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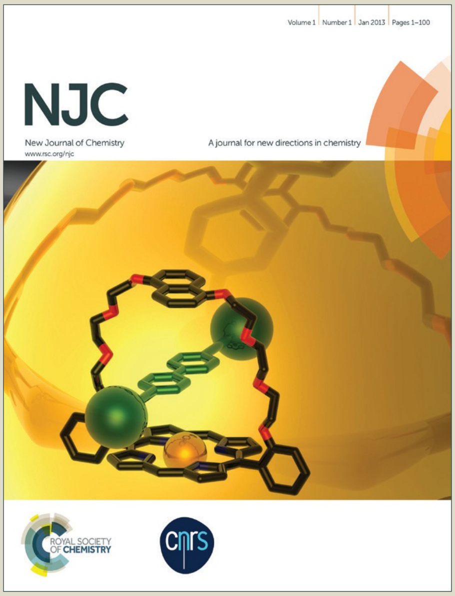

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A novel 2D infinite M_3L_2 cage-based Cd(II) Microporous Coordination Polymer with a tripodal carboxylic acid ligand and solvent-dependent luminescence properties†

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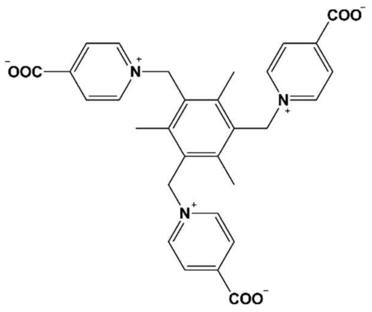
A novel M_3L_2 cage-based microporous coordination polymer assembled by six-coordinated Cd(II) ion and flexible tricarboxylic ligand has been designed and synthesized. The solvent-dependent luminescence properties revealed that the title coordination polymer have an obvious enhanced luminescent in the solvent of CH_2Cl_2 and $CHCl_3$.

Considering that cage-based compounds, especially, metal organic complexes can serve as the very effective encapsulation for functional guest molecules, its self-assemble and applications have been well studied and summarized.[1] M_3L_2 type cage-like complexes as the minimum metal organic cage, were commonly synthesized by using a tripodal pyridine-containing or imidazole-containing ligand with low-coordinated metal ions, such as: Ag^+, Pt^{2+} and Pd^{2+}.[2] Interestingly, the Sun group has firstly reported the single crystal structure of a discrete M_3L_2 cage-like complex which assembled with a tetrahedral Zinc(II) centers.[3] Later, another discrete M_3L_2 cage were obtained by the assemble of Cu(II) salt and a flexible tri(oxamate)-base ligand.[4] On the other hand, although a silver(I) coordination polymer chain linked by SO_4^{2-} through non-coordination bond containing M_3L_2 cage has been assembled nearly.[5] However, there is no related reports when using a carboxyl-containing ligand even with upper 4-coordinated metal ions, such as: Zn^{2+} and Cd^{2+} to assemble the 1D, 2D or 3D structures by the stronger coordination bond. This maybe owing to the various coordinated modes of the carboxyl and the steric hindrance of the high coordinated metal ions. It is well known that the widely used polycarboxylic ligands play an important role in the constructing of various metal organic complexes. So, the fully using of polycarboxylic ligands to construct special structural and functional metal organic complexes is very urgent.



Scheme 1. The structure of **L** ligand.

The self-assemble of Microporous Coordination Polymers (MCPs) is a highly topical area of current research, in which has yielded many fascinating architectures and has been founded enormous potential applications in catalysis[6], capture and degradation of toxic gases[7], NLO optics[8], biomedical imaging[9] and molecular sensor[10]. Among the fruitful production of functional MCPs reported to date, luminescent MCPs can be viewed as the most promising class of materials, due to their potentially applications in materials. In fact, recently, some luminescent MCPs have been succeeded in sensing of solvents, such as, DMF, acetone and water.[11] Considering the widely using of MCPs, the study of solvent-dependent luminescence properties in common solvents is necessary.

Herein, we used a bowl-shaped tripodal carboxyl acid ligand, 1,1',1''-((2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene))tris (pyridine-1-ium-4-carboxylate) (named **L** , as shown in Scheme 1) [12] and cadmium ion which has a distorted octahedral configuration, to construct a M_3L_2 cage which expanded by 1,3,5-benzenetricarboxylic acid (H_3BTC) to form a 2D infinite M_3L_2 cage-based framework $[(BTC)_{2/3}(L)_{2/3}Cd]\bullet(H_2O)_{1.5}\bullet(DMF)_{0.5}$ (compound **1**) §. The 3D structure of compound **1** was formed by the hydrogen bonds and π-π stacking between the 2D planer structures. To the best of our knowledge, this is the first MCP based on M_3L_2 cage

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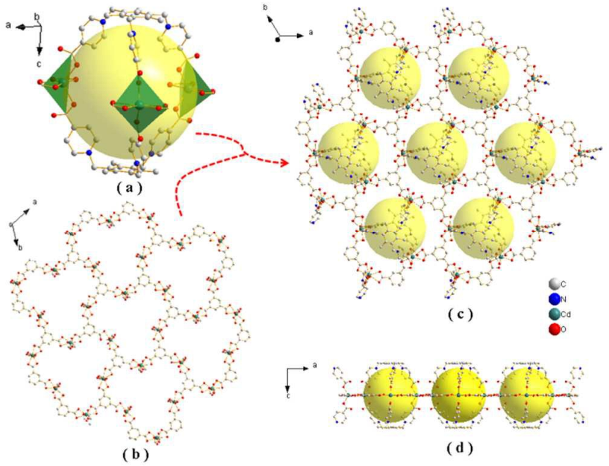

Figure 1. (a) The structure of M_3L_2 cage in compound **1**. (b) The 2D planar structure constructed by BTC^{3-} and Cd^{2+}. The 2D structures of compound **1** in **c** direction (c) and **b** direction (d), respectively. The H atoms are omitted for clarity. The solvent molecules were removed from the single crystal x-ray diffraction data, so not to be represented in the structure of compound **1**.

constructed by Cd(II) ions and flexible tripodal carboxyl-containing ligands. What is more, the solvent-dependent luminescence properties revealed that compound **1** have an obvious enhanced luminescent in the solvents of CH_2Cl_2 and $CHCl_3$, respectively.

Single-crystal X-ray diffraction reveals that compound **1** crystallizes in the centrosymmetric trigonal space group R-3c, which is associated with the point group C3v(3m). The asymmetric unit contains a half Cd(II) atom, one third **L** ligand and one third BTC^{3-}(Figure S8). As shown in Fig. 1a, the Cd atom occupies the centre of a distorted octahedron defined by two carboxylates in bidentate chelating mode from two different BTC^{3-} ligands and two carboxylates in monodentate coordination mode from two independent **L** ligands. The Cd—O bond lengths range from 2.27(2) to 2.49(7) Å, which are comparable with those reported in other Cd(II)-carboxylic complexes.[13] The O—Cd—O angles range from 51.5 (5) to 139.6(2)° and the tetrahedron length range from 4.03(9) to 5.77(1) Å. In the viewpoint of **L** ligand, three methylene-4-carboxylic acid group of **L** orientate to the same side of basic phenyl group, which results in a bowl-shaped configuration of **L**. Two **L** ligands just which opposite faced are linked by three Cd(II) ions to form the interesting M_3L_2 cage (Figure 1a). The diameter of the cage is about 12.6 Å. Then each M_3L_2 cage is linked by six BTC^{3-} to form a 2D well coplanar structure (Figure 1c). In the side of BTC^{3-}, each BTC^{3-} is linked by three BTC^{3-} which coordinated by Cd(II) ions to form a 2D plane(Figure 1b). So, the resulted M_3L_2 based MCP is obtained due to the contribution of **L** ligand and BTC^{3-}. Because of C-H···O hydrogen bonds and π-π stacking (Figure 2), the 2D coplanar structures link each other to form the 3D architecture.

The solid diffuse reflectance spectrum revealed that compound **1** was a wide-gap semiconductor with band gap of 3.45 eV (Figure S5). The photoluminescent properties of **L** ligand, H_3BTC and compound **1** in solid state were investigated at ambient temperature (Figure S6). Upon excitation at 300 nm, peaks at 372, 397 nm for H_3BTC, 402, 460 nm for **L** ligand, and 399, 462 nm for compound **1** were found in photoluminescence spectrum, respectively. Compared with the free **L** ligand, the emission band locations of compound **1** was comparable but with an increasing band height. It may be attributed to the coordination effect of the ligands to Cd ions, which increased the structural rigidity and reduce the nonradiative decay of the intraligand.[12]

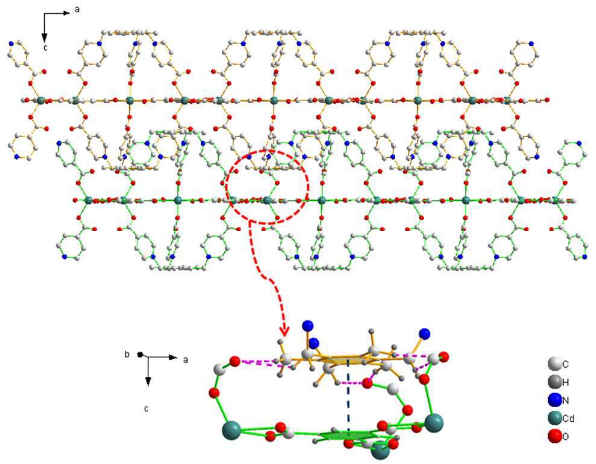

Figure 2. The 3D structure of compound **1** is resulted by the interaction of 2D structures in **b** direction (different color display different 2D structures) The H atoms and solvent molecules are omitted for clarity; the interactions between the 2D structures are clearly showed in the blow. The pink dot line is on behalf of the C-H···O hydrogen bond, while the black line is the π-π stacking.

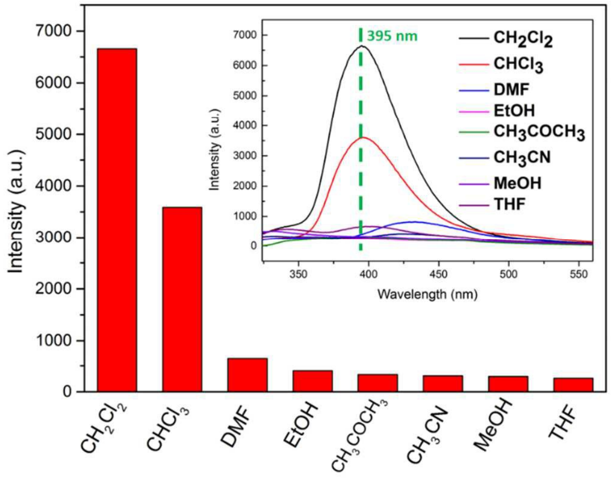

Figure 3. The PL intensities at 395 nm of compound **1** which in suspension in various pure organic solvents under the same testing conditions. The insert picture showed the real photoluminescent spectra of compound **1** in suspension in organic solvents when excited at 300 nm.

What is more, the most interesting feature is that its PL spectrum is largely dependent on the solvent molecules, particularly in the case of CH_2Cl_2 and $CHCl_3$. As shown in Figure 3, comparing with DMF, ethanol, acetone, acetonitrile, methanol and THF, the intensities of compound **1** suspended in CH_2Cl_2 and $CHCl_3$ were greatly enhanced. The other kinds of solvents did not exhibit some changes in 395 nm. In order to give a possible fluorescent enhancement mechanism, the solvent-exchanged samples have been conducted the ^{1}H-NMR and TGA experiments. The results of ^{1}H-NMR revealed that both CH_2Cl_2 and $CHCl_3$ can not exchange with the gust molecules in the framework of compound **1** (Figure S7). The result of TGA experiments further proved no exchange between the CH_2Cl_2 and $CHCl_3$ and gust molecules (Figure S3). So, the probably reason can be owing to the solvent-dependent surface-enhanced fluorescent which have been studied in the field of the capped Au or Ag metallic nanostructures, mono-layer organic structure and the quant dots[14]. Although some fluorescent MOFs relying on guest molecules have been observed previously, [11] most examples are in the solvents of DMF, acetone and water through solvent-exchange. Here, we have presented a rare example of obvious surface-enhanced luminescent in the solvent of CH_2Cl_2 and $CHCl_3$. To the best of our knowledge, such kinds of halomethane solvents for fluorescent MOFs has not previously been reported

In summary, we have designed and synthesized a 2D infinite M_3L_2 cage-based MCP which assembled by six-coordinated Cd(II) ion and a flexible tricarboxylic ligand. The solvent-dependent luminescence properties revealed that compound **1** have an obvious enhanced luminescent in the solvent of CH_2Cl_2 and $CHCl_3$. The results could immensely expand the design and synthesis of special cage-based MCPs assembled with well-designed ligand and medium coordinated metal ions, and hence, pushing the application of cage-based MCPs in the functional materials filed by encapsulation with functional guest molecules. The guest functionalized MCPs will have widely applications in nonlinear optics, biological imaging and drug delivery depend on the function of the gust molecules. And some potential halomethane sensor will be found in the field of MCPs. Further work for preparing new stable cage-based MCPs functionalized with nonlinear optical molecule is in progress.

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Notes and references

§ To the solution of **L** ligand (0.0340g, 0.065 mmol) and H_3BTC (0.0210 g, 0.100 mmol) in 4 mL DMF and 1 mL H_2O, was added the solution of $Cd(NO_3)_2•4H_2O$ (0.0462 g, 0.150 mmol) then added 1 drops of 6 mol/L HCl. The mixture was heated to 90 °C in a sealed vial for 72 h, then allowed to cool down to room temperature. The colorless block crystals (0.0174 g) of **1** were obtained by filtration and washed with DMF and CH_2Cl_2 three times, respectively. Yield 60.42 % (based on **L** ligand). Calcd for $C_{27.5}H_{26.5}O_{10}CdN_{2.5}$ (Mr= 664.4): C, 49.71; H, 4.02; N, 5.27 %. Found: C, 49.90; H, 3.85; N, 5.41 %. FT-IR (KBr pellet, cm^{-1}): 3416 s, b, 3114 w, 3053 w, 1619 vs, 1576 vs, 1438 m, 1370 vs, 1250 w, 1206 w, 1161 w, 1129 w, 1104 w, 1043 w, 935 w, 876 w, 799 w, 770 m, 732 m, 696 w.

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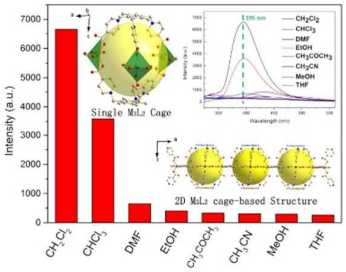

Text:

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