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Synthesis, structure, and photoluminescent property of a trinuclear Cd^{II} complex based on semi-rigid bis(imidazole-4,5-dicarboxylate) ligand

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ABSTRACT

A new 3D complex, $\{[Cd_3(HL)_2(H_2L)(H_2O)_4]\cdot 2H_2O\}_n$ (**1**) (H_4L = 1,1′-(1,4-phenylenebis(methylene))bis(1H-imidazole-4,5-dicarboxylic acid), has been hydrothermally synthesized and characterized by elemental analyses, IR, TG, and X-ray single-crystal diffraction. Complex **1** is the first framework based on Cd^{II} ion and semi-rigid *bis*-IDC ligand. The (6,6)-net architecture of **1** is built from H_2L^{2-} ligands linking 1D chain-like $[Cd_3(HL)_2]_n$ SBUs, which formed by HL^{3-} anions bridging two kinds of metal centers. In addition, complex **1** was demonstrated to display strong blue-violet fluorescence emission in the solid state at room temperature.

The design and synthesis of coordination polymers (CPs), often referred to as metal–organic frameworks (MOFs), have been extensively studied not only stemming from their appealing structural and topological novelty but also owing to their tremendous potential applications in microelectronics, fluorescence, nonlinear optics, magnetism, porous materials and heterogeneous catalysis [1–4]. It is well known that the self-assembly of CPs is highly influenced by the structural character of the ligands, coordination trend of the metal ions, and other factors such as the temperature, templates, counterions, pH value of the solution, and solvent system [5,6]. Among them, tactical synthesis or selection of the organic ligand and controlling reaction condition are key factors for achieving expected CPs [7]. The syntheses of new N-heterocyclic carboxylic acid ligands are a long-standing fascination of chemists, and so far, many pyridine-based, imidazole-based, pyrazine-based and triazole-based carboxylic acids have been reported, but the study of their analog and derivative ligands is still underdeveloped [8,9].

In recent years, imidazole-4,5-dicarboxylic acid (H_3IDC) and its 2-position substituted analog ligands have attracted upsurging research interest owing to the excellent performance on the construction of nanostructures and MOFs [10]. However, the derivate ligands of H_3IDC with two IDC groups remain largely unexplored. Prompted by this interesting finding, we design and synthesis a new H_3IDC derivative ligand, namely 1,1′-(1,4-phenylenebis(methylene))bis(1H-imidazole-4,5-dicarboxylic acid) (H_4L), by using 1,4-dibenzyl group linking two identical H_3IDC molecules [11]. We are interested in the use of H_4L as organic linker in combination with Cd^{II} ion adopting d^{10} configuration to construct new CPs based on the following considerations: (i) H_4L and its anions possess multiple potential coordination sites from two IDC groups and can be partially or fully deprotonated at different pH values, therefore, providing various acid-base type coordination modes; (ii) the oxygen-rich and nitrogen-rich backbone of H_4L may help in constructing supramolecular networks via hydrogen bonds and π–π aromatic interactions; and (iii) H_4L has bigger size and two IDC groups can freely twist around the $–CH_2–$ spacers to meet the requirements of the coordination geometries in the assembly process. In this work, we reported the synthesis and characterization of a new trinuclear d^{10} metal polymer, $\{[Cd_3(HL)_2(H_2L)(H_2O)_4]\cdot 2H_2O\}_n$, which exhibits 3D 6-connected framework assembly of *bis*-deprotonated ligands linking 1D chain-like SBUs by the employment of H_4L.

Crystalline products of **1** was hydrothermally synthesized by reacting $Cd(NO_3)_2\cdot 4H_2O$ (0.1 mmol), H_4L (0.05 mmol), dimethylamine hydrochloride (0.2 mmol) and H_2O (10 mL) at 150 °C [12], and characterized by elemental analysis, IR and single crystal X-ray diffraction, and the phase purity of the bulk sample was identified by powder X-ray diffraction (PXRD) (Fig. S1).

The single crystal X-ray analysis [13] indicates that complex **1** crystallizes in the triclinic system space group $P-1$ and the asymmetrical unit of **1** contains two crystallography independent Cd^{II} ions, one HL^{3-} ligand, a half of H_2L^{2-} ligand, two coordination water molecules and a lattice water molecule. As shown in Fig. 1a, Cd1 ion lies at an inversion center and is six-coordinated by two nitrogen atoms (Cd1–N5, 2.273(4) Å; Cd1–N5A, 2.273(4) Å) and two oxygen atoms (Cd1–O9, 2.408(4) Å; Cd1–O9A, 2.408(4) Å) from two separate H_2L^{2-} anions, and two oxygen atoms (Cd1–O4, 2.272(4) Å; Cd1–O4A, 2.272(4) Å) from two isolated HL^{3-} anions in a slightly distorted octahedral environment. Different from Cd1,

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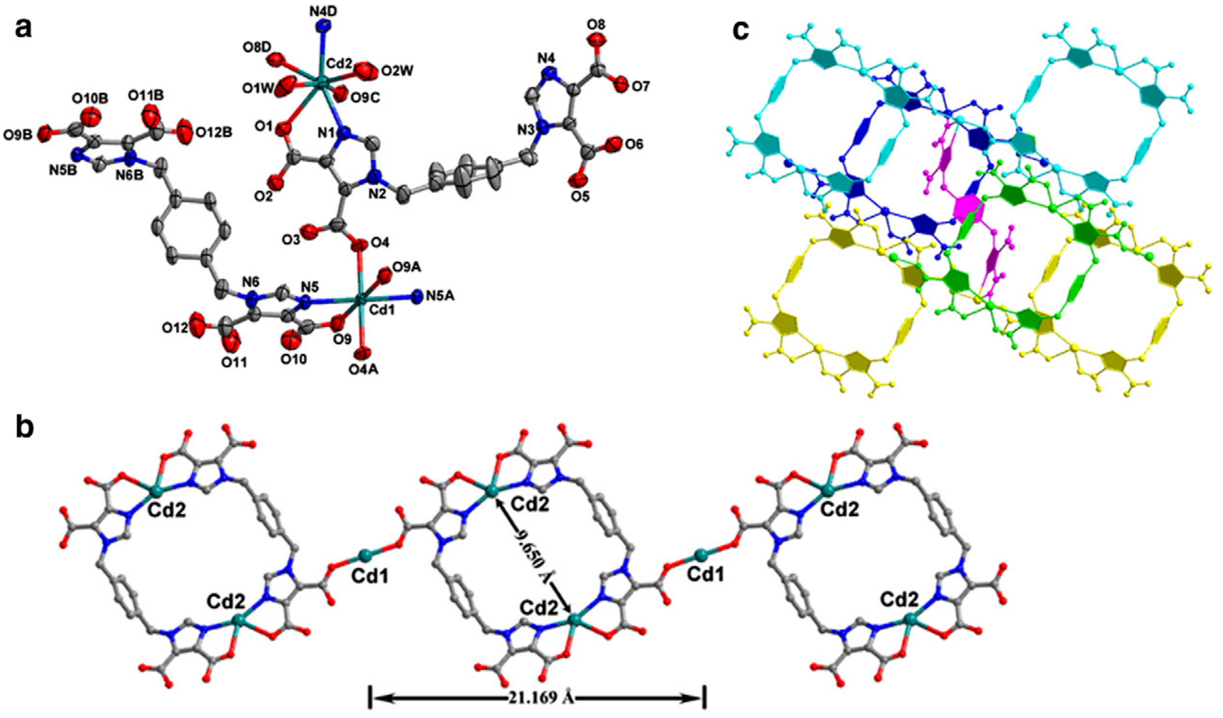
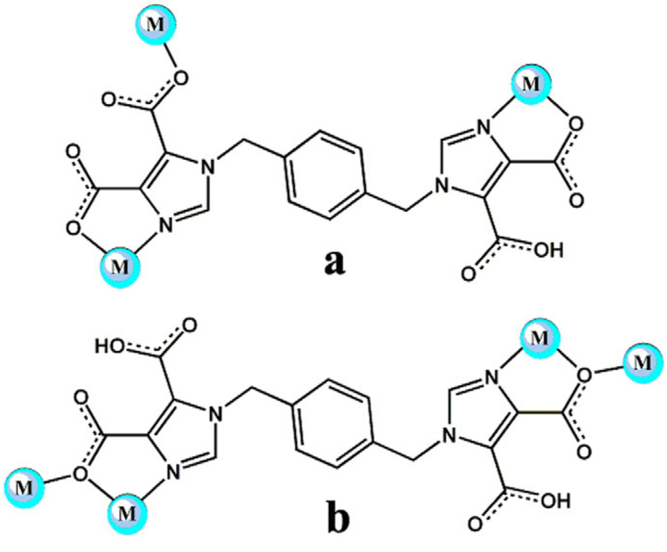


Fig. 1. (a) View of the coordination environment of Cd^{II} ions in **1** with thermal ellipsoids drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Symmetry codes: A, −x, −y, −z; B, −x + 1, −y + 1, −z; C, −x + 1, −y, −z; D, −x + 2, −y, −z + 1. (b) The 1D chain formed by HL^{3-} bridging two different metal centers. (c) View of four 1D chain-like SBUs connected by the H_2L^{2-} anion.

Cd2 adopts a pentagonal bipyramid coordination geometry and surrounded by two nitrogen atoms (Cd2–N1, 2.278(4) Å; Cd2–N4D, 2.297(4) Å) and two oxygen atoms (Cd2–O1, 2.491(4) Å; Cd2–O8D, 2.461(4) Å) from two individual HL^{3-} ligands, and one oxygen atom (Cd2–O9C, 2.408(4) Å) from one H_2L^{2-} ligand as well as two terminal water molecules (Cd2–O1W, 2.293(4) Å; Cd2–O2W, 2.633(5) Å). In complex **1**, the H_4L ligands were deprotonated into HL^{3-} and H_2L^{2-} fashions in the presence of dimethylamine, respectively, and they exhibit two different types of coordination modes, as depicted in Scheme 1. One acts as a tridentate connector adopting μ_3-*k*N,O: *k*N′, O′: *k*O″ coordination mode linking three Cd^{II} ions (Scheme 1a) in *bis*-N,O-chelating and O-monodentate fashions, in which the dihedral angle between two imidazole rings and the benzene ring are 75.86° and 76.30°. The other serves as tetradentate ligand bridging four Cd^{II} centers and displays a μ_4-*k*N,O: *k*N′,O′: *k*O: *k*O′ coordination mode via *bis*-N,O-chelating and *bis*-O-monodentate fashions with the dihedral angle of 83.10° between the aromatic rings. It is worth noting that all carboxylate groups and the attaching aromatic rings are almost coplanar in two different coordination modes.



Scheme 1. Coordination modes of the HL^{3-} and H_2L^{2-} ligands in complex **1**.

Interestingly, two adjacent Cd2 metal centers were interconnected by two HL^{3-} ligands with the *cis–gauche* conformation leading to the formation of a $Cd_2(HL)_2$ ring, in which the Cd2···Cd2 separation is 9.650 Å. The neighboring $Cd_2(HL)_2$ rings link with each other by sharing the Cd1 nodes giving rise to a one-dimensional (1D) infinite $[Cd_3(HL)_2]_n$ chain with the shortest Cd1···Cd1 distance of 21.169 Å (Fig. 1b). Each 1D $[Cd_3(HL)_2]_n$ chain can be considered as a secondary building unit (SBU). The four identical chain-like $[Cd_3(HL)_2]_n$ SBUs are further connected by the H_2L^{2-} anion with *trans* conformation (Fig. 1c) resulting to a three-dimensional (3D) co-valent framework (Fig. 2). Although a large number of complexes based on the new designed N-heterocyclic carboxylic acid ligands have been reported. To the best of our knowledge, such complex constructed from semi-rigid H_3IDC derivative ligand bearing *bis*-IDC groups have not been observed in coordination polymers.

To further understand the structure of **1**, topological analysis by reducing multidimensional structure to simple node-and-linker net was performed. Three Cd^{II} ions were μ_2-bridged by two caboxylate oxygen atoms from two H_2L^{2-} ligands to form a trinuclear cluster. Each trinuclear cluster is surrounded by six trinuclear clusters and can be considered as a six-connected node (Fig. 3a). On the basis of the simplification above, complex **1** possesses a classical non-interpenetrating 6-connected a-Po net with the Schläfli symbol of $(4^{12} \cdot 6^3)$ based on the trinuclear cadmium nodes, which is assigned to the pcu net (Fig. 3b).

The thermal stability of **1** has been examined by using thermogravimetric (TG) analyzer from 40 to 1000 °C under flowing nitrogen at a heating rate of 10 °C/min. From the TG curve (Fig. S2), **1** shows a three-step weight loss. The first weight loss of 2.05% (cal. 2.14%) is assigned to the liberation of two lattice water molecules which occurred in the range of approximate 40–70 °C. The second weight loss of 4.12% (cal. 4.28%) between 100 and 150 °C is ascribed to the

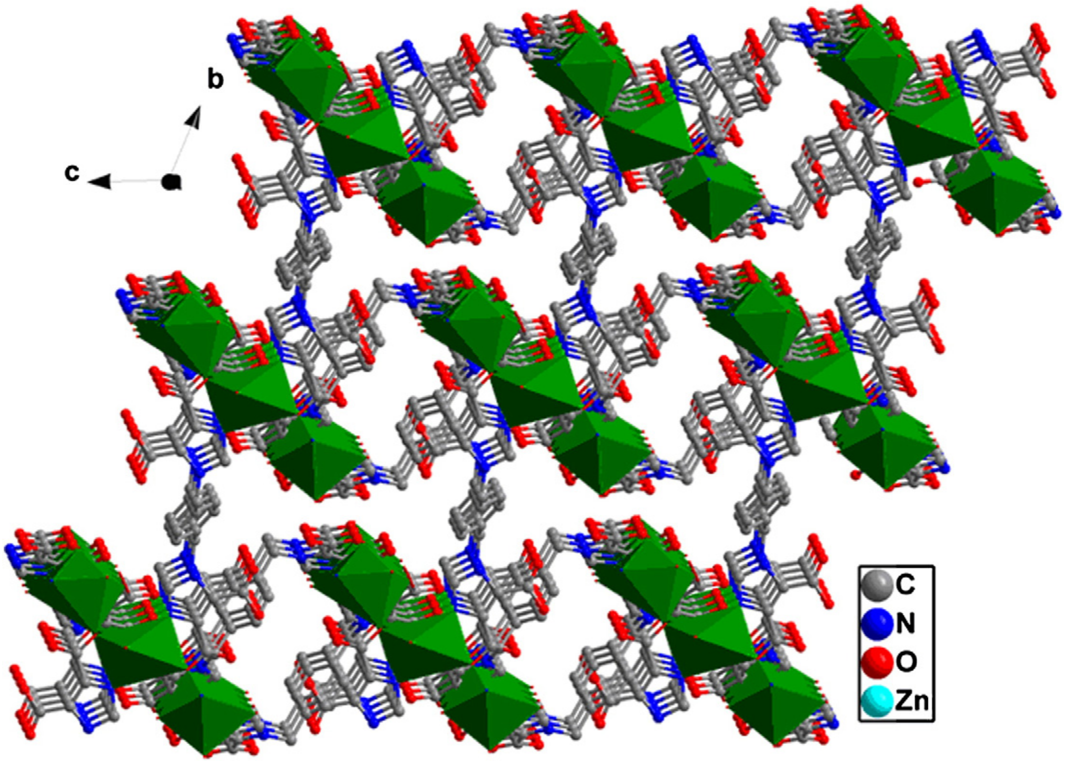


Fig. 2. Polyhedral view of the 3D framework of complex **1**.

loss of four coordination water molecules. The last loss of 70.03% (cal. 70.66%) occurs from 315 to 810 °C, which corresponds to the complete decomposition of the samples. After the decomposition, the final product may be CdO.

The photoluminescent properties of the free H_4L ligand and Cd^{II} complex **1** in the solid state were investigated at room temperature and relevant emission spectra are shown in Fig. 4. The free H_4L ligand shows an emission band centered at 435 nm upon excitation at 364 nm, which can be assigned to the $\pi \rightarrow \pi*$ transitions [14]. In contrast to the free ligand, complex **1** has an emission at 432 nm under the same conditions and merely blue-shifted by ~2 nm. This emission is assignable as an intraligand transition of the H_4L ligand. Since the heteroatoms of the heterocyclic aromatic ligand will have decreased π and π∗ orbital energies (the HOMO and LOMO, as well as orbitals with energies close to these, may not be significantly contributed by the Cd metal atoms, so that LMCT can be excluded from consideration) [15]. The features of the highest occupied (HOMO) and the lowest unoccupied (LUMO) frontier orbitals are shown in Fig. S3. Obviously, the electron densities of the singlet state of HOMO and LUMO reside the ligands all [16], suggesting that the emission band of complex can be attributed to ligand-to-ligand charge transfer (LLCT). The enhancement in luminescence may be ascribed to an increase in the conformational rigidity of the H_4L ligand due to their coordination to the Cd^{II} ion, resulting in a decrease in the nonradiative decay of the intraligand excited states.

In conclusion, an interesting 3D Cd^{II} complex, $\{[Cd_3(HL)_2(H_2L)(H_2O)_4]\cdot 2H_2O\}_n$, has been successfully synthesized and structurally characterized, which is constructed by two different configuration ligands linking metal centers. In this work, we explore the coordination characteristics of *bis*-IDC system ligand for the first time. Moreover, complex **1** displays blue–violet fluorescent property indicating that the polymer may have potential applications in optical materials. Further work on this ligand and its metal complexes is still explored in our laboratory.

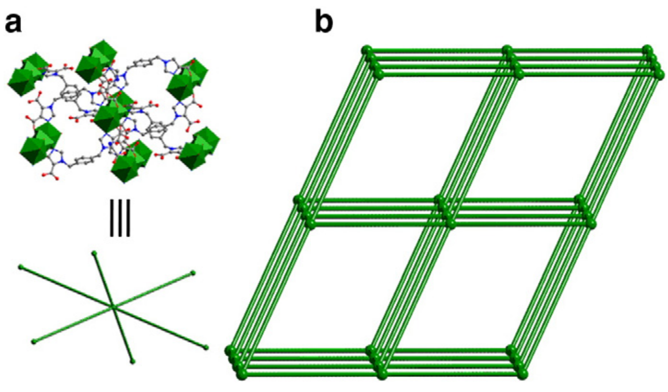


Fig. 3. (a) View of 6-connected node in **1**. (b) A schematic representation of a-Po network of **1**.

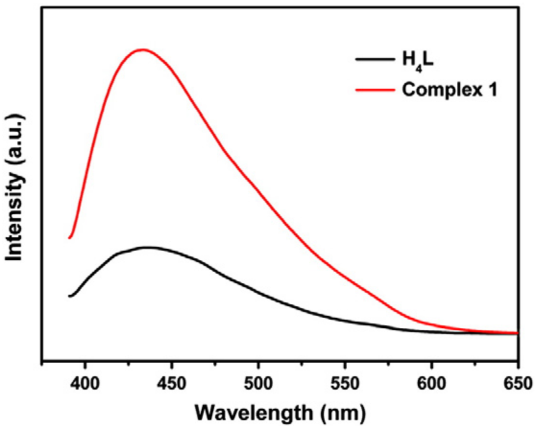


Fig. 4. The solid-state photoluminescent spectra of the free H_4L and complex **1** at room temperature.

Acknowledgments

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited to the Cambridge Crystallographic Data Centre, CCDC No. 687253 for complex **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2014.01.004.

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[11] Synthesis of 1,1′-(1,4-phenylenebis(methylene))bis(1H-imidazole-4,5-dicarboxylic acid) (H_4L). A mixture of 1H-imidazole-4,5-dicarbonitrile (3.54 g, 30 mmol) and NaOH(1.32 g, 33 mmol) in DMF (30 mL) was stirred at 70 °C for 2 h, and the 1,4-bis(chloromethyl)benzene (2.62 g, 15 mmol) was added. The mixture was cooled to room temperature after being stirred at 70 °C for 24 h and poured into 200 mL of ice water. A white solid formed immediately, which was isolated by filtration. The above white solid was added into 40 mL of NaOH solution (20%), and the reaction mixture was refluxed for 4 h at 120 °C. The obtained clear solution was cooled to room temperature and acidified (pH = 2) with dilute HCl solution. The obtained white solid product H_4L was filtered and washed with water until free from acid. Yield: 65%.

[12] Synthesis of complex 1: A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (30 mg, 0.1 mmol), H_4L (20 mg, 0.05 mmol), Dimethylamine hydrochloride (16 mg, 0.2 mmol) and deionized water (10 ml) in a 23 mL Teflon reactor, and then was heated at 150 ºC for 72 h; colorless block crystals were obtained. Elemental Anal. Calc. (%) for it: C, 38.60; H, 2.75; and N, 10.00. Found: C, 38.65; H, 2.73; and N, 10.06%.

[13] Crystal data for complex 1, $Mr = 1680.10$, triclinic, $P-1$, $a = 9.227(4)$ Å, $b = 13.564(5)$ Å, $c = 13.866(6)$ Å, $\alpha = 112.464(5)°$, $\beta = 99.523(6)°$, $\gamma = 100.855(5)°$, $V = 1520.2(11)$ Å^3, $Z = 1$, $R_1 = 0.0439$ ($I > 2\delta(I)$). Intensity data were collected on a Bruker SMART APEXII CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å) at room temperature. The structure was solved

by the direct method and refined by the fullmatrix least-squares method on F^2 using the SHELXTL crystallographic software package.

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