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Syntheses, structures and properties of three 4-fold interpenetration coordination polymers based on two different *dia* interpenetrating modes

Xiu-Yuan Li [a], Chen-Xiao Han [a], Ke-Fen Yue [a,*], Yong-Liang Liu [b], Chun-Sheng Zhou [b], Yuan-Feng Hou [a], Tian He [a], Ni Yan [a]

[a] *Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of the Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710069, PR China*
[b] *Department of Chemistry, Shang Luo University, Shang Luo 726000, PR China*

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Three new 4-fold interpenetrated coordination polymers based on two different *dia* interpenetrating modes have been prepared successfully, namely $[Cu_{0.5}(bib)_{0.5}(tftpa)_{0.5}]_n$ (**1**), $\{[Zn_{0.5}(bib)_{0.5}(tftpa)_{0.5}]\cdot 0.5H_2O\}_n$ (**2**) and $[Cd(bib)(tftpa)(EtOH)]_n$ (**3**) (bib = 1,4-bis(2-methyl-imidazol-1-yl)butane, H_2tftpa = tetrafluoroterephthalic acid). Complexes **1** and **3**, with the same octahedral metal center, are obtained as 4-fold interpenetrated *dia* coordination frameworks; however, complex **2**, with a tetrahedral metal center, presents a 4-fold *dia* network with an uncommon [2 + 2] mode of interpenetration. All of the polymers contain right- and left-handed helices that are constructed alternatively and each helix is built up from $[M_2(tftpa)(bib)]_n$. Additionally, thermogravimetric curves and luminescent emissions of **2** and **3** have been studied.

1. Introduction

In recent years, much attention has been paid to the rational design and construction of coordination polymeric frameworks in the field of supramolecular chemistry and crystal engineering, owing to their intriguing structures and potential properties in various areas, such as gas adsorption, heterogeneous catalysis, ion exchange and so on [1–6]. It has been proved that the structures of coordination polymers (CPs) have a close relationship with their functions. However, the prediction and design of target CPs are still fraught with enormous challenges [7,8]. Many investigations have been dedicated to finding new synthetic strategies [9–11], and an effective approach is to adopt mixed-ligand systems [12–14]. In general, the occurrence of interpenetration can be ascribed to the presence of a large solvent accessible volume in a single network [15,16], but “nature abhors a vacuum” [17–19], even at the molecular level, so large empty voids tend to become smaller by framework interpenetration [20–22], and interpenetration makes the whole framework more stable.

In this paper, we chose the flexible ligand 1,4-bis(2-methylimidazol-1-yl) butane as an N-donor ligand, since the long spacer $-(CH_2)_4-$ is a good candidate for interpenetrated structures [23–25], and the rigid tetrafluoroterephthalic acid as an auxiliary linker for the construction of CPs in order to satisfy and mediate the geometric requirements of the metal centers. Herein we have prepared three 4-fold interpenetration CPs with 6^6 *dia* topology, namely, $[Cu_{0.5}(bib)_{0.5}(tftpa)_{0.5}]_n$ (**1**), $\{[Zn_{0.5}(bib)_{0.5}(tftpa)_{0.5}]\cdot 0.5H_2O\}_n$ (**2**) and $[Cd(bib)(tftpa)(EtOH)]_n$ (**3**) (bib = 1,4-bis(2-methylimidazol-1-yl)butane, H_2tftpa = tetrafluoroterephthalic acid) through solvothermal or diffusion methods. Their crystal structures, topological and thermogravimetric analyses and luminescent properties have been investigated.

2. Experimental

2.1. Materials and general methods

All reagents and solvents employed were commercially available and used without further purification. Fourier transform infrared spectra were determined with a FT-IR 170 SX (Nicolet) spectrophotometer, and the samples were prepared as KBr pellets in the range 4000–400 cm^{-1}. Elemental analyses for carbon, hydrogen and

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* Corresponding author. Tel.: +86 29 81535026.
E-mail address: ykflyy@nwu.edu.cn (K.-F. Yue).

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nitrogen atoms were performed with a Perkin-Elmer 2400C Elemental analyzer. Fluorescent spectra for the solid samples were measured with a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Thermogravimetric analyses were carried out with a NETZSCH TG 209 thermal analyzer under a nitrogen atmosphere with a heating rate of 10 K/min between ambient temperature and 1000 °C. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å).

2.2. Synthesis of $[Cu_{0.5}(bib)_{0.5}(tftpa)_{0.5}]_n$ (**1**)

A mixture of bib (21.8 mg, 0.1 mmol), H_2tftpa (23.8 mg, 0.1 mmol) and $Cu(NO_3)_2{\cdot}3H_2O$ (24.2 mg, 0.1 mmol) in a mixture of DMF (2 mL) and distilled water (8 mL) was stirred under ambient conditions. The mixture was then placed into a Teflon-lined stainless steel (20 mL) container, heated at 130 °C for 3 days and then cooled to room temperature at a rate of 5 °C min^{-1}. After cooling to room temperature, blue needle-shaped crystals of **1** that were fit for crystal X-ray analysis were obtained in 72% yield. *Anal.* Calc. for $C_{20}H_{18}CuF_4N_4O_4$: C, 46.38; H, 3.50; N, 10.82. Found: C, 46.49; H, 3.61; N, 10.72%. IR data (KBr, cm^{-1}): 3446(s), 3129(m), 2945(w), 1630(vs), 1469(s), 1372(s), 1249(m), 1157(m), 1120(w), 985(s), 745(vs), 686(m).

2.3. Synthesis of $\{[Zn_{0.5}(bib)_{0.5}(tftpa)_{0.5}]{\cdot}0.5H_2O\}_n$ (**2**)

A mixture of bib (21.8 mg, 0.1 mmol), H_2tftpa (23.8 mg, 0.1 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (29.7 mg, 0.1 mmol) in a mixture of ethanol (2 mL) and distilled water (8 mL) was stirred under ambient conditions. The mixture was then placed into a Teflon-lined stainless steel (20 mL) container, heated at 130 °C for 3 days and then cooled to room temperature at a rate of 5 °C min^{-1}. After cooling to room temperature, colorless block-shaped crystals of **2** that were fit for crystal X-ray analysis were obtained in 75% yield. *Anal.* Calc. for $C_{20}H_{20}ZnF_4N_4O_5$: C, 44.63; H, 3.72; N, 10.41. Found: C, 44.55; H, 3.96; N, 10.72%. IR data (KBr, cm^{-1}): 3456(s), 2073(w), 1620(s), 1473(m), 1449(m), 1393(m), 1278(w), 1157(m), 1121(m), 986(m), 747(m), 615(m), 505(w).

2.4. Synthesis of $[Cd(bib)(tftpa)(EtOH)]_n$ (**3**)

To a mixture of bib (21.8 mg, 0.1 mmol) and H_2tftpa (23.8 mg, 0.1 mmol) in 5 mL EtOH, triethylamine was added dropwise to give a clear solution. The mixture was layered onto a solution of $Cd(Ac)_2{\cdot}2H_2O$ (26.6 mg, 0.10 mmol) in 5 mL distilled water, and then kept at room temperature. After 2 weeks, colorless block-shaped crystals of **3** that were fit for crystal X-ray analysis were obtained in 59% yield. *Anal.* Calc. for $C_{22}H_{24}CdF_4N_4O_5$: C, 43.12; H, 3.95; N, 9.14. Found: C, 43.81; H, 4.21; N, 8.96%. IR data (KBr, cm^{-1}): 3446(s), 2939(w), 1623(s), 1540(w), 1501(m), 1449(s), 1387(s), 1283(m), 1153(m), 1095(w), 987(s), 889(w), 747(s), 680(m), 468(w).

2.5. Crystallography

Single crystal X-ray diffraction analyses of complexes **1**–**3** were carried out on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated Mo Kα radiation source (λ = 0.71073 Å) at 296(2) K. The diffraction data were integrated using the SAINT program and semi-empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL program package [26]. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically. The hydrogen atoms of water molecules in **2** and one of –OH groups in **3** were located by difference Fourier maps and refined by the riding mode. Crystal data and structure refinements for **1**–**3** and selected bond distances and angles for **1**–**3** are listed in Tables 1 and S1.

3. Results and discussion

3.1. Structure description of $\{[Cu_{0.5}(bib)_{0.5}(tftpa)_{0.5}]_n\}$ (**1**)

X-ray single-crystal diffraction analysis reveals that **1** crystallizes in the centrosymmetric monoclinic *P*2/*c* space group. As depicted in Fig. 1a, the asymmetric unit contains a half Cu(II) ion, a half bib ligand and a half tftpa ligand. The six-coordinated Cu(II) center exhibits a distorted octahedral geometry, $[CuN_2O_4]$, with four oxygen atoms (O1, O2) from two separate tftpa ligands (Cu(1)-O(1) 1.955(6), Cu(1)-O(2) 2.753(6) Å), and two nitrogen atoms (N1) from different bib ligands (Cu(1)-N(1) 1.974(7) Å). Due to the Jahn–Teller effect, the bond distance of Cu(1)-O(2) is longer than Cu(1)-O(1). Each tftpa ligand adopts the bis-bidentate chelating mode to bridge the Cu(II) ions, forming 1D zigzag chains with a Cu···Cu separation of 10.9691 Å and Cu···Cu···Cu angle of 93.734(3)°. Synchronously, the *trans*-conformation of the bib ligand extends such 1D chains (the distance between two adjacent Cu(II) ions is 13.7021 Å and Cu···Cu···Cu angle is 63.867(5)°) to afford a 3D *dia* network with the point symbol 6^6 and the long symbol $6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2{\cdot}6_2$ (Fig. 1b). Interestingly, **1** presents a 1D tetragonal helical channel along the *b* axis. Each helix is built up by $[Cu_2(tftpa)(bib)]_n$ along the *b* axis with a helical pitch of 38.2560 Å. Right- and left-handed helices are constructed alternatively (Fig. 1c), and the connected modes of all these helices induce the racemic nature of **1** [27,28]. **2** and **3** have the same helical structures view along the *a* axis, and will not be discussed below. In order to stabilize the overall network, the large cavities within the structure are completely filled by three other independent frameworks, and thus a 4-fold interpenetrating framework is formed (Fig. 1d).

3.2. Structure description of $\{[Zn_{0.5}(bib)_{0.5}(tftpa)_{0.5}]{\cdot}0.5H_2O\}_n$ (**2**)

Complex **2** crystallizes in the centrosymmetric orthorhombic space group *Pnna* and the asymmetric unit of **2** is composed of a half Zn(II) ion, a half bib ligand, a half tftpa ligand and a half lattice water (Fig. 2a). The coordination of each Zn(II) ion is completed by

Table 1
Crystal data and structure refinements for **1**–**3**.

Complex	1	2	3
Molecular formula	$C_{20}H_{18}CuF_4N_4O_4$	$C_{20}H_{20}ZnF_4N_4O_5$	$C_{22}H_{24}CdF_4N_4O_5$
Formula weight	517.92	537.77	612.85
Temperature	296(2)	296(2)	296(2)
Crystal system	monoclinic	orthorhombic	triclinic
Space group	*P*2/*c*	*Pnna*	$P\bar{1}$
a (Å)	9.561(3)	18.1037(18)	8.9246(16)
b (Å)	9.564(2)	13.8016(14)	11.0620(19)
c (Å)	14.495(3)	9.3201(10)	12.490(2)
α (°)	90	90	96.362(3)
β (°)	125.187(13)	90	91.334(2)
γ (°)	90	90	97.685(3)
V ($Å^3$)	1083.3(5)	2328.7(4)	1213.6(4)
ρ (g/cm^3)	1.588	1.534	1.677
F(000)	526	1096	616
Reflections collected	5205	12132	6021
Goodness-of-fit on F^2	1.067	1.004	1.101
R_1[a] [$I > 2\sigma(I)$]	0.0997	0.0320	0.0350
wR_2[b] [$I > 2\sigma(I)$]	0.1613	0.0682	0.1063

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$.
[b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.