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In Situ Synthesis and Ferroelectric, SHG Response, and Luminescent Properties of a Novel 3D Acentric Zinc Coordination Polymer

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Supporting Information

ABSTRACT: The 3D acentric metal−organic framework (MOF) of $[Zn(Mitz)Cl]_n$ [**1**; Mitz = 3-tetrazolyl-6-methyl-5-(4-pyridyl)-2-pyridone] was obtained from in situ [2 + 3] cycloaddition reactions of milrinone [=3-cyano-6-methyl-5-(4-pyridyl)-2-pyridone] with sodium azide in the presence of $ZnCl_2$ as the Lewis acid. The compound is a typical ferroelectric material with an electric hysteresis loop showing a remnant polarization (P_r) of ca. 0.21 $\mu C/cm^2$ and a coercive field (E_c) of 2600 V/cm. Powdered samples of **1** display strong second-harmonic-generation responses of ∼2 times larger than that of KH_2PO_4. Photoluminescent study show that complex **1** and the milrinone ligand exhibit maximal emission peaks at around 409 and 401 nm, respectively, in the solid state at room temperature.

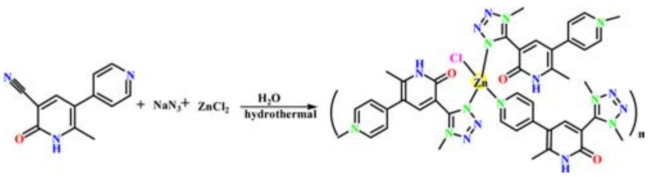
Since the discovery of the first ferroelectric crystal Rochelle salt in 1920 by Valasek[1] and the first research of nonlinear optical second-harmonic-generation (SHG) response from ruby in 1961 by Franken et al,[2] a great number of new noncentrosymmetric compounds with ferroelectric and SHG response have been synthesized and investigated intensively from the viewpoints of fundamental physics and technological applications.[3,4] Currently, the search for new classes of ferroelectric materials is of especially immense interest because of their versatile applicability to modern electric devices such as memory elements, filtering devices, and high-performance insulators.[5] However, to the best of our knowledge, most of the attention in this field has been focused on developing ferroelectric inorganic compounds such as KH_2PO_4 (KDP), $BaTiO_3$, and $LiNbO_3$;[5] studies toward the development of ferroelectric materials based on metal−organic frameworks (MOFs)[6] are still rare.

To be a ferroelectric material, the structure must meet the following four conditions: (i) it should be asymmetric; (ii) it must have a polarizable functional group; (iii) it should have the ability of spontaneous polarization; (iv) the polarization orientation can be changed with a change of the electric field. The recent works by Xiong et al. showed that in situ [2 + 3] cycloaddition chiral ligand synthesis[7] under hydrothermal reaction conditions provided a convenient and simple route to novel chiral MOFs and applications of these materials in ferroelectric behavior, SHG responses, nonlinear optics, and molecular recognition and separation.[8] As we all know, constructing a MOF that crystallizes in 1 of the 10 polar point groups (1, *m*, 2, *mm*2, 3, 3*m*, 4, 4*mm*, 6, and 6*mm*)[5a] is essential for ferroelectric behavior. As summarized by Lin et al.,[9] on the one hand, many crystals are acentric but not chiral because of the presence of helices of both handedness[10,11] in an achiral single crystal or equal probability for the formation of chiral crystals of both handedness such as "utp" net; on the other hand, both chiral and acentric structures can be formed from an achiral building block.[12] So, we can infer that not only chiral MOFs but also acentric MOFs that crystallizes in the above-mentioned 10 polar point groups may also have ferroelectric behavior.[13] Keep this in mind: we were intrigued with the possibility of constructing an acentric (not chiral) MOF that would crystallize in 1 of the 10 polar point groups, by using an appropriate acentric organic ligand as the building block.

Fortunately, by in situ [2 + 3] cycloaddition reactions of milrinone [=3-cyano-6-methyl-5-(4-pyridyl)-2-pyridone][14] with sodium azide in the presence of $ZnCl_2$ as the Lewis acid, we obtained a novel 3D acentric zinc coordination polymer, $[Zn(Mitz)Cl]_n$ [**1**; Mitz = 3-tetrazolyl-6-methyl-5-(4-pyridyl)-2-pyridone]. Herein, we report the synthesis of MOF **1**, which displays interesting ferroelectric behavior, strong SHG responses, and green luminescent properties.

As shown in Scheme 1, MOF **1** was prepared under hydrothermal reaction conditions. A heavy-walled Pyrex tube containing a mixture of milrinone (0.0422 g, 0.2 mmol), $ZnCl_2$ (0.0272 g, 0.2 mmol), NaN_3 (0.039 g, 0.6 mmol), and water (2.5 mL) was frozen, sealed under vacuum, and then placed inside an oven at 160 °C. The golden block crystals for **1** were obtained after 24 h of heating. Yield: 0.0584 g, 87.2%, $C_{12}H_9N_6ClOZn$ (354.07) on the basis of milrinone. Calcd for **1**: C, 40.67; H, 2.54; N, 23.72. Found: C, 40.88; H, 2.51; N, 23.66. IR (KBr, cm^{-1}): 3414(m), 1621(w), 1613(s), 1590(s), 1451(s), 1428(m), 1360(w), 1131(m), 1019(m), 811(w), 750(w), 641(w), 453(w).

Scheme 1. Preparation of MOF 1



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A pale-yellow crystal of **1** with dimensions of 0.30 mm × 0.20 mm × 0.20 mm was selected for single-crystal X-ray diffraction (XRD). The data were collected on a Bruker P4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ A) at 293 K using the $\theta-2\theta$ scan technique and corrected for Lorentz−polarization and absorption effects. The crystal structure was solved by direct methods with the *SHELXS-97* program.[15,16] Detailed information about the crystal data and structure determination for the title compound are summarized in Table 1.

Table 1. Crystal Data and Structure Refinement for 1

complex	**1**
empirical formula	$C_{12}H_9ClN_6OZn$
M_w	354.07
system	orthorhombic
space group	$Pna2_1$
a (Å)	8.438(2)
b (Å)	9.605(1)
c (Å)	17.969(3)
V (Å^3)	1434.2(4)
D_c (mg/m^3)	1.640
Z	4
μ(Mo Kα)/mm^{-1}	1.905
reflns collected	7448
GOF on F^2	1.036
R1 [$I > 2\sigma(I)$]	0.0701
wR2 (all data)	0.1781

In a comparison of the IR spectra of the product formation of **1** and the reaction substrate (milrinone and NaN_3), the absence of peaks at about 2300 and 2100 cm^{-1} suggests that the cyano group and the N_3^- anion have turned into the tetrazole group with several newly formed typical tetrazolyl group peaks ranging from 1613 to 1451 cm^{-1}.[7]

As shown in Figure 1 and Table 1, compound **1** belongs to the orthorhombic crystal system, with acentric space group $Pna2_1$, which belongs to the polar point group $mm2$ and $Z = 4$. The central metal zinc adopts four coordination modes, which are connected by two α-N atoms from different tetrazole groups, one N atom from the pyridyl group, and one Cl atom. Interestingly, the bond distance of Zn1−Cl1 [2.260(3) Å] is obviously longer than Zn1−N6#1 = 2.027(9) Å, Zn1−N1 = 2.024(8) Å, and Zn1−N46#2 = 2.124(7) Å, and all of the bond angles (such as N6#1−Zn1−N1) of the tetrahedron are between 90.1(3)° and 125.9(3)°, suggesting that the central zinc metal in MOF **1** lies in a highly unsymmetrical fashion.[17]

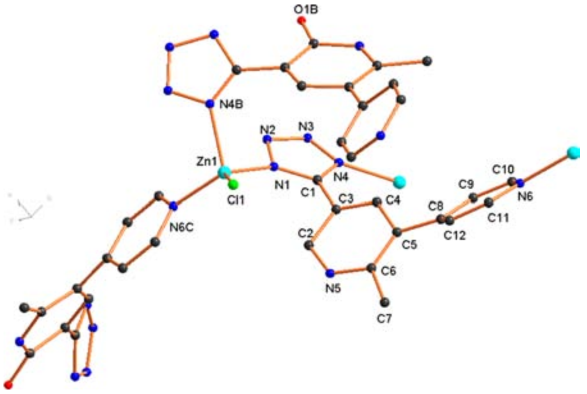

Figure 1. Asymmetric unit view of **1** showing each Zn center located in a highly distorted tetrahedral coordination geometry. Selected bond lengths (Å) and angles (deg): Zn1−N6#1 2.027(9), Zn1−N1 2.024(8), Zn1−N4#2 2.124(7), Zn1−Cl1 2.260(3); N6#1−Zn1−N1 108.3(3), N6#1−Zn1−N4#2 106.7(3), N1−Zn1−N4#2 90.1(3), N6#1−Zn1−Cl1 115.3(2), N1−Zn1−Cl1 125.9(3), N4#2−Zn1−Cl1 105.7(3). Symmetry code for **1**: #1, $-x - {}^1/_2, y - {}^1/_2, z + {}^1/_2$; #2, $x + {}^1/_2, -y - {}^5/_2, z$; #3, $x - {}^1/_2, -y - {}^5/_2, z$; #4, $-x - {}^1/_2, y + {}^1/_2, z - {}^1/_2$.

MOF **1** shows a unique 3D acentric structure. As shown in Figure SI, each milrinone tetrazole ligand in MOF **1** acts as a tridentate ligand linking three different Zn atoms through two μ^1-N atoms (N1−Zn1 and N4−Zn1A) of tetrazole and one μ^1-N atom (N6−Zn1B) of pyridine. Interestingly, all of the neighboring tetrazole groups of different ligands link adjacent Zn atoms to form a linear chain along the a axis, and then these linear chains are further linked by bridging pyridyl groups to form a 2D structure parallel to the ac plane; such building blocks are further cross-linked by bridging Zn atoms and ligands, thereby extending the structure into a 3D network (Figure SII).

To exactly describe the topological structure of compound **1**, we simplified the top structure by application of a topological approach (TOPOS software analysis).[18−22] As shown in Figure 2 (left), the top net has two three-connected topologically equivalent nodes representing either the Zn^{II} center or an averaged ligand position, so the overall structure can be simplified to an unusual (3,3)-connected network with Schäfli symbol (10,3).[23−25] Despite the coordination figure of the Zn center being 4, it should be viewed as three-connected because the auxiliary ligand does not connect any other metals and cannot be regarded as a bridging link. Closer examination indicated that the network had an extended Schäfli symbol of $10_2 \cdot 10_4 \cdot 10_4$ and a c10 number of 622 and was therefore a (10,3)-d net called "utp" according to Cory et al.'s work.[18,21,23,25]

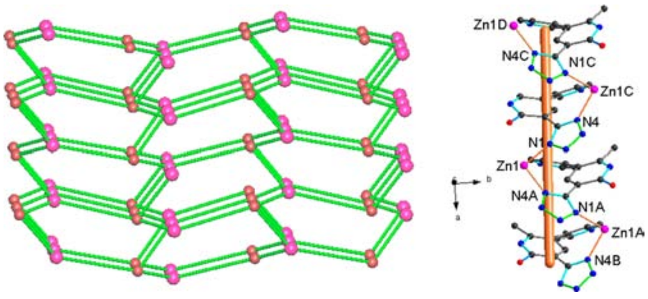

Figure 2. View (left) of **1** in the ab plane with an overlay of the (10,3)-d topological net, which projects a (6,3) net in which the purple nodes stand for Zn atoms and the brown nodes represent the simplified ligand. View (right) along the c axis showing one of the helicals linked by the tetrazole moiety of the ligand. Color code: Zn, purple; O, red; N, blue; C, black. Symmetry code: A, $x + {}^1/_2, -y - {}^5/_2, z$; B, $1 + x, y, z$; C, $x - {}^1/_2, -y - {}^5/_2, z$; D, $-1 + x, y, z$.

The (10,3)-a net is the most symmetrical three-connected 3D net.[26] Different from the (10,3)-a net, the (10,3)-d net has both left- and right-handed helices in the structure. As shown in Figure 2, we can clearly observe an alternate helix along the a axis resulting in an overall racemic network in **1** (right side of Figure 2). In addition, compared to works of Cory et al.,[23,24] we can infer that the net is a noninterpenetrated "utp" net. The interpenetration is not possible because the building blocks deviate from ideal geometries, producing a rather distorted and congested (10,3)-d net.

Because **1** crystallizes in the acentric space group $Pna2_1$, which belongs to 1 of the 10 polar point groups (1, *m*, 2, *mm*2, 3, 3*m*, 4, 4*mm*, 6, and 6*mm*) required for ferroelectric properties. Figure 3 clearly shows that there is an electric hysteresis loop in **1** (a typical ferroelectric feature) with a remnant polarization (P_r) of ca. 0.21 μC/cm^2 and a coercive field (E_c) of ca. 2.60 kV/cm. Saturation of the spontaneous polarization (P_s) of **1** occurs at ca. 0.51 μC/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 μC/cm^2),[1] but significantly smaller than that found in KDP (P_s = 5.0 μC/cm^2).

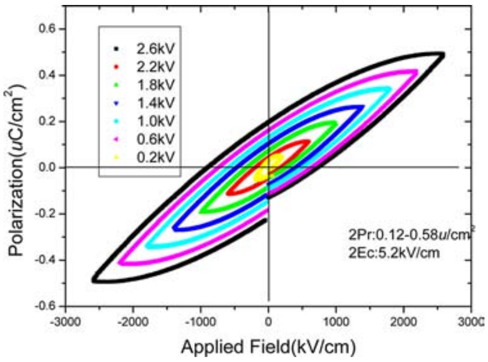

Figure 3. Electric hysteresis loop observed by virtual ground mode in a powdered sample of **1** in the form of a pellet using an RT6000 ferroelectric tester at room temperature.

Because **1** crystallizes in the acentric space group $Pna2_1$, its optical property was examined. As we expected, powdered samples **1** display strong SHG responses of ~2 times larger than that of KDP; this implies that **1** is a dipolar active compound. However, because of the approximate estimation of the SHG strength, the deuteration effect on nonlinear optics is not evident in our experiments.[27]

As shown in Figure SV in the Supporting Information, the powder XRD of compound **1** shows that its products are very highly crystalline. The results also revealed that the reaction was quantitative because no starting materials were detected. Their stimulated powder XRD pattern based on crystal structure analysis allowed unambiguous identification via comparison of the experimental and computed powder XRD patterns.

In summary, we have successfully synthesized a novel 3D acentric zinc coordination polymer **1** with a topological (10,3)-d net called "utp". It displays an interesting ferroelectric property and SHG responses. Thus, it opens a new avenue for exploring functional molecule-based materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Emission spectra, a TGA curve for **1**, powder XRD patterns, and measurement of electric hysteresis loop. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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