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A Solvothermally in Situ Generated Mixed-ligand Approach for NLO-Active Metal–Organic Framework Materials

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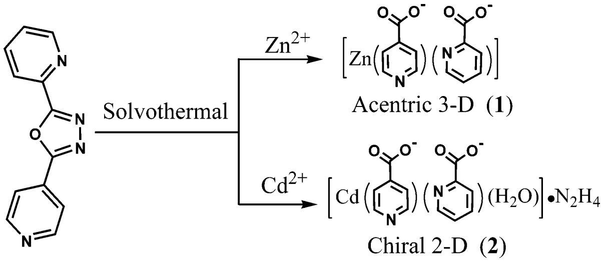
The synthesis and crystal structures of two new NLO-active coordination polymers, [Zn(2-pc)(4-pc)] and [Cd(2-pc)(4-pc)(H$_2$O)]·N$_2$H$_4$ (2-pc = 2-pyridine carboxylate, 4-pc = 4-pyridine carboxylate), bridged by in situ generated mixed ligands under solvothermal treatment is described.

Crystal engineering based on noncentrosymmetric metal–organic frameworks (MOFs) using asymmetric bridging ligands as building blocks has attracted much attention because acentric MOFs have potential applications as second-order nonlinear optical (NLO) materials, in which significant progress in the generation of acentric MOFs using a single kind of bridging ligands and d^{10} metal ions has been demonstrated, although it is still a formidable challenge.[1–4] We believe that MOFs constructed with mixed bridging ligands might have a higher probability to exhibit NLO activity, although such a strategy still remains unexplored. However, control of the construction of MOFs with mixed-ligand bridges such that they have polarity and chirality requires rational design of the ligands and appropriate synthetic techniques.

Meanwhile, the hydro(solvo)thermal technique has recently been successfully applied to synthesize MOFs with in situ generated carboxylate ligands via the hydrolysis of α,β-diketone,[5] cyano,[6] ester,[2] and C=C[7] groups. More importantly, the in situ generation of ligands seems to play an important role in the formation of the crystal structures and favors acentric crystallization.[2] This fact encourages us to explore unprecedented in situ generation of two different organic ligands from one precursor as a strategy for assembling acentric MOF crystals under hydro(solvo)thermal conditions.

Scheme 1. Self-Assembly of the in Situ Generated, Acentric Bridging Ligands with Zn(II) or Cd(II) Ions



Therefore, we extended our study on solvothermal ligand reactions[8] to include solvothermal reactions using 2-(2-pyridyl)-5-(4-pyridyl)-1,3,4-oxadiazole (PPO)[3e] (Scheme 1) and metal acetates, in which PPO bears different functional groups. Fortunately, a new in situ solvothermal hydrolysis reaction on PPO took place, giving rise to two new, colorless crystalline MOFs, namely, [Zn(2-pc)(4-pc)] (**1**) and [Cd(2-pc)(4-pc)(H$_2$O)]·N$_2$H$_4$ (**2**) (2-pc = 2-pyridine carboxylate, 4-pc = 4-pyridine carboxylate), bridged by two asymmetric

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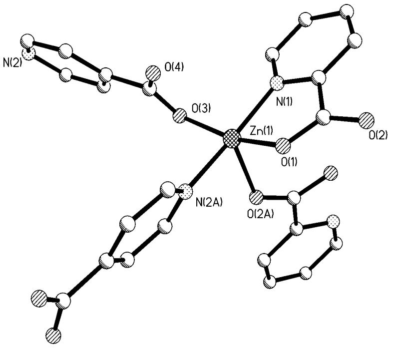

Figure 1. Coordination environment of the metal atom in **1**.

ligands 2-pc and 4-pc.[9] **1** and **2** crystallize in the acentric and chiral space groups $Pna2_1$ and $P2_1$, respectively. Obviously, the PPO oxadiazole group was broken up into the two carboxylate groups of 2-pc and 4-pc during the reaction, resulting in the formation of MOFs in the same 1:1:1 molar ratio of metal to 2-pc to 4-pc.

The crystal structure[10] of **1** reveals that each metal atom is five-coordinated by two nitrogen atoms from one 2-pc and one 4-pc ligands and three oxygen atoms from one 4-pc and two 2-pc ligands [Zn−N, 2.013(3)−2.024(3) Å; Zn−O, 1.934(2)−2.220(3) Å; N−Zn−N, 172.63(11)°; O−Zn−O, 97.51(11)−164.20(11)°; N−Zn−O, 79.64(10)−95.99(11)°] in a distorted trigonal-bipyramidal geometry (Figure 1). The Zn(II) ions are linked by syn-anti carboxylate groups from 2-pc ligands into infinite helical chains with a pitch of 6.012(3) Å along a 2_1 screw axis in the *c* direction. Interestingly, such chains crystallize in both (*P*) right-handed and (*M*) left-handed fashions, as shown in Figure 2a,b and are extended to a three-dimensional (3-D) network through the 4-pc bridges, as illustrated in Figure 2c. Thus, the zinc ions act as 4-connected nodes and are linked by the 2-pc and 4-pc linkers to form the 3-D network. Topological analysis shows that **1** is a new example of the nonuniform 4-connected 3-D nets predicted by Wells,[11] as shown in Figure 2d, being characterized by a short vertex symbol ($6^3.8^2.10$).[12]

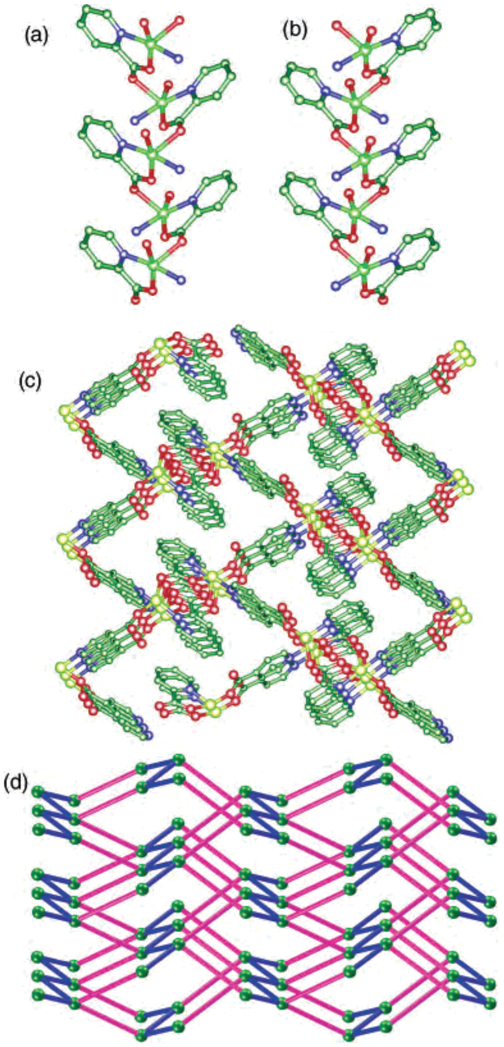

Figure 2. (a) *P* helix and (b) *M* helix along the *c* axis in **1** (4-pc ligands were omitted for clarity), and (c) 3-D net and (d) topological $6^3.8^2.10$ net in **1**.

In **2**, the Cd(II) atom exhibits a distorted pentagonal-bipyramidal geometry [Cd−N, 2.357(4)−2.397(4) Å; Cd−O, 2.272(3)−2.609(4) Å; N−Cd−N, 91.2(2)°; O−Cd−O, 51.9(2)−152.5(2)°; N−Cd−O, 69.10(14)−173.5(4)°], being additionally ligated by one aqua ligand when compared to that in **1** (Figure 3).[10] Differently, **2** has a layer structure, featuring homochiral, right-handed (*P*) helices with a pitch of 8.618(1) Å formed by the Cd(II) ions and syn-anti carboxylate groups of 2-pc ligands (Figure 4) that are related by the 2_1 screw axes in the *b* direction. Such chains are extended to a nonuniform 2-D (4,4) grid through 4-pc bridges

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(9) Typical experiments for the syntheses of **1** and **2**: To an aqueous solution (8 mL) of $Zn(MeCO_2)_2 \cdot 6H_2O$ (0.058 g, 0.2 mmol) for **1** or $Cd(OAc)_2 \cdot 2H_2O$ (0.1 mmol) for **2** was slowly added a methanol solution (8 mL) of 2-(2-pyridyl)-5-(4-pyridyl)-1,3,4-oxadiazole (PPO) (0.045 g, 0.2 mmol). The mixture was stirred at room temperature for 30 min. The mixture was placed in a 23-mL Teflon-lined autoclave and heated at 140 °C for 36 h. The autoclave was then cooled to room temperature over a period of 8 h at a rate of 5 $°C \cdot h^{-1}$, and **1** or **2** as colorless crystals were collected by filtration, washed with water, and dried in air. Phase-pure crystals of **1** or **2** were obtained by manual separation. The final yields were 60% and 65% based on M for **1** and **2**, respectively. Anal. Calcd (%) for **1**: C, 46.56; H, 2.60; N, 9.05. Found: C, 46.48; H, 2.59; N, 9.09. Calcd for **2**: C, 35.44; H, 3.47; N, 13.78. Found: C, 35.50; H, 3.45; N, 13.82.

(10) Crystal diffraction intensities for **1** and **2** were collected at 293 K on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using SADABS. The structures were solved with direct methods and refined with the full-matrix least-squares technique based on F^2 using the SHELXTL program package. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically (C−H = 0.96 Å); the water hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystal data for **1**: $C_{12}H_8N_2O_4Zn$, orthorhombic, space group $Pna2_1$, M_r = 309.59, a = 21.795(5) Å, b = 9.318(3) Å, c = 6.012(3) Å, V = 1221.0(7) Å^3, Z = 4, ρ_{calcd} = 1.684 $g \cdot cm^{-3}$, μ = 2.022 mm^{-1}, $F(000)$ = 624, 6426 collected reflections, 2248 unique reflections (R_{int} = 0.0249), R1 = 0.0321, wR2 = 0.0780, Flack parameter x = 0.04(2), GOF = 1.028 for all data. Crystal data for **2**: $C_{12}H_{14}CdN_4O_5$, monoclinic, space group $P2_1$, M_r = 406.67, a = 9.600(1) Å, b = 8.618(1) Å, c = 11.478(1) Å, β = 107.693(2)°, V = 904.7(2) Å^3, Z = 2, ρ_{calcd} = 1.493 $g \cdot cm^{-3}$, μ = 1.231 mm^{-1}, $F(000)$ = 404, 5463 collected reflections, 3457 unique reflections (R_{int} = 0.0182), R1 = 0.0353, wR2 = 0.1012, Flack parameter x = −0.03(4), GOF = 1.141 for all data.

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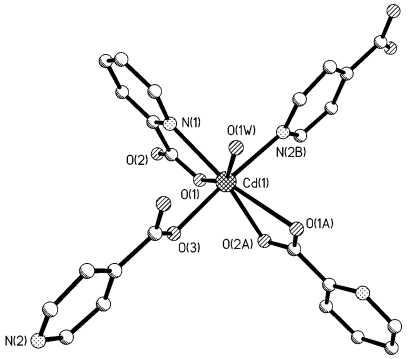

Figure 3. Coordination environment of the metal atom in **2**.

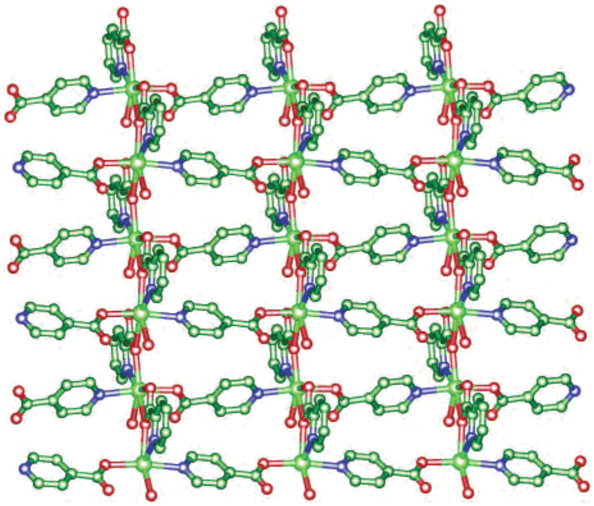

Figure 4. Top view of the chiral 2D net along the *c* axis in **2**.

(Figure 4). The guest N_2H_4 molecules derived from the hydrolysis of PPO are clathrated between the layers (Figure S1 in the Supporting Information).

Preliminary quasi-Kurtz powder second-harmonic generation (SHG) measurements[13] on powdered **1** and **2** exhibited modest SHG efficiencies approximately 3.5 and 1.5 times than that of KDP, respectively. TGA analyses showed that **1** was decomposed at 455 °C (Figure S2 in the Supporting Information), whereas **2** had a weight loss of ca. 11.9% in the temperature range of 100−253 °C, corresponding to the loss of one aqua ligand and one lattice hydrazine molecule per formula unit (calcd 12.3%), and no obvious weight loss then up to 320 °C (Figure S3 in the Supporting Information). Both **1** and **2** are insoluble in common solvents owing to their neutral 3-D and 2-D polymeric structures, and they might serve as potential candidates for practical NLO applications.

It is noteworthy that we failed in preparing both **1** and **2** via direct reactions of the Zn(II) and Cd(II) salts, respectively, with a 1:1 mixture of 2-pc and 4-pc under very similar reaction conditions, which led to white microcrystalline products exhibiting no SHG effect. This fact implies that **1** and **2** might be unable to be prepared directly from a mixture of 2-pc and 4-pc. Therefore, it can be concluded that the in situ ligand generation is propitious to the formation of acentric crystals of **1** and **2**, although further studies are needed to better understand this phenomenon.

In summary, this work implies that self-assembly of MOFs via solvothermal in situ generation of mixed organic ligands might be a useful route in controlling both the stoichiometries and crystal structures and hence presents a new synthetic approach for NLO-active and even other functional MOF materials constructed by mixed organic ligands.

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Supporting Information Available: X-ray crystallographic files in CIF format, TGA curves, IR data, and additional plots for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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