2D Chiral Uranyl(VI) Coordination Polymers with Second-Harmonic Generation Response and Ferroelectric Properties

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The in situ hydrothermal reactions of $UO_2(NO_3)_2$ with 1-oxo-4-cyanopyridine (ocpy) and ethyl (*S*)-lactate (e-la) afforded two unprecedented chiral 2D neutral luminescent square grids, uranyl-bis(1-oxo-4-pyridylcarboxylate) $UO_2(opyca)_2$ (**1**) and homochiral uranyl-bis[(*S*)-lactate] (**2**). Their solid-state structures, preliminary optical and photoluminescent properties are reported.

Introduction

The crystal engineering strategy has provided many advantages to construct chiral or polar supramolecular motifs with many useful physical properties, especially the nonlinear optical properties [second harmonic generation (SHG) response].[1,2] Enantiopure or homochiral metal-organic coordination polymers have found some applications in selective enantio-separation and asymmetric catalysis.[3] Apart from those achievements, however, as Ward et al. pointed out,[1a] the prediction of crystal structures based solely on the structure of their molecular components still remains unexplored and crystal engineering has not developed to the stage where a desired structure (or crystal symmetry) can be ensured. One of the foremost challenges not only in organic solid-state chemistry, but also in supramolecular materials design with SHG properties, essentially requires crystallization in noncentrosymmetric space groups (those lacking inversion symmetry). Moreover, a noncentrosymmetric polar packing arrangement is a requirement for a number of macro-physical properties, such as piezoelectricity, pyroelectricity, and ferroelectricity as well as SHG, which describes the capacity of a material to double the frequency of incident light. A ferroelectric material is one which can be switched rapidly between different states by means of an external electric field. Such materials may be useful in a variety of new technologies, such as electric-optical devices, information storage, switchable NLO (nonlinear optical) devices and light modulators. Recently, some polar and chiral metal-organic coordination polymers have been used as SHG materials with metal ions such as Zn^{2+}, Cd^{2+}, and Ag^{+}.[2] To this end, chiral or enantiopure organic-inorganic hybrid coordination polymers containing the uranium(VI) ion, to the best of our knowledge, remain unexplored and unknown, although there has been much current interest in multi-dimensional U^{VI} coordination polymers which have widespread properties such as fluorescence and zeolite-likeness.[4−6] To our surprise, the in situ hydrothermal reactions of $UO_2(NO_3)_2$ with 1-oxo-4-cyanopyridine (ocpy) and ethyl (s)-lactate(e-la) afford two unprecedented chiral 2D neutral luminescent square grids, uranyl-bis(1-oxo-4-pyridylcarboxylate) $UO_2(opyca)_2$ (**1**) and homochiral uranyl-bis[(*S*)-lactate] (**2**). Herein, we report their synthesis, solid state structures, fluorescent and optical properties (1).

Results and Discussion

The hydrolysis reaction of $UO_2(NO_3)_2$ with ocpy under hydrothermal reaction conditions gave **1**, as shown by the absence of the cyano group peak (ca. 2200 cm^{-1}) and appearance of a strong carboxylate peak at 1600 cm^{-1} in its IR spectrum. The hydrolysis reaction of $UO_2(NO_3)_2$ with e-la under hydrothermal reaction conditions yielded **2**, as confirmed by the appearance of the carboxylate peak (ca. 1600 cm^{-1}).

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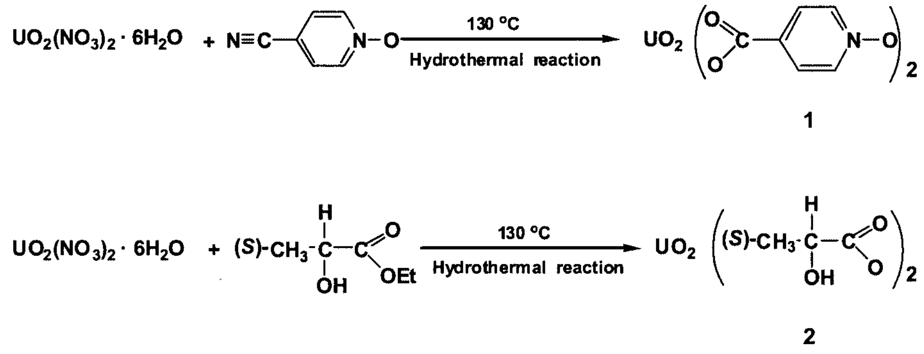

Scheme 1

These in situ hydrolysis reactions or in situ ligand syntheses provide an excellent route to novel metal-organic coordination polymer construction for chemists.[7]

The solid-state structure of **1** (Figure 1a) has a slightly distorted pentagonal bipyramid as the local coordination geometry around each U atom center, defined by seven oxygen atoms from two carboxylate groups, two N-oxide and two oxo groups. Thus, there are two kinds of opyca ligands, one serves as a tridentate spacer, and the other acts as a bidentate linker. Overall each opyca ligand bridges two U atom centers, resulting in the formation of a 2D square grid network with dimensions of 10.07 × 10.04 Å (Figure 1b). The relationship between two layers in the packing diagram in **1** should be an ABAB-type stack, as observed (Supporting Information). No interpenetration was observed in **1**. To the best of our knowledge, this is the first example of neutral square networks containing an U atom as the connecting node.[8]

Like **1**, the local coordination geometry around each U atom center in **2** can best be described as a distorted pentagonal bipyramid. However, there are two crystallographically different U centers (Figure 2a). There are also three kinds of lactate ligands: One serves as a bidentate ligand to chelate one U atom using two oxygens from one carboxylate and one hydroxy group; the second lactate ligand acts as a bidentate bridge to link two U atoms using one carboxylate group; the third lactate ligand is a monodentate terminal group with coordination of its carboxylate to one U atom. Such coordination results in the formation of a 2D brick-wall type grid network with approximate dimensions of 3 × 6.04 Å (Figure 2b). The relationship between two layers is also an ABAB-type stack (Supporting Information). No interpenetration was found in **2**.

Compounds **1** and **2** crystallize in the chiral space groups $P2_12_12_1$ and $P2_1$ respectively. These two space groups belong to the crystal classes 222 and 2, respectively, where their optical activity can occur as a specific physical effect. Preliminary experimental results show that **1** and **2** display powder SHG efficiencies ca. 0.4 and 0.1 times that of urea. Due to **2** having a polar point group (C_2) which theoretically can display potential ferroelectric property. However **1**, with a point group of D_2, fails to do that in principle.

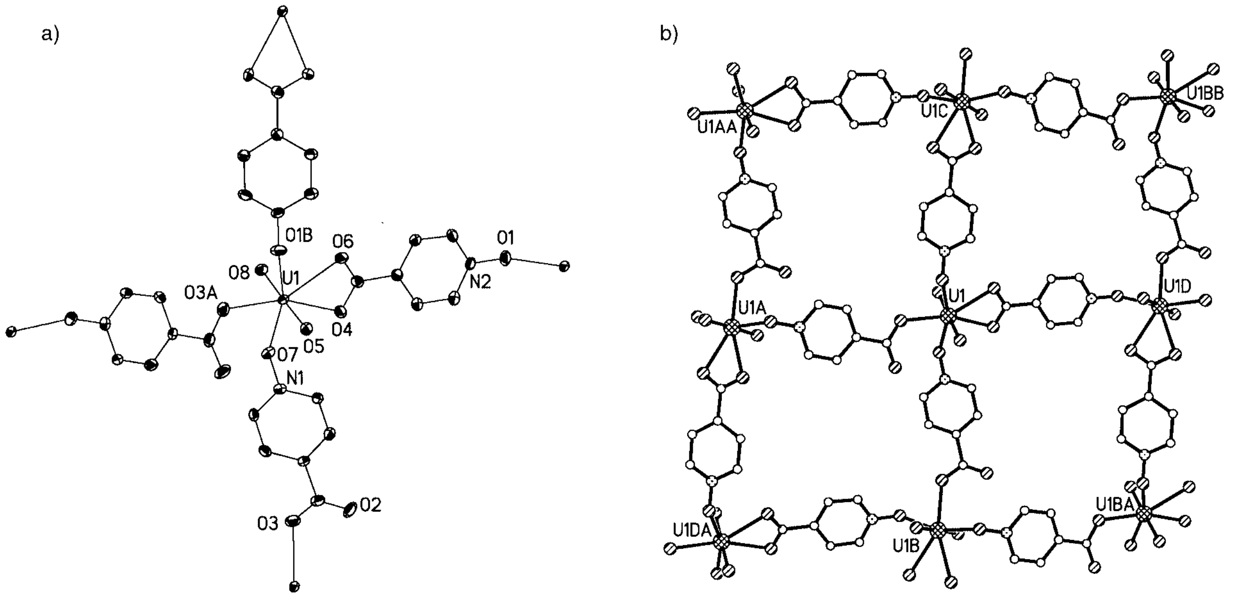

Figure 1. (a) An asymmetric unit of **1** in which thermal ellipsoids are drawn at the 30% probability level; (b) a 2D square grid representation of **1**

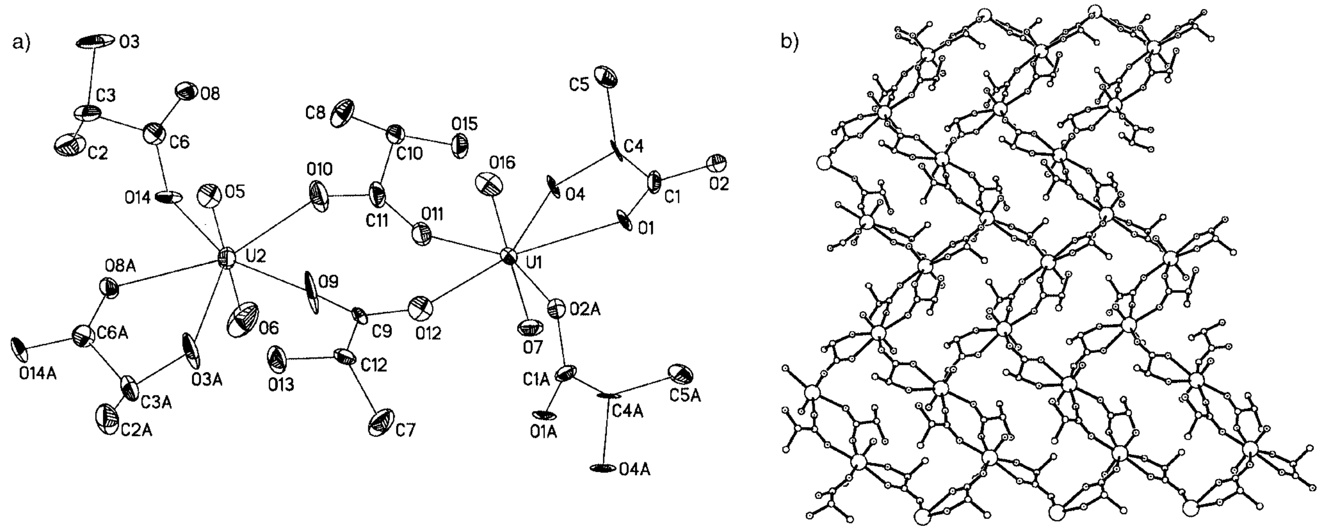

Figure 2. (a) An asymmetric unit of **2** in which thermal ellipsoids are drawn at 30% probability level; (b) a 2D brick-wall representation of **2**

Experimental results indicate that **2** exhibits a low ferroelectric behavior (Figure 3), while **1** does not [Figure 4 shows that there is a weak electric hysteresis loop which is a ferroelectric feature with a remanent polarization (Pr) of 0.12 $\mu C \cdot cm^{-2}$ and coercive field (Ec) of 5 $kVcm^{-1}$. The saturation spontaneous polarization (Ps) of **2** was not observed, probably due to current leakage]. Maybe H-bonds and the layered structure are responsible for **2**'s ferroelectric behavior.[9] Furthermore, **1** and **2** are thermally stable up to 250 and 300 °C, respectively, and are insoluble in common solvents. On the other hand, both **1** and **2** exhibit strong green fluorescent emission at room temperature (Figure 4), which is typical for the uranyl fluorescent spectrum. Thus, **1** represents the first neutral luminescent molecular box with uranyl.[10]

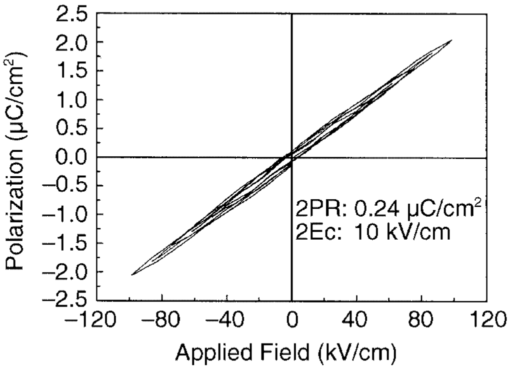

Figure 3. An electric hysteresis loop of **2** was observed by Virtual Ground Mode in a powdered sample in the form of a pellet using an RT6000 ferroelectric tester at room temperature while the sample was immerged in insulating oil; the measurement was performed using ac-pulse

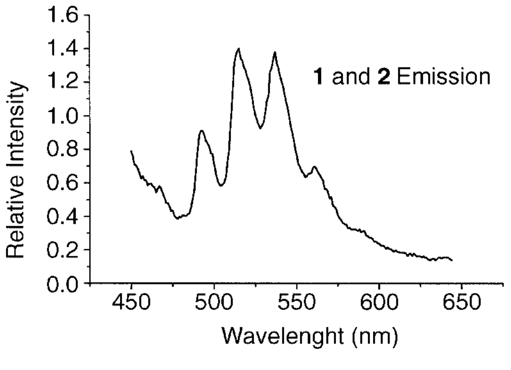

Figure 4. Fluorescent emission spectra of **1** and **2** in the solid state at room temperature

The synthesis of chiral or homchiral novel UO_2-coordination polymer self-assembled through in situ ligand hydrolysis is an extension of a crystal engineering strategy, which is very useful for functional materials design, while the properties of **1** and **2** perhaps make them potential candidates for fluorescent and opto-electronic information storage materials.

Experimental Section

Caution: Compounds containing UO_2^{2+} should be handled with great care (no skin contact or respiration).

Preparation of 1: Hydrothermal treatment of $U(NO_3)_2 \cdot 6H_2O$ (1.0 mmol, 0.502 g), 1-oxo-4-cyanopyridine (2.0 mmol, 0.240 g) and H_2O (2 mL) over 4 days at 130 °C yielded yellowish block crystals of **1** (0.355 g, only one pure phase) in 65% yield based on 1-oxo-4-cyanopyridine. $C_{12}H_8N_2O_8U$ (546.23): calcd. C 26.45, H 1.53, N 5.60; found C 26.36, H 1.47, N 5.13. IR spectrum (KBr): $\tilde{\nu}$ = 3449 cm^{-1} (w), 3112 (w), 3039 (w), 1644 (s), 1617 (w), 1583 (w), 1562 (w), 1540 (m), 1491 (w), 1425 (s), 1352 (s), 1226 (m), 1210 (s), 1177 (m), 1150 (w), 924 (m), 916 (s), 876 (m), 784 (m), 683 (w), 642 (m), 559 (w), 467 (w).

Preparation of 2: Hydrothermal treatment of $U(NO_3)_2 \cdot 6H_2O$ (1.0 mmol, 0.502 g) and ethyl (*S*)-lactate (2.0 mL, 17.6 mmol, 2.084 g) over 4 days at ca. 80−100 °C yielded yellowish block crystals of **2** (0.202 g, only one pure phase) in 45% yield based on $U(NO_3)_2 \cdot 6H_2O$. $C_6H_{10}O_8U$ (448.17): calcd. C 16.07, H 2.23; found

C 16.12, H 2.31. IR spectrum (KBr): $\tilde{\nu}$ = 3449 cm^{-1} (br., w), 2989 (w), 1620 (m), 1562 (br.,s), 1471 (m), 1432 (w), 1372 (w), 1314 (w), 1261 (m), 1118 (m), 1048 (m), 940 (s), 865 (w), 787 (w), 767 (w), 557 (m), 477 (w).

Crystal Data for 1: $C_{12}H_8N_2O_8U$, M_r = 546.23 g·mol^{-1}, orthorhombic, $P2_12_12_1$, a = 7.1116(5), b = 13.4060(10), c = 14.9176(11) Å, $\alpha = \beta = \gamma$ = 90.00°, V = 1422.22(18) Å^3, Z = 4, D_c = 2.551 Mg·m^{-3}, R_1 = 0.0240, wR_2 = 0.0659, T = 293 K, μ = 11.459 mm^{-1}, S = 0.518. The crystal was twinned.

Crystal Data for 2: $C_6H_{10}O_8U$, M_r = 448.17 g·mol^{-1}, monoclinic, $P2_1$, a = 8.2854(5), b = 8.1836(5), c = 15.1707(9) Å, $\alpha = \gamma$ =90°, β = 92.9830(10)°, V = 1027.25(1) Å^3, Z = 4, D_c = 2.898 Mg·m^{-3}, R_1 = 0.0660, wR_2 = 0.1732, T = 293 K, μ = 15.823 mm^{-1}, S = 1.333, Flack χ = 0.04(3).

The structures were solved by Direct methods using the program SHELXTL (Sheldrick, 1997).[11] All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent carbon atoms. The final difference Fourier map was found to be featureless. CCDC-215386−215387 (**1** and **2** respectively) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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