An effective approach for constructing acentric heterometallic-organic framework with catalytic activity

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ABSTRACT

A new acentric heterometallic–organic framework, [CdMg (btec)(DMF)(H$_2$O)$_3$] (**1**) (H$_4$btec = 1,2,4,5-benzene tetracarboxylic acid), has been solvothermally synthesized. It features a 4-connected net with typical **pts** topology. To the best of our knowledge, compound **1** is the first example of Cd–Mg heterometallic organic framework based on the H$_4$btec ligand. Compound **1** has potential unsaturated metal sites after the removal of coordination water molecules, so it shows good catalytic activity on the diethylzinc addition to benzaldehyde. The photoluminescent property of **1** is also investigated.

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Heterometallic-organic frameworks (HMOFs) are of great current interest not only due to their many practical applications in luminescence, magnetism, and heterogeneous catalysis [1–3], but also due to their impressive structural diversity in architectures [4–7]. In particular, acentric HMOFs offer many advantages on designing nonlinear optical (NLO) materials [8,9]. Moreover, HMOF-based catalysis has become a hot topic in recent years, but it is still in an immature phase [10]. A common structural feature of those reported HMOF-based catalysts is the presence of coordinatively unsaturated metal sites (CUSs) as Lewis acid sites [11,12]. CUSs can offer a promising tool in catalysis because regular arrangements and well-defined environments of metal centers in the pore channels induce regioselectivity and shape- or size-selectivity towards guest molecules or reaction intermediates. In the case of Lewis acid catalyzed reactions, the availability of CUSs is a key requirement [13]. MOF materials with removable solvent molecules occupying coordination sites of metals provide a versatile and convenient route to produce these functional CUSs [14]. Thus, the generation of CUSs by thermal activation is an effective approach for improving the catalytic performance of MOFs. Some MOFs with CUSs, such as HKUST-1 and MIL-101 [15,16], have been successfully applied to catalyze some organic reactions including the cyanosilylation of benzaldehyde [17] and epoxide ring opening [18,19]. The asymmetric addition reaction of diethylzinc with benzaldehyde is one of the convenient routes to

produce industrial phenylpropanol, and is also a typical reaction to evaluate the catalytic property of new MOF [20].

In addition, templated synthesis is of great importance in the design and syntheses of functional materials [21]. A remarkable variety of templates which include solvents [22] and ammonium cations [23] have been utilized in the syntheses of HMOFs. Alkylammonium cations are perhaps the popular ones among these various templates. They have taken critical templating roles in the syntheses of artificial zeolites [24,25]. However, so far templated HMOF materials with tetra-alkylammonium cations are rarely synthesized.

In this work, we report a new acentric heterometallic-organic framework, [CdMg(btec)(DMF)(H$_2$O)$_3$] (**1**) (H$_4$btec = 1,2,4,5-benzene tetracarboxylic acid), which is solvothermally synthesized and structurally characterized by single-crystal X-ray diffraction, IR spectrum and elemental analysis. The dehydrated sample has a good catalytic activity on the reaction of diethylzinc addition to benzaldehyde, so the unsaturated metal sites may play the key role in the reaction. The photoluminescent property of **1** is also investigated.

Compound **1** was solvothermally synthesized with the Cd(CH$_3$COO)$_2$/Mg(NO$_3$)$_2$/H$_4$btec/(Et)$_4$NBr/1,4-diazabicyclo[2.2.2]octane molar ratio being 1:1:1:1:0.5 in mixed H$_2$O and DMF solvent (v: v = 1: 2) at 100 °C for 2 days. Single-crystal X-ray diffraction reveals that **1** crystallizes in space group of Pna2(1) [30]. As shown in Fig. 1a, the asymmetric unit of **1** consists of one Cd(II) ion, one Mg(II) ion, one btec$^{4−}$ ligand, one coordinated DMF and three coordinated H$_2$O molecules. Cd1 is coordinated by seven oxygen atoms from four carboxylate groups from four ligands. Mg1 is octahedrally coordinated by six oxygen donors from three waters, one DMF, and two carboxylate oxygen atoms from two btec$^{4−}$ ligands. The Cd–O and Mg–O bond lengths are normal. The Cd centers and Mg centers are alternately linked by the carboxylate groups into an infinite linear chain along the b-axis. The distances

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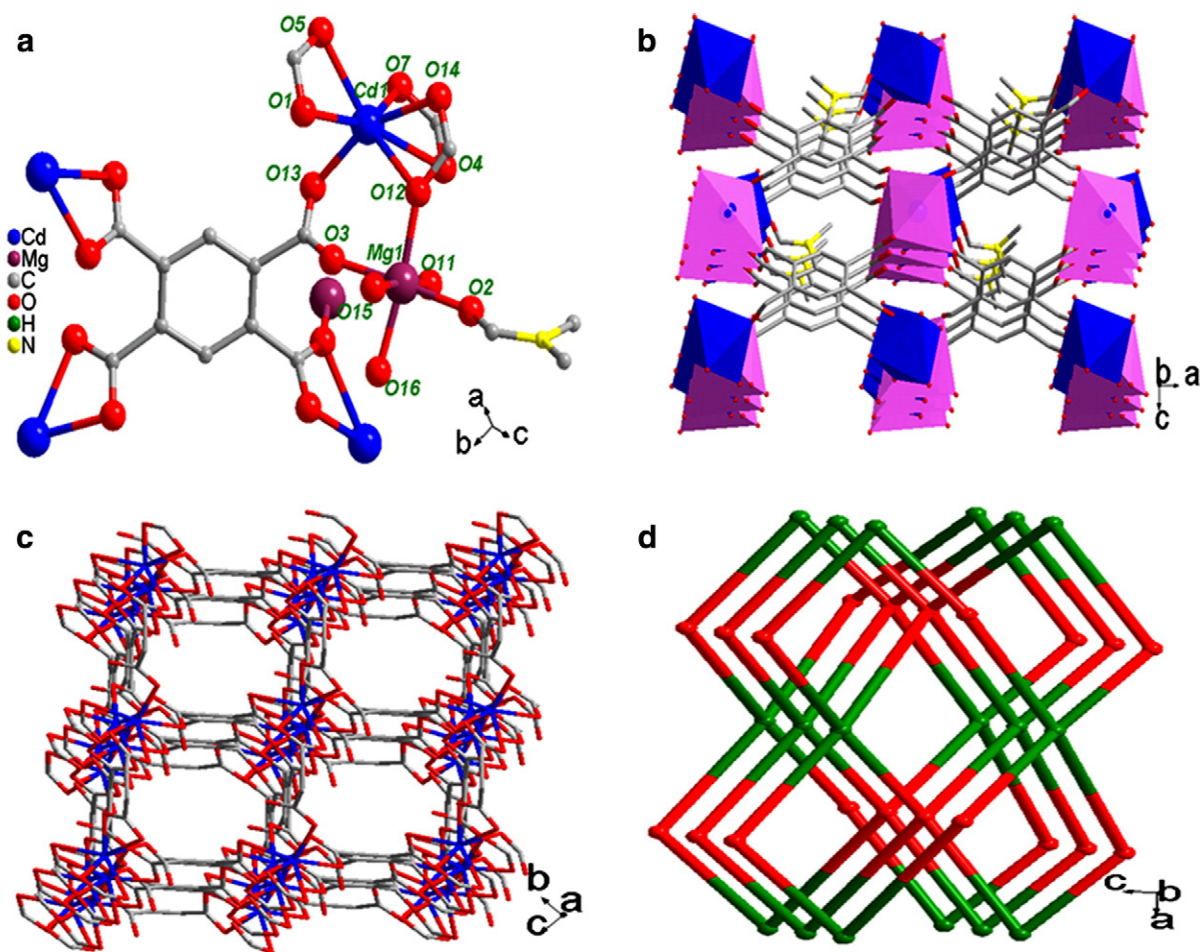E-mail addresses: zhanghuabin@fjirsm.ac.cn (H.-B. Zhang), csm@fzu.edu.cn (S.-M. Chen).

Fig. 1. (a) The coordination environment in compound **1** with hydrogen atoms and lattice water molecules omitted for clarity. (b) The 3-D structure of **1** with two kinds of polyhedron (Cd (blue) and Mg (pink) as a polyhedron center, respectively). (c) View of the 3-D structure of **1** (Mg ions are filtered out) along *a* axis. (d) The 4-connected **pts** topology of **1**.

between neighboring metal centers in the chain are 3.844(1) Å and 5.431(3) Å, respectively. Each btec^{4-} anion adopts the (k^2)-(k^2)-$(k^1$-$k^1)$-$(k^2$-$\mu_2)$-μ_6-coordination mode (Chart S1). The resulting chains are further linked by the btec^{4-} ligands into a 3D framework (Fig. 1b). To further understand the structure of **1**, topological analysis by reducing the multidimensional structure to a simple node-and-linker net was performed. Apparently, the cadmium and magnesium centers can be viewed as a node that is connected by sharing carboxylic groups, and the betc^{4-} can be defined as a four-connected node. The network can be defined as a four-connected **pts** topology with the point symbol of $(4^2 \cdot 8^4)$ (Fig. 1d) [26]. If the Mg ions are removed from the framework, the remaining anionic structure of **1** is still a 3D network with identical topology (Fig. 1c).

The phase purity was identified by powder X-ray diffraction (PXRD). The major peak positions of the PXRD pattern of the bulk solids of **1** matched well with those of the simulated pattern obtained from single-crystal data, indicating the phase purity of the sample (Fig. S3). TGA of **1** indicates that the weight loss of about 11.5% between 119 and 200 °C corresponds to the full liberation of coordinated water molecules, which corresponds well to the molecular formula of compound **1**. After 300 °C, a sharp decomposition of the framework is assigned to coordinated DMF molecules and btec^{4-} ligands (Fig. S4), which indicates that **1** has good thermal stability. Besides, compound **1** also exhibits high chemistry stability in n-hexane, DMF and water. As shown in Fig. S6, the IR spectrum of **1** indicated that the strong and sharp band at 1618 cm^{-1} can be attributed as characteristic absorption bands of the carboxylate groups. The UV–vis diffuse absorption spectra of **1** and thermal treated sample of **1** (under 200 °C), which clearly

indicate their absorption edges, are about 348 nm and 426 nm, respectively as shown in Fig. S5. The calculation results show that their energy gaps are 3.56 ev and 2.91 ev, respectively [27].

To evaluate the catalytic activity of compound **1**, we used the diethylzinc addition to benzaldehyde as a test reaction (Fig. 2a). Activated
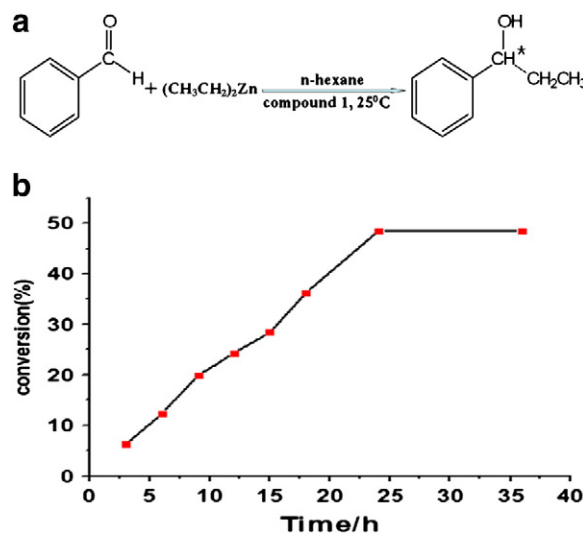

Fig. 2. (a) The asymmetric addition reactions of diethylzinc with benzaldehyde. (b) The conversion of phenylpropanol with time for compound **1**.

catalyst **1** (24 mg) dried under vacuum at 200 °C for 2 h was placed in a 25 ml Schlenk flask and then vacuumized for 10 min. The n-hexane (2 ml) solvent was added via syringe under nitrogen. After the mixture stirred for 30 min, benzaldehyde (0.25 ml) and diethylzinc (in n-hexane, 0.75 ml) were added. The new mixture was stirred under nitrogen at 25 °C. In a certain time interval, a small amount of solution was taken out and quenched with saturated NH_4Cl solution and ethyl acetate. The composition of the reaction mixture was determined by gas chromatograph (GC) analysis (Fig. S3). We can observe racemic phenylpropanol (R- and S-) with the same yield in the products. After 24 h, the reaction led to a 48.6% conversion of benzaldehyde and it is basically stopped (Fig. 2b). The PXRD pattern of **1** after catalysis is consistent with that of the as-synthesized sample, which reveals the good chemical stability of **1** (Fig. S3). Besides, several parallel experiments have been carried out by using the metal salt, free organic ligand, as well as the mixture of metal salts and organic ligand under the similar reaction conditions, which showed nearly no catalytic effect (Fig. S2). We may draw the conclusion that the unsaturated metal sites in compound **1** may play the key role in the catalytic reaction. The cycle catalytic experiment has also been carried out, but the conversion of benzaldehyde is very low (Fig. S2). The weak recycling performance of the catalytic activity should be attributed to the idea that active metal sites might be coordinated by water molecules coming from air and the reactants.

Considering the excellent photoluminescent properties of some Cd(II)-carboxylate MOFs, solid-state luminescent properties of **1** and H_4btec have been investigated at room temperature. As shown in Fig. 3, the H_4btec displays a broad emission with peak at 512 nm which can be assigned to the π–π* transition. Compared with free ligand, the emission of **1** has a stronger blue-shifted emission with a maximum emission at around 440 nm, which should be assigned to the ligand-to-metal charge-transfer (LMCT) band [28,29]. Luminescence properties of MOFs can be dramatically affected by the coordination environment of metal centers, arrangement of luminophores, species of guest molecules, and so forth. Thus, the luminescent behavior of thermal treated sample (200 °C for 2 h) was also studied. The emission spectrum of the thermal treated sample exhibits a similar pattern emission but with great enhancement relative to compound **1**. This phenomenon suggests that the solvent molecules are effective non-radiative relaxers to quench luminescence.

In this communication, an experiment is carried out under the similar synthesis conditions without $(Et)_4NBr$, but we fail to obtain compound **1**. Thus we speculate that $(Et)_4NBr$ may play the role in the reaction as structure directing agent (SDA). In summary, a new acentric heterometallic-organic framework with 4-connected **pts** topology has been successfully synthesized. It showed catalytic activity on the diethylzinc addition to benzaldehyde. The strong fluorescent emission of **1** may make it a potentially useful photoactive material.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2014.01.021.

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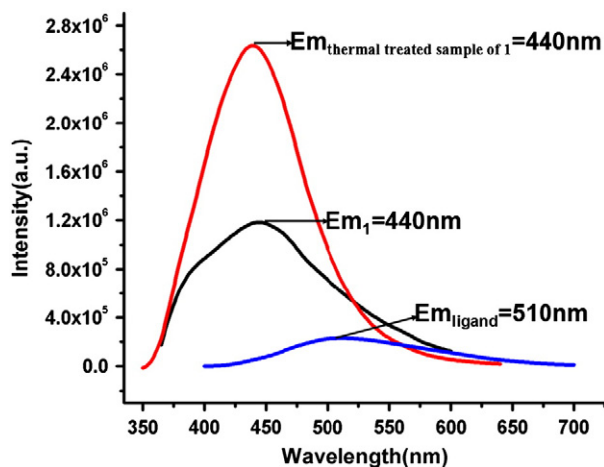

Fig. 3. The emission spectra of **1** and free ligand in the solid state at room temperature (blue: free ligand; black: sample; red: thermal treated sample of **1** (200 °C for 2 h).

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[30] All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Synthesis of $[Cd(btec)Mg(DMF)(H_2O)_3]$ (1): a mixture of $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.0584 g, 0.22 mmol), $Mg(NO_3)_2$ (0.0558 g, 0.22 mmol), H_4btec (0.0626 g, 0.25 mmol), 1,4-diazabicyclo[2.2.2] octane (0.02081 g, 0.18 mmol), $(Et)_4NBr$ (0.0454 g, 0.22 mmol), 6 ml mixture of N, N-dimethylformamide (DMF) and H_2O (v: v = 4: 2) were stirred to give a colorless turbid solution. The mixture was heated at 100 °C for 2 days, and then cooled to room temperature. The colorless-block crystals were filtered off, washed with fresh DMF and dried in air. Anal. Calcd. For $C_{13}H_{15}CdNMgO_{12}$ (%): C, 30.35; N, 2.72; H, 2.92. Found: C, 30.44; N, 2.71; H, 3.09. Cd: Mg = 1: 1 (mol · mol^{-1}). IR (solid KBr pellet v/cm^{-1}): 3550 m, 3424 s, 1614 s, 1385 m, 1141 m, 614w (Fig. S6). Crystal data for 1: $C_{13}H_{15}CdNMgO_{12}$, Mw = 513.95, orthogonal, a = 17.6167(1) Å, b = 9.1946(6) Å, c = 10.7005(7) Å, V = 1733.3(2) Å^3, T = 293(2) K, space group $Pna2(1)$, Z = 4, 4609 reflections measured, 2315 independent reflections (R_{int} = 0.0273). The final R_1 value was 0.0277 (I > 2σ(I)). The final $wR(F^2)$ value was 0.0842 (I > 2σ(I)). The goodness of fit on F^2 was 1.054. The structure of 1 was solved by direct methods and refined on F^2 by full-matrix, least-squares methods using the SHELXL-97 program package [31].