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Ferroelectric Metal−Organic Framework with a High Dielectric Constant

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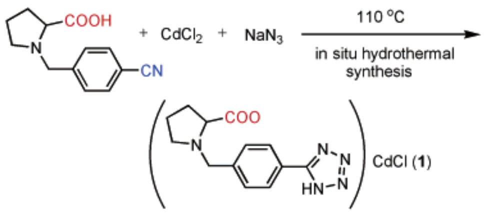
The search for new classes of ferroelectric materials is of immense current interest due to their versatile applicability to modern electric devices such as memory elements, filtering devices, and high-performance insulators.[1] The high permittivity (dielectric constant [ϵ_o])[2] properties of ferroelectric materials have also made them important in the development of dielectric resonators and filters for microwave communication systems.[3] In recent years, much of the attention in this field has been focused on developing ferroelectric inorganic compounds such as KH_2PO_4(KDP), $BaTiO_3$, and $LiNbO_3$.[1] In contrast, studies toward developing ferroelectric materials based on metal−organic frameworks (MOF)[4] have remained sparse. This is surprising in view of recent works by us and others which showed that in situ (2+3) cycloaddition chiral ligand synthesis[5] under hydrothermal reaction conditions provided a convenient and simple route to novel MOFs and the applications of these materials in catalysis, gas storage, nonlinear optics, and molecular recognition and separations.[6] In this context, we were intrigued with the possibility of constructing a MOF that would crystallize in one of the 10 polar point groups essential for ferroelectric behavior, by using an appropriate homochiral organic ligand as building block. Herein, we report the synthesis of novel 3D MOF (**1**) in which **1** displays ferroelectric behavior associated with dielectric loss and thus a relaxation process, which, to our knowledge, is unprecedented.

Colorless block compound **1** was prepared by hydrothermal reaction of *N*-(4-cyanobenzyl)-(*S*)-proline with $CdCl_2$ and excess NaN_3 at 110 °C for 2 days. Product formation was based on elemental analyses and IR spectroscopic measurements revealing two peaks at stretching frequencies typical for that of a carboxylate and tetrazoyl group formed from in situ (2+3) cycloaddition of *N*-(4-cyanobenzyl)-(*S*)-proline with NaN_3 in the presence of $CdCl_2$ as Lewis acid catalyst (Scheme 1).

Scheme 1



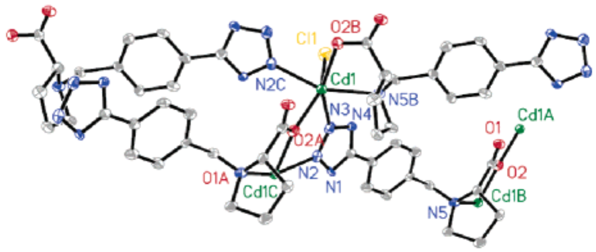


Figure 1. Asymmetric unit representation of **1** with a slightly distorted octahedral Cd coordination geometry. Typical bond distances (Å): Cd1−Cl1 2.305(3), Cd1−N3 2.3417(8), Cd1−O2A 2.264(6), Cd1−O2B 2.372(7), Cd1−N2C 2.309(7), Cd1−N5B 2.369(7).

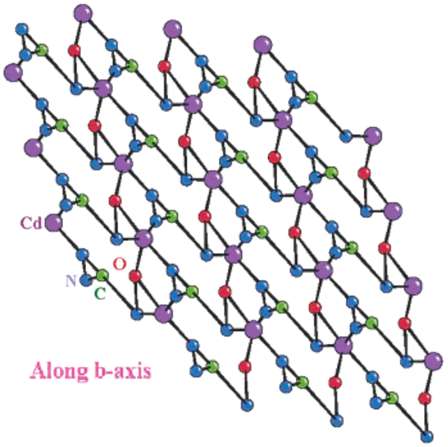


Figure 2. A simplified 2D network along the *b*-axis. The longest straight black lines, triangular C−N−C and O−N units represent the benzyl, tetrazoyl, and pyrrolidinyl groups, respectively.

X-ray single crystal determination of **1** reveals that the Cd center sits in a slightly distorted octahedron that is composed of three N atoms from two tetrazoyl groups and a pyrrolidinyl group, and a terminal Cl atom as well as two O atoms from two carboxylate groups. Each *N*-(4-(1*H*-tetrazol-5-yl)benzyl)proline (H-TBP) ligand acts as a pentadentate bridging linker that connects five Cd atoms, which gives the 3D framework depicted in Figure 1.[7] Notably, an O atom from the carboxylate group of the H-TBP ligand binds to a Cd center that is also linked to a N atom from the pyrrolidinyl ring to give a stable five-membered ring. A second five-membered ring is found along the Cd1−N3−N2−Cd1C−O2A bonding sequence with the μ_2-O atom from the H-TBP carboxylate group connecting two Cd ions that are also linked together via two N atoms from the tetrazoyl group. The C−C, C−N, C−O, and Cd−Cl distances are unexceptional and comparable to those reported in the literature. Figure 2 shows a simplified net representation of **1** along the *b*-axis that consists of three types of nets: (a) a nine-membered ring formed from four N atoms, two C atoms, an O atom, and two Cd atoms; (b) a five-membered ring formed from two N atoms, an O atom, and two Cd atoms; and (c) two different three-membered rings, the first arising from a tetrazoyl group acting as a μ_2-linker and the second arising from chelation of the five-membered proline ring. Interestingly, a view along the *a*-axis reveals

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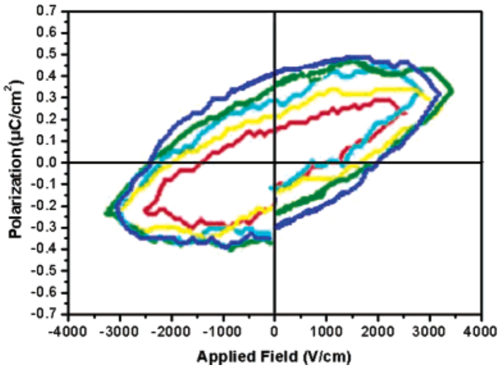

Figure 3. Electric hysteresis loop of a pellet obtained from a powdered sample of **1** observed by Virtual Ground Mode using an RT6000 ferroelectric tester at room temperature.

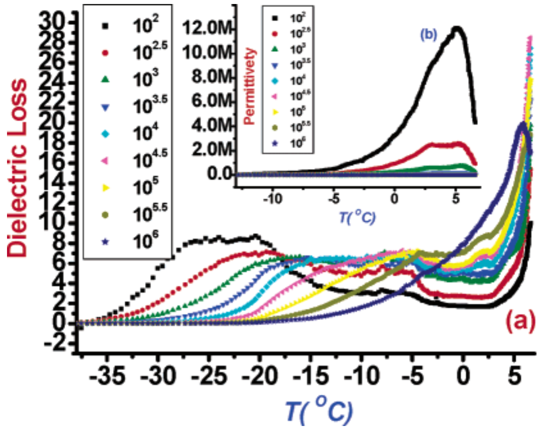

Figure 4. (a) Temperature dependence of the dissipation factor (or loss component = dielectric loss, tanδ = ϵ_2/ϵ_1) of the dielectric response at different frequencies (Hz). (b) Temperature dependence of the real part of the dielectric response of **1** at different frequencies (Hz) (inset).

that it is similar to that along the *b*-axis, while a view along the *c*-axis shows simple rectangles. To our knowledge, the formation of this 3D framework is unprecedented in the literature (see Supporting Information).

Since **1** crystallizes in the noncentric space group (C_c), which belongs to the polar point group (C_s), its optical property was examined. Our preliminary measurements on a powdered sample of **1** suggest that it is SHG (second harmonic generation) active with approximate responses of 10 times that of KDP (KH_2PO_4); this implies that **1** is a dipolar active compound.

In this work, the ferroelectric behavior of **1** was also examined given that point group C_s is 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}) required for such materials. Figure 3 clearly shows there is an electric hysteresis loop in **1** (a typical ferroelectric feature) with a remnant polarization (P_r) of ca. 0.38 $\mu C \cdot cm^{-2}$ and coercive field (E_c) of ca. 2.10 $kV \cdot cm^{-1}$. Saturation of the spontaneous polarization (P_s) **1** occurs at ca. 0.50 $\mu C \cdot cm^{-2}$, which is significantly higher than that for a typical ferroelectric compound (e.g., $NaKC_4H_4O_6 \cdot 4H_2O$, Rochelle salt; usually $P_s = 0.25\ \mu C \cdot cm^{-2}$). As shown in Figure 4, a relaxation process was also observed, suggesting that dielectric loss changes with temperature at different frequencies with the peak maxima obeying Arrhenius equation $\tau = \tau_o \exp(H/kT)$, where T = absolute temperature; k = Boltzmann's constant; H = activation energy; and τ_o = inverse of the frequency factor.

For a Debye peak, the condition for the peak is $\omega\tau = 1$. The equation can therefore be rewritten as $\ln f = -\ln(2\pi\tau_o) - H/kT_p$, where T_p = temperature of the peak, $\omega = 2\pi f$, and f = vibration frequency.

Thus, we can approximately estimate the activity energy H and relaxation time τ_o from Figure 4a. The average H and τ_o are ca. 1.96 eV and $1.60 \times 10^{-5.5}$ s, respectively. This suggests that the relaxation process (peak) is probably associated with dipolar Cd−Cl bond vibration or the displacement of the proton on the tetrazoyl group.[8] Notably, the permittivity at low frequencies reaches a maximum value (1.2×10^7, 5 °C, 100 Hz), which rapidly drops by 100-fold at relatively high frequency ($10^{3.5}$ Hz); this is similar to that for perovskite-related oxide $CaCu_3Ti_4O_{12}$ (10^5) which was reported to display a 1000-fold reduction.[9] This discrepancy suggests the presence of a dipole relaxation at low frequencies and is in good agreement with the dielectric loss measurement; recall that permittivity (ϵ) = $\epsilon_1(\omega) - i\epsilon_2(\omega)$, where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are the real (dielectric constant) and imaginary (dielectric loss) parts, respectively. The frequency dependence of the dielectric constant ϵ_1 at ca. 6.6 °C indicates ϵ_1 rapidly decreases with an increase in frequency, which further supports the presence of a dipole relaxation process, while ϵ_1 remains unchanged ($\epsilon_o = 38.6$, estimated from the slope) at ca. −53.8 °C. Interestingly, dielectric loss tanδ does not change with frequencies (see Supporting Information).

In summary, a novel 3D ordered ferroelectric MOF was prepared through employing cycloaddition chiral ligand synthesis under hydrothermal reaction conditions. This class of materials provides a new impetus to examining the potential applications of MOF as ferroelectric materials.

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Supporting Information Available: Detailed experimental procedures, IR spectroscopic data, additional ORTEP views, and X-ray crystallographic cif files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Crystal data of **1**: $C_{13}H_{14}ClN_5O_2Cd$, $M = 420.14$, monoclinic, C_c, $a = 9.0860(7)$ Å, $b = 24.088(4)$ Å, $c = 7.7691(14)$ Å, $\beta = 115.028(2)°$, $V = 1540.7(5)$ Å^3, $Z = 4$, $D_c = 1.811$ Mg m^{-3}, $R_1 = 0.0554$, $wR_2 = 0.1268$, $\mu = 1.604$ mm^{-1}, $S = 1.029$; Flack = 0.10(6).

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