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Two Chiral Nonlinear Optical Coordination Networks Based on Interwoven Two-Dimensional Square Grids of Double Helices

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ABSTRACT: Two new chiral two-dimensional coordination networks, $ZnL_2(H_2O)_2$ (1) and $CdL_2(H_2O)_2$ (2) [L = 1,2,2-trimethyl-3-(pyridin-4-ylcarbamoyl)cyclopentanecarboxylic acid], have been synthesized and structurally characterized by single X-ray structure analysis, featuring very unusual interwoven (4,4) square grids of double helices. The frameworks exhibit high thermal stability as confirmed by thermogravimetric analysis and powder X-ray diffraction studies. The unique chiral networks attributed to the chiral organic linker have led to their nonlinear optical properties.

Introduction

The design and synthesis of noncentrosymmetric solid state materials is one of the most important and challenging goals of the chemistry and materials science community. The unique functions and properties of such noncentrosymmetric solid state materials such as second harmonic generation (SHG) and ferroelectricity are heavily dependent on their framework structures, so extensive effort to rationalize the structure– property relationship has been spent over the past two decades.^{1–11} Pioneered by Lin,¹ previous research on the nonlinear optical materials has been mainly focused on the construction of acentric metal–organic coordination polymers (MOCPs) by making use of nonsymmetrical organic linkers.^{12–21}

The incorporation of chiral organic linkers into the coordination networks can enforce the construction of noncentrosymmetric solid state materials and thus induce their nonlinear optical properties at witnessed in the growing number of nonlinear optical chiral coordination networks.^{22–40} Motivated by Bu with respect to the design and construction of homochiral coordination networks from D-camphoric acid, 41-43 we developed a new chiral and helical organic linker to have both D-camphor and pyridyl moieties for their coordination to metal ions and thus the construction of chiral coordination networks (Scheme 1). Herein, we report two new chiral twodimensional (2D) coordination networks, $ZnL_2(H_2O)_2$ (1) and $CdL_2(H_2O)_2$ (2) [L = 1,2,2-trimethyl-3-(pyridin-4-ylcarbamoyl)cyclopentanecarboxylic acid], of very unusual interwoven (4,4) square grids of double-helix structures exhibiting nonlinear optical, luminescent, and ferroelectrical properties.

Experimental Section

General Procedures. All the chemicals were commercially available and used without further purification. (1R,3S)-1,2,2-Trimethylcyclopentane-l,3-dicarbonyl chloride (**3**) was synthesized according to ref 44. ¹H and ¹³C NMR spectra were recorded on a Bruker Advance DMX500 spectrometer using tetramethysilane (TMS) as an internal standard. Infrared spectra (IR) were recorded on a Thermo Fisher Nicolet iS10 spectrometer using KBr pellets. Elemental analyses for C, H, and N were performed on an EA1112 microelemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected in the $2\theta = 5-60^{\circ}$ range on an X'Pert PRO diffractometer with Cu K α radiation ($\lambda = 1.542$ Å) at room temperature. Thermogravimetric analyses (TGA) were conducted on a Netszch TGA 209 F3 thermogravimeter with a heating rate of 10/min in an N₂ atmosphere. Luminescence spectra for the solid samples were recorded with a Hitachi F4500 fluorescence spectrometer. The photomultiplier tube voltage was 700 V, and the scan speed was 240 nm/min. The slit widths were both 2.5 nm for excitation and emission spectra. The second-order nonlinear optical intensity was estimated by measuring a powder sample $61-90 \ \mu m$ in diameter relative to KDP. A pulsed Q-switched Nd:YAG laser at a wavelength of 1064 nm was used to generate second-order harmonic generation (SHG signals). The backscattered SHG light of 532 nm was collected and detected with a photomultiplier through a monochromator. The ferroelectric properties of solid state samples are measured from a powdered sample in the form of a pellet using a Premier II ferroelectric tester (Radiant Technologies, Inc.) at room temperature, and the electric hysteresis loop was observed by Virtual Ground Mode (the measurement is ac, and the frequency is 10 Hz).

X-ray Collection and Structure Determination. Crystallographic measurements for 1 and 2 were taken on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector using graphitemonochromatic Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K. The determinations of the unit cells and data collections for the crystals of 1 and 2 were performed with CrysAlisPro. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.4 ' All structures were determined by direct methods and refined by the full-matrix least-squares method with the SHELX-97 program package.46 All non-hydrogen atoms, including solvent molecules, were located successfully from Fourier maps and were refined anisotropically. H atoms on C atoms were generated geometrically. The H atoms of the water molecules and amine groups were clearly visible in difference maps and were handled in the subsequent refinement with fixed isotropic displacement parameters. Crystallographic data are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2.

Synthesis of (*Z*)-1,8,8-Trimethyl-4-(pyridin-4-ylimino)-3-oxabicyclo-[3.2.1]octan-2-one (4). To the suspension of 4-pyridinamine (7.52 g, 80 mmol) in CH₂Cl₂ at 0 °C was added (1*R*,3*S*)-1,2,2-trimethylcyclopentane-1,3-dicarbonyl chloride (3) (4.74 g, 20 mmol) in portions.



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Table 1. Crystallographic Data Collection and Refinement Results for 1 and 2

	1	2
chemical formula	C30H42N4O8Zn	C30H42N4O8Cd
formula weight	652.05	699.09
temperature (K)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073
crystal system	monoclinic	monoclinic
space group	C_2	C_2
<i>a</i> (Å)	19.3447(9)	19.8930(7)
$b(\mathbf{A})$	8.9864(5)	9.0654(3)
$c(\dot{A})$	9.2291(5)	9.4049(3)
β (deg)	95.750(5)	99.598(3)
$V(A^3)$	1596.3(1)	1672.3 (1)
Z	2	2
density (calculated g/cm ³)	1.357	1.388
absorbance coefficient (mm ⁻¹)	0.823	0.704
F(000)	688	724
crystal size (mm ³)	$0.34 \times 0.28 \times 0.09$	$0.44 \times 0.34 \times 0.20$
goodness of fit on F_2	1.036	1.014
$\tilde{R}1, WR2 [I > 2\sigma(I)]^{a}$	0.0340, 0.0447	0.0203, 0.0410
R1, wR2 (all data) a^{a}	0.0401, 0.0455	0.0204, 0.0410
largest difference peak and hole $(e/Å^3)$	0.241, -0.177	0.252, -0.164

a
R1 = $\sum(|F_{o}| - |F_{c}|) / \sum |F_{o}|; wR2 = [\sum w(|F_{o}| - |F_{c}|^{2}) / \sum wF_{o}^{2}]^{1/2}$.

Table 2. Selected Bond Lengths (angstroms) and Angles (degrees) for $1 \mbox{ and } 2$

1^a				
$Zn(1) - O(2)^i$	1.935(2)	$O(2)^{i}_{} - Zn(1) - N(1)$	96.67(9)	
Zn(1) - N(1)	2.060(2)	$O(2)^{n} - Zn(1) - N(1)$	110.75(9)	
$O(2)^{i} - Zn(1) - O(2)^{ii}$	135.9(1)	$N(1)-Zn(1)-N(1)^{iii}$	102.5(1)	
	2	b		
$Cd(1) - O(2)^{i}$	2.223(2)	$N(1)-Cd(1)-N(1)^{iii}$	93.8(1)	
$Cd(1) - O(3)^{i}$	2.470(2)	$O(2)^{i}-Cd(1)-O(3)^{i}$	54.95(6)	
Cd(1) - N(1)	2.303(2)	$O(2)^{ii} - Cd(1) - O(3)^{i}$	108.81(8)	
$O(2)^{i} - Cd(1) - O(2)^{ii}$	155.5(1)	$N(1) - Cd(1) - O(3)^{i}$	141.81(8)	
$O(2)^{i} - Cd(1) - N(1)$	87.80(8)	$N(1)^{iii} - Cd(1) - O(3)^{i}$	91.37(8)	
$O(2)^{ii} - Cd(1) - N(1)$	109.18(8)	$O(3)^{i} - Cd(1) - O(3)^{ii}$	107.3(1)	

 a For 1: (i) – x + 1, y + 1, –z – 1; (ii) x, y + 1, z + 1; (iii) – x + 1, y, –z. b For 2: (i) – x + 1, y + 1, –z – 1; (ii) x, y + 1, z + 1; (iii) – x + 1, y, –z.

The solution was allowed to stir at 0 °C for 5 h and then warmed to room temperature and allowed to stir overnight. Silica gel column chromatography with an eluent of ethyl acetate and dichloromethane (1:1, v/v) afforded a pure white solid (2.58 g, 50% yield): ¹H NMR (CDCl₃) δ 8.49 (d, 2H), 6.82 (d, 2H), 2.90 (t, 1H), 2.32 (m, 1H), 2.13 (m, 1H), 1.99 (m, 2H), 1.25 (s, 3H), 1.15 (s, 3H), 1.05 (s, 3H).

Synthesis of 1,2,2-Trimethyl-3-(pyridin-4-ylcarbamoyl)cyclopentanecarboxylic Acid (L). A mixture of (Z)-1,8,8-trimethyl-4-(pyridin-4-ylimino)-3-oxabicyclo[3.2.1]octan-2-one and triethylamine (1 mL) was stirred at 50 °C in water for 24 h. The precipitate was filtered off, and the filtrate was removed in vacuo to give the crude product, 1,2,2-trimethyl-3-(pyridin-4-ylcarbamoyl)cyclopentanecarboxylic acid, as a white solid (80% yield): ¹H NMR (DMSO) δ 10.06 (s, 1H), 8.41 (d, 2H), 7.59 (d, 2H), 2.92 (t, 1H), 2.46 (m, 1H), 2.04 (m, 1H), 1.76 (m, 1H), 1.42 (m, 1H), 1.19 (s, 6H), 0.78 (s, 3H); ¹³C NMR (DMSO) δ 177.274, 173.081, 150.776, 146.115, 113.759, 56.139, 54.023, 46.710, 32.656, 23.031, 22.978, 22.209, 21.677; MS (ESI) exact mass calcd for C₁₅H₂₀N₂O₃ [M + H]⁺ 277.2, found 277.1, [M - H]⁻ 275.2, found 275.0; HRMS (ESI) exact mass calcd for C₁₅H₂₀N₂O₃ [M + H]⁺ 277.1547, found 277.1540.

Synthesis of $ZnL_2(H_2O)_2(1)$. A mixture of $ZnNO_3 \cdot 6H_2O(0.0295 \text{ g}, 0.1 \text{ mmol})$ and L (0.0552 g, 0.2 mmol), ethanol (2.5 mL), water (2.5 mL), and DMF (5 mL) were sealed into a 20 mL Teflon cup. The vessel was heated at 120 °C for 2 days. After the mixture had slowly cooled to room temperature, colorless block crystals were obtained in 80% yield. Anal. Calcd for $C_{30}H_{42}N_4O_8$ [Zn (%)]: C, 55.26; H, 6.49; N, 8.59. Found: C, 55.14; H, 6.51; N, 8.37. IR (KBr, cm⁻¹): 3552(s), 3323(s), 3228(w), 3160(w), 3070(w), 2978(s), 1693(s), 1596(s), 1513(s), 1458(w), 1434(w), 1402(w), 1360(w), 1331(w), 1313(s), 1213(s), 1175(s), 1068(w), 1026(s), 842(s), 781(w), 538(w), 519(w).

Synthesis of CdL₂(**H**₂**O**)₂ (**2**). Complex **2** was prepared via a procedure similar to that of **1**, except that Cd(NO₃)₂·4H₂O was used instead of ZnNO₃·6H₂O (70% yield). Anal. Calcd for C₃₀H₄₂N₄O₈ [Cd (%)]: C, 51.54; H, 6.06; N, 8.01. Found: C, 51.63; H, 6.09; N, 7.76. IR (KBr, cm⁻¹): 3535(s), 3371(s), 3235(w), 3163(w), 3077(w), 2976(s), 1690(s), 1598(s), 1511(s), 1430(s), 1360(s), 1311(w), 1213(s), 1176(s), 1126(w), 1018(s), 928(w), 891(w), 839(s), 781(w), 610(w), 535(w), 484(w).

Results and Discussion

The single-crystal X-ray diffraction studies reveal that both 1 and 2 have a 2D polymeric structure crystallizing in monoclinic space group C_2 . As depicted in Figure 1, the Zn(II) center lies on a crystallographic 2-fold axis and is coordinated to two pyridyl nitrogen atoms and two carboxylate oxygen atoms that come from four different L ligands in compound 1. The bond angles about the Zn tetrahedron range from 96.71(9) to 135.7(1) Å and deviate slightly from those of a perfect tetrahedron. The Cd(II) in compound 2 has a slightly different coordination environment and is six-coordinated to two pyridyl nitrogen atoms and four oxygen atoms from two cleating carboxylate group. The local coordination geometry about the Cd(II) center can best be described as a distorted octahedron with the bond angles ranging from 87.80(8)° to 155.5(1)°.

The most interesting structural features are their chiral and helical network structures, apparently attributed by the chiral and helical geometry of the bridging ligand L. Typically, coordination networks of diamond topology will be selfassembled from such pyridylcarboxylate organic linkers as exemplified in Lin's works.¹ Here the bend and helical nature of organic linker L have led to the formation of the 2D (4,4) wavelike grids that are interwoven with each other to occupy the large void space within the wavelike grids (Figure 2a). It should be noted that right-handed double-helical chains



Figure 1. ORTEP drawing (with thermal ellipsoids at 50% probability) showing the coordination environment of the metal site in 1 (a) and 2 (b).



Figure 2. (a) Perspective views of the single (4,4) wavelike grid constructed from double right-handed helices. (b) Space filling and perspective views of one right-handed helix along the *b* axis. Color code: Zn, azury; oxygen, red; nitrogen, blue.



Figure 3. Schematic showing the parallel arrangement of (a) double right-handed helices and (b) 2D interwoven grids in a staggered arrangement.



Figure 4. Packing diagrams of compound **1** of the ABAB sequence with views along (a) the *c* axis and (b) the *b* axis.

(Figure 2b) are distinguishable in the (4,4) network along the b axis. Because the right-handed helix of the L is predetermined by the R-c and S-c in the ligand, the coordinated tetrahedron for Zn or the octahedron for Cd would only form the right-handed forms and thus induces the absolute right-handed



Figure 5. TGA curves for 1 and 2 under nitrogen.

 2_1 -helical chains along the *b* axis in both structures. The period of helical chains is 17.973 Å, as the double of the *b* parameter of the unit cell. These double helices are in an orderly arrangement with the zinc or cadmium atoms functioning as hinges to result in a homochiral 2D sheet (Figure 3). To the best of our knowledge, coordination networks **1** and **2** are the first example of MOCPs exhibiting such unique interwoven (4,4) square grids of double-helix structures. These interwoven (4,4) square grids of double helices are alternately stacked in ABAB packing (Figure 4)

Both compounds 1 and 2 exhibit quite high thermal stability as shown in thermogravimetric analysis (TGA) (Figure 5). For 1, the TGA curve shows the weight loss of interlayer water molecules (calculated, 5.15%; observed, 4.94%) in the temperature range of 100-175 °C. The host framework is stable up to ca. 316 °C. For 2, the TGA curve shows the weight loss of interlayer water molecules (calculated, 5.52%; observed,



Figure 6. PXRD patterns of 1 and 2 (calculated, black; as-synthesized, blue; activated at 180 °C in vacuum for 12 h, red).

5.39%) in the temperature range of 100-145 °C. The host framework is stable up to ca. 316 °C. The powder X-ray diffraction patterns (PXRD) of dehydrated samples 1 and 2 (after removal of guest water molecules as the sample is heated to 180 °C in vacuum) indicate that the host framework also matches those of the pristine samples, suggesting their structures are intact after removal of solvent water molecules (Figure 6).

We conducted the quasi-Kurtz second harmonic generation (SHG) measurements on powdered samples to confirm their acentricity as well as to evaluate their potential application as second-order NLO materials.⁴⁷ Preliminary experimental results indicate that both 1 and 2 display SHG efficiencies that are approximately 2.8 and 2.6 times that of KDP, respectively. The modest powder SHG response of 1 and 2 may be attributed to a comparable short donor–acceptor system, which is essential for second-order optical nonlinearity. However, their SHG responses are systematically stronger than those 2D coordination networks containing a comparable length donor–acceptor system, ^{1,13,19,48} indicating the obvious effects of the chirality and helices on SHG efficiency.

The photoluminescence spectra of 1 and 2 were investigated in the solid state at room temperature (Figure 7). Upon excitation of 1 and 2 at 365 nm, intense bands in the emission spectra are observed at 437 nm for 1 and 440 nm for 2. This emission can be attributed to the intraligand emission from L. Free L exhibits a luminescence at ca. 453 nm upon excitation at 365 nm in the solid state at room temperature. The enhancement and blue shift (from ca. 453 to 437 nm) of the emission of the L in 1 compared to that of free ligand may be attributed to the coordination bond between the ligand and



Figure 7. Photoluminescence spectra of 1 (red), 2 (blue), and L (black) in the solid state at room temperature.



Figure 8. Electronic hysteresis loops of powdered samples in the form of pellets of 1 using a Premier II ferroelectric tester at room temperature.

Zn(II), which increases the rigidity of the ligand and reduces the loss of energy by radiationless decay of the intraligand emission excited state.^{12,49}

Compounds 1 and 2 both crystallize in space group C_2 , which belongs to one of the 10 polar point groups $(C_1, C_s, C_2, C_{2\nu}, C_4, C_{4\nu}, C_3, C_{3\nu}, C_6$, and $C_{6\nu}$).^{7,17,50,51}To detect the ferroelectricity, the hysteresis loops of electric polarization were measured on a powdered sample of 1 (Figure 8). At room temperature, the remnant polarization (Pr) is ca. 0.1280 μ C/cm² for 1 with a coercive field (Ec) of ca. 12 kv/cm. Saturation of the spontaneous polarization (Ps) in 1 occurs at 0.25 μ C/cm², which is the same as a typical ferroelectric compound (e.g., NaKC₄H₄O₆·4H₂O, Rochelle salt; usually Ps = 0.25 μ C/cm²), but much smaller than that found in KDP ($\approx 5 \mu$ C/cm²).

In conclusion, the incorporation of a new chiral and helical organic linker has led to two novel coordination networks of unique interwoven (4,4) square grids of double-helix structures, exhibiting nonlinear optical properties. The power to synthesize a variety of chiral and helical organic linkers with typical binding sites such as carboxylate and pyridyl groups for their coordination with metal ions and/or metalcontaining clusters has provided the promise to construct a series of novel chiral and helical coordination networks of diverse structures; thus, some novel functional nonlinear optical coordination networks will be emerging in the future.

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Supporting Information Available: X-ray data of 1 and 2 in CIF format and figures of asymmetric units. This material is available free of charge via the Internet at http://pubs.acs.org.

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