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A Strategy for Synthesis of Ionic Metal-Organic Frameworks

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For the first time, we designed and synthesized a new kind of ionic metal-organic framework with lanthanide ions and a carboxyl-functionalized ionic liquid, including $[Er_4(\mu_3\text{-}OH)_4(\mu_2\text{-}O)_{0.5}OL_4(H_2O)_3]\cdot Br_{2.90}\cdot Cl_{1.10}\cdot 2H_2O$ (MOF-**1**) and $[PrL(H_2O)_4Cl]\cdot Br\cdot H_2O$ (MOF-**2**).

Porous hybrid inorganic−organic solids have been extensively studied recently due to their interesting structures coupled with their promising applications in gas storage, separation, and catalysis.[1] The pore size/shape and overall porous activity can be tuned by rationally designing the appropriate ligands.[2] However, metal-organic frameworks (MOFs) are predominantly built up from the neutral organic molecules containing N and O donors as bridging links. And, introducing a functional part into open-framework structures may open a new era in the design of new materials.

Traditionally, ionic liquids (ILs), as potential environmentally benign reaction media, have been successfully used in catalysis reactions, separations, electrochemistry, and so on.[3] A variety of functionalized ILs have been developed in order to modify their physical and chemical properties for wider applications.[4,5] Until now, there are no reports of lanthanide MOFs using ILs as bridging links. Due to their high coordination number and variable coordination environments of lanthanide ions, the introduction of polynuclear clusters into MOFs may lead to new materials that possess fascinating structures and special properties.[6]

Herein, a carboxyl-functionalized IL, 1,3-dimethylcarboxylic acid imidazolium bromine, $[(CH_2COOH)_2im]Br$ (H_2LBr), was synthesized and characterized. And the imidazolium-centered dicarboxylate as the bridging ligand was introduced into the construction of lanthanide coordination polymers for the first time. Reactions of $LnCl_3\cdot 6H_2O$ (Ln = Er or Pr) with imidazolium dicarboxylic acid in the mixed solvents result in two novel ionic MOFs,[7,8] including $[Er_4(\mu_3\text{-}OH)_4(\mu_2\text{-}O)_{0.5}OL_4(H_2O)_3]\cdot Br_{2.90}\cdot Cl_{1.10}\cdot 2H_2O$ (MOF-**1**) and $[PrL(H_2O)_4Cl]\cdot Br\cdot H_2O$ (MOF-**2**).

The asymmetric unit of MOF-**1** contains four crystallographically independent Er(III) atoms, and each Er(III) atom is eight-coordinate. Three types of coordination modes of the complete deprotonated ligands L^- are present in the structure: (1) each carboxylate group of the L^- ligand adopts a bridging bidentate mode; (2) one carboxylate group of L^- ligands adopts a bridging bidentate mode, while the other adopts a bridging monodentate mode; (3) each carboxylate group of the L^- ligand adopts a chelating bidentate mode. The average distances of $Er-O(H_2O)$, $Er-O(\mu_3\text{-}OH)$, and $Er-O(COO^-)$ are 2.395, 2.338(6), and 2.333 Å, respectively.

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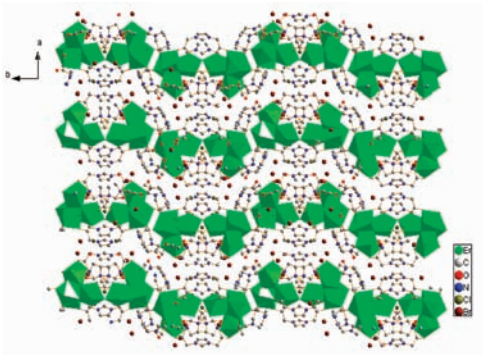

Figure 1. 1D chain in MOF-**1** viewed along the *b* axis. Polyhedra represent ErO_8 (H atoms are omitted for clarity).

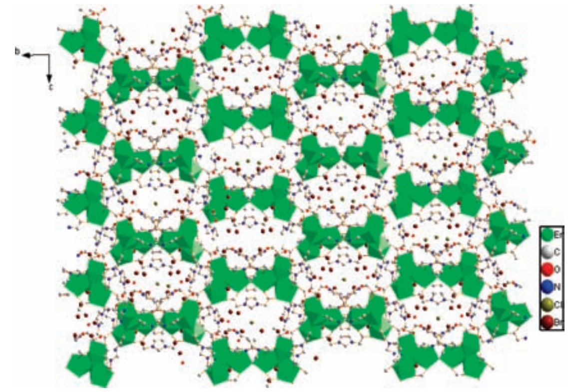

Figure 2. View of MOF-**1** down the *a* axis. Polyhedra represent the ErO_8 (H atoms and hydrogen bonds are omitted for clarity).

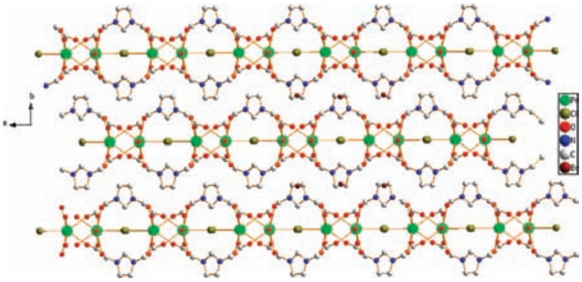

Figure 3. 1D chains of MOF-**2** along the *a* axis (H atoms and hydrogen bonds are omitted for clarity).

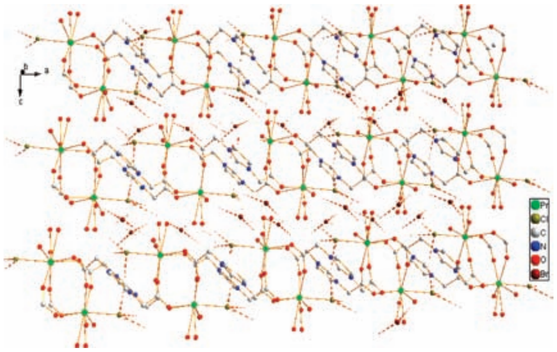

Figure 4. View of MOF-**2** in the *ac* plane. Hydrogen bonds from Br and Cl atoms shown as dotted lines (H atoms are omitted for clarity).

The cubanelike $[Er_4(\mu_3\text{-}OH)_4]^{8+}$ cores exist in the structure, and each μ_3-OH interlinks four unique Er(III) atoms, with nonbonding Er···Er distances of 3.692(5)−3.781(5) Å and angles Er···Er···Er of 58.73−61.07°. A little distortion of the core from a perfect cube is reflected by the values of Er−O(μ_3-OH)−Er (103.5−108.7°, average 106.6°) and O(μ_3-OH)−Er−O(μ_3-OH) (68.40(2)−72.20(2)°, average 70.25°). All of these structural parameters compare well with those in $[Er_4(\mu_3\text{-}OH)_4(Val)_5(H_2O)_{10}](ClO_4)_8$ and $[Er_4(\mu_3\text{-}OH)_4(Glu)_3(H_2O)_8](ClO_4)_5$.[6b] Each tetranuclear cluster is linked through ligands resulting in a unique inorganic chain along the *b* axis (Figure 1), with an Er1···Er1 distance of 4.863 Å and a nonlinear Er1−O(19)−Er1 angle of 135.2°. The chains link to each other through ligands leading to a 3D framework, as depicted in Figure 2. The framework contains circular channels down the *a* axis, which encapsulate highly disordered Br^- and Cl^- ions, as well as noncoordinating water molecules. Three kinds of hydrogen-bonding interactions exist in MOF-**1**: (1) hydrogen bonds (C−H···Br/Cl) between the hydrogen of carboxylate ligands and out-of-order Br^-/Cl^- ions, (2) hydrogen bonds (O−H···Br) between the hydrogen of μ_3-OH's and out-of-order Br^- ions, and (3) hydrogen bonds (O−H···Br) between the hydrogen of coordinated water and out-of-order Br^- ions.

Notably, the structure of MOF-**2** is completely different from that of MOF-**1**. In MOF-**2**, Pr(III) is nine-coordinate, including one chlorine, eight oxygen atoms of carboxylate ligands, and water molecules. The distances of Pr−O(H_2O) are 2.445−2.584 Å, and those of Pr−O(COO^-) are 2.425−2.461 Å. The average distance of Pr−O (2.481 Å) is comparable to that of 2.473(12) Å in [Pr(4,4′-Hbpdc)(4,4″-bpdc)$(H_2O)_2$][9] and 2.418(3) Å in $[Pr(C_6H_{11}NO)_6Cl)]Cl_2$,[10] which have neutral carboxylic acids as ligands. The distance of Pr−Cl (2.765(17) Å) can be compared to that in $[Pr(C_6H_{11}NO)_6Cl)]Cl_2$ (2.757(2) Å). The Pr(III) atoms are linked via bridging imidazolium carboxylic acid forming 1D chains along the *a* axis (Figure 3). And the hydrogen bonds bring the moieties into a 2D network in the *ac* plane, as seen in Figure 4. In fact, there are two types of hydrogen bonds in MOF-**2**: (1) hydrogen bonds (O−H···Br/Cl) between the hydrogen of coordinated water and Br^- (Cl) and (2) hydrogen

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(7) Synthesis for $[Er_4(\mu_3\text{-}OH)_4(\mu_2\text{-}O)_{0.5}OL_4(H_2O)_3]\cdot Br_{2.90}\cdot Cl_{1.10}\cdot 2H_2O$ (MOF-**1**): The mixture of $ErCl_3\cdot 6H_2O$ (0.0511 g, 0.134 mmol), H_2LBr (0.524 g, 0.198mmol), an aqueous solution of NaOH (1.0 mL, 0.30 mmol), H_2O (1 mL), and EtOH (9 mL) was heated in a 23 mL capacity stainless-steel reactor with a Teflon liner at 150 °C for 3 days and then cooled to room temperature. Pale-pink prismy crystals of MOF-**1** were obtained. Yield: 0.889 g (90%). Anal. calcd for $C_{28}H_{42}Br_{2.90}Cl_{1.10}Er_4N_8O_{26.50}$ (Found): C, 18.13 (17.82); H, 1.44 (1.45); N, 6.04 (5.94)%. IR data (KBr, cm^{-1}): 3379, 1613, 1448, 1409, 1316, 1176, 774, 674. For $[PrL(H_2O)_4Cl]\cdot Br\cdot H_2O$ (MOF-2): Green crystals of MOF-**2** were prepared in the same manner as above. Yield: 13.4 mg (20%). Anal calcd for $C_7H_{17}BrClN_2O_7$ (Found): C, 16.89 (16.47); H, 3.45 (3.33); N, 5.63 (5.51)%. IR (KBr, cm^{-1}): 3376, 1668, 1616, 1391, 1315, 1170, 969, 840, 777, 667.

(8) Crystal data for MOF-1: $M = 1854.47$, $T = 113(2)$ K, $\lambda = 0.71073$ Å, orthorhombic, *Pnma*, $a = 25.0161(8)$ Å, $b = 31.9509(12)$ Å, $c = 13.2163(6)$ Å, $V = 10563.6(7)$ Å^3, $Z = 8$, $D_{calcd} = 2.332$ Mg m^{-3}, $\mu = 8.627$ mm^{-1}, GoF = 1.180, $R_{int} = 0.0781$, $R_1 = 0.0551$, wR_2(all) = 0.1373. CCDC 673122. For MOF-2: $M = 497.50$, $T = 113(2)$ K, $\lambda = 0.71073$ Å, monoclinic, *C*12/*m*1, $a = 8.7533(18)$ Å, $b = 17.854(4)$ Å, $c = 8.6180(17)$ Å, $V = 1339.3(5)$ Å^3, $Z = 4$, $D_{calcd} = 2.467$ Mg m^{-3}, $\mu = 6.850$ mm^{-1}, GoF = 1.093, $R_{int} = 0.0390$, $R_1 = 0.0243$, wR_2(all) = 0.0662. CCDC 673123.

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bonds (C−H···Cl) between the hydrogen of the carboxylate ligand and chlorine.

In summary, we have developed a rational synthetic approach toward MOFs using a carboxyl-functionalized IL as a bridging link. To the best of our knowledge, compounds **1** and **2** represent the first examples of ionic lanthanide coordination frameworks based on ILs. This work demonstrates that introducing a functional part into an open framework opens up new possibilities in crystal engineering and the fabrication of new materials. Therefore, following the strategy proposed in this work, it is expected that more and more adjustable functionalized MOFs can be designed and synthesized with novel structures and wider applications in the future.

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Supporting Information Available: Description of the H_2LBr ligand and its coordination modes in the MOFs. Crystallographic data for MOF-**1** and MOF-**2** and full details of the structures of the coordination polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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