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Chiral coordination polymer as a luminescence sensor for small organic molecules

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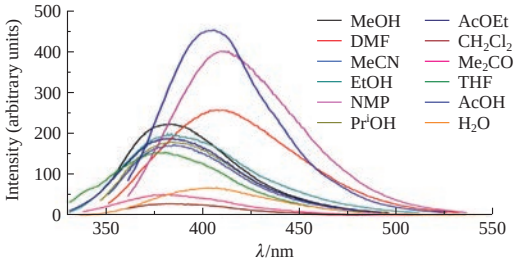
The new coordination polymer $\{[Cd_2(bptc)(H_2O)_6]\cdot 2H_2O\}_n$, where H_4bptc is 3,3′,5,5′-biphenyltetracarboxylate, has been synthesized hydrothermally and characterized. In this complex, $bptc^{4-}$ as tridentate ligands connect the Cd^{2+} cations to form a chiral 2D layer, which crystallizes in the orthorhombic chiral space group *C*222. The compound exhibits the properties of luminescence sensor for organic molecules.



The design of chemical sensors is of great interest to researchers.[1–4] Recently, luminescent coordination polymers have been intensively studied because of their inherent properties such as easily designed crystal structures, stable frameworks, a wide range of thermal stability, and systematically tunable luminescence properties.[5–11] For example, Zheng and co-workers exploited two Ln-MOFs with pyridyl Lewis basic sites as remarkably selective and sensitive bifunctional luminescence sensors for metal ions and small organic molecules.[12] Here, we describe a new chiral framework of $\{[Cd_2(bptc)(H_2O)_6]\cdot 2H_2O\}_n$ **1**. The new coordination polymer was obtained under solvothermal conditions.† The crystal structure‡ and luminescent sensing performance were studied in detail.

The X-ray crystallographic analysis has revealed that complex **1** crystallizes in the orthorhombic chiral space group *C*222.[15,16] Figure 1(*a*) shows that both Cd(1) and Cd(2) cations are seven-

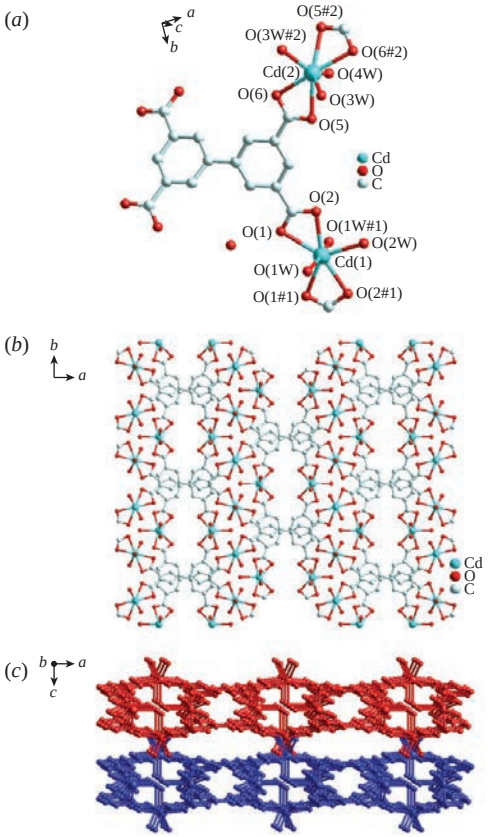


Figure 1 (*a*) Coordination environment of the Cd^{2+} cation in a molecule of complex **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = *x*, 1 – *y*, 2 – *z*; #2 = 0.5 – *x*, –0.5 – *y*, *z*. (*b*) Schematic representation of a single 2D layer formed by Cd^{2+}, $bptc^{4-}$ of compound **1**. (*c*) Schematic view of the structure of complex **1**.

† Commercially available reagents and solvents of reagent grade were used without additional purification.

Preparation of $\{[Cd_2(bptc)(H_2O)_6]\cdot 2H_2O\}_n$ **1**. A mixture of $Cd(NO_3)_2\cdot 4H_2O$ (30.8 mg, 0.1 mmol) and H_4bptc (33.0 mg, 0.1 mmol) was dissolved in distilled water (2 ml) and DMF (2 ml). The final mixture was sealed in a 15 ml Parr Teflon-lined stainless-steel vessel and heated at 95 °C for 3 days; then, the reaction system was cooled to room temperature. Colorless block crystals of **1** thus obtained were washed with water and dried under ambient conditions. Yield 71% (based on H_4bptc). Found (%): C, 27.61; H, 3.16. Calc. for $C_{32}H_{44}Cd_4O_{32}$ (%): C, 27.64; H, 3.19.

‡ *Crystal data for complex* **1**: $C_{32}H_{44}Cd_4O_{32}$, M = 1390.27, orthorhombic, space group *C*222, a = 24.9257(15), b = 11.7081(5) and c = 7.4148(4) Å, V = 2163.9(2) Å^3, Z = 2, d_{calc} = 2.134 g cm^{-3}, μ(MoKα) = 2.048 mm^{-1}, F(000) = 1368, T = 293(2) K, 8298 reflections measured, 1908 independent reflections (R_{int} = 0.0431), final R_1 [$I > 2\sigma(I)$] = 0.0267, $wR(F^2)$ = 0.0606, GOF = 1.029. The measurements were performed on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[13] Hydrogen atom positions were fixed geometrically at calculated distances. A semiempirical absorption correction was applied using SADABS.[14]

CCDC 1856044 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

coordinated with a pentagonal bipyramid geometry, which is formed by five oxygen atoms from two bidentate chelating carboxyl groups and one water molecule in the equatorial plane, and other two oxygen atoms from two water molecules in the perpendicular plane. Both Cd atoms lie on a twofold axis. In addition, the atoms O(2W) and O(4W) are disordered on the same symmetry element. The Cd cations are connected by $bptc^{4-}$ ligands to give a 2D structure, as shown in Figure 1(*b*),(*c*).

The photoluminescent properties of solid H_4bptc and compound **1** were studied at room temperature (Figure S2, Online Supplementary Materials). The free H_4bptc ligand in the solid state exhibited a strong emission at about 365 nm, which is presumably due to π–π* transitions. Compound **1** exhibited the emission at about 391 nm similar to that of the ligand. Compared to the free H_4bptc ligand, the emission band of **1** is 26 nm red-shifted. For compound **1**, abundant lattice water molecules fill the network to form important weak forces, which stabilize the framework and enhance the rigid structure.[17]

Commonly used organic solvents are known to exert adverse effects on human health and the environment. Novel sensing materials based on luminescent coordination polymers have been widely used in the detection of small organic molecules by the obvious diversifications of luminescent signals caused by pollutants.[18–20] In this context, a luminescence sensing experiment was carried out to explore the effect of guest molecules on compound **1**. The luminescent properties of compound **1** in suspensions in organic solvents were systematically investigated. Finely ground as-synthesized compound **1** (5 mg) was immersed in different organic solvents (5 ml) and ultrasonicated for 2 h. Figure 2 shows that its luminescent intensity is largely dependent on solvent molecules, probably, due to different interactions of the chromophores in **1** with the solvents. Evidently, acetone and dichloromethane exerted the most significant quenching effect, whereas acetic acid and *N*-methylpyrrolidone (NMP) had the lowest quenching effect. Detailed experiments were undertaken to examine the sensitivity of the emission response of **1** towards acetone. Compound **1** dispersed in NMP was considered as the standard emulsion **1**–NMP. It was found that the luminescence intensity of the **1**–NMP quickly decreased with the addition of acetone (Figure S3) and the luminescence intensity of the **1**–acetone was quickly enhanced with the addition of NMP (Figure S4).

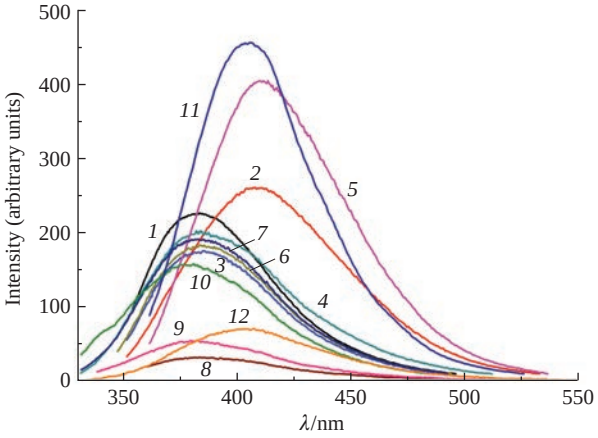


Figure 2 Luminescence emission of compound **1** in different solvents: (*1*) MeOH, (*2*) DMF, (*3*) MeCN, (*4*) EtOH, (*5*) NMP, (*6*) Pr^iOH, (*7*) AcOEt, (*8*) CH_2Cl_2, (*9*) Me_2CO, (*10*) THF, (*11*) AcOH and (*12*) H_2O.

In summary, we have synthesized the new chiral coordination polymer $\{[Cd_2(bptc)(H_2O)_6]\cdot 2H_2O\}_n$ **1** based on the H_4bptc ligand. The photoluminescence properties of solid H_4bptc, compound **1** as well as compound **1** in suspensions in different organic solvents were investigated. The revealed solvent-dependent luminescence properties are of interest for the sensing of dichloromethane and acetone, which are very harmful to humans.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.01.012.

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