Dimethyl 4-chloropyridine-2,6-dicarboxylate was synthesized according to the literature.^[27,28] ¹H NMR spectra were performed with a Bruker Avance DMX500 spectrometer using tetramethylsilane (TMS) as an internal standard. Infrared spectra (IR) were recorded with a Thermo Fisher Nicolet iS10 spectrometer using KBr pellets. Elemental analyses for C, H, N were performed with an EA1112 microelemental analyzer manufactured by Thermo Electron Corporation. Powder X-ray diffraction (PXRD) patterns were collected in the $2\theta = 3-60^{\circ}$ range with an X'Pert PRO diffractometer with Cu- K_a ($\lambda = 1.541$ Å) radiation at room temperature. Thermogravimetric analyses (TGA) were carried out with a Netzsch TG209F3 with a heating rate of 1 K·min⁻¹ in a nitrogen atmosphere. Luminescence spectra for the solid samples were recorded with a Hitachi F4500 fluorescence spectrometer. The photomultiplier tube voltage was 700 V and the scan speed was 240 nm per min, while the slit widths of excitation and emission spectra were 2.5 nm and 2.5 nm for H₃cpda and 1, 1.0 nm and 1.0 nm for 2, respectively.

4-Carbomethoxyphenylboronic Acid Pinacol Ester: Methyl 4-bromobenzoate (10 g, 46.5 mmol), bis(pinacolato)diboron (15.35 g, 60.3 mmol), KOAc (13.7 g, 139.5 mmol), and Pd(PPh₃)₂Cl₂ (0.5 g, 0.7 mmol) were dissolved in 1,4-dioxane (250 mL), subsequently the mixture was heated at 80 °C for 4 h. After cooling to room temperature, the precipitate was filtered off, and the filtrate was removed under reduced pressure. The residue was purified by silca gel columnchromatography with petroleum ether/ethyl acetate (8:1) to give 4carbomethoxyphenylboronic acid pinacol ester in 60% yield based on methyl 4-bromobenzoate. ¹H NMR (CDCl₃): $\delta = 1.37$ (s, 12 H), 3.93 (s, 3 H), 7.88 (d, 2 H), 8.04 (d, 2 H). 5-(4-Carboxyphenyl)-2,6-Pyridinedicarboxylic Acid (H₃cpda): A mixture of dimethyl 4-chloropyridine-2,6-dicarboxylate (6.89 g, 30 mmol), 4-carbomethoxyphenylboronic acid pinacol ester(9.43 g, 36 mmol), KI (24.9 g, 150 mmol), K₂CO₃ (12.4 g, 90 mmol), and CsF (13.67 g, 90 mmol) was dissolved in dried 1,4-dioxane (250 mL), which was purged with argon and stirred for half an hour at room temperature. Afterwards, Pd(PPh₃)₄ (0.4 g, 0.035 mmol) was added and the mixture was heated at 90 °C for 8 h. After cooling to room temperature, the precipitate was filtered off, and the filtrate was removed under reduced pressure. The residue was purified by silca gel columnchromatography with dichloromethane/ethyl acetate (40:1) to give dimethyl 5-(4-carboxyphenyl)pyridine-2,6-dicarboxylate as a white solid. A suspension of diester in 1 M NaOH was stirred at 80 °C for 2 h. The solution was cooled with ice and acidied with HCl to pH 2. The white precipitate was collected to give H₃cpda in 65% yield based on dimethyl 4-chloropyridine-2,6-dicarboxylate. ¹H NMR (DMSO): $\delta = 8.03$ (d, 2 H), 8.08 (d, 2 H), 8.49 (s, 2 H) ppm. C14H9NO6: calcd. C 58.54; H 3.16; N 4.88%; found: C 58.03; H 3.10; N 4.74%.

Zn₇O(cpda)₃(OH)₃ (1): Zn(NO₃)₂·6H₂O (0.0223 g, 0.075 mmol), H₃cpda (0.0144g, 0.05 mmol), HCl (12 mol·L⁻¹, 20uL), H₂O (6 mL), and ethanol(2 mL) were added into a 25 mL Teon high temperature kettle and kept at 170 °C for 48 h. After the mixture had slowly cooled to room temperature, colorless rhombus-like crystals were obtained in 75% yield based on Zn(NO₃)₂·6H₂O. C₄₂H₂₁N₃O₂₂Zn₇: calcd. C 36.59; H 1.52; N 3.05%; found: C 36.90; H 1.63; N 3.11%. **IR** (KBr): $\bar{\nu} = 3480$ (s), 1687 (s), 1646 (m), 1604 (s), 1572 (m), 1463 (w), 1445 (w), 1410 (m), 1385 (m), 1329 (m), 1261 (w), 1077 (w), 1011 (w), 905 (w), 862 (w), 778 (m), 748 (w), 699 (w), 530 (w) cm⁻¹.

[**Tb**(**H**₂**cpda**)(**Hcpda**)(**H**₂**O**)[•](**H**₂**O**) (2): A mixture of Tb(NO₃)₃· 6H₂O (0.012 g, 0.025 mmol), H₃cpda (0.0144 g, 0.05 mmol), HCl (12 mol·L⁻¹, 20 µL), and H₂O (8 mL) was added into a 25 mL Teon high temperature kettle and kept at 120 °C for 48 h. After the mixture was slowly cooled to room temperature, colorless rod-like crystals were obtained in 55% yield based on Tb(NO₃)₃·6H₂O. C₂₈H₁₉N₂O₁₄Tb: calcd. C 43.84; H 2.48; N 3.65%; found: C 43.65; H 2.41; N 3.66%. **IR** (KBr): $\tilde{v} = 3440$ (s), 1681 (s), 1596 (s), 1450 (m), 1420 (m), 1350 (m), 1315 (w), 1286 (m), 1185 (w), 1129 (w), 1071 (w), 1014 (w), 918 (w), 859 (w), 809 (w), 773 (m), 764 (m), 728 (m), 532 (w) cm⁻¹.

X-ray Data Collection and Structural Determination: Crystallographic measurement for complex 1 and 2 was taken with a Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphitemonochromatic Mo- K_{α} radiation ($\lambda = 0.71073$ Å) at 293 K. The determination of the unit cells and data collections for the crystals of 1 and 2 were performed with CrysAlisPro. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.^[29] The structure was solved by direct methods, and rened by a full-matrix leastsquare method with the SHELX-97 program package.[30] All non-hydrogen atoms including solvent molecules were located successfully from Fourier maps and were rened anisotropically. Hydrogen atoms on carbon atoms were generated geometrically. The hydrogen atoms of the water molecules were clearly visible in different maps and were handled in the subsequent renement with xed isotropic displacement parameters. Crystallographic data for 1 and 2 are summarized in Table 1, the selected bond lengths and angles are listed in Table S1 and S2 (Supporting Information), respectively.

ARTICLE

	1	2
Chemical formula	C ₄₂ H ₂₁ N ₃ O ₂₂ Zn ₇	C ₂₈ H ₁₉ N ₂ O ₁₄ Tb
Formula weight	1377.21	766.37
Temperature /K	293(2)	293(2)
Wavelength /Å	0.71073 A	0.71073
Crystal system	rhombohedral	monoclinic
Space group	RĪ	C2/c
a /Å	13.6884(10)	28.2602(11)
b /Å	13.6884(10)	6.9089(3)
<i>c</i> /Å	39.877(3)	30.2153(10)
a /°	90	90
β /°	90	99.598
γ /°	120	90
V/A^3	6470.8(8)	5816.9(4)
Ζ	6	8
Density (calcd.) /g·cm ⁻³	2.121	1.750
Absorbance coefcient /mm ⁻¹	3.921	2.507
F(000)	4080	3024
Crystal size /mm ⁻³	$0.35 \times 0.28 \times 0.22$	$0.32 \times 0.26 \times 0.22$
Goodness of t on F_2	1.034	1.144
$R_1, wR_2[I > 2\sigma(I)^{\mathrm{a}})$	0.0243, 0.0566	0.0801, 0.2159
R_1 , wR_2 (all data) ^{a)}	0.0301, 0.0588	0.0945, 0.2260
Largest difference peak and hole /e•Å ⁻³	0.358, -0.544	3.823, -2.342

 Table 1. Crystallographic data collection and renement result for 1 and 2.

a) $R_1 = (|F_0| - |F_c|) / \sum |F_0|; wR_2 = |\sum w (|F_0| - |F_c|^2) / \sum w F_0^2]^{1/2}.$

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-899464 (1) and CCDC-899465 (2) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam. ac.uk)

Supporting Information (see footnote on the first page of this article): Figures S1–S5: PXRD patterns of 1 and 2; the excitation spectra of H_3 cpda ligand and complexes 1 and 2. Table S1 and S2: Selected bond lengths and angles for complexes 1 and 2.

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