Supramolecular Engineering of Chiral and Acentric 2D Networks. Synthesis, Structures, and Second-Order Nonlinear Optical Properties of Bis(nicotinato)zinc and Bis{3-[2-(4-pyridyl)ethenyl]benzoato}cadmium

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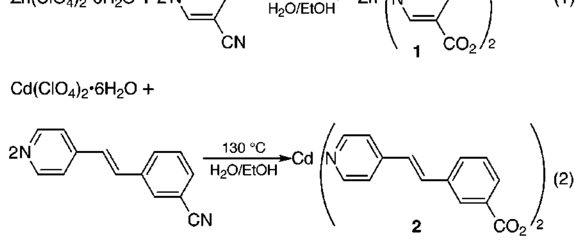
Noncentrosymmetric organization of molecular building blocks is an essential requirement for a bulk material to exhibit second-order nonlinear optical (NLO) effects,[1] and the construction of such acentric supramolecular assemblies presents a great challenge to conventional synthetic methodologies.[2] Herein we wish to report the development of a rational synthetic approach toward chiral and acentric, NLO-active 2D polymeric metal−organic coordination networks.

Construction of metal−organic coordination frameworks via metal coordination-directed self-assembly processes has proven to be a fertile field.[3] Metal−ligand coordination can also counteract unfavorable centric interactions such as dipole−dipole repulsions, and thus present a unique opportunity for the construction of acentric polymeric coordination networks.[4] Of particular interest are bipyridine-based discrete and infinite square (and rhombohedral) grids which have been extensively explored in recent years and now seem to be ubiquitous.[5] Despite the potential importance of chiral and acentric square assemblies in second-order NLO applications, their synthesis has thus far remained virtually unexplored.[6] To this end, we have explored the synthesis of chiral and acentric 2-D square grids using bifunctional bridging ligands, *m*-pyridinecarboxylates, as linking groups. When coordinated to a metal center in a *cis*-octahedral fashion, the bent configuration of the *m*-pyridinecarboxylate linking group can accommodate the planar arrangement of the metal centers so that an infinite 2-D square network can be obtained. The metal centers in such a *cis*-octahedral environment have a maximum of C_{2v} symmetry. The lack of a center of symmetry on either the metal center or the bridging ligand will ensure the acentricity (and chirality in some cases[7]) of the square network itself. Equally important is the introduction of the electronic asymmetry (push−pull effects) through the bifunctional *m*-pyridinecarboxylate linking group; such an electronic asymmetry is essential for second-order optical nonlinearity. We report here the synthesis, X-ray structures, second-order NLO properties, and high thermal stabilities of two 2D square grids: bis(nicotinato)zinc, **1**, and bis{3-[2-(4-pyridyl)ethenyl]benzoato}cadmium, **2**.

Compound **1** was obtained as colorless rectangular plate crystals in 74.3% yield by reacting $Zn(ClO_4)_2{\cdot}6H_2O$ and 3-cyanopyridine under hydro(solvo)thermal conditions (eq 1).[8] While the IR spectrum of **1** clearly indicates the absence of characteristic peaks for perchlorate groups and for cyano groups, the presence of two strong peaks at 1566 and 1403 cm^{-1} suggests the formation of carboxylate groups during the reaction.[9] The nicotinate (3-pyridinecarboxylate) group evidently results from the hydrolysis of 3-cyanopyridine.[10] **2** was prepared similarly in 66% yield by reacting $Cd(ClO_4)_2{\cdot}6H_2O$ and 4-(3-cyanostyryl)pyridine at 130 °C (eq 2).[11]



A single-crystal X-ray diffraction study of **1** reveals an infinite square grid consisting of six-coordinate Zn centers and bridging nicotinate groups (Figure 1).[12] **1** crystallizes in the chiral space group $P4_32_12$. The Zn center lies on a crystallographic 2-fold axis; the asymmetric unit contains one Zn center and one *exo*-tridentate nicotinate group. The Zn center coordinates to two carboxylate groups and to two pyridyl nitrogen atoms of four different nicotinate groups in a *cis* configuration to result in an infinite 2-D square grid. The two carboxylate groups bind to the Zn center in a highly unsymmetrical, semichelating fashion with a Zn−O2 distance of 1.998(5) Å and a Zn−O4 distance of 2.383(5) Å. The overall geometry around the Zn center is thus a highly distorted

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[7] The particular disposition of the pyridyl nitrogen atom in the *m*-pyridinecarboxylate linking group often results in C_2 symmetry on the *cis*-octahedral metal centers, thereby affording chiral 2D polymeric networks.

[8] In a typical synthesis, $Zn(ClO_4)_2{\cdot}6H_2O$ (0.186 g, 0.5 mmol) and 3-cyanopyridine (0.105 g, 1.0 mmol) were thoroughly mixed in H_2O (0.07 mL) and ethanol (0.3 mL) in a heavy-walled Pyrex tube. After heating at 130 °C for 48 h, colorless rectangular plate crystals of **1** (0.115 g, 74.3%) were obtained.

[9] Anal. Calcd for $C_{12}H_8N_2O_4Zn$, **1**: C, 46.5; H, 2.59; N, 9.05. Found: C, 46.1; H, 2.57; N, 9.00. Anal. Calcd for $C_{24}H_{20}N_2O_4Cd$, **2**: C, 59.9; H, 3.59; N, 4.99. Found: C, 59.1; H, 3.55; N, 5.11.

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[11] (3-Cyanostyryl)pyridine was prepared by Heck reaction between 3-bromobenzonitrile and 4-vinylpyridine.

[12] X-ray single-crystal diffraction data for both **1** and **2** were collected on a Siemens SMART CCD diffractometer. Crystal data for **1**: tetragonal, space group $P4_32_12$, with $a = 7.7094(2)$ Å and $c = 20.3266(7)$ Å, $U = 1208.1(1)$, Z = 4, $D_{\mathrm{calc}} = 1.70$ g/cm^3, $T = 198$ K, Mo Kα radiation ($\lambda = 0.71073$ Å). Least-squares refinement based on 1030 reflections with $I > 3\sigma(I)$ and 124 parameters led to convergence, with a final value of $R = 0.067$ and $R_w = 0.071$. Flack parameter = 0.53(5). Crystal data for **2**: orthorhombic, space group *Fdd*2, with $a = 20.6215(4)$ Å, $b = 36.4257(2)$ Å, and $c = 6.2408(1)$ Å, $U = 4687.8(1)$ Å^3, $Z = 8$, $D_{\mathrm{calc}} = 1.59$ g/cm^3, $T = 198$ K, Mo Kα radiation ($\lambda = 0.71073$ Å). Least-squares refinement based on 1143 reflections with $I > 1.5\sigma(I)$ and 199 parameters led to convergence, with a final value of $R = 0.029$ and $R_w = 0.031$. Flack parameter = 0.57(12). The fact that both structures have a Flack parameters of ~0.5 suggests that crystals of **1** and **2** used for X-ray diffraction are probably twinned.

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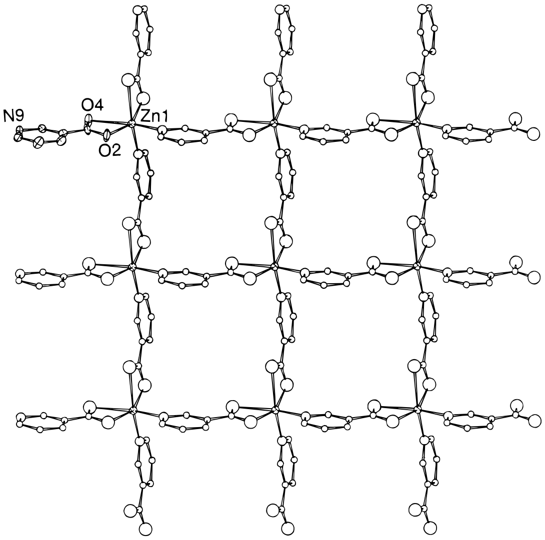

Figure 1. View of the 2D square grid structure of **1**. The ellipsoids represent the asymmetric unit and all the Zn atoms. The circles with increasing sizes represent C, N, and O, respectively.

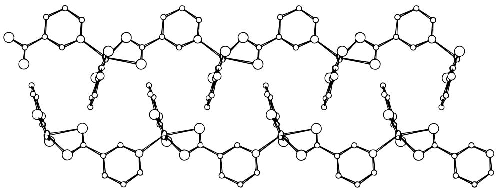

Figure 2. Interdigitation of adjacent square grids in **1** as viewed down the *b* axis. The $\pi-\pi$ stacks formed between the pyridyl rings are clearly visible.

octahedron. Each Zn center in **1** has C_2 molecular symmetry. All the Zn centers in **1** are chiral and have the same handedness (δ). Compound **1** represents the first chiral 2D square grid. At first glance, there seems to be void space in **1** with a Zn−Zn separation of 7.71(1) Å. A closer examination reveals that the pyridine rings of the nicotinate groups intrude into the square cavities in **1** to result in interdigitation of the 2-D square networks (Figure 2). The interdigitated pyridyl rings form $\pi-\pi$ stacks with a centroid-to-centroid distance of 4.18 Å (the shortest distance between interdigitated pyridyl rings is 3.64 Å). The interdigitation of pyridyl rings from adjacent square grids has efficiently filled all the void space; no solvent molecules are enclathrated in **1**.

Compound **2** crystallizes in the acentric space group *Fdd*2. The Cd center lies on a crystallographic 2-fold axis, with one Cd center and one bridging 3-[2-(4-pyridyl)ethenyl]benzoate group in the asymmetric unit. The Cd center coordinates to two carboxylate groups and to two pyridyl nitrogen atoms of four different 3-[2-(4-pyridyl)ethenyl]benzoate groups in a *cis* configuration to result in an infinite 2-D rhombohedral grid (Figure 3). The Cd−Cd−Cd angles in each rhombohedron are 84.5 and 95.5°. Similar to **1**, the two carboxylate groups bind to the Cd center in a highly unsymmetrical, semichelating fashion with a Cd1−O4 distance of 2.273(6) Å and a Cd1−O2 distance of 2.484(4) Å. Each Cd center adopts a highly distorted octahedral geometry. Owing to the larger length of the 3-[2-(4-pyridyl)ethenyl]benzoate bridging ligand *vs* the nicotinate group, there is a large void space within the rhombohedral grid in **2** (the Cd−Cd separations are 12.93(1) Å). These large cavities have been effectively filled via the interweaving of three independent rhombohedral grids in the *ac* plane (Figure 4); no enclathration of solvent molecules is observed in **2**. Each Cd center in **2** possesses a C_2 local symmetry, and is thus chiral. However, the Cd centers in adjacent layers of 3-fold interwoven rhombohedral grids have opposite chirality; compound **2** is therefore a 2D racemate.

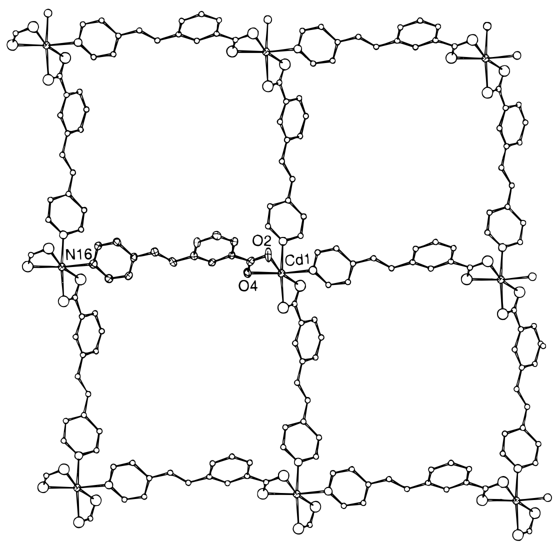

Figure 3. View of the 2D rhombohedral grid structure of **2**. The ellipsoids represent the asymmetric unit and all the Cd atoms. The circles with increasing sizes represent C, N, and O, respectively.

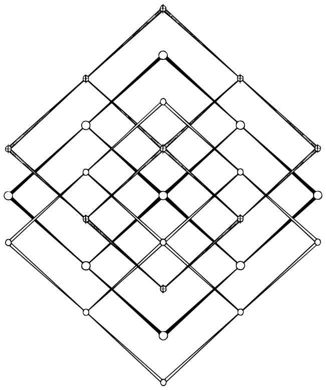

Figure 4. A schematic showing the interweaving of three independent rhombohedral grids in the *ac* plane in **2**.

Preliminary Kurtz powder second harmonic generation (SHG) measurements on compounds **1** and **2** confirm their acentricity.[13] **1** shows a modest powder SHG efficiency ($I^{2\omega}$ of 2 *vs* α-quartz), whereas **2** exhibits a powder SHG efficiency larger than technologically important $LiNbO_3$ ($I^{2\omega}$ of 1000 *vs* α-quartz).[14] Compounds **1** and **2** also exhibit remarkable thermal stabilities. Thermogravimetric analyses show that **1** and **2** have onset decomposition temperatures of 420 and 360 °C, respectively. The insolubility of **1** and **2** in common solvents also makes them potential candidates for practical NLO applications.

In summary, we have developed a rational synthetic approach toward acentric solids based on 2-D square (or rhombohedral) coordination networks using unsymmetrical linking groups. We are currently extending this strategy to the synthesis of other chiral and acentric supramolecular assemblies.

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Supporting Information Available: TGA data, details of powder SHG measurements, and crystallographic data for **1** and **2** (10 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[13] Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3798.
[14] $LiNbO_3$ has a relative powder SHG signal of 600 *vs* α-quartz.[12]