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A two-dimensional Cd(II) coordination polymer: [Cd(1,4-BDOA)(1,10-phen)] · H_2O with strong blue fluorescent emission constructed by benzene-1,4-dioxydiacetate ligand

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Abstract

Hydrothermal reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with 1,10-phen and 1,4-$BDOAH_2$ yields a two-dimensional cadmium(II) coordination polymer, [Cd(1,4-BDOA)(1,10-phen)] · H_2O, in which CdN_2O_5 pentagonal bipyramids are linked together to construct a lamellar structure. It exhibits strong blue fluorescent upon photoexcitation.

Keywords: Cd(II) Carboxylate coordination polymer; Benzene-1,4-dioxyacetic acid; Hydrothermal synthesis; Fluorescent property

In recent years, extensively attention has been focused on the design and synthesis of cadmium(II) carboxylate coordination polymers for their intriguing structural motifs, photoluminescent properties and other potential applications in molecular-based materials [1–4]. Some rigid aromatic carboxylic acids such as isophthalic acid or the related species are often chosen to fabricate these supramolecular architectures [5,6]. The flexible benzene-1,4-dioxydiacetic acid (1,4-$BDOAH_2$), analogue to phthalic acids, possesses the versatile binding fashions and the capability of forming coordination architectures of diverse sizes and shapes, etc., and hence it is an attractively choice for the construction of coordination polymers [7,8]. However, the coordination chemistry and structural properties of cadmium(II) polymers based on 1,4-$BDOAH_2$ ligand have been documented very little to date. Recently, we have reported the structure of one 1D polymer, $[Cd(1,4\text{-}BDOA)(imidazole)_3]_n$, (**I**), in which the Cd(II) atom exists in a distorted octahedral coordination sphere and this ligand acts in a $\eta^1{:}\eta^1{:}\eta^1{:}\mu_2$ bridging mode [9] (Scheme 1). Herein is described the synthesis, structure, thermal and luminescent properties of a novel two-dimensional (2D) cadmium(II) polymer, [Cd(1,4-BDOA)(1,10-phen)] · H_2O (**II**), with the 1,4-$bdoa^{2-}$ ligand showing the unprecedented $\eta^1{:}\eta^1{:}\eta^1{:}\eta^1{:}\mu_2$ and $\eta^1{:}\eta^2{:}\eta^1{:}\eta^2{:}\mu_4$ modes. Moreover, it also exhibits a strong blue fluorescent emission in the solid state.

Hydrothermal reaction of $Cd(NO_3)_2 \cdot 4H_2O$ with 1,10-phen, 1,4-$BDOAH_2$ and NaOH in the molar ratio of 1:1:1:2 at 433 K (five days) leads to the formation of colorless prismatic crystals of **II** in 67% yield based on cadmium. Anal. Calc. for $C_{22}H_{18}N_2O_7Cd$: C, 49.41; H, 3.39; N, 5.24. Found: C, 49.68; H, 3.49; N, 5.09%.

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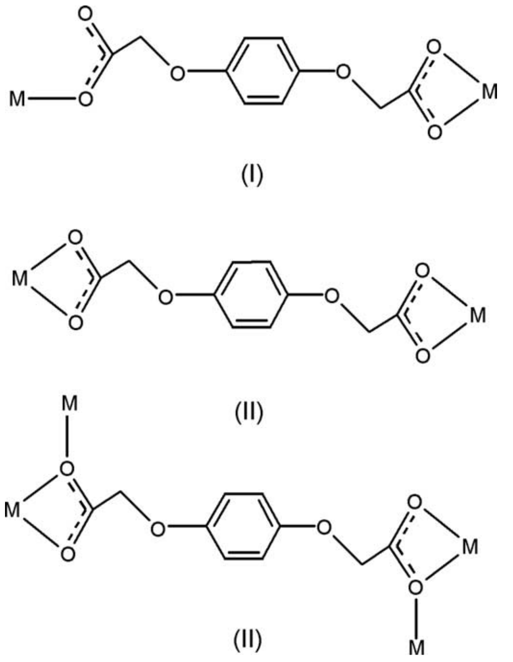

Scheme 1. The coordination modes of 1,4-BDOA^{2-} group in the Cd complexes (**I**) and (**II**): (**I**) $\eta^1:\eta^1:\eta^1:\eta^1:\mu_2$; (**II**) $\eta^1:\eta^1:\eta^1:\eta^1:\mu_2$; (**III**) $\eta^1:\eta^2:\eta^1:\eta^2:\mu_4$.

IR (KBr, cm^{-1}): 3438w [ν(O–H)]; 1606m [ν_{asym}(OCO$^-$)]; 1417s, 1332s [ν_{sym}(OCO$^-$)]; 1217s, 1067s [ν_{asym}(COC), ν_{sym}(COC)]; 856m, 727s [δ(C–H)].

The molecular structure of **II** is shown in Fig. 1, and it is established by single crystal X-ray diffraction analysis [10–12]. Two crystallographically independent "half" 1,4-bdoa^{2-} ligands occupy different inversions in the middle of the benzene rings, respectively. Each Cd atom displays a distorted pentagonal bipyramidal geometry, with five carboxylate oxygen donors from three 1,4-bdoa^{2-} ligands, two nitrogen donors from one bidentate chelating 1,10-phen ligand. It is noted that the C1–C2–O3–C3 and C6–C7–O6–C8 torsion angles are −73.7(3)° and 69.4(3)°, respectively. Whereas in the reported **I**, the oxyacetate groups and benzene ring are almost coplanar, with the torsion angles being −174.2(3)° and 178.7(2)°, respectively. This demonstrates that the 1,4-BDOA^{2-} ligand has remarkable flexibility corresponding to the rigid aromatic carboxylic acid ligand such as terephthalate. It is obviously observed from the reported complex, [Cd(bipy)(terephthalate)(H_2O)]$_n$, (**III**), in which the dihedral angles of the two carboxyl groups and the phenyl are 5.63° and 12.58°, respectively [13].

In 2D coordination polymer, there are two coordination types of 1,4-BDOA^{2-} ligands that are distinguished by their direction bridging Cd atoms (Fig. 2). In the former case, two CdN_2O_5 pentagonal bipyramids are combined by the carboxyl O2 and O2$^{\text{i}}$ atoms to form a binuclear unit. There is a crystallographic inversion center between the two Cd atoms whose separation is 3.84 Å. All the binuclear units are joined by the carboxylate groups in a $\eta^1:\eta^2:\eta^1:\eta^2:\mu_4$ mode to produce a 1D chain, with the Cd···Cd distances of 11.91 and 14.22 Å, respectively. In the latter case, infinite chains are further connected together by another carboxylate groups in a $\eta^1:\eta^1:\eta^1:\eta^1:\mu_2$ mode, generating a 2D porous architecture parallel to (1 1 0). Adjacent Cd···Cd distance is 11.80 Å, which is significantly shorter than the corresponding Cd···Cd distance of 15.01 Å in **I**, but somewhat longer than that in **III** (11.30 Å). Moreover, there exist π–π stacking interactions between the adjacent 1,10-phen rings [centroid–centroid distance = 3.68(2) Å] and intramolecular hydrogen bonds, which are formed between the free water molecules and carboxylate oxygen atoms [O···O distances, 2.951(6) and 3.082(6) Å], resulting in a three-dimensional (3D) supramolecular network.

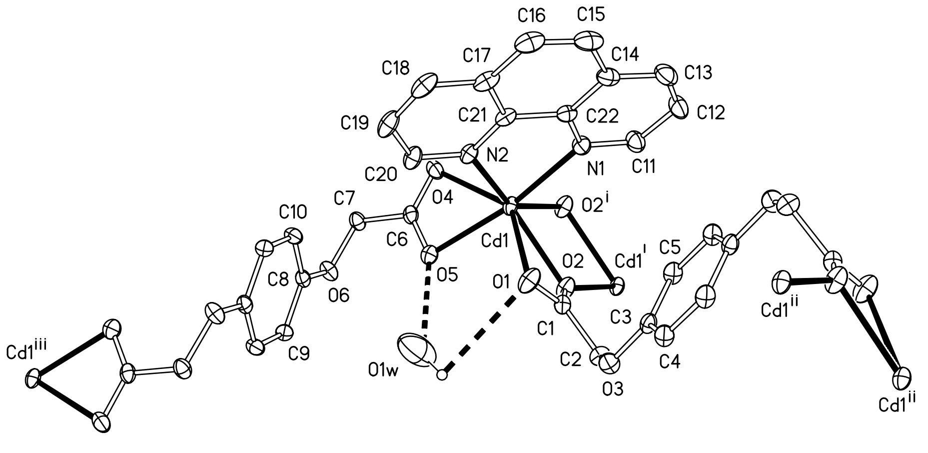

Fig. 1. The coordination environments of the Cd$^{\text{II}}$ atom in **II** (at 30% probability level). Selected bond distances (Å) and angles (°): Cd(1)–O(2)$^{\text{i}}$ 2.3365(19); Cd(1)–N(1) 2.347(2); Cd(1)–O(1) 2.581(2); Cd(1)–N(2) 2.339(2); Cd(1)–O(2) 2.343(2); Cd(1)–O(4) 2.451(2); Cd(1)–O(5) 2.341(2) and O(2)$^{\text{i}}$–Cd(1)–O(5) 103.86(8); O(2)$^{\text{i}}$–Cd(1)–O(2) 69.93(8); O(2)–Cd(1)–O(1) 52.12(6); N(1)–Cd(1)–O(1) 89.31(8); N(2)–Cd(1)–N(1) 71.45(8); N(2)–Cd(1)–O(4) 86.97(7). Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x+2, -y, -z+1$.

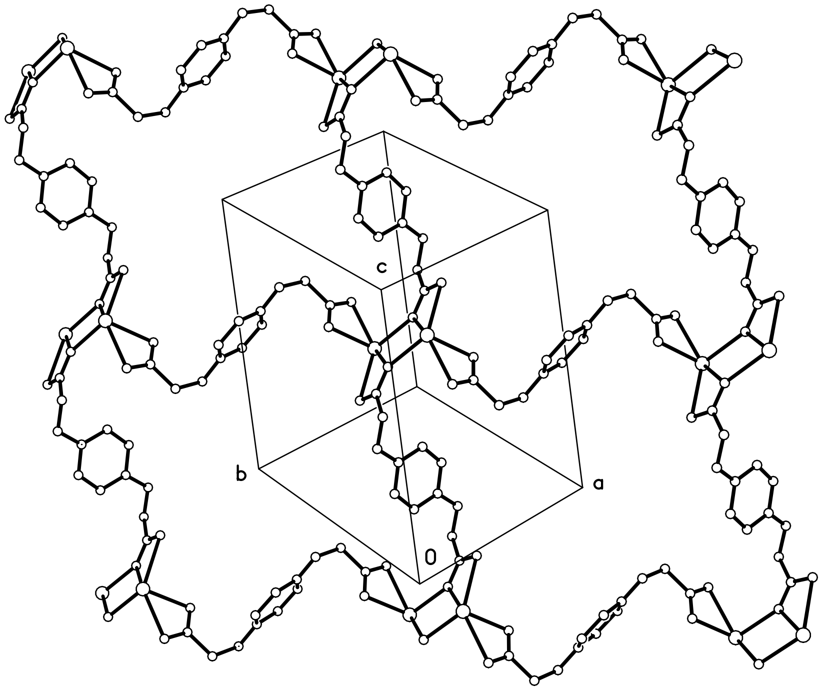

Fig. 2. Two-dimensional network structure of **II** with phen and water molecules omitted for clarity.

In the IR spectra of **II**, the observation of a strong and broad v(OH) absorption around 3438 cm^{-1} is coherent with the presence of hydrogen bonds or water molecules. The $v_{asym}(OCO^-)$ and $v_{sym}(OCO^-)$ absorptions appear in 1606, 1427 and 1332 cm^{-1}, respectively, and the values of $\Delta(OCO^-)$ suggest there are different coordinated modes of the carboxylate groups [14].

TG results show that the first weight loss of 3.67% from 317 to 594 K corresponds to the loss of the lattice water molecule (Calc. 3.36%), and then the loss steps are observed continuously with the burning 1,4-$BDOA^{2-}$ group and 1,10-phen ligand in the range of 594–822 K. The final residual weight is 23.77% (Calc. 24.01%) corresponding to CdO. This suggests that its skeleton possesses higher thermal stability.

The fluorescent emission spectrum of **II** was measured in solid state at room temperature (as shown in Fig. 3). Upon photoexcitation at 258 nm, it exhibits two intense fluorescent emission bands at 483, 419 nm and one weak fluorescent emission band at 320 nm. Since free 1,4-$BDOAH_2$ ligand is observed the similar photoemissions at 316 and 416 nm at the same photoexcitation condition, the emission bands at 320 and 419 nm come from the intraligand fluorescent emissions in **II**. Whereas the strong blue emission, $\lambda_{max} = 483$ nm, may be assigned to the ligand-to-metal-charge-transfer (LMCT) [15,16]. The **II** may be a candidate for light emitting device for its high thermal stability and the insolubility in many common solvents.

In conclusion, a novel cadmium polymer based on 1,4-$bdoa^{2-}$ ligand has been synthesized by the hydrothermal reaction, in which CdN_2O_5 pentagonal bipyramids are joined by 1,4-$BDOA^{2-}$ ligands with the unprecedented $\eta^1:\eta^1:\eta^1:\eta^1:\mu_2$ and $\eta^1:\eta^2:\eta^1:\eta^2:\mu_4$ modes to form a lamellar structure. Its skeleton is thermally stable up to 594 K, and its strong blue fluorescent emission of $\lambda_{max} = 483$ nm shows that it may be promising as optoelectronic devices. Further study about this subject is underway and will be reported in a full paper.

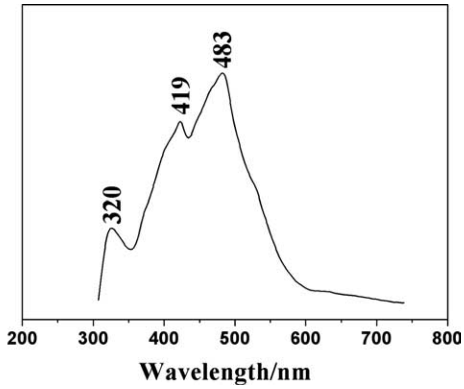

Fig. 3. The emission spectrum of **II** measured in solid state at room temperature.

Acknowledgements

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Appendix A. Supplementary data

Crystal data and structure refinement, atomic coordinates, bond lengths and angles, IR, PL and TG results of the complex were available from the authors on request.

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Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.inoche.2005.01.020.

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[10] Crystal data for $C_{22}H_{18}N_2O_7Cd$: triclinic, $P\bar{1}$, unit cell para. $a = 9.1880(18)$ Å, $b = 10.925(2)$ Å, $c = 11.907(2)$ Å, $\alpha = 65.23(3)°$, $\beta = 75.63(3)°$, $\gamma = 89.58(3)°$. $V = 1044.9(5)$ Å^3, $Z = 2$, $D_c = 1.700$ g/m^3, $\mu = 1.093$ mm^{-1}, $F(000) = 536$. Data collections ($3.26 \leqslant \theta \leqslant 27.30°$) were performed at 293 K on RIGAKU RAXIS–RAPID single X-ray diffractometer (Mo Kα, $\lambda = 0.71073$ Å) for **1**. The structures were solved with direct methods (SHELXS-97) [11] and refined by full-matrix least squares (SHELXL-97) [12]. Unique reflections were obtained from a total of 4619 measured reflections ($R_{\text{int}} = 0.0165$). Structure solution and refinement based on 4116 independent reflections with $I > 2\sigma(I)$ and 295 parameters gave the final $R = 0.0290$, $wR = 0.0669$ and $S = 1.068$.

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