*Inorg. Chem.* **2001,** *40,* 4516−4517

# A New Metal−Organic Polymer with Large Grid Acentric Structure Created by Unbalanced Inclusion Species and Its Electrospun Nanofibers

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*Received May 18, 2001*

Crystal engineering of metal−organic polymers with functional building blocks may produce intriguing structures and properties.[1] Mimicking zeolite structures, metal−organic polymers can be deliberately designed to have micropores and large open channels. More importantly, metal−organic polymers may have properties that are not shown by zeolites, such as solubility. Soluble coordination polymers have shown interesting properties, such as moisture absorption and delivery of drugs.[2] Designing metal−organic polymers incorporated with both covalent and hydrogen bonds may achieve these properties. Hydrogen bond containing complexes may be used for generating metal−organic nanofibers[3] and as chemotherapeutic agents.[4] It has been reported that submicron fibers represent a new approach to semipermeable membranes.[5] While there has been great interest in the preparation of nanofibers, the studies on metal−organic polymers are rare.[3] Here we report new mixed-bonding acentric framework metal−organic polymers, $[(H_2O)_2Zn(BPY)(BPEN)_2]\cdot 1.75(BPEN)\cdot 0.25(BPY)\cdot 2NO_3\cdot 4.45H_2O$ (BPY = 4,4′-bipyridine; BPEN = *trans*-1,2-bis(4-pyridyl)ethylene) **1**, and its isostructural cadmium analogue **2**, created by unbalanced inclusion guest species, and **1** has been fabricated into nanofibers by electrospinning.

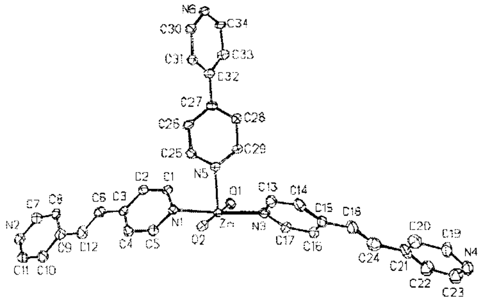

**Figure 1.** View of the basic part of the polymer showing the atom numbering scheme. Thermal ellipsoids are 40% equiprobability envelopes, with hydrogen atoms omitted. This unit has essentially two-fold symmetry.

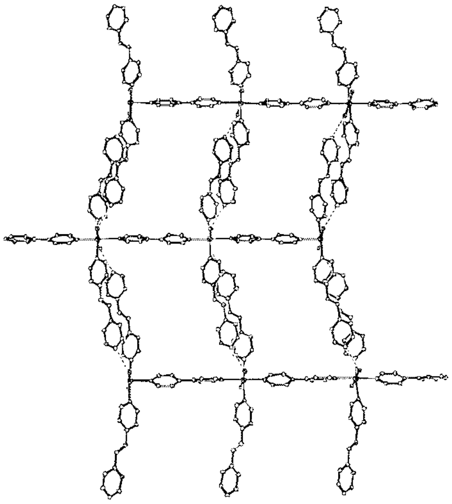

**Figure 2.** View of polymer chains and the networks, with the large rectangular grids where anions and various solvent molecules reside.

The reaction of $Zn(NO_3)_2\cdot 6H_2O$ (0.1487g) or $Cd(NO_3)_2\cdot 4H_2O$ (0.1543g) with BPY(0.0781g) and BPEN (0.1842g) in the mole ratio of 1:1:2 under hydrothermal conditions at 120 °C for 3 days produced yellow−orange crystals of **1** (79% yield) and **2** (75% yield), and they are suitable for single-crystal X-ray diffraction analysis.[6] Based on the unit cell information and the preliminary structural solution from a quick data set of **2**, it is concluded that **2** is isostructural with **1**.[6] The repeat unit of **1** with mixed-ligand bent-T-shape geometry, showing the numbering scheme, is shown in Figure 1, and the two-dimensional network structure of **1** is shown in Figure 2. The structure consists of octahedral Zn atoms coordinated by two BPY linear molecules, and the BPY−Zn−BPY chains are extended along the *b* axis. The BPY−Zn−BPY chains are then linked by double BPEN linear chains with mixed covalent and hydrogen bonds to result in a two-dimensional framework structure. The remaining two sites around the Zn metal atoms are coordinated by two water molecules. The water molecules form hydrogen bonds to the noncoordinated nitrogen atoms on the double BPEN bridging molecules (O(1)−H(1A)···N(4) 2.748(3); O(2)−H(2A)···N(2) 2.806(3) Å). Each of the double bridging BPEN molecules contains both coordinated and hydrogen-bonded N-donors; the two BPEN molecules are paired at each terminal side, with one nitrogen atom covalently bonded to the metal and one nitrogen atom hydrogen-bonded to the oxygen on the water molecule, and this double head and tail

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(1) See, for example: (a) Zaworotko, M. J. *Chem. Commun*. **2001**, 1. O'Keeffe, M.; Eddaoudi, M.; Li, H.; Reineke, T. and Yaghi, O. M. *J. Solid State Chem*., **2000**, *152*, 3. Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D. and Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474. (b) Keller, S. W. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 247. Talley, C. E.; Bean, A. C. and Albrecht-Schmitt, T. E. *Inorg. Chem*. **2000**, *39*, 5174. Lu, J. Y. and Babb, A. M. *Chem. Commun*. **2001**, 821. Lu, J. Y. and Babb, A. M. *Inorg. Chem*. **2001**, *40*, 3261.

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(6) Crystal data for **1**: FW, 1184.15; space group, *Cc*; cell dimensions $a = 17.929(1)$, $b = 11.459(1)$, $c = 28.581\ (1)$ Å, $\beta = 98.403(1)°$, $U = 5809.1(5)$ Å$^3$, $Z = 4$, Dcalc = 1.354 g cm$^{-3}$, $\mu = 0.496$ mm$^{-1}$, $T = 223(2)$ K. Final R indices $[I > 4\sigma(I)]$: R1 = 0.0305, wR2 = 0.0735. The Laue symmetry was determined to be 2/m, and from the systematic absences noted, the space group was shown to be either *Cc* or *C*2/*c*. Although the main polymeric framework fits well on a two-fold axis, the remaining anions and solvents do not conform to this symmetry and necessitate refinement in the lower symmetry space group *Cc*. Both of the anions were found to be disordered over two slightly different positions, and so each of the four orientations was refined as an ideal rigid body. Additionally, one of the two interstitial BPEN molecules was found to be replaced by BPY and water 25% of the time. Unit cell dimensions for **2**: Monoclinic, space group *Cc*, $a = 17.848(9)$, $b = 11.733(9)$, $c = 28.936\ (9)$ Å, $\beta = 98.48(2)°$. Elemental analysis: for complex **1**, Calcd. C, 58.27; H, 5.14; N, 14.19. Found: C, 58.48; H, 4.89; N, 13.91. Complex **2**, Calcd. C, 56.04; H, 4.94; N, 13.65. Found: C, 56.63; H, 4.45; N, 13.17.

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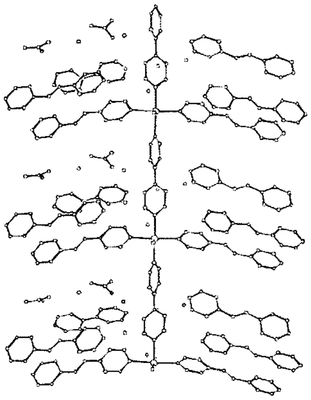

**Figure 3.** View of the polymeric chain along the *b* axis, including anions and solvents. The breaking of the two-fold symmetry of the core polymer by the interstitial material is clear. Only one orientation of each disordered group is shown at any site.

connection feature propagated to link the chains into a two-dimensional network. While the single hydrogen-bonded organic bridges have been observed in several compounds, such as $[Cu(bipy)(H_2O)_2(FBF_3)_2 \cdot bipy$,[7] $[Mn(CO)_3(OH)]_4 \cdot 2(bipy) \cdot 2MeCN$,[8] and $Co(NCS)_2(bipy)(H_2O)_2 \cdot bipy$,[9] the double bridging feature with both covalent and hydrogen bonds is more interesting. The mixed ligand network rings create large rectangles with Zn····Zn distances of 11.459 × 14.667 Å. The two-dimensional networks are assembled in such a way that the zinc atoms are located close to the centers of the cavities of adjacent 2-D nets. There are about thirty-four molecules and anions (molecules included are seven BPEN, one BPY, eight nitrates, and eighteen water molecules) in the cavities per unit cell volume. Numerous hydrogen-bonding interactions among the inclusion species are present in the structure. In total, there are 64 hydrogen-bonding interactions per unit cell volume. The included BPY, nitrates, and water molecules in the network structure are dominantly on the left side of the BPY−Zn−BPY chains (Figure 3). This left-side handedness of the inclusion species breaks down the two-fold symmetry of the network and results in an acentric coordination polymer. There are many frameworks with acentric space groups reported;[10] this mixed-bonding acentric structure is unique in that it was created by unbalanced guest species and utilizes double bridges of both covalent and hydrogen bonds.

Alternatively, the structure may be viewed as a one-dimensional covalent-bonded polymer with elongated BPEN sidearms, which are further stacked into two-dimensional nets by the $\pi$-$\pi$ interactions between the BPEN sidearms from the neighboring chains. It should be noted that the inclusion capability and the hydrogen bonding of the compound are essential elements for the soluble property of the complex.

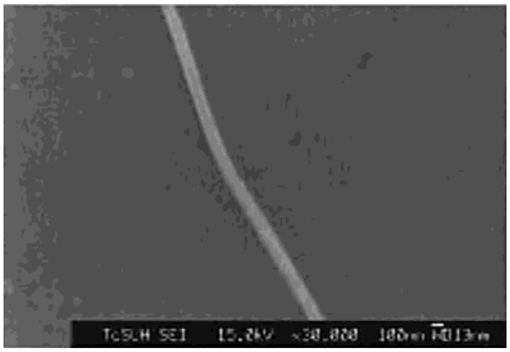

**Figure 4.** Scanning electron micrograph of electrospun nanofiber.

Complex **1** was dissolved in 10 mL of water or DMF to form a saturated metal−organic polymer solution,[11a] an electric field (25 kV) was then applied to the capillary tube filled with the solution held by its surface tension at the end of the capillary, and the applied field created a charged jet from the solution of **1**.[11b] The solvent evaporated during the travel course and left behind charged fibers that were collected on a fiber-collection screen. The diameter and morphology of the nanofibers were studied using an optical microscope and a scanning electron microscope (Figure 4). The diameters of the fibers range from 60 nm to 4 $\mu$m.

In summary, we have synthesized two new acentric framework metal−organic polymers created by unbalanced inclusion guest species. The new metal−organic polymer has been fabricated into nanofibers using electrospinning techniques. The metal−organic nanofibers and their properties are being explored in our laboratory.

**Acknowledgment.** The authors thank the financial support from the Welch Foundation and assistance from Dr. J. D. Korp in crystallography. This work made use of MRSEC/TCSUH Shared Experimental Facilities supported by the National Science Foundation and the Texas Center for Superconductivity at the University of Houston.

**Supporting Information Available:** Crystallographic tables and CIF file. These materials are available free of charge via the Internet at http://pubs.acs.org.

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(10) See, for example: Lin, W.; Wang, Z.; Ma, L. *J. Am. Chem. Soc*. **1999**, *121*, 11249. Burrows, A. D.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *Chem. Commun*. **1996**, 97.

(11) (a) The stability of **1** was confirmed by FTIR spectra before and after the recrystallization in water or DMF. (b) The electrospinning process was employed for over three decades in industries. See for example, Simons, H. L. U.S. Patent #3,280,229, 1966.