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Urothermal synthesis of two photoluminescent cadmium coordination polymers

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ABSTRACT

Two new Cd coordination polymers, $[Cd(5\text{-Nisp})(e\text{-urea})]_n$ (**1**), and $[Cd_2(5\text{-Hisp})_2(e\text{-urea})_2(en)]_n$ (**2**), (where 5-Nisp = 5-nitroisophthalate; 5-Hisp = 5-hydroxyisophthalate; e-urea = ethyleneurea; en = 1,2-ethanediamine), have been urothermally synthesized by using ethyleneurea hemihydrate as the solvent. Single-crystal X-ray diffraction analyses reveal that both **1** and **2** have linear chain sub-structures linked by 5-Nisp ligands or 5-Hisp ligands into three-dimensional frameworks. The thermogravimetric behavior and the photoluminescent properties of **1** and **2** were studied.

Coordination polymers have attracted considerable attention in recent years due to their interesting properties and promising applications in the areas of heterogeneous catalysis, magnetism, nonlinear optics, gas storage, and separation etc. [1]. The solvents play an important role in the self-assembly process of the metal organic frameworks (MOFs), and the well-known synthetic methods including hydrothermal, solvothermal and ionothermal synthesis [2–4] have been established and widely used. At the current stage, the urothermal synthesis of MOFs remains in the initial stage [5].

To construct novel architectures, different functional groups such as sulfonate, nitro and hydroxy groups have been attached to benzene-polycarboxylate [6–8]. Recently, supramolecular Cd frameworks based on 5-nitroisophthalic acid (5-Nisp) and 5-hydroxyisophthalic acid (5-Hisp) ligands have been systematically studied [7,8]. The carboxyl groups of 5-Nisp or 5-Hisp may be completely deprotonated and bond to metal centers, which may form secondary building units to construct frameworks with novel structural features. On the other hand, one-dimensional chain is the basic building block [9,10] in the structures of coordination polymers. The chain can be zig-zag, linear, ladder, or helix. Herein, we report the urothermal synthesis, structures and photoluminescent properties of two interesting compounds $[Cd(5\text{-Nisp})(e\text{-urea})]_n$ (**1**; e-urea = ethyleneurea) and $[Cd_2(5\text{-Hisp})_2(e\text{-urea})_2(en)]_n$ (**2**; en = 1,2-ethanediamine), which have linear chain sub-structures linked by 5-Nisp ligands or 5-Hisp ligands into three-dimensional frameworks.

Compounds **1** and **2** were urothermally synthesized through the assembly of $Cd(NO_3)\cdot 6H_2O$ in ethyleneurea hemihydrate at 120 °C for 3 days, with 5-Nisp or 5-Hisp, respectively [11]. A single crystal X-ray analysis reveals that $[Cd(5\text{-Nisp})(e\text{-urea})]_n$ (**1**) crystallizes in an orthorhombic form with chiral space group $P2_12_12_1$ [12]. The flack parameter of −0.02(3) demonstrates the homochirality of a single crystal. Spontaneous resolution occurs here and the bulk sample is racemic because of the achiral precursors. As shown in Fig. 1a, the Cd1 is octahedrally coordinated with six oxygen atoms, among which, four oxygen atoms (O1, O2, O3, O4) are from four carboxyl groups of four different 5-Nisp ligands, and two μ_2-O (O7, O7a) are from two e-urea molecules. The 5-Nisp ligand acts as a μ_4-linker, using its four oxygen atoms to bond to four Cd atoms. The e-urea acts as the μ_2-bridge to link two adjacent Cd atoms. So the e-urea molecules link the Cd atoms to form a 1D chain, the adjacent Cd atoms are further linked by the carboxyl groups of 5-Nisp ligands (Fig. 1b). Then these chains are connected by the aromatic rings of the 5-Nisp ligands to form the 3D framework (Fig. 1c), which includes a 1D channel along the *a*-axis filled by the coordinate e-urea molecules.

A single crystal X-ray analysis reveals that **2** crystallizes in a monoclinic $P2(1)/n$ space group. [12] As shown in Fig. 2a, the asymmetric unit of **2** consists of two crystallographically independent Cd centers, two 5-Hisp ligands, two e-urea molecules and one en having half occupation factor. Cd1 is six-coordinated by four oxygen atoms (O1, O3, O7, O9) from different carboxyl groups of two 5-Hisp ligands,

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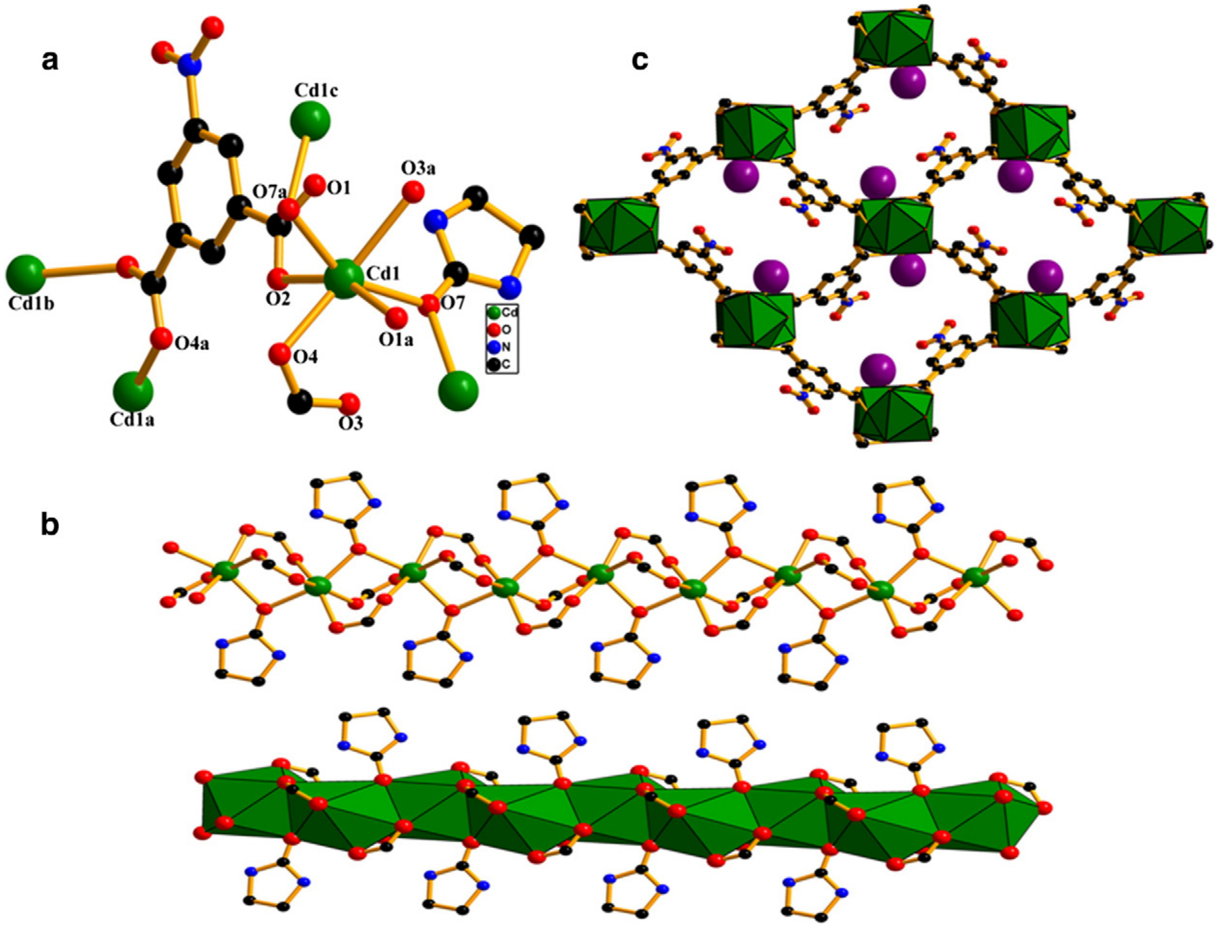

Fig. 1. (a) The coordination environment in **1**, H atoms were omitted for clarity; (b) the chain in **1**; (c) The three-dimensional structure of **1** viewed along the *a*-axis, the aubergine balls indicate the e-urea ligands.

and two oxygen atoms (O11, O12) from two coordinated e-urea molecules. Differently, Cd2 is eight-coordinated by four oxygen atoms (O1, O2, O8, O9) from two chelating carboxyl group of 5-Hisp ligands, two single coordinated oxygen atoms (O4, O6) from two carboxyl groups of 5-Hisp ligands, and two oxygen atoms (O11, O12) from two coordinated e-urea molecules. Two 5-Hisp ligands have the same coordination modes. Each of them acts as a μ_4-linker, using its four oxygen atoms to bond to four Cd atoms. Two e-urea molecules act as μ_2-linker to link adjacent Cd atoms to form a Cd_2(e-urea)$_2$ subunit (SBU). Then the Cd_2(e-urea)$_2$ SBUs are linked by the carboxyl groups of 5-Hisp ligands to form a chain (Fig. 2b). Then these chains are connected by the aromatic rings of the 5-Hisp ligand to form the 3D framework through μ_2-ligands (Fig. 2c). The 3D structure exhibits 1D channels along the *a*-axis, which are blocked with coordination solvent and en molecules generated from the decomposition of e-urea (Fig. s3) [13].

Some Cd-(5-Nisp) and Cd-(5-Hisp) framework structures synthesized from hydrothermal or solvothermal methods have been previously reported [7a,14]. The structures of **1** and **2** presented are totally different from those reported Cd-(5-Nisp) and Cd-(5-Hisp) compounds, because the additional e-urea ligands coming from the solvent have been part of the framework structure. Thus, the e-urea used for synthesis is not only an effective solvent, but also a structure-directing agent which helps to build the framework structure. In this work, we found that 1D chain is the basic building block for **1** and **2**. However, the chains in two compounds are totally different. In **1**, the e-urea molecules link Cd atoms to form a 1D chain. In **2**, two e-urea molecules link two adjacent Cd atoms to form a Cd_2(e-urea)$_2$ SBU, which are further linked by the carboxyl groups of 5-Nisp ligands to form the 1D chain.

Thermal gravimetric analysis (TGA) of **1** indicates that the compound **1** has thermal stability up to 350 °C. The compound of **2** has thermal stability up to 330 °C (Fig. s1). After that temperature, the frameworks decompose.

Powder X-ray diffraction (PXRD) were measured to confirm the phase purity and to examine the crystallinity of bulk sample (Fig. s2). The simulative (black line) and experimental (red line) X-ray powder diffraction pattern for compound **1** and compound **2** are compared, respectively. The diffraction (XRD) peaks are corresponded well in position, indicating the phase purity of the experimental compounds.

The fluorescent emission spectra of compounds **1** and **2** were measured in the solid state at room temperature. Compound **1** (Fig. 3a) has one intense emission at 440 nm upon photoexcitation at the λex = 350 nm. Compound **2** has one intense emission at 473 nm upon photoexcitation at λex = 350 nm (Fig. 3b). These results indicate that the emission bonds correspond to the intraligand charge transfers ($n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$) [7a,14]. Such luminescent properties of **1** and **2** are similar to those observed in other Cd-(5-Nisp) and Cd-(5-Hisp) frameworks [13].

In summary, we report here two new compounds **1** and **2** synthesized by using the e-urea as the solvent. The 1D chain is the basic building block in two compounds. The different numbers of e-urea

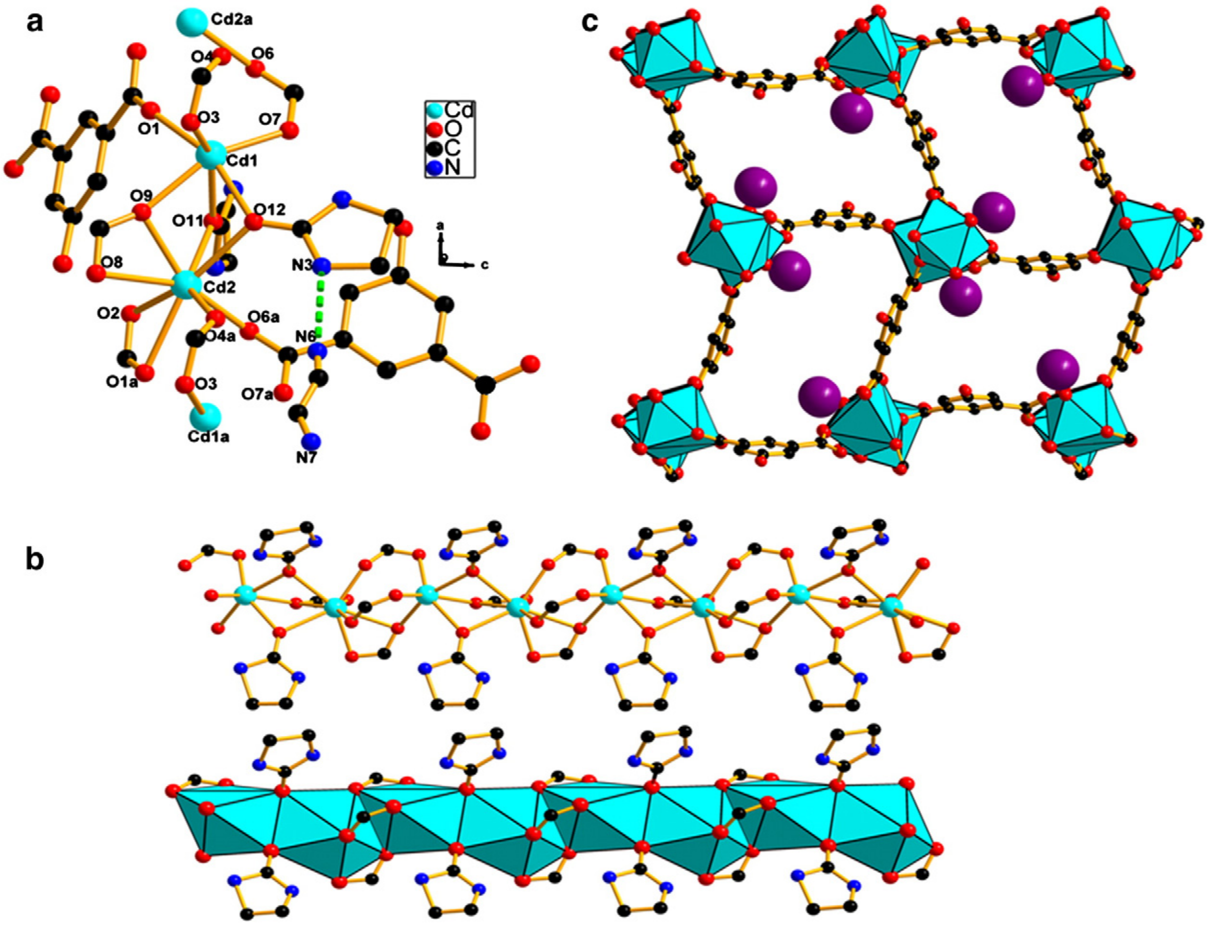

Fig. 2. (a) The coordination environment in **2**, H atoms were omitted for clarity; (b) the chain in **2**; (c) the three-dimensional structure of **2** viewed along the *a*-axis, the aubergine ball indicate the e-urea ligands.

molecules in two compounds result in different chains, which further affect the final framework and symmetry. The results demonstrated that the e-urea is an effective solvent and structure-directing agent for the construction of MOFs.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2013.01.030.

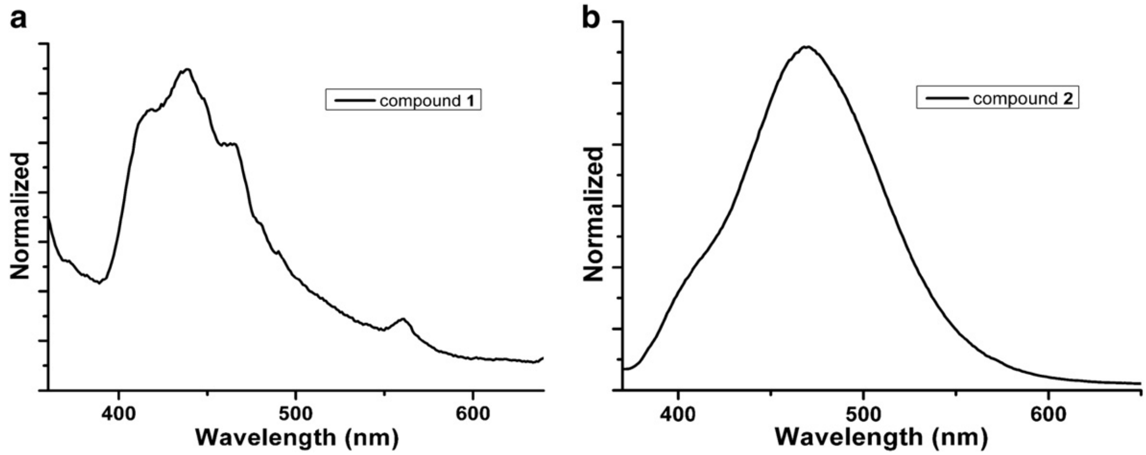

Fig. 3. Solid-state emission spectra of **1** (a) and **2** (b) at room temperature.

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[12] X-ray crystallographic study: Diffraction intensities of **1** and **2** were collected at 293 K direction methods and difference Fouriersynthese (Mo-Ka, $\lambda = 0.71073$ Å). The crystallographic calculations were conducted using SHELXL-97 programs. Crystal date for **1**: $C_{11}H_9CdO_7N_3$, $M = 407.61$, *orthorhombic*, $a = 6.7547(8)$ Å, $b = 11.0302(9)$ Å, $c = 17.1073(19)$ Å, $\beta = 90^o$, $V = 1274.6(2)$ $Å^3$, $T = 293(2)$ K, space group $P2_12_12_1$, $Z = 4$, 10975 reflections measured, 2905 independent reflections ($R_{int} = 0.0295$). The final $R1$ values were 0.0180 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0636 ($I > 2\sigma(I)$). The final $R1$ values were 0.0197 (all data). The final $wR(F^2)$ values were 0.0639 (all data). The goodness of fit on F^2 was 0.784. Crystal date for **2**: $C_{23}H_{24}Cd_2O_{12}N_5$, $M = 787.27$, *monoclinic*, $a = 7.152(2)$ Å, $b = 18.283(5)$ Å, $c = 19.947(6)$ Å, $\beta = 90.395(7)^o$, $V = 2608.3(13)$ $Å^3$, $T = 293(2)$ K, space group $P2(1)/n$, $Z = 4$, 6447 reflections measured, 3938 independent reflections ($R_{int} = 0.0214$). The final $R1$ values were 0.0406 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1021 ($I > 2\sigma(I)$). The final $R1$ values were 0.0501(all data). The final $wR(F^2)$ values were 0.1074 (all data). The goodness of fit on F^2 was 1.030.

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