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Three 1D coordination polymers based on bipyridinium carboxylate ligands: Photochromism

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ABSTRACT

With the self-assembly reaction of $TM(NO_3)_2$ (TM = Cd, Cu) and two bipyridinium carboxylate ligands, three one-dimensional (1D) double chain-like coordination polymers (CPs) $\{[Cd_{0.5}(CEbpy)(H_2O)]NO_3{\cdot}H_2O\}_n$ (**1**), $\{[Cu_{0.5}(CEbpy)(H_2O)]NO_3{\cdot}H_2O\}_n$ (**2**), $\{[Cu(BCEbpy)(H_2O)_2]NO_3{\cdot}Br{\cdot}4H_2O\}_n$ (**3**), (CEbpy = 1-carboxyethyl-4,4′-bipyridine, BCEbpy = 1,1′-bis(carboxyethyl)-4,4′-bipyridine) have been synthesized and structurally characterized. Compounds **1** and **2** exhibit electron-transfer (ET) photochromism due to the generation of viologen radicals, while the photochromic behavior of compound **3** is a redox process, which is rarely reported in bipyridinium complexes. Furthermore, the photoinduced radicals in **1**–**3** have long-lived lifetime after irradiation.

1. Introduction

Built by linking inorganic nodes with functional organic unites rationally, coordination polymers (CPs) have provided more and more great promise for applications in separation, gas sorption, sensing, catalysis and drug delivery in the past few decades [1]. It is a burgeoning interest to develop photoactive CPs in this field, which are essential as practical photo-functional materials [2]. Moreover, the photochemical properties of the complexes can be modulated by the connection of photoactive organic units and different metal centers, resulting in more stimuli in response to the smart chemical system [3]. Insight into structure-property relationships and direct guidance for the rational construction of CPs with adjustable photosensitive properties still remains a challenge [4].

Viologen-based ligands with carboxylates have multiple potential coordination sites, including terminal N and O atoms [5]. This diversified coordination mode between the organic linker and metal species not only provides more opportunities for constructing various framework structures, but also adjusts the chromic properties of the resulting CPs [6]. One of the interesting properties of viologen complexes is their photochromism, which produces highly colored free radical by photoinduced electron transfer (PET) from the donor to the acceptor [7]. Up to now, many efforts have been made on designing and synthesizing the bipyridinium-based coordination compounds with ligands containing different photochromic unites to show interesting structural control and property tailoring [8].

It is difficult to get a stable coloration form based on the complex of the species, which limits its application as an optical switch in air, since the viologen radical is highly sensitive to oxidation [9]. Therefore, metal-ligand coordination can be an effective method to overcome the unstable disadvantages of viologen components as a synthetic strategy [10]. The formation of interpenetrating structural motif of the metal-ligand complex helps to stabilize the free radicals generated in situ and reduces the distance between functional components [11]. In addition, the close packing pattern of the network increases the interaction of the ligands and creates multiple bridges for electron transfer [12].

The formation of a cross-linked polymer structure has been reported as a method of inhibiting the oxidation of viologen radicals [13]. The condensing packing mode protects the photo-generated free radicals and restricts back electron transfer as diffusion controlled in the crystalline state by incorporating the viologen fragment into interlaced network [14]. In this paper, two viologen-based ligands with carboxylates have been selected with $TM(NO_3)_2$ (TM = Cd, Cu) to construct three one-dimensional (1D) double cross-linked chain-like coordination polymers$\{[Cd_{0.5}(CEbpy)(H_2O)]NO_3{\cdot}H_2O\}_n$ (**1**), $\{[Cu_{0.5}(CEbpy)(H_2O)]NO_3{\cdot}H_2O\}_n$ (**2**), $\{[Cu(BCEbpy)(H_2O)_2]NO_3{\cdot}Br{\cdot}4H_2O\}_n$ (**3**), (CEbpy = 1-carboxyethyl-4,4′-bipyridine, BCEbpy = 1,1′-bis(carboxyethyl)-4,4′-bipyridine). Compounds **1**–**3** all exhibit photochromism after irradiation via Hg lamp and the photoproducts are stable for months. The close packing pattern provides the opportunity for intramolecular electron transfer and the long-lived charge separation states.

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2. Experimental section

2.1. Materials and methods

All chemicals used in the synthesis were purchased from commercial sources without further purification. CEbpy and HBCEbpyBr were synthesized according to the literature method [15]; A Rigaku Ultima IV-185 diffractometer was used to collect X-ray powder diffraction (PXRD) patterns; A Vario EL III CHNOS elemental analyzer was used to perform elemental analysis of C, H and N; A Varian Cary 5000 UV–vis spectrophotometer was used to perform UV–vis diffuse reflectance spectrum at room temperature; A Nicolet 5DX spectrometer by use of KBr pellets was made to obtain FT-IR spectra (4000–500 cm^{-1}); A HTG-3 equipment in the range 30–800 °C at 10 °C·min^{-1} was used to carry out thermogravimetric (TG) experiments in air; A Bruker A300-10/12 spectrometer was used to record electron paramagnetic resonance (EPR) spectrum at room temperature.

2.1.1. Synthesis of 1

$Cd(NO_3)_2{\cdot}4H_2O$ (30.8 mg, 0.1 mmol) was added into a 10 mL aqueous solution of CEbpy (42.8 mg, 0.2 mmol) and then stirred for 5 min. After mixed and filtered, the filtrate in the beaker was left for slow evaporation in air at room temperature. Two weeks later, some yellow block crystals were got in 25.4% yield (based on CEbpy). Elemental analysis: Anal. Calcd for $C_{12}H_{14}Cd_{0.5}N_3O_7$: C, 39.08; H, 3.80; N, 11.40%. Found: C, 38.68; H, 3.62; N, 11.92%. IR (KBr, cm^{-1}): 3477, 3414, 2924, 1617, 1539, 1407, 1257, 1087, 873, 618.

2.1.2. Synthesis of 2

The procedure was similar to the synthesis of compound **1**, except $Cd(NO_3)_2{\cdot}4H_2O$ (30.8 mg, 0.1 mmol) was replaced by $Cu(NO_3)_2{\cdot}3H_2O$ (24.2 mg, 0.1 mmol). Some blue block crystals were got in a week in 23.6% yield (based on CEbpy). Elemental analysis: Anal. Calcd for $C_{12}H_{14}Cu_{0.5}N_3O_7$: C, 41.86; H, 4.07; N, 12.21%. Found: C, 42.17; H, 3.88; N, 11.97%. IR (KBr, cm^{-1}): 3474, 3412, 3054, 2918, 2850, 2362, 1617, 1384, 1225, 1113, 926, 872, 826, 770, 725, 624.

2.1.3. Synthesis of 3

$Cu(NO_3)_2{\cdot}3H_2O$ (24.2 mg, 0.1 mmol) was added into a 10 mL aqueous solution of HBCMbpyBr (35.3 mg, 0.1 mmol) and then stirred for 5 min. The filtrate was left for slow evaporation after the reaction at room temperature. Blue block crystals were got in two weeks in 25.4% yield (based on HBCEbpyBr). Elemental analysis: Anal. Calcd for $C_{14}H_{24}BrCuN_3O_{13}$: C, 28.68; H, 4.10; N, 7.17%. Found: C, 28.37; H, 3.97; N, 6.88%. IR (KBr, cm^{-1}): 3547, 3469, 3413, 3056, 2362, 1639,1616, 1559, 1448, 1384, 1292, 1197, 1126, 873, 824, 736, 622.

The powder X-ray diffraction experimental spectra of the as-synthesized three compounds were in good agreement with the simulated samples, confirming that the solid phase was pure (Fig. S1).

2.1.4. X-ray crystallorgraphy

The X-ray diffraction data of compounds **1–3** were collected on an Oxford Gemini diffractometer using graphite monochromated Mo-Kα (λ = 0.71073 Å) at 293 K. SCALE3 ABSPACK scaling algorithm was used for an empirical absorption correction with spherical harmonics [16]. SHELXTL-97 program was used to solve and refine the structures by direct method and full-matrix least-squares techniques on F^2 performed [17]. All non-hydrogen atoms were refined anisotropically. The crystallographic data of **1–3** is listed in Table 1, and selected bond lengths and bond angles are listed in Table S1.

3. Results and discussion

3.1. Structural description

Since compounds **1** and **2** are isostructural, **2** is discussed in detail.

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

Compound	1	2	3
CCDC code	1813671	1813670	1813672
Empirical formula	$C_{12}H_{14}Cd_{0.5}N_3O_7$	$C_{12}H_{14}Cu_{0.5}N_3O_7$	$C_{14}H_{24}BrCuN_3O_{13}$
Formula weight	368.46	344.03	585.81
Crystal size (mm)	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.2	0.3 × 0.2 × 0.2
Crystal system, space group	triclinic P-1	triclinic P-1	monoclinic $P2_1/c$
a (Å)	7.8993 (5)	7.9048 (6)	8.7872 (5)
b (Å)	9.5494 (5)	9.8328 (11)	16.3287 (8)
c (Å)	10.3909 (4)	9.9409 (15)	15.0239 (8)
α (°)	107.066 (4)	69.955 (12)	90
β (°)	93.435 (5)	89.052 (9)	91.0130 (10)
γ (°)	95.509 (5)	82.159 (8)	90
Volume ($Å^3$)	742.65 (7)	718.69 (15)	2155.3 (2)
Z	2	2	4
Dc ($g{\cdot}cm^{-3}$)	1.648	1.590	1.805
F (000)	374.0	355.0	1188.0
$m\mu$ (mm^{-1})	0.814	0.841	2.939
R_1/wR_2, [$I \geq 2\sigma(I)$]	0.0327, 0.0814	0.0930, 0.2377	0.0329, 0.0964
R_1/wR_2, (all data)	0.0355, 0.0831	0.1016, 0.2407	0.0382, 0.1045

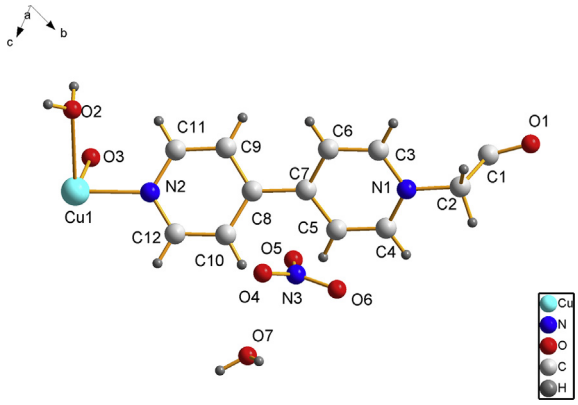

Fig. 1. Ball-and-stick graph representation of a selected unit of compound **2**.

Crystallizing in the triclinic space group *P-1*, compound **2** contains a half Cu^{2+} ion, one CEbpy ligand, one coordinated and one dissociative water molecule, and one charge-balancing NO_3^- anion (Fig. 1). The structure of **2** shows that the expanded structure forms a macrocyclic homodimer comprising two monosubstituted bipyridinium CEbpy ligands which are bridged directly to the copper center through the terminal *N*-center and carboxylate groups. One oxygen of the carboxylate group binds to the metal copper center, and at the cis position, the terminal *N*-center of CEbpy ligand is bonded. The macrocyclic homodimers coordinate to form a 1D double ladder chain where each Cu^{2+} center is bound by two nitrogen and two oxygen atoms from four different CEbpy ligands and two water molecules, completing a little distorted octahedron coordination sphere (Fig. 2a), which joins the neighbouring chains through hydrogen bonds of the dissociative water molecules and the charge-balancing NO_3^- anions (O (2)–H···O (6), 2.209 Å; O (7)–H···O (4), 2.152 Å; O (7)–H···O (1), 2.302 Å; O (2)–H···O (7), 1.907 Å) (Fig. 2d) to give a 3D framework (Fig. 2e). From the comparison of two compounds, compounds **1** and **2** own the same structure and packing geometry but different hydrogen bonds. The 1D double chain of **1** joins another neighbouring chain through hydrogen bonds (O (3)–H···O (4), 2.144 Å; O (7)–H···O (3), 1.879 Å; O (7)–H···O (2), 1.980 Å) (Fig. 2b) to give the 3D framework (Fig. 2c). Furthermore, there also exists face-to-face π···π interactions in **1** and **2** contributing to the stabilization of the 3D structures.

Crystallizing in the monoclinic space group $P2_1/c$, compound **3** contains one Cu^{2+} ion, one BCMbpy ligand, two coordinated and four dissociative water molecules, and one charge-balancing NO_3^- anion