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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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1. Materials and Methods

All the reagents and solvents were commercially available and used as received. The powder X-ray diffraction patterns (PXRD) were collected with a scan speed of 0.5 s/deg on a Bruker Advance D8 (40 kV, 40 mA) diffractometer with Cu radiation (λ= 1.54056 Å) at room temperature. FT-IR data were recorded on VERTEX 80 with KBr pellets in the 4000 – 400 cm^{-1} region. Elemental analyses (EA) for C, H and N were performed on Vario ELIII. TGA data were obtained on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 10 °C min^{-1} under N_2 atmosphere. Diffuse reflectance spectrum were recorded on a U-41000 Spectrophotometer (Liquid) using $BaSO_4$ powder as a 100% reflectance reference. The solid state luminescence spectra were given by F-4500 FL spectrophotometer (EX Slit: 10.0 nm, EM Slit: 10.0 nm and PMT Voltage: 500 V). The fluorescence properties of compound **1** in different solvents were given by F-4500 FL spectrophotometer (EX Slit: 10.0 nm, EM Slit: 10.0 nm and PMT Voltage: 500 V). Sample treated: In the fluorescence measurements of different solvents, 2 mg of well-grounded compound **1** were added in 3 mL of different organic solvents. After treatment by ultrasonication for 3h, the mixtures were aged for 3 days in order to form stable suspensions before the fluorescence measurements. In the 1H-NMR measurements, the title compound **1** was immerged in the solvents of CH_2Cl_2 and $CHCl_3$ overnight, respectively, and dry in the room temperature. Then, the treated sample was immerged in the deuterated solvent of d_6-DMSO for 6 h. At last, the liquid supernatant was collected for the ^{1}H-NMR experiment. In the CH2Cl2-exchanged TGA measurements, the samples were immerged in the solvent of CH_2Cl_2 overnight and dry in the room temperature.

2. X-ray crystallography

Single-crystal X-ray crystallographic studies: Data were collected on a Bruker Smart APEX II diffractometer with a CCD area detector. Raw data collection and reduction were done using APEX2 software.[1] Adsorption corrections were applied using the SADABS routine. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package.[2] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms of L ligand and H_3BTC were calculated in ideal positions with isotropic displacement parameters. Free solvent molecules of DMF and water for compound were highly disordered, and were unsuccessful to locate and refine the solvent peaks. The diffuse electron densities resulting from the these residual solvent molecules were removed from the data set using the SQUEEZE routine of PLATON and refined further using the data generated.[3] The contents of the solvent region are not represented in the unit cell contents in crystal data. The final formula of compound **1** was calculated from elemental analysis and TGA data, so the final formula and formula weight are different from those expected from the data set which is removed the diffractions of guest molecules. Crystal data for **1**: $C_{27.5}H_{26.5}O_{10}N_{2.5}Cd$, FW=664.4, Trigonal, space group R-3c, a=17.9949(7) Å, c=64.9775(8) Å, V=18221(2) Å^3, Z=18, d_{calcd}=0.986 gm^{-3}, $R_1(I>2s(I))=0.0626$, wR_2(all data)=0.2203, GOF=1.012. CCDC 1402379 (**1**) contains the supplementary crystallographic data for this communication. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. PXRD with rietveld refinements.

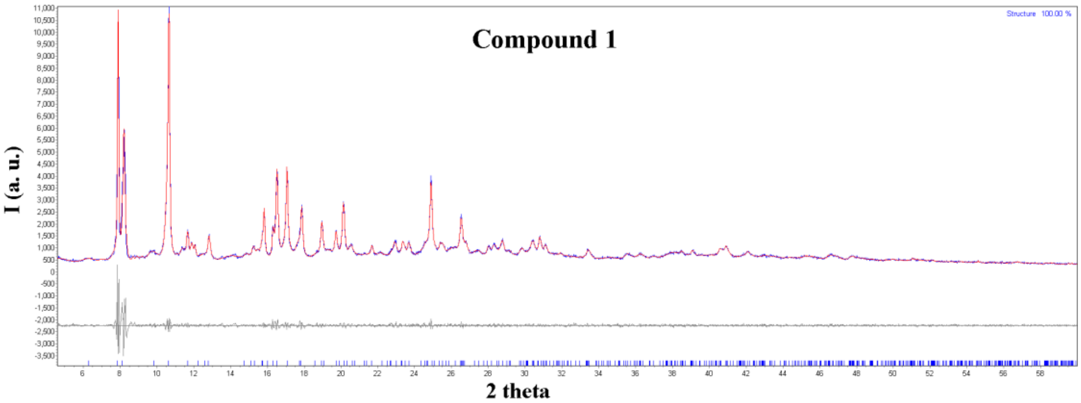


Figure S1. The Rietveld refinements of compound **1**: the red line is the best fitted, the blue line is as-synthesized and the gray line is the difference. The Bragg positions are marked as blue bars. The best fitting results for **1**: a = 17.975(2), c = 65.20(1) Å, which is in an excellent agreement with the single crystal x-ray diffraction results.

4. TGA, DTG and PXRD for the sample in DMF, air and after thermal treatment.

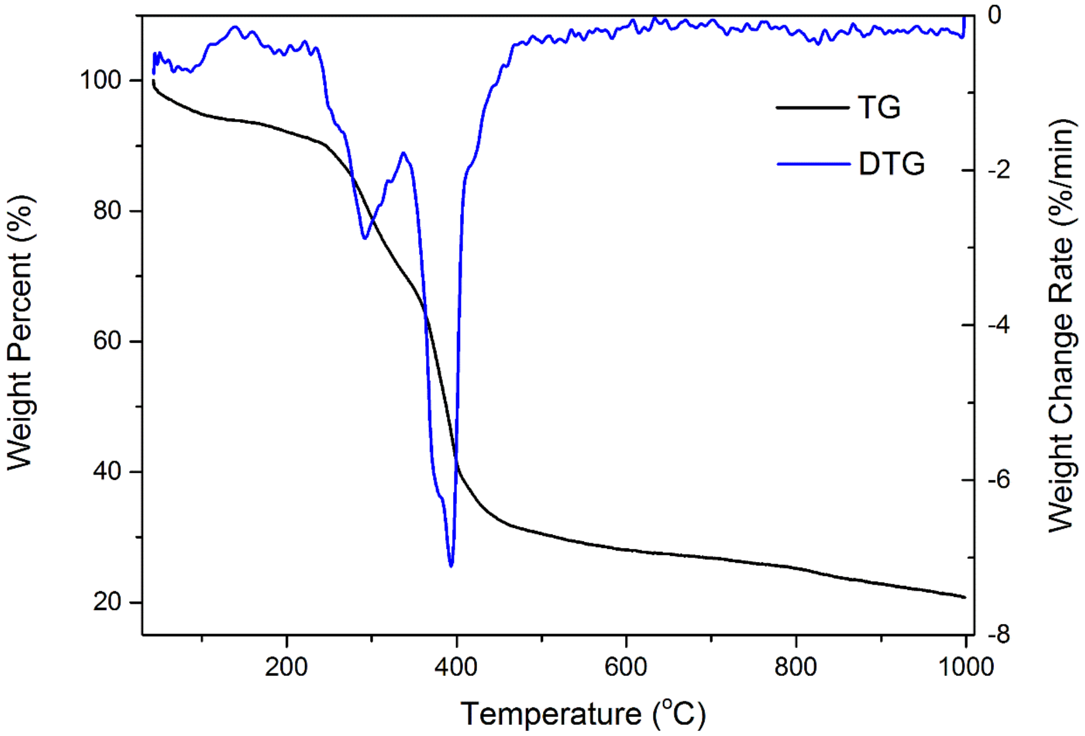


Figure S2. TGA plots of compound **1**. The weight loss of 4.7 % (calcd 4.1 %) from r.t. to ca. 95 °C is assigned to the release of guest water molecules and the weight loss in the range of ca. 95 – 250 °C is assigned to the remove of guest DMF molecules (exptl 5.8 %; calcd 6.4 %). From ca. 250 to ca. 340 °C, the weight loss of 20.3 % (calcd 19.9 %) is assigned to the release of BTC^{3-}. Above 340 °C, it started to lose its L ligand as a result of thermal decomposition. The residue (exptl 28.2 %) is about the mixture of CdO (calcd 19.2 %) and carbon at ca. 600 °C.

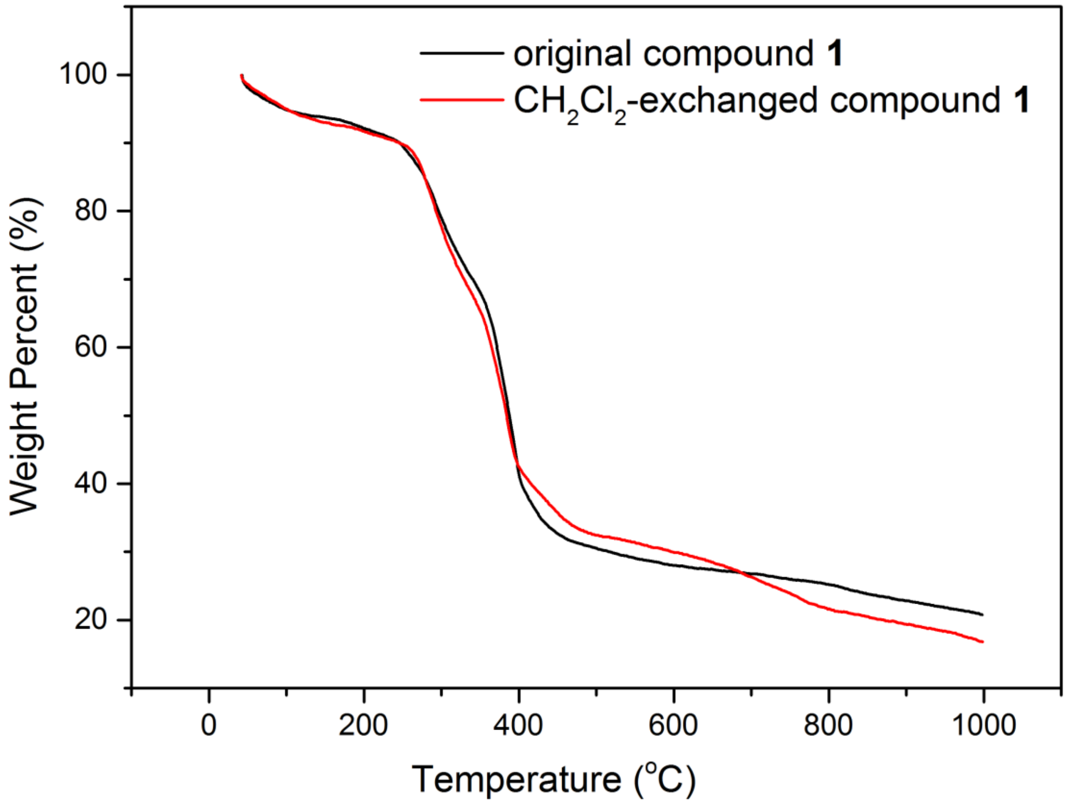


Figure S3. The TGA experiments of the original and the so-called "CH_2Cl_2-exchanged" samples carried out in the same conditions. With the little difference what may be caused by the system error of the thermogravimetric analyzer, we think the guest molecules are not exchanged.

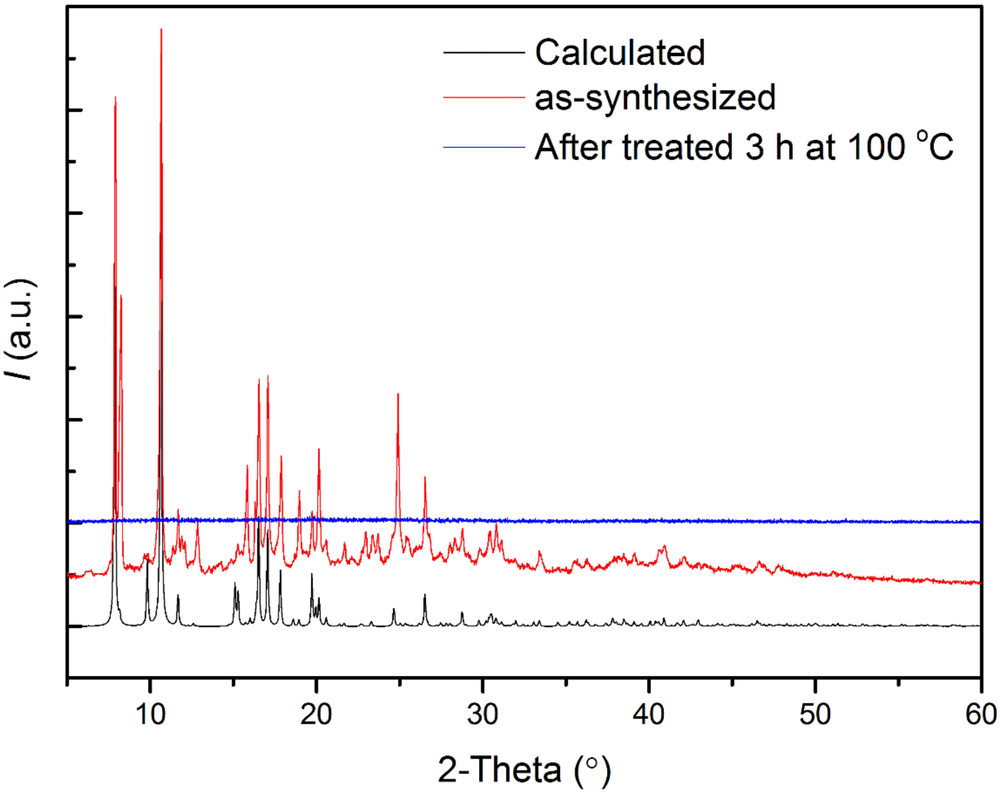


Figure S4. The PXRD patterns of compound **1.** The black line was calculated, the red line was the sample placed in DMF for two weeks and then in air for two weeks, the blue line was the sample after being heated to 100 °C and then maitained for 3 h. The red line contained many peaks and matched the black line beautifully, while the blue line was an approximately straight one which indicated that the framework was collapsed and changed into amorphous phase after loosing some guest molecules. Those revealed that compound **1** was very stable in the solvent (DMF) or air, but unstable after thermal treatment which was the reason for not to carry out the porosity measurements (BET Measurement with N_2).

5. Diffuse reflectance spectrum

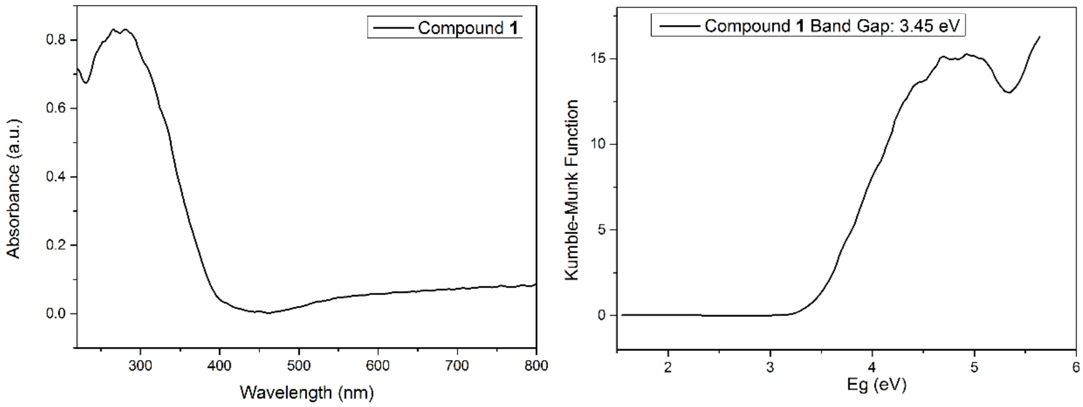


Figure S5. The solid-state diffuse reflectance UV-Vis spectra for compound **1**. The result of right picture was treated with Kumble-Munk fuction. The band gap of compound **1** is 3.45 eV.

6. Solid-state emission spectra

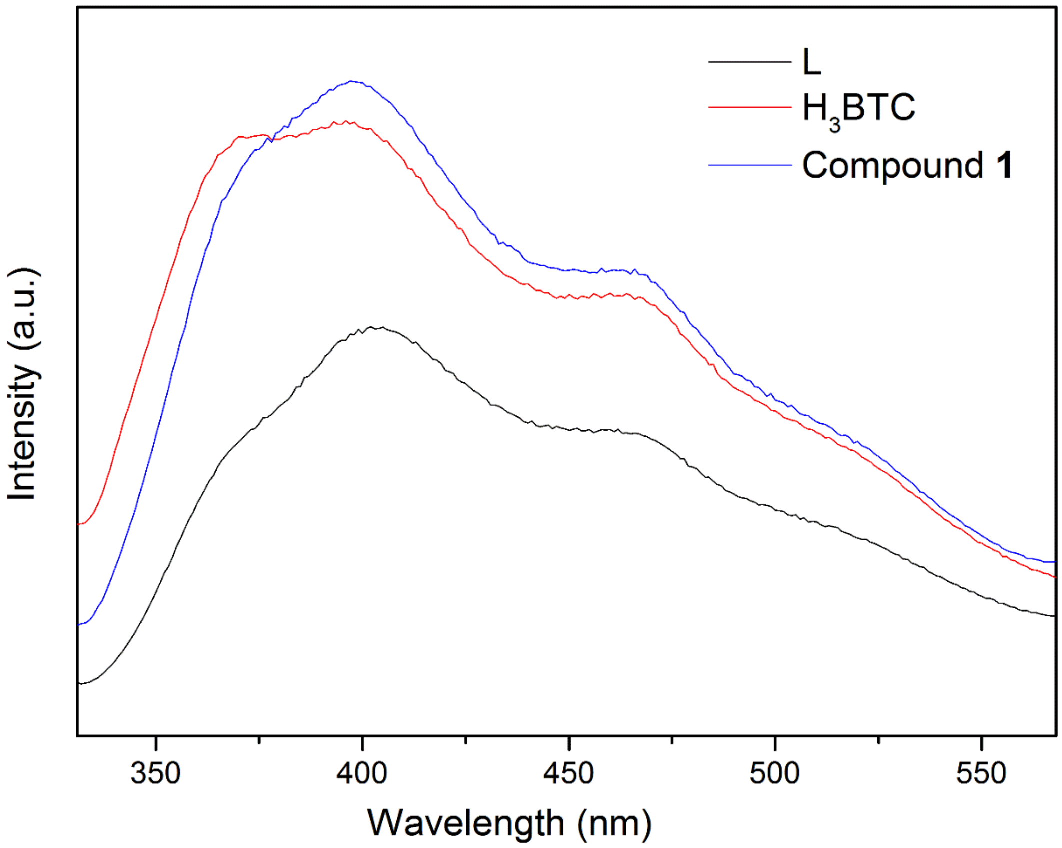
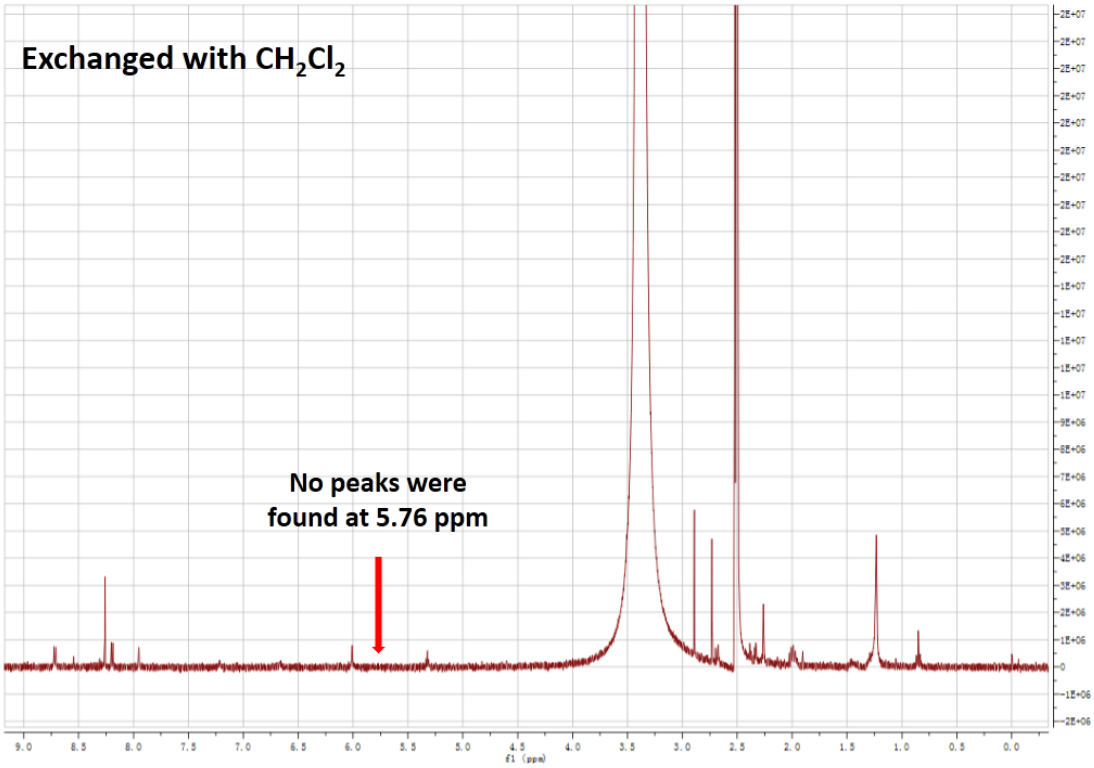


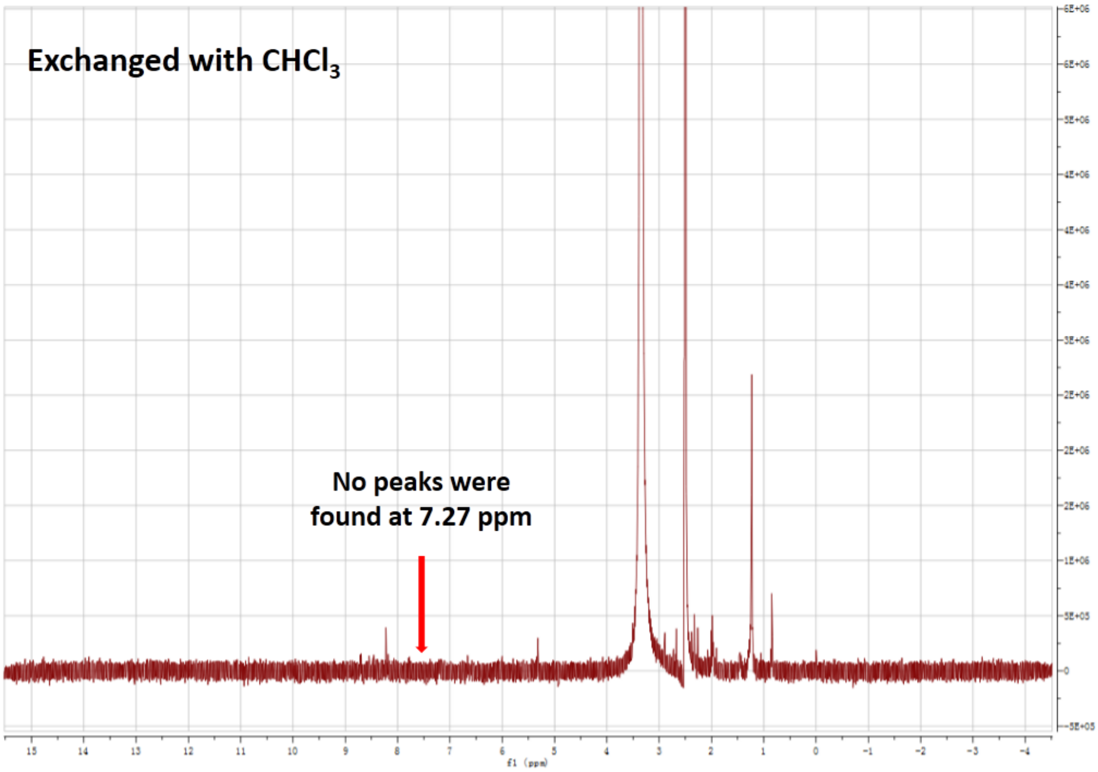
Figure S6. The solid-state emission spectra for **L** ligand, H_3BTC and compound **1** (excited at 300 nm).

7. ^{1}H-NMR of the guest-exchanged liquid supernatant



Exchanged with CH_2Cl_2

No peaks were found at 5.76 ppm



Exchanged with $CHCl_3$

No peaks were found at 7.27 ppm

Figure S7. The ^{1}H-NMR experiments of liquid supernatant in CH_2Cl_2-exchanged and $CHCl_3$-exchanged compound **1** with d_6-DMSO.

8. Additional structural figures

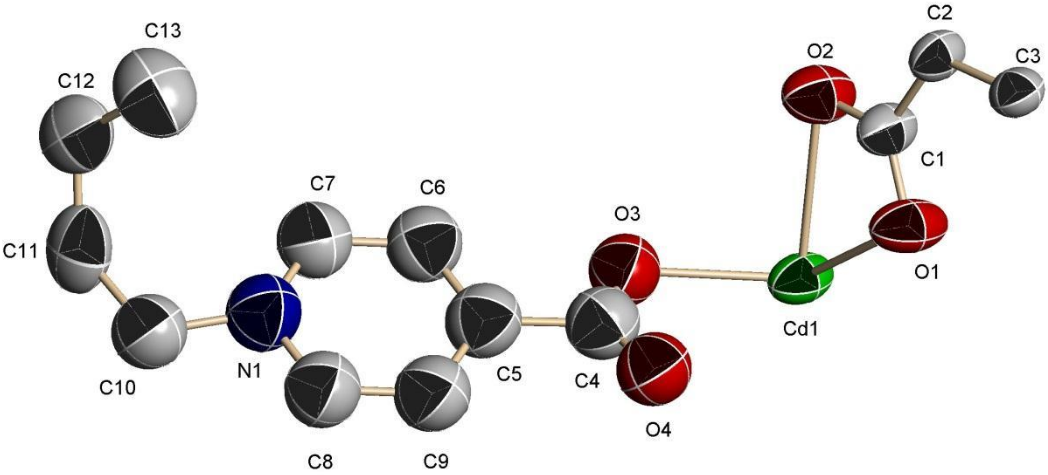


Figure S8. The asymmetric unit of compound **1**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

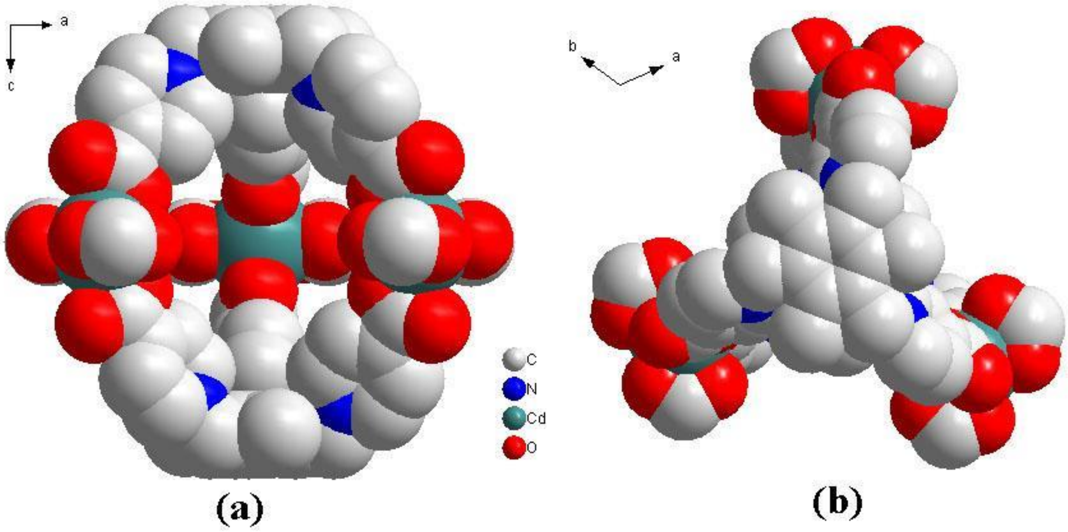


Figure S9. The space filling of M_3L_2 cage in compound **1**. At **b** (a) and **c** (b) directions. Hydrogen atoms are omitted for clarity.

Reference:

[1] Bruker AXS, SAINT Software Reference Manual, Madison, WI, **1998**

[2] G. M. Sheldrick, Acta Crystallogr. Sect. A **2008**, 64 112.

[3] A. L. Spek, J. Appl. Crystallogr. **2003**, 36, 7–13.