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Homochiral helical coordination polymers constructed from achiral ligand of 5-(3-pyridyl)-isophthalic acid

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ABSTRACT

Reactions of achiral 5-(3-pyridyl)-isophthalic acid (H_2L) with Co^{2+} and Ni^{2+} under solvothermal conditions yield two new homochiral helical coordination polymers $[Co(L)(H_2O)_2]_n$ (**1**), $[Ni(L)(H_2O)_2]_n$ (**2**). Single crystal X-ray diffraction analyses show that complexes **1** and **2** are isomorphous with infinite 3D structures and they both contain two enantiomers, **1a** and **1b** for Co and **2a** and **2b** for Ni, crystallizing in the chiral hexagonal space groups $P6_5$ and $P6_1$, respectively. The enantiomeric nature of them is confirmed by the results of CD spectra. The optical properties of them were investigated in terms of diffuse reflectance, IR and fluorescent spectra, which both exhibit strong luminescence. The electronic band structure along with the density of states (DOS) calculated by the DFT method indicate that compound **1** pose an energy band gap of 3.58 eV and that the origin of the emission band may be mainly ascribed to charge transfer (ILCT) where the charges are transferred between the O-2p state and C-2p state.

1. Introduction

Recently, there has been increasing interest in creating chiral coordination polymer because they are highly attractive for asymmetric catalysis, chiral separation and other applications requiring noncentrosymmetric crystal structures such as nonlinear optical devices [1–5]. The control of helicity at the supramolecular level is a fascinating challenge for chemists that have made great efforts to introduce helicity into artificial systems [6–11]. Lin and coworkers have presented that three different approaches have thus far been utilized to construct homochiral solids [12,13]. In the first approach, homochiral helical coordination polymer can be built from achiral components. In the second approach, an enantiopure co-ligand can be used to direct homochiral crystallization of an intrinsically chiral MOFs that is built from achiral metal nodes and bridging ligands. The third and most reliable strategy is that utilizes metal ions or metal clusters as nodes and chiral multifunctional ligands as linkers [6,14–16]. Although these methods have been successfully used in the preparation of chiral coordination polymer, it is generally quite difficult that homochiral solids were constructed from achiral precursors without any enantiopure additives [17–20].

In this context, we selected achiral 5-(3-pyridyl)-isophthalic acid (H_2L) as an attractive building block in order to obtain novel homochiral coordition polymers. In the case of H_2L, although it belongs to the rigid ligand category, the C–C bond between pyridine ring and benzene ring can turn over/rotate to different extents in order to meet the steric requirement upon metal complexation, and thus readily affords steady coordination structures [21–23]. To a certain extent, this type of ligand with the twisted binding sites will induce the formation of helical structures when linked by a linear metal-connecting point. Herein, we report the construction of two new homochiral helical coordination polymers with this ligand and the crystal structures and optical properties of the two complexes $[M(L)(H_2O)_2]_n$ ($M = Co^{2+}$ (**1**) and Ni^{2+} (**2**)).

2. Experimental

2.1. Syntheses

2.1.1. Synthesis of $[Co(L)(H_2O)_2]_n$ (1)

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.04 mmol), 5-(3-pyridyl)-isophthalic acid (H_2L) (0.04 mmol), NaOH (0.08 mmol) and water (10 mL) was loaded into a 25 mL Teflon-lined autoclave, and heated

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at 413 K for 2 d, after which it was cooled to room temperature at a rate of 2.4 °C/h. Red prismatic crystals of the title complex that are stable in air were obtained by filtration of the result solution (yield: 52% based on Co). IR (cm^{-1}): 3381.25(s),1601.11(w), 1535.02(s),1487.59(w),1450.85(s),1411.55(s),1380.36(s),1303.97(vw), 1198.26(vw),1115.24(w),1056.38(vw),931.17(vw),906.38(vw), 844.62(vw),817.39(vw),773.84(s),723.39(w),705.43(s),652.43(w), 538.03(vw). *Anal.* Calc. for (**1**): C, 46.43; H, 3.30 N, 4.17. Found: C, 46.49; H, 3.37; N, 4.23%.

2.1.2. Synthesis of $[Ni(L)(H_2O)_2]_n$ (2)

Green crystals of complex **2** were obtained as the same process of **1** except for the dosage of reactant ($Ni(NO_3)_2 \cdot 6H_2O$ (0.04 mmol), 5-(3-pyridyl)-isophthalic acid (H_2L) (0.04 mmol), NaOH (0.08 mmol) and water (10 mL)) (Yield: 54% based on Ni). IR (cm^{-1}): 3390.60(vs), 1614.86454(s),1574.11(s),1531.89(s),1488.66(s),1463.50(w),1451.17 (s),1408.88(s),1379.19(s),1306.52(w),1198.87(vw),1060.74(vw), 1032.25(vw),933.96(vw),906.06(w),820.21(w),775.32(w),724.48(w), 706.09(w),653.66(w). *Anal.* Calc. for (**2**): C, 46.57; H, 3.31; N, 4.18. Found: C, 46.66; H, 3.35; N, 4.25%.

2.2. X-ray single crystal structure determination

The single crystals of **1** and **2** were mounted on a glass fiber for the X-ray diffraction analysis, respectively. Data was collected on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. The intensity data were collected with an ω scan technique and corrected for *LP* factors as well as for absorption by the multiscan method [24]. The structures were solved by direct methods and refined on F^2 with full-matrix least-squares techniques using Siemens SHELXTL™ version 5 package of crystallographic software [25]. The final refinements included anisotropic displacement parameters for all non-hydron atoms and a secondary extinction correction. All H atoms of coordinated water molecules were placed in calculated positions, with O–H distances of 0.85 Å, and refined in riding mode with $U_{iso}(H)$ values of 1.5 $U_{eq}(O)$. Other H atoms were allowed to ride on their respective parent atoms with C–H distances of 0.93 Å, and were included in the refinement with isotropic displacement parameters $U_{iso}(H) = 1.2\ U_{eq}$ (C). A summary of the crystal data, data collection parameters and convergence results are compiled in Table 1. Selected bond lengths are given in Table S2.

2.3. Physical measurements

All the reagents were commercially purchased and used without further purification. Elemental analyses (C, H and N) were carried out with a Perkin-Elmer 2400 II elemental analyzer. Photoluminescence analyses were performed on an Edinburgh FLS920 fluorescence spectrometer. IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellet in the range of 4000–400 cm^{-1}. The UV–Vis spectra were recorded at the room temperature on a computer-controlled PE Lambda 900 UV–Vis spectrometer equipped with an integrating sphere in the wavelength range 200–2000 nm. A $BaSO_4$ plate was used as a reference, on which the finely ground powder of the samples were coated. The absorption spectrum was calculated from reflection spectrum by the Kubelka–Munk function [26]: $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient that is practically wavelength independent when the particle size is larger than 5 μm, and R is the reflectance. Thermogravimetry–differential thermal analyses (TG–DTA) were performed on a PerkinElmer Diamond thermoanalyzer under a N_2 atmosphere in the range of 30–800 °C at a heating rate of 20 °C/min. Solid-state CD spectra were measured on KBr disks with a solid-state dedicated universal chiroptical spectrophotometer (UCS-1: JASCO J-800KCM) [27].

Table 1
Crystal collection and structure refinement parameters for **1** and **2**.

Compounds	1a	2a
Empirical formula	$C_{13}H_{11}CoNO_6$	$C_{13}H_{11}NiNO_6$
Formula weight (g mol^{-1})	336.16	335.94
Space group	$P6_5$	$P6_5$
a (Å)	10.2357(3)	10.1816(5)
c (Å)	20.3953(12)	20.441(3)
V (Å^3)	1850.53(13)	1835.2(3)
Z	6	6
λ (Mo Kα) (Å)	0.71073	0.71073
Data/restraints/parameters	3061/7/202	2704/7/203
Collected reflections	17513	15652
Independent reflections	3061	2704
Observed reflections (R_{int})	3061 (0.0380)	2704 (0.0542)
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0326, 0.0798	0.0478, 0.1421
R_1, wR_2 (for all reflections)	0.0387, 0.0833	0.0493, 0.1456
Flack value	−0.010(14)	0.00(3)
Goodness-of-fit on F^2	0.998	1.035
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ (e/Å^3)	0.388 and −0.338	0.412 and −0.576

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

2.4. Computational procedures

The crystallographic data of **1** determined by X-ray was used to calculate the electronic band structure. Calculation of the electronic band structure along with density of states (DOS) was carried out with density functional theory (DFT) using one of the three nonlocal gradient corrected exchange–correlation functional (GGA-PBE) and performed with the CASTEP code [28], which uses a plane wave basis set for the valence electrons and norm-conserving pseudopotential for the core electrons [29]. The number of plane waves included in the basis was determined by a cutoff energy E_c of 600 eV. Pseudoatomic calculations were performed for H-1s^1, C-2s^{2}2p^2, N-2s^{2}2p^3, O-2s^{2}2p^4, and Co-3d^{7}4s^2. The parameters used in the calculations and convergence criteria were set by the default values of the CASTEP code [30]. The calculations of linear optical properties were also made in this work. CASTEP calculated the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function. The $\varepsilon_2(\omega)$ can be thought of as detailing the real transitions between occupied and unoccupied electronic states. The real and imaginary parts were linked by a Kramers–Kronig transform [31]. This transform was used to obtain the real part $\varepsilon_1(\omega)$ of the dielectric function.

3. Results and discussion

3.1. Crystal structure

The structure of **1** and **2** are researched by the single-crystal X-ray diffraction analysis. The results show that complexes **1** and **2** are isomorphous with infinite 3D structures and they both contain two enantiomers, **1a** and **1b** for Co and **2a** and **2b** for Ni, crystallizing in the chiral hexagonal space groups $P6_5$ and $P6_1$, respectively. The enantiomeric nature of **1a** and **1b** can be simply represented by their mirror structures (Fig. 1). Since **1a** and **1b** are enantiomers, only the structure of **1a** is detailed here. **1**a crystallizes in the chiral hexagonal $P6_5$ space group and adopts left-handed and right-handed helixes. The absolute structure in the $P6_5$ space group was determined by a Flack parameter of −0.010(14) using the least-squares method (Table 1). As shown in Fig. 1, the asymmetric unit of **1a** consists of one Co^{2+} ion, one 5-(3-pyridyl)-isophthalic acid ligand and two coordinated water