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# A Multifunctional 3D Ferroelectric and NLO-Active Porous Metal−Organic Framework

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The construction of porous metal−organic frameworks (MOFs) is of great interest due to their potential applications in host−guest molecular interactions, catalysis, gas storage, and separation.[1] One of current efforts focuses on introducing additional functionalities into porous MOFs, for instance, porous MOF based magnets.[2] Since the discovery in 1920, ferroelectric materials have demonstrated remarkable utility in microwave devices, semiconductor chips, and miniature X-ray and neutron sources.[3] Notably, ferroelectric complexes are increasingly attractrive in the assembly of predesigned organic spacers.[4] On the other hand, second-order nonlinear optical (NLO) materials have also undergone rapid development owing to the versatile applicability of optoelectronic devices and photonics technologies.[5] Hence, incorporation of both ferroelectric and second-order NLO properties into porous MOFs may lead to novel multifunctionality in the resultant materials.

The basic requirement for ferroelectric and second-order NLO properties is that the material must be noncentrosymmetric. The synthesis of noncentrosymmetric porous MOFs is a highly interesting and challenging task.[6] To lower the energy of system, the symmetric information in organic motifs or molecular building blocks (MBBs) is likely to transmit to the whole framework.[7] Herein, we will report the use of a tetracarboxylic ligand $H_4X$[8] ($H_4X$ = tetrakis[4-(carboxyphenyl)oxamethyl]methane acid) with Zn(II) metal centers, to generate a ferroelectric and NLO-active porous MOF $[Zn_2(X)(CH_3CH_2OH)]\cdot 3H_2O$ (**1**) with chiral secondary building units (SBUs).

The structure of complex **1** was solved by a single-crystal X-ray diffraction method in noncentrosymmetric space group $C_c$ (point group $C_s$). The asymmetric unit contains one $X^{4-}$ ion, one ethanol molecule, two crystallographic-independent Zn(II) ions, and three guest water molecules. As depicted in Figure S1, the Zn1(II) ion is bonded by two chelated and two bridging carboxylate groups to form a $ZnO_6$ octahedron. The Zn2(II) ion is five-coordinated by one ethanol molecule and four carboxylate oxygen atoms in a distorted trigonal bipyramid. It is notable that, although each of the four carboxylate groups in the $X^{4-}$ ligand connects the two kinds of Zn(II) polyhedra, the connection modes for carboxylate groups are different: The first carboxylate group (O5−C12−O6) links Zn1 and Zn2 through a chelating/bridging mode, and the two Zn atoms are further bridged by other two carboxylate groups with a Zn1····Zn2 distance of 3.178 Å and Zn1−O6−Zn2 angle of 101.08° (Figure S2a); the second carboxylate group (O7−C19−O8) links Zn1C and Zn2D through a chelating/bridging mode, but the two Zn atoms are not connected by any bridging carboxylate groups with a Zn1C····Zn2D distance of 4.266 Å and Zn1C−O7−Zn2D angle of 142.73° (Figure S2b); the third carboxylate group (O11−C33−O12) connects Zn1A and Zn2A with a bridging mode, and the group lies in the equatorial basal plane of the Zn2A trigonal bipyramid (Figure S2c); the fourth carboxylate group (O9−C26−O10) connects Zn1B and Zn2B through a bridging mode, but the group is in the axial direction of the Zn2B trigonal bipyramid (Figure S2d). Thus the four carboxylate groups of the $X^{4-}$ ligand connect four dinuclear Zn units through different complexation modes to form chiral SBUs (Figure 1a), leading to the formation of noncentrosymmetric complex **1**. The framework of the complex possesses cross-linked diamond (dia) topology: if ignoring the bonding of Zn2−O7, the complex can be simplified as 3D $6^6$-dia networks which are 3-fold interpenetrated and further cross-linked via a Zn2−O7 connection (Figure S4). Through sharing dinuclear Zn units, the chiral building block is extended into a three-dimensional porous framework (Figure 1b). The open channels with cross sections of ca. ∼8.6 × 8.6 Å$^2$ are filled with lattice water molecules. The solvent-accessible volume is ∼1539 Å$^3$ per unit cell, and the pore volume ratio was calculated to be 34.4% by the PLATON program.[9]

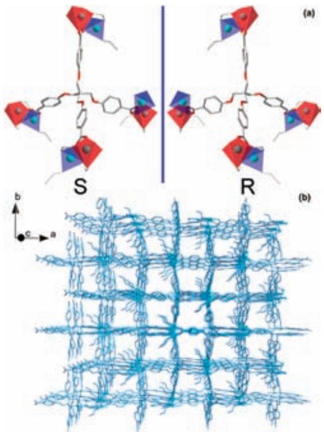

***Figure 1.*** (a) Two kinds of chiral tetrahedral SBUs. (b) Perspective view of the microporous framework: Zn, azury; C, gray; O, red. Lattice water molecules are omitted for clarity.

Thermogravimetric analysis (TGA) of complex **1** under a nitrogen flow reveals a weight loss of 10.6% (calcd 11.9%) from 60 to 175 °C for the removal of lattice water molecules and coordinated EtOH, and the weight loss of 6.9% between 60 to 100 °C may be attributed to the removal of lattice water molecules (calcd 6.4%). The powder X-ray diffraction patterns (PXRD) of dehydrated sample **1b** (after removal of guest water molecules by heating the sample to 120 °C in vacuum) indicates that the host framework is

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retained as compared to that of as-prepared sample **1**. Furthermore, immersing **1b** into $H_2O$ at 25 °C generates **1c**, whose PXRD pattern is almost identical to that of **1a** (simulated, Figure S6), indicating the complete recovery of the structure.

The $N_2$ adsorption isotherm of complex **1** at 77 K (Figure S7) displays a type I sorption behavior. Fitting the BET equation to the $N_2$ adsorption isotherm gives a total pore volume of 0.155 $cm^3\ g^{-1}$ at $P/P_0 = 0.975$. The apparent surface area was calculated using the Langmuir method to be 479 $m^2\ g^{-1}$ (367 $m^2\ g^{-1}$ BET), which confirms the permanent porosity of complex **1**. The pore size is estimated to be 8.74 Å (Figure S8) which is consistent with the aperture size obtained from the crystal structure data. The methane adsorption isotherm shows type-I sorption behavior with an uptake of 2.5 wt % at 80 bar and 295 K (Figure 2). After removal of the terminal bonded EtOH, the amount of hydrogen uptake (36.2 $cm^3\ g^{-1}$) is 272% of that (13.3 $cm^3\ g^{-1}$) before the removal of ethanol at 77 K (Figure 2, inset). It should be noted that very large isosteric heats of $H_2$ adsorption were calculated at low loadings, with a value of 12.46 kJ $mol^{-1}$ at zero loading (CPO-27-Ni, 13.5 kJ $mol^{-1}$)[10] (Figure S11).

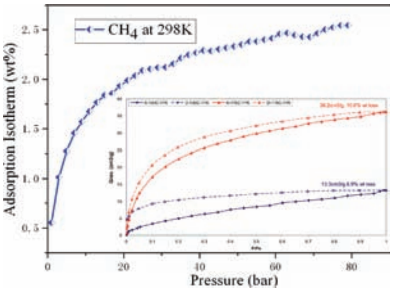

*Figure 2.* Adsorption isotherm of methane at 298 K, and $H_2$ adsorption−desorption isotherms (77 K, inset) activated at 100 °C (blue) and 175 °C (red).

Complex **1** crystallizes in the point group $C_s$, belonging to one of the 10 polar point groups ($C_1$, $C_s$, $C_2$, $C_{2v}$, $C_4$, $C_{4v}$, $C_3$, $C_{3v}$, $C_6$, $C_{6v}$). To detect the ferroelectricity, the hysteresis loops of electric polarization were measured on a single crystal of complex **1** (Figure 3). At 283 K, the remnant polarization (Pr) is ca. 0.01 $\mu C\ cm^{-2}$.

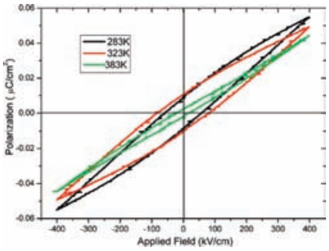

*Figure 3.* Polarization ($P$) versus applied field ($E$) hysteresis loops from a single crystal sample.

We also studied the temperature dependence of dielectric permittivity of a powder sample at 10 kHz, 90 kHz, and 1 MHz (Figure S13) and found that the progress of lattice water removal is consistent with the TGA result. Furthermore, the measurement of second harmonic generation (SHG)[11] shows that complex **1** exhibits an SHG efficiency ∼2.5 times that of potassium dihydrogen phosphate (KDP; KDP is a commercially available NLO reference material and has a $I^{2\omega}$ of ∼10 versus α-quartz). To the best of our knowledge, complex **1** represents the first successful attempt to prepare ferroelectric and NLO-active porous MOFs from chiral tetracarboxylate building blocks.

In summary, we have presented a 3D microporous framework with chiral tetrahedral SBUs constructed by different connections of four carboxylate groups to zinc units. The presence of the chiral SBUs resulted in the formation of a noncentrosymmetric complex **1** with interesting ferroelectric and NLO properties. This work may exploit facile entry for incorporation multifunctionalities into porous MOFs for the preconceived needs in material designs.

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**Supporting Information Available:** Coordination environment of $X^{4-}$ ion, TGA curve, XRPD patterns, Pore size distribution, Nitrogen adsorption isotherm, Isosteric heats of $H_2$ adsorption, Temperature dependence of dielectric permittivity, IR spectrum, Selected bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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