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Synthesis and structure of a cobalt coordination polymer based on 2,8-di(pyridin-4-yl)dibenzothiophene and 4,4-dicarboxydiphenylsulfone

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Abstract: A new coordination polymer $\{[Co_2(DPDBT)_2(DCPS)_2(H_2O)](H_2O)\}_n$ (**1**) [DPDBT = 2,8-di(pyridin-4-yl)dibenzothiophene, H_2DCPS = 4,4′-dicarboxydiphenyl sulfone], was synthesized under solvothermal conditions. Complex **1** exhibits a 2D structure with two different kinds of binuclear cobalt cluster units. The UV/Vis spectra of **1** and of the ligands were investigated, indicating that complex **1** is a potential wide gap semiconductor material.

Keywords: binuclear cluster unit; cobalt complex; mixed ligand; UV/Vis spectrum.

1 Introduction

Coordination polymers are currently under intense academic and industrial investigations, because of their potential applications in the fields of photochemistry [1], molecular magnetism [2], gas adsorption and separation [3], heterogeneous catalysis [4], nonlinear optics [5], as well as their artistic architectures [6–8]. In the self-assembly processes of coordination polymers, using mixed ligands is undoubtedly a good choice for the construction of new polymeric structures with greater tunability than that only present with a single type of ligand [9, 10]. Coordination polymers based on pyridyl ligands with excellent coordination ability have attracted more and more attention due to their novel architectures and special properties [11, 12].

Recently, we synthesized a new V-shaped pyridyl ligand, 2,8-di(pyridin-4-yl)dibenzo[b,d]thiophene (DPDBT) [10, 13], which may be regarded as a rigid ligand (Scheme 1). Meanwhile, we adopted 4,4′-dicarboxydiphenyl sulfone (H_2DCPS) [14] as a co-ligand to react with the DPDBT ligand and various bivalent metal salts. A coordination polymer with an intriguing structure was obtained under solvothermal conditions, namely $\{[Co_2(DPDBT)_2(DCPS)_2(H_2O)](H_2O)\}_n$ (**1**). Complex **1** was characterized by elemental analysis, IR spectra, and powder and single crystal X-ray crystallography. The UV/Vis spectra of **1** and the ligands were investigated.

2 Results and discussion

2.1 Crystal and molecular structure of $\{[Co_2(DPDBT)_2(DCPS)_2(H_2O)](H_2O)\}_n$ (1)

Complex **1** and the Cd(II) complex $\{[Cd_2(DPDBT)_2(DCPS)_2(H_2O)](H_2O)\}_n$ with the same ligand composition as reported in [13] have very similar molecular and crystal structures despite the utilization of different bivalent metal salts. As $\{[Cd_2(DPDBT)_2(DCPS)_2(H_2O)](H_2O)\}_n$ [13], complex **1** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ (Table 1). The differences in the cell constants do not point to isotypism. The coordination geometry around the Co^{2+} atoms is depicted in Fig. 1. The Co–O lengths are in the range of 2.039(1)–2.267(1) Å, and the Co–N lengths are 2.138(8)–2.149(2) Å. They are both close to that of the reported Co

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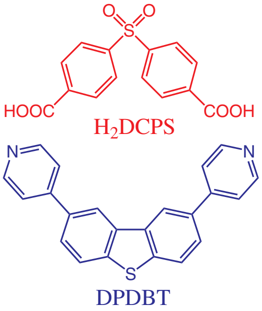

Scheme 1: Structures of ligands DPDBT and H_2DCPS.

complex $\{[Co_2(BPPA)(hfipbb)_2(H_2O)(DMF)_2](H_2O)_4\}_n$ (Co–N 2.120(2) Å, Co–O 2.052–2.224 Å, BPPA = bi(4-pyridylphenyl)amine, H_2DCPS = 4,4′-dicarboxydiphenyl sulfone) [8].

There are two kinds of binuclear cobalt units $[Co_2(CO_2)_2]$ (Fig. 1), in which the Co1···Co1#3 and Co2···Co1#1 distances are 4.012(8) and 4.518(8) Å, respectively. There are three different types of bonding modes for the carboxylate groups in **1**: monodentate (O1–C72–O2), chelate (O3–C59–O4), and bridging bidentate (O5–C58–O6 and O7–C45–O8). The dihedral angles between two phenyl rings of $DCPS^-$ anions are 75.3° and 77.3°. For $DCPS^{2-}$ anions connecting two cobalt cluster units, the $[Co_2(CO_2)_2]$–S–$[Co_2(CO_2)_2]$ angles are 105.8° and 123.9°.

Table 1: Crystallographic data of $\{[Co_2(DPDBT)_2(DCPS)_2(H_2O)](H_2O)\}_n$ (**1**).

Complex	**1**
Empirical formula	$C_{72}H_{46}Co_2N_4O_{13}S_4$
Formula weight	1421.23
T, K	296(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	15.5070(10)
b, Å	16.6545(10)
c, Å	17.7571(19)
α, deg	99.0360(10)
β, deg	97.7370(10)
γ, deg	117.4260(10)
V, Å^{-3}	3906.4(5)
Z	2
D_{calcd}, g m^{-3}	1.21
$\mu(MoK_\alpha)$, mm^{-1}	0.6
$F(000)$, e	1456
θ range, deg	1.19–25.00
hkl range	±18, ±19, −19→9
Refl. collected/unique/R_{int}	22 031/13 681/0.015
Data/restraints/ref. param.	13 681/3/849
Goodness-of-fit on F^2	1.020
R_1/wR_2 [$I > 2\sigma(I)$]	0.0401/0.1171
R_1/wR_2 (all data)	0.0470/0.1219
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.95/−0.99

For the DPDBT molecules, the angle N3–S1–N4 is 75.19°, and N1–S2–N2 is 77.01°. The dihedral angles between pyridyl and adjacent phenyl rings of the BPPA molecules in **1** are 34.91°, 25.17°, 29.37°, and 17.92°. The crystal structure of **1** along the crystallographic *a* axis is shown in Fig. 2.

2.2 UV/Vis spectra

The UV/Vis absorption spectra of free H_2DCPS and DPDBT ligands were obtained in the crystalline state at room temperature (Fig. 3). The H_2DCPS and DPDBT ligands exhibit absorption bands in the ranges of 200–310 and 200–480 nm, respectively, which can be ascribed to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions of the ligands. A lower energy band from 510 to 665 nm for complex **1** can be attributed to the spin-allowed d–d transition of the d^7 (Co^{2+}) cation [15, 16]. The diffuse reflectance data have been transformed into a Kubelka–Munk function to obtain the band gaps (E_g). As shown in Fig. 4, the E_g value assessed from the steep absorption edge is 2.40 eV.

2.3 Powder X-ray diffraction measurements

To confirm whether the crystal structure is truly representative of the bulk material tested in the photochemical studies, powder X-ray diffraction (PXRD) was carried out for complex **1**. The experimental and computer-simulated patterns are shown in Fig. 5, proving that the bulk synthesized material and the measured single crystal for **1** are the same.

3 Conclusion

In summary, a new coordination polymer has been successfully synthesized by self-assembly of DPDBT and carboxylate ligands $DCPS^{2-}$ and Co^{2+} ions under solvothermal conditions. Complex **1** shows a 2D structure containing two different binuclear cobalt units. The band gap (E_g) value assessed from the steep absorption edge is 2.40 eV.

4 Experimental section

4.1 Materials and physical measurements

The carboxylic acid H_2DCPS, and other reagents and solvents employed were commercially available. The DPDBT

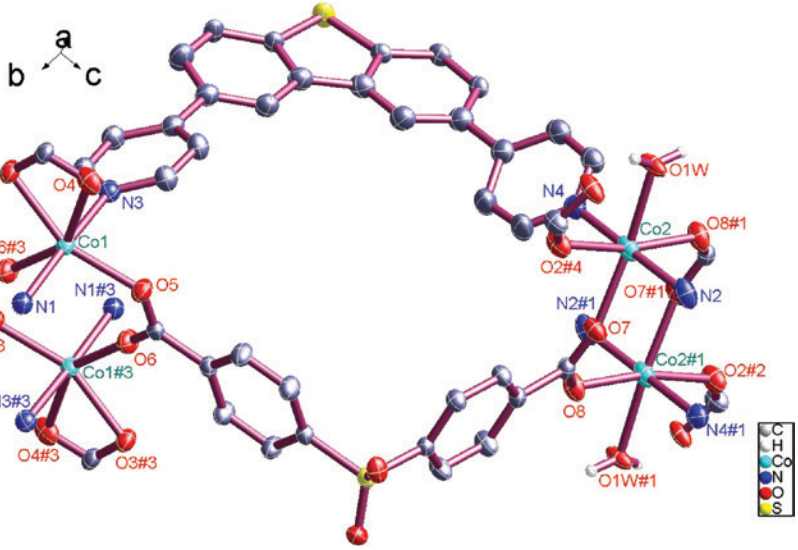

Fig. 1: Coordination environments of the Co^{2+} atoms in **1**. Most hydrogen atoms are omitted for clarity (30 % ellipsoid probability). Symmetry codes: #1 = $-x, -y, 2-z$; #2 = $-1+x, -1+y, 1+z$; #3 = $-x, 1-y, 1-z$; #4 = $1-x, 1-y, 1-z$.

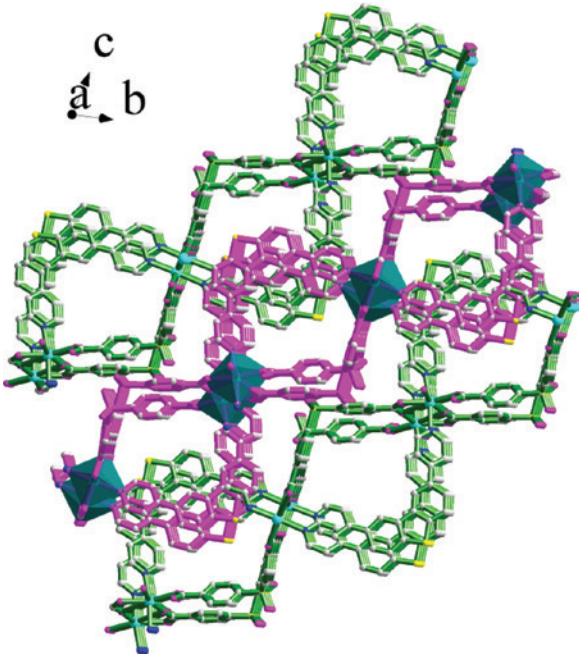

Fig. 2: Crystal structure of **1** seen along the crystallographic *a* axis.

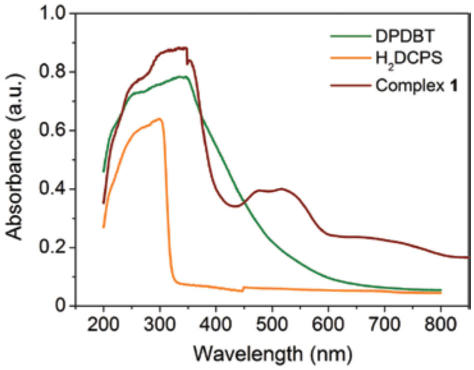

Fig. 3: UV/Vis absorption spectra of **1** and the ligands at room temperature.

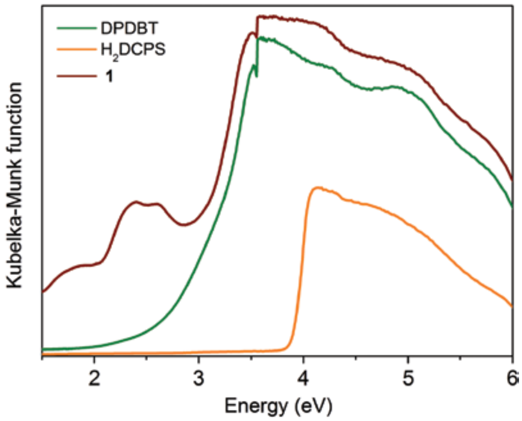

Fig. 4: Kubelka–Munk plots as a function of the energy of **1** and the ligands at room temperature.

ligand was synthesized by Suzuki cross-coupling reaction [10, 13]. The crystal sample was stored in mother solutions until the study of its properties. The IR absorption spectrum of complex **1** was recorded in the range of 400–4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets. C, H, and N analysis was carried out with a Perkin Elmer 240C elemental analyzer. The UV/Vis absorption

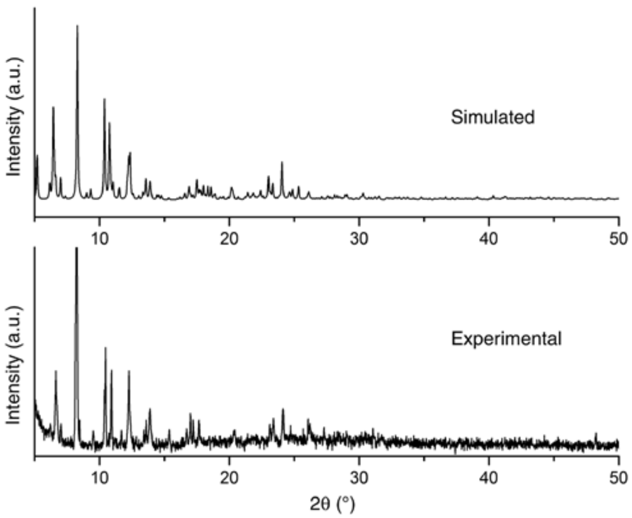

Fig. 5: Powder X-ray diffraction pattern of complex **1**.

spectrum was recorded by a Shimadzu UV-3600 spectrometer for the solid phase.

4.2 Syntheses of $\{[Cd_2(DPDBT)_2(DCPS)_2(H_2O)](H_2O)\}_n$ (1)

A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (58.2 mg, 0.2 mmol), DPDBT (67.6 mg, 0.2 mmol), and 4,4′-dicarboxydiphenyl sulfone (60.12 mg, 0.20 mmol) was dissolved in 15 mL of DMF-H_2O (*v*/*v*, 1:1). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (25 mL) under autogenous pressure and heated at 90 °C for 3 days. Red crystals of **1** were collected in 77 % yield based on DPDBT ligand. – $Co_2C_{72}H_{48}N_4O_{14}S_4$: calcd. C 60.08, H 3.36, N 3.89; found: C 59.97, H 3.43, N 3.81. – IR (KBr, cm^{-1}): 3429 (s), 1672 (s), 1612 (s), 1556 (s), 1470 (m), 1399 (s), 1324 (m), 1295 (s), 1226 (w), 1162 (s), 1136 (w), 1098 (s), 1070 (w), 1014 (w), 839 (w), 807 (s), 780 (w), 742 (s), 720 (w), 697 (w), 621 (s), 580 (s), 464 (w).

4.3 X-ray crystallography

Intensity measurements were made on a Bruker Smart-1000CCD diffractometer with graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) by using a φ–ω scan mode at 296(2) K. Lp corrections were applied. An absorption correction was done using SADABS [17]. The structure was solved by Direct Methods [18] with SHELXTL (version 6.10) [18] and refined by full-matrix least squares on F^2 with SHELXTL [19]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were generated geometrically. It should be noted that the guest molecules in complex **1** are too disordered to be modeled properly in the refinement. Therefore, the respective electron density was removed with the routine SQUEEZE in PLATON [20, 21]. The details

Table 2: Selected bond lengths (Å) and bond angles (deg) for $\{[Co_2(DPDBT)_2(DCPS)_2(H_2O)](H_2O)\}_n$ (**1**).[a]

Distances			
Co(1)–O(6)#1	2.0391(15)	Co(1)–O(5)	2.0654(15)
Co(1)–N(3)	2.1388(19)	Co(1)–N(1)	2.1414(19)
Co(1)–O(3)	2.1579(15)	Co(1)–O(4)	2.2671(17)
Co(2)–O(8)#2	2.0594(15)	Co(2)–O(7)	2.0772(16)
Co(2)–O(2)#3	2.1069(16)	Co(2)–N(4)	2.147(2)
Co(2)–N(2)	2.149(2)	Co(2)–O(1W)	2.162(2)
Angles			
O(6)#1–Co(1)–O(5)	122.58(7)	O(6)#1–Co(1)–N(3)	90.22(7)
O(5)–Co(1)–N(3)	90.81(7)	O(6)#1–Co(1)–N(1)	87.79(7)
O(5)–Co(1)–N(1)	87.91(7)	N(3)–Co(1)–N(1)	176.58(7)
O(6)#1–Co(1)–O(3)	89.00(6)	O(5)–Co(1)–O(3)	148.41(6)
N(3)–Co(1)–O(3)	88.00(7)	N(1)–Co(1)–O(3)	94.75(7)
O(6)#1–Co(1)–O(4)	147.89(7)	O(5)–Co(1)–O(4)	89.52(7)
N(3)–Co(1)–O(4)	89.69(6)	N(1)–Co(1)–O(4)	93.48(7)
O(3)–Co(1)–O(4)	58.91(6)	O(8)##2–Co(2)–O(7)	105.47(7)
O(8)#2–Co(2)–O(2)#3	168.87(7)	O(7)–Co(2)–O(2)#3	85.56(7)
O(8)#2–Co(2)–N(4)	87.77(7)	O(7)–Co(2)–N(4)	92.11(8)
O(2)#3–Co(2)–N(4)	90.33(8)	O(8)#2–Co(2)–N(2)	88.05(7)
O(7)–Co(2)–N(2)	86.34(8)	O(2)#3–Co(2)–N(2)	94.30(8)
N(4)–Co(2)–N(2)	174.98(8)	O(8)#2–Co(2)–O(1W)	84.46(8)
O(7)–Co(2)–O(1W)	169.55(8)	O(2)#3–Co(2)–O(1W)	84.63(8)
N(4)–Co(2)–O(1W)	91.55(11)	N(2)–Co(2)–O(1W)	90.81(11)

[a] Symmetry transformations used to generate equivalent atoms: #1 = $-x, 1-y, 1-z$; #2 = $-x, -y, 2-z$; #3 = $1-x, 1-y, 1-z$.

of the crystal and refinement data are given in Table 1. Selected bond lengths and bond angles are listed in Table 2.

PXRD measurements were done on a Bruker D8 Advance X-ray diffractometer using MoK_α radiation (λ = 0.71073 Å), the X-ray tube being operated at 40 kV and 40 mA.

CCDC 1439158 contains the supplementary crystallographic data for this paper. These 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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