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Homochiral 1D Zinc–Quitenine Coordination Polymer with a High Dielectric Constant

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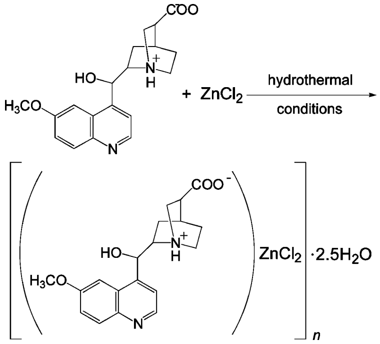
Heat treatment of a solution of MeOH and water containing the quitenine ligand HQA [HQA = 6-methoxyl-(8*S*,9*R*)-cinchonan-9-ol-3-carboxylic acid] and $ZnCl_2$ at 70 °C to give the one-dimensional (1D) chain coordination polymer $\{(HQA)(ZnCl_2)(2.5H_2O)\}_n$ (**1**). The local coordination geometry around the zinc center in **1** displays a slightly distorted tetrahedron, with the HQA ligand adopting a zwitterionic moiety similar to that found in natural amino acids. Measurements on a powdered sample of **1** reveal a strong second-harmonic-generation response of ca. 20 times larger than that for KDP (KH_2PO_4). Notably, measurements on the dielectric properties of **1** showed that the 1D chain coordination polymer exhibited a dipolar chain relaxation process and a high dielectric constant ($\epsilon_0 = 37.3$).

The search for new classes of materials with high dielectric constants (ϵ_0) has come under increasing scrutiny in recent years because of their potential applications in resonators, filters, and other key components in microwave communication systems.[1] However, only a limited number of materials have been developed to meet the stringent property requirements imposed by operating frequencies, required power levels, and types of applications. To date, the tantalate $Ba_3ZnTa_2O_9$ ($\epsilon_0 \approx 30$) is the only commercially available dielectric inorganic material that is known to display the required low dielectric loss.[2] In addition, while there have been a vast number of studies on pure inorganic compounds, examples on hybrid inorganic−organic coordination polymers (which would possess the advantageous properties of both inorganic and organic compounds) as dielectric materials have remained sparse.[3] This is surprising in view of the fact that the development of such compounds that can either delocalize or localize charge (with respective $\epsilon_0 \ll 0$ and $\epsilon_0 > 0$) in a manner comparable to that exhibited by a metal and an insulator, respectively, is highly desirable. The design and synthesis of high dielectric constant materials [a compound with a dielectric constant greater than that of silicon nitride ($\epsilon_0 > 7$)] has thus hitherto remained a significant challenge.[4] In general, a high dielectric constant ($\epsilon_0 > 1000$) is related to either ferroelectric behavior that displays a dipole moment in the absence of an external electric field or relaxor behavior in high electric fields.[4] Herein we report the synthesis and crystal structure of the homochiral one-dimensional (1D) coordination polymer $\{(HQA)(ZnCl_2)(2.5H_2O)\}_n$ (**1**), which was shown to exhibit a high dielectric constant ($\epsilon_0 = 37.3$) and dielectric loss characteristic of a relaxation process (Scheme 1).

Scheme 1



Heat treatment of a solution of MeOH and water containing HQA and $ZnCl_2$ at 70 °C gave homochiral **1** as a colorless block compound. IR spectroscopic analysis of **1** revealed two

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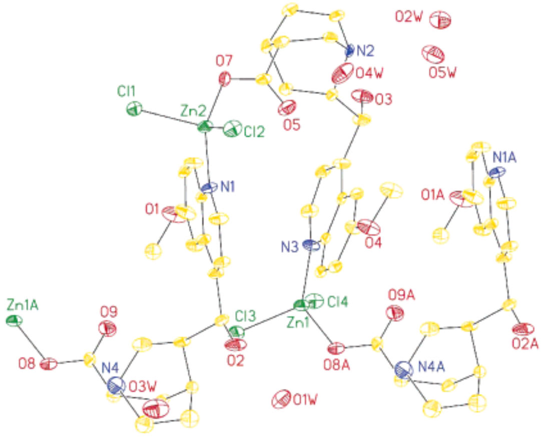

Figure 1. Asymmetric unit view of **1** showing each Zn center located in a slightly distorted tetrahedral coordination geometry. Typical bond distances (Å): Zn−Cl, 2.244(2), 2.206(2), 2.261(2), 2.265(2); Zn−N, 2.054(6), 2.073(5).

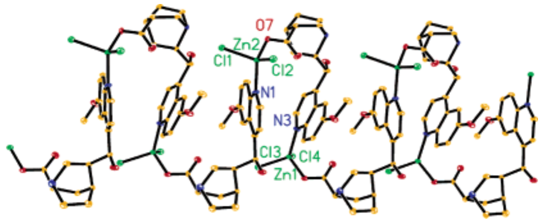

Figure 2. 1D wavelike chain representation of **1**.

peaks at 1621(s) and 1591(m) cm^{-1} that are assigned to the ν(CO) stretching of the carboxylate group and a peak at 1679(m) cm^{-1} that suggested the presence of the zwitterionic moiety. In addition, two broad peaks at 3430(s) and 3377(s) cm^{-1} indicated the presence of uncoordinated water molecules.

X-ray crystal structure analysis of **1** reveals that there are two crystallographically independent Zn centers.[5] As depicted in Figure 1, two Cl anions and the N atom of the quinoline ligand along with an O atom originating from the carboxylate group are coordinated to a Zn center to form a slightly distorted tetrahedral coordination geometry around the Zn metal ion. Thus, each quitenine ligand acts as a bidentate spacer that links two Zn centers and leads to the formation of a 1D chain coordination polymer (Figure 2). To balance the charges in **1**, the N atom of the quinicludine ring is protonated, which results in the formation of a zwitterionic moiety similar to that found in natural amino acids. Figure 3 reveals the packing mode of each wavelike chain adopting AA-type packing, which is thought to prevent cancellation of the dipolar moment. Furthermore, each small dipolar moment unit (small dark arrow) is composed of a protonated quinicludine and a carboxylate group, which are marked as + and − charge, respectively. As shown in Figure 4, the dipolar moment in each chain is marked as a long purple arrow (μ_1 and μ_2). The total dipolar moment ($\mu > 0$) marked as a long red arrow must not be equal to zero. Prior to this work, only one other example of this class of metal−organic framework was known, which described the synthesis of a homochiral three-dimensional Cd−QA coordination polymer (zeotype) and its usefulness as a chiral sieve to resolve racemic 2-butanol.[3d]

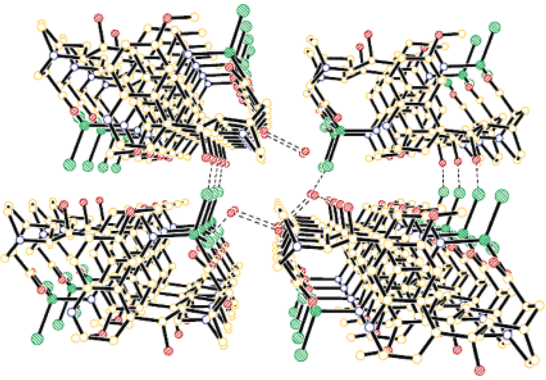

Figure 3. Packing view of **1**.

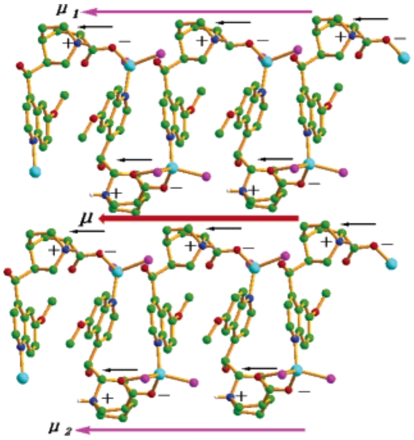

Figure 4. Perspective view of two chains along the *a* axis with the dipolar moment direction in **1**. The red arrow is the total dipolar moment (μ), while the purple arrows are the chain dipolar moments μ_1 and μ_2.

In this work, we have examined the optical properties of **1** in view of the fact that the compound crystallizes in a chiral space group ($P1$), which belongs to polar point group (C_1). Our preliminary results on a powdered sample of **1** indicate that it is second-harmonic-generation (SHG) active and exhibits a response that is approximately 20 times greater than that reported for KDP.[6] Such a strong SHG response could be due to the presence of intramolecular charge separation in **1**, which could be due to the zwitterionic moiety generating a large dipole moment μ ($\mu = qd$, where q is charge and d is distance); this would not be unreasonable in view of the fact that there are a number of literature examples that report the use of zwitterions as a means to enhance the SHG response.[7] Furthermore, the ligand HQA has been previously shown to be a good donor−acceptor chromophore, which is essential for nonlinear optical materials.[7e] However, a measurement of the dipole moment proved difficult because of the very small distances between the charges.

As mentioned above, the space group $P1$ is associated with the point group C_1, which is one of the 10 polar point groups (C_1, C_2, C_s, C_{2v}, C_4, C_{4v}, C_3, C_{3v}, C_6, and C_{6v}) required for

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(5) Crystal data of **1**: $C_{38}H_{54}Cl_4N_4O_{13}Zn_2$, $M_r = 1047.39$, triclinic, $P1$ (No. 1), $a = 9.048(4)$ Å, $b = 9.274(4)$ Å, $c = 13.587(6)$ Å, $\alpha = 100.925(9)°$, $\beta = 92.436(7)°$, $\gamma = 96.813(9)°$, $V = 1109.1(8)$ Å^3, $Z = 1$, $D_c = 1.568$ Mg m^{-3}, R1 = 0.0498, wR2 = 0.0988, $\mu = 1.389$ mm^{-1}, $S = 0.989$, Flack = 0.022(13).

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ferroelectric behavior.[8] Our experimental results reveal that **1** displays very weak ferroelectric behavior (see the Supporting Information). Nevertheless, measurement of dielectric loss clearly indicates that there is a relaxation process (Figure 4), that the dielectric loss changes in **1** with temperature at different measuring frequencies at the maximum peak, and that the relaxation process obeys the empirical Vogel−Fulcher relationship given in eq 1,[9] where F = frequency,

$$F = F_0 \exp[-E_a/K_B(T - T_m)] \qquad (1)$$

E_a = activation energy, K_B = Boltzmann's constant, and T = temperature (T_m is the maximum peak's temperature).

From Figure 5, E_a and the relaxation time ($\tau_0 = 1/2\pi F_0$) are estimated as 0.63 eV and 1.6×10^{-20} s, respectively.[10] As a result of the very weak ferroelectric behavior, the process could most probably be due to chain microvibration that results in an overall chain−chain dipolar relaxation process. This would be in good agreement with the presence of a 1D-ordered chain structural net. It is interesting to note that the dielectric constant (ϵ_1) at low frequencies reaches a maximum value (2.06×10^6 at 1.5 °C and 100 Hz; see the Supporting Information), which rapidly drops by ca. 100-fold at a relatively high frequency of 10^4 Hz. This behavior is similar to that found for the perovskite-related oxide $CaCu_3Ti_4O_{12}$ (10^5), which has been previously reported to display a 1000-fold reduction.[4] This discrepancy would further support the presence of a dipolar chain relaxation at low frequencies and would be consistent with the strong SHG response and dielectric loss measurements; recall that permittivity (ϵ) = $\epsilon_1(\omega) - i\epsilon_2(\omega)$ (Figure 6), 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 (ϵ_0 = 37.3 as estimated from the gradient in Figure 5) at a temperature of ca. −22.0 °C indicates that while ϵ_1 remains unchanged within a frequency range of $0.1044 \times 10^3 - 1 \times 10^6$ Hz, it increases smoothly from 37.6 to 39.1 within the 45−1044-Hz frequency range. In contrast, ϵ_2 remains unchanged within the measured frequency range, which could be due to low dielectric loss behavior. Again, such a feature would support the presence of a dipolar chain relaxation process rather than a ferroelectric process. To our knowledge, this is the first example of a metal−organic coordination polymer exhibiting such a relaxation process and a high dielectric constant.

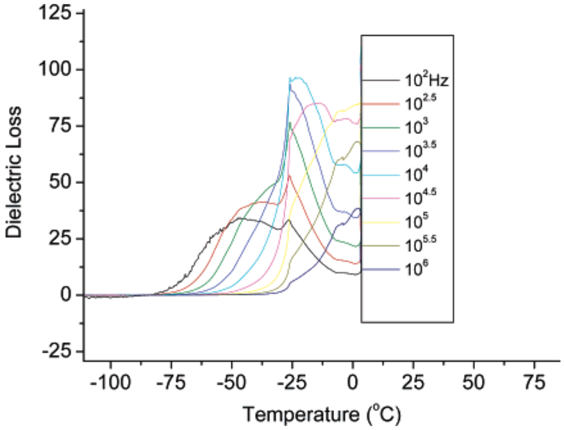

Figure 5. Temperature dependence of dielectric loss (ϵ_0) at different frequencies.

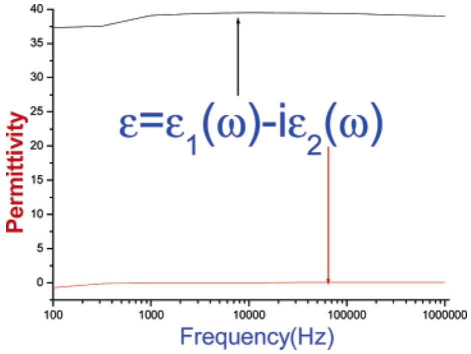

Figure 6. Frequency dependence of permittivity [$\epsilon = \epsilon_1(\omega) - i\epsilon_2(\omega)$] of **1** at ca. −22.0 °C in which ϵ_1 and ϵ_2 are the respective real and imaginary parts of permittivity. Dielectric loss = ϵ_2/ϵ_1.

In summary, we report herein the synthesis of a novel 1D metal−organic coordination polymer that was demonstrated to exhibit a high dielectric constant. In addition to their applications in catalysis, gas storage, nonlinear optics, and molecular recognition and separations,[11] we showed the potential utility of hybrid inorganic−organic coordination polymers as high-dielectric constant materials, which provides a new impetus in this field of materials science.

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Supporting Information Available: Detailed experimental procedures, additional figures, and X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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