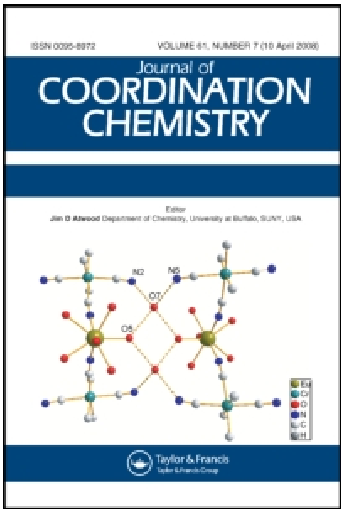

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A new three-connected metal-organic coordination polymer with helical motifs: synthesis, crystal structure and photoluminescence

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A new three-connected metal-organic coordination polymer with helical motifs: synthesis, crystal structure and photoluminescence

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An interesting metal-organic network with helical motifs, $\{[Zn_2(mpdc)_2(bpy)(H_2O)_2]\cdot 2H_2O\}$ (**1**, mpdc = 2,6-dimethyl pyrdine-3,5-dicarboxylate), was synthesized under hydrothermal conditions, and characterized. Single-crystal X-ray structural analysis indicates that the title compound crystallizes in a monoclinic lattice, $P2(1)/c$ with $a = 7.811(2)$, $b = 12.324(3)$, $c = 15.794(4)$A, $\beta = 98.206(4)^\circ$, $Z = 2$, $V = 1504.8(7)\,\text{Å}^3$, $D_c = 1.704\,\text{Mg}\,\text{m}^{-3}$, $F(000) = 816$, $R_1 = 0.0379$, $wR_2 = 0.0807$. In the structure of **1** the helical strands composed of $[Zn(mpdc)(H_2O)]$ array in an interlacing fashion, and trap solvated water molecules to assemble a novel supramolecular network. Compound **1** exhibits strong photoluminescence in the solid state at room temperature.

Keywords: Coordination polymer; Helical structure; Zinc; Supramolecular architecture; Photoluminescence

1. Introduction

Metal-organic frameworks (MOFs) have diverse topological structures and promising potential applications [1]. Various topologies of MOFs have been reported and reviewed [2], some of which are similar to natural minerals, such as rho-ZMOF [3], $[Zn(mim)_2\cdot H_2O]_\infty$(SOD) [4], and $[Zn(eim)_2\cdot 2H_2O]_\infty$(ANA) [4]. Design and synthesis of MOFs with helical structures have attracted attention for the relation to biological phenomena such as molecular recognition and information storage (exemplified by the double helix of DNA and the α helix of proteins) [5]. For construction of MOFs or supramolecular architectures, pyridine dicarboxylic acids (PDCs) have been ultilized because of their versatile coordination modes as well as hydrogen-bonding donors or acceptors [6], but alkyl- or aryl-substituted PDCs have not been well explored [7]. Our interest has focused on coordination chemistry of substituted pyridine-3,5-dicarboxylic acids [8]. Herein, we report a new photoluminescent metal-organic architecture with helical motifs.

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2. Experimental

2.1. *General methods*

All chemicals in these syntheses are of reagent grade and used as purchased without further purification. Infrared (IR) spectra are recorded from KBr pellets in the range of 400–4000 cm^{-1} on a Nicolet Impact 410 FT-IR spectrometer. Elemental analyses are performed on a Perkin–Elmer 2400 element analyzer. Thermogravimetric analyses are performed with a Mettler Toledo TGA/SDTA 851e analyzer in N_2 with a heating rate of 5°C min^{-1} from 30 to 800°C. Excitation and emission spectra were obtained on a RF-5301PC spectrofluorimeter equipped with a 450 W xenon lamp as the excitation source; the measurement of solid state samples was performed at room temperature.

2.2. *Synthesis*

2,6-Dimethylpyridine-3,5-dicarboxylic acid (**H_2mpdc**) was prepared by hydrolyzing diethyl 2,6-dimethylpyridine-3,5-dicarboxylate [9].

2.2.1. $\{[Zn_2(mpdc)_2(bpy)(H_2O)_2]\cdot 2H_2O\}$ (1). A solution of H_2O (10 mL) containing H_2mpdc (0.2 mmol), 4,4′-bipyridine (bpy, 0.4 mmol), $Zn(NO_3)_2\cdot 6H_2O$ (0.2 mmol) and Et_3N (0.04 mL) is sealed in a reactor of 23 mL and heated at 120°C for 72 h, then cooled to room temperature. Colorless crystals are washed with ethanol (3 × 3 mL) to give **1** (0.04 g, 54% yield). Elemental analysis Calcd (%) for $C_{28}H_{30}O_{12}N_4Zn_2 = \{[Zn_2(mpdc)_2(bpy)(H_2O)_2]\cdot 2H_2O\}$: C 45.12, H 4.06, N 7.52; found C 45.08, H 3.98, N 7.49. FT-IR (KBr) (cm^{-1}): 3300 (m), 3051(m), 3021(m), 1602 (s), 1551(m), 1426(m), 1380(vs), 1078(m), 833(m) and 642(m).

2.3. *Crystallographic studies*

A suitable single crystal is glued to a thin glass fiber and mounted on a Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å)) operating at 50 kV and 40 mA. Intensity data are collected at room temperature. Data processing is performed using the SAINT processing program. The structure is solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL-97 [10]. All hydrogen atoms of hydrogen bonds, and non-hydrogen atoms are easily found from the difference Fourier maps and refined anisotropically. The crystallographic data and details on refinement for **1** are summarized in table 1. Selected bond distances are listed in table 2. Hydrogen bonding parameters are summarized in table 3.

3. Result and discussion

$\{[Zn_2(mpdc)_2(bpy)(H_2O)_2]\cdot 2H_2O\}$ (**1**) (mpdc = 2,6-dimethyl- pyridine-3,5-dicarboxylate) is obtained by reacting of $Zn(NO_3)_2$ with H_2mpdc and 4,4′-bipyridine(bpy) in H_2O in the presence of triethylamine (pH = 6) at 120°C. X-ray diffraction analyses reveal

Table 1. Crystallographic data and structure refinement summary for **1**.

Formula	$C_{28}H_{30}N_4O_{12}Zn_2$
Fw	745.32
Size (mm^3)	$0.34 \times 0.21 \times 0.10$
Crystal system	Monoclinic
Space group	$P2(1)/c$
a (Å)	7.811(2)
b (Å)	12.324(3)
c (Å)	15.794(4)
α (°)	90
β (°)	98.206(4)
γ (°)	90
V (A^3)	1504.8(7)
Z	2
T (K)	298(2)
Wavelength (Å)	0.71073
ρ_{Calcd} (Mg m^{-3})	1.704
F(000)	816
θ (°)	2.10–25.0
Reflections collected	7699
Independent reflections	2568 [R(int) = 0.0497]
Data/parameters	2568/224
Goodness-of-fit on F^2	1.008
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0381$, $wR_2 = 0.0807$
R indices (all data)	$R_1 = 0.0690$, $wR_2 = 0.0949$

Table 2. Selected interatomic distances (Å) and angles (°) for **1**.

Zn(1)–O(3)	1.953(3)
Zn(1)–O(5)	1.977(3)
Zn(1)–O(1)	1.983(3)
Zn(1)–N(2)	2.062(3)
O(3)–Zn(1)–O(5)	101.81(13)
O(3)–Zn(1)–O(1)	122.01(12)
O(5)–Zn(1)–O(1)	118.49(15)
O(3)–Zn(1)–N(2)	113.49(13)
O(5)–Zn(1)–N(2)	106.10(13)
O(1)–Zn(1)–N(2)	106.10(13)

Table 3. Hydrogen bonding parameters in **1**.[a]

X–H ··· Y	X–H	H ··· Y	X ··· Y	∠X–H ··· Y
O5–H15 ··· O4#1	0.810	1.914	2.724	178.45
O5–H16 ··· O6	0.775	1.840	2.613	175.10
O6–H17 ··· N1#2	0.831	1.953	2.783	175.91
O6–H18 ··· O2#3	0.814	1.946	2.754	171.54

[a] Symmetric code: #1: $-x+1$, $y+1/2$, $-z+3/2$; #2: $x+1$, $-y+1/2$, $z-1/2$; #3: $x+1$, y, z.

that **1** crystallizes in the space group $P2(1)/c$. The compound is stable in air and insoluble in common organic solvents such as methanol, ethanol, acetonitrile, acetone and DMF. X-ray powder diffraction pattern proves **1** is a pure phase.

The coordination environment of zinc is illustrated in figure 1(a). The Zn center adopts a tetrahedral coordination (ZnO_3N) by binding to one nitrogen atom of

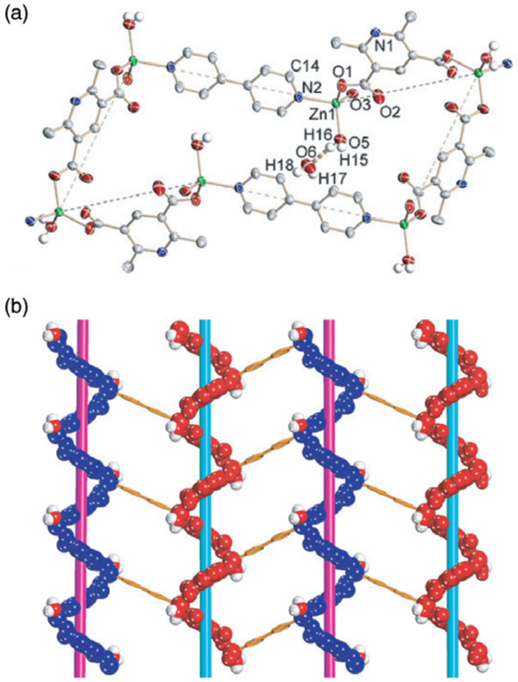

Figure 1. (a) Thermal ellipsoid (50%) plot of a chair-like six-membered ring of **1**. (b) Covalent helical strands composed of [Zn(mpdc)(H_2O)] were bridged by bpy ligands to form a 2-D network viewed along the [010] direction. CH_3 groups and hydrogen atoms of (Ar) C–H bonds are omitted for clarity. Blue *M*-(left-handed) strands, red *P*-(right-handed) strands, and brown stick bpy ligands.

bpy ligand, one oxygen of H_2O and two oxygen atoms from different carboxylate groups of two $mpdc^{2-}$ ligands in monodentate mode (table 1). The unit of $[Zn_6(bpy)_2(mpdc)_4(H_2O)_6]$ is a chair-like six-membered ring with a pore with ca 17 Å × 11 Å (figure 1a and figure S1b). Furthermore, the *M*- and *P*-helical strands composed of [Zn(mpdc)(H_2O)], are bridged by bpy ligands to form an extended 2-D coordination polymeric network along *bc* plane (figure 1b).

These 2-D polymeric layers form a periodically ordered 3-D surpamolecular network along the [010] direction (figures 2 and 3), in which the *M*-and *P*-helical strands interlace with each other (figure S2). The channel with diameter of ca 2 Å encircled by four adjacent layers is occupied by H_2O molecules *via* strong hydrogen bonds (O5 ··· O6 2.613 Å, O6 ··· N1 2.783 Å, O6 ··· O2 2.754 Å) (table 3). Two types of interaction stabilize the 3-D supramolecular framework: the hydrogen bonds (table 3) and the parallel $\pi \cdots \pi$ stacking interactions with face-to-face distances of 3.60 Å between bpy and $mpdc^{2-}$ ligands [11].

The thermogravimetric analysis (TGA, N_2) for **1** reveals weight loss of 4.5% below 200°C corresponding to loss of free water (Calcd: 4.8%) (figure 4). As reported in our previous work on a cadmium complex [8], **1** also exhibits strong photoluminescence in solid state at room temperature. The emission maximum at $\lambda = 462$ nm of **1** can be assigned to ligand-metal charge transfer, while emission maximum of H_2mpdc at 472 nm (upon excitation at $\lambda = 367$ nm) can be attributable to the $\pi^* \rightarrow n$ transitions (figure 5) [12].

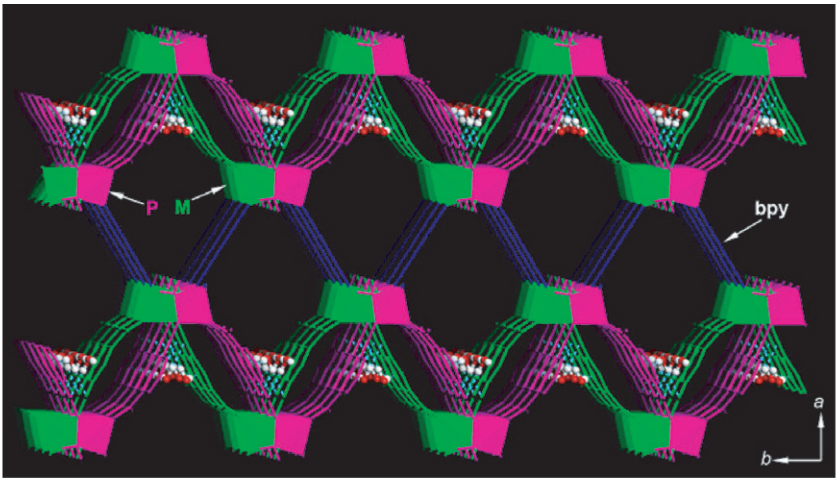

Figure 2. Perspective of water molecules trapped by the interlacing *P*-(right-handed) and *M*-(left-handed) helical strands.

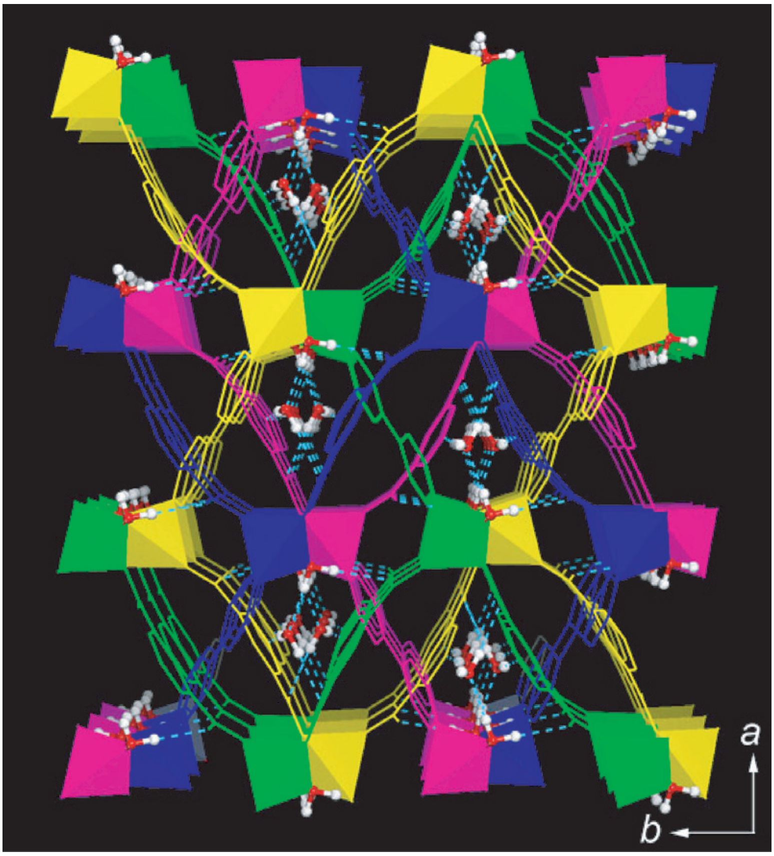

Figure 3. (a) The 3-D supramolecular framework (different layers represented with colors). The channel circled by four adjacent layers hosts equivalents of solvated water molecules through strong hydrogen bonds.

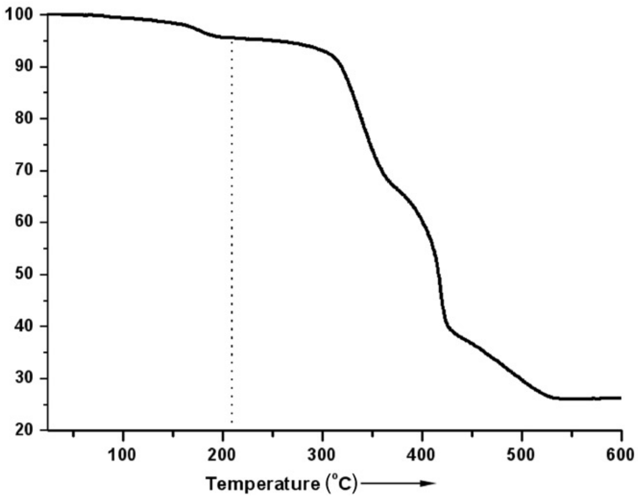

Figure 4. TGA (N_2) plot of compound **1**.

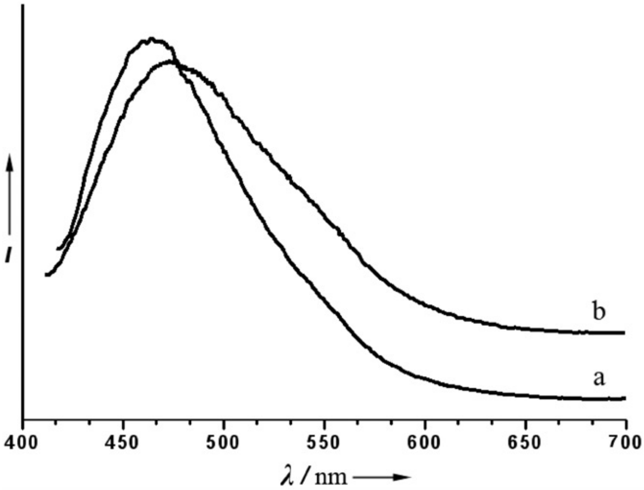

Figure 5. Emission spectra of (a) **1** ($\lambda_{max} = 462$ nm) and (b) H_2mpdc ligand ($\lambda_{max} = 472$ nm), upon excitation at 367 nm in solid state at room temperature.

4. Conclusion

We synthesized an interesting metal-organic network of $\{[Zn_2(mpdc)_2(bpy)(H_2O)_2] \cdot 2H_2O\}$with helical motifs by using mpdc^{2-} ligands, a derivative of pyridyldicarboxylates, as V-shaped spacers. The interlacing helical-strands of $[Zn(mpdc)(H_2O)]$ trap solvated water molecules to construct interesting 3-D supramolecular network with the participation of 4,4′-bipyridine. As expected, **1** exhibits strong photoluminescence in the solid state at room temperature.

Supplementary materials

CCDC-609979 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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