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A Polar Luminescent Zn Polymer Containing an Unusual Noninterpenetrated utp Net

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A new Zn coordination polymer with the mixed ligands of 1,3,5-benzenetricarboxylate and 1,3-bis(4-pyridyl)propane has been hydrothermally synthesized, and an unusual distorted noninterpenetrated utp [or (10,3)-d] net has been defined.

In the past decade, the remarkable progress in crystal engineering has provided a wide range of coordination polymers with potential applications as functional solid materials and new topologies.[1] Analysis of the network topology has proven to be a useful tool in the design and interrogation of crystal structures.[2,3] Recently, some new topologies [i.e. (8,4)[4]] and many of the previously unrecognized networks (i.e., $CdSO_4$,[5] NbO,[6] $SrAl_2$,[7] quartz,[8] dual quartz,[9] moganite[10]) have been enumerated or identified. Among these structures, the three-connected (10,3) nets are particularly interesting because many of them have large voids and channels inside the frameworks and they can be chiral in many cases.[11] Up to now, more than 12 different (10,3) nets have already been defined by Wells[3a,b] and Koch and Fischer.[12] The (10,3)-d (or utp) net is special in some sense compared to the chiral higher symmetry (10,3)-a (srs). Although it resembles a (10,3)-a net in the sense that it has 4-fold helices, these are alternating left- and right-handed and the whole net is therefore racemic. To our knowledge, of the utp type, there are currently only three known examples assigned in the papers. Two H-bonded complexes {resorcinol[13a] and $[Co(2,2'\text{-biimidazole})_3]\cdot 0.5DMF\cdot 0.8H_2O$[13b]} and a 3D polymer $[Co(NO_3)(1,4\text{-bis}(3\text{-pyridyl})\text{-}2,3\text{-diaza-}1,3\text{-butadiene})_{1.5}]\cdot H_2O$[13c] represent this topology. Both of the two metal coordination complexes exhibit an interpenetrated

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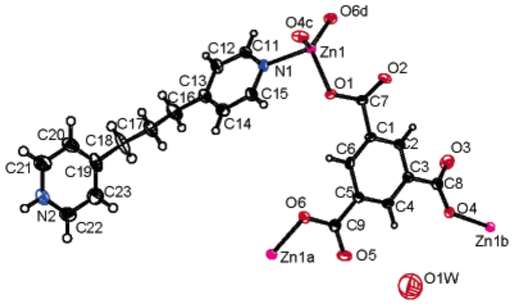

Figure 1. ORTEP drawing of the molecular structure of complex **1**. Symmetry codes: (a) $-x, -1 - y, -^1/_2 + z$; (b) $^1/_2 + x, -3/2 - y, z$; (c) $-^1/_2 + x, -^3/_2 - y, z$; (d) $-x, -1 - y, ^1/_2 + z$.

utp net. However, a coordination polymer with a noninterpenetrated utp net has not been reported to date.

As a highly symmetric triangular ligand, 1,3,5-benzenetricarboxylate (BTC) is a good selection for the construction of a (10,3) net. A self-assembly reaction of BTC and $Zn(NO_3)_2$ gives a chiral complex $[Zn_2(BTC)(NO_3)](H_2O)(C_2H_5OH)_5$ with a srs net.[14] Our strategy is based upon the coordination of a d-block metal (Zn^{II}) with the BTC ligand and a long but flexible ligand 1,3-bis(4-pyridyl)propane (BPP) as the auxiliary (second) ligand.[15] As the BPP ligand was added to the Zn−BTC system, the reticular construction was changed drastically. In this Communication, we describe an unusual distorted noninterpenetrated utp net in a Zn^{II} metal−organic polymer $[Zn(BTC)(HBPP)]_n \cdot nH_2O$ (**1**).

Complex **1** was hydrothermally synthesized at 160 °C.[16] The structure of the complex was identified by satisfactory elemental analysis, IR, and X-ray diffraction.[17] X-ray diffraction of the complex indicates that it crystallized in noncentrosymmetric space group $Pna2_1$. Its Fourier transform IR spectrum showed the expected absorptions for the symmetric and asymmetric vibrations of BTC (1632 and 1435 cm^{-1}) and a H-bonded water (3419 cm^{-1}). It showed no absorptions for any protonated BTC (1730−1690 cm^{-1}), indicating the complete deprotonation of H_3BTC.

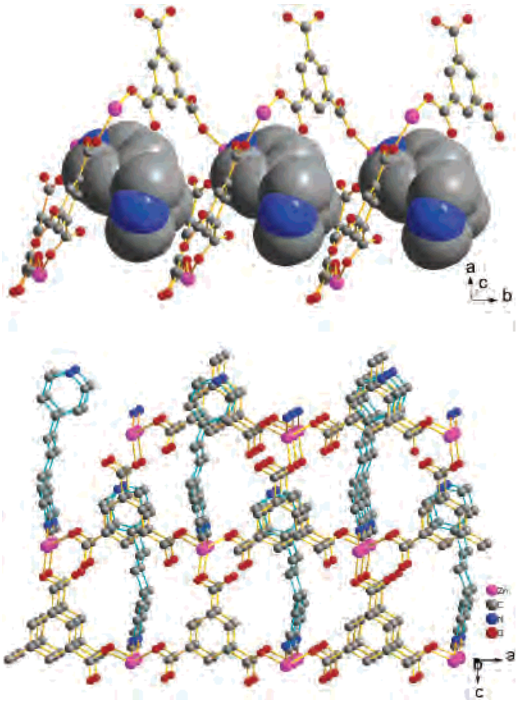

Figure 2. Top: view of the 1D helix-encapsulated BPP ligands. Bottom: packing diagram of complex **1**, showing the large channels along the *b* axis and the orientation of the BPP ligands.

The crystal structure of **1** is illustrated in Figure 1. Each BTC ligand bridges three Zn^{II} ions in a trigonal-planar fashion by its three carboxylate groups in the monodentate mode [Zn−O = 1.923(5), 1.948(5) and 1.951(4) Å, respectively]. Each Zn atom locates at the center of a distorted tetrahedral geometry with three O donors from three individual carboxylate groups and one N donor from the terminal BPP ligand [Zn−N = 2.063(6) Å]. While one of the two BPP pyridyl groups is protonated, the auxiliary BPP ligand does not bridge Zn^{II} ions in the net. The BTC ligand adopts two carboxylate groups to link the Zn centers to give a 1D cylindrical 6_1 helix in the *b* direction (Figure 2). The Zn−Zn distances bridged by BTC are in the range of 8.15−10.64 Å, and the repeating period in the helical column is about 7.89 Å. The diameter of the helical column is about 11.22 Å. Each helical column is occupied by a BPP ligand. The uncoordinated pyridine ring of the BPP ligand is parallel to the benzene ring of the BTC ligand, but no interactions are found between them. From another point of view, it is the BPP ligand that molds the formation of such a helix. The third carboxylate group of the BTC ligand binds to the unsaturated site of the Zn center of other helices, resulting in the final 3D architecture. Because of the presence of large template BPP ligands, no interpenetrated phenomenon is found. Another interesting feature of the complex is that all uncoordinated ends of the BPP ligands are extended to the same direction, so no center of inversion can be found and the whole framework is polar.

If BPP ligands are ommited, the Zn atom can be looked at as a three-coordinate nonplanar node with triangular-pyramidal geometry. Because the BTC ligand can be looked at as a planar three-coordinate node, the whole network can

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(16) A mixture of $ZnSO_4 \cdot 7H_2O$ (0.287 g, 1.0 mmol), BPP (0.198 g, 1.0 mmol), benzene-1,3,5-tricarboxylate acid (0.105 g, 0.5 mmol) with NaOH (0.040 g, 1.0 mmol), and 15 mL of water was placed in a Parr Teflon-lined stainless steel vessel (25 cm^3), and then the vessel was sealed and heated to 160 °C. The temperature was held for 3 days, and then the reactant mixture was cooled at a rate of 0.5 °C min^{-1} to lead to the formation of colorless crystals of **1** (yield = about 35% based on Zn; final pH = 5.2). Anal. Calcd for **1**: C, 53.95; H, 4.12; N, 5.72. Found: C, 53.99; H, 4.22; N, 5.69. IR (solid KBr pellet, v/cm^{-1}) for complex **1**: 3419 (m), 1633 (vs), 1567 (m), 1435 (s), 1366 (s), 1227 (m), 1099 (w), 1030(m), 767 (s), 718 (s), 615 (w).

(17) Crystal data for **1**: $C_{22}H_{20}N_2O_7Zn$, $M_r = 489.77$, colorless crystal (0.25 × 0.20 × 0.15 mm), orthorhombic, space group $Pna2_1$, $a = 19.0972(12)$ Å, $b = 7.8864(5)$ Å, $c = 13.7586(8)$ Å, $V = 2072.2(2)$ Å^3, $Z = 4$, $T = 293(2)$ K, $\rho_{calcd} = 1.570$ g cm^{-1}, $F(000) = 1008$, $\mu = 1.234$ mm^{-1}, Flack = 0.04(2), R1(wR2) = 0.0460 (0.1228), and $S = 1.026$ for 2318 reflections with $I > 2\sigma(I)$.

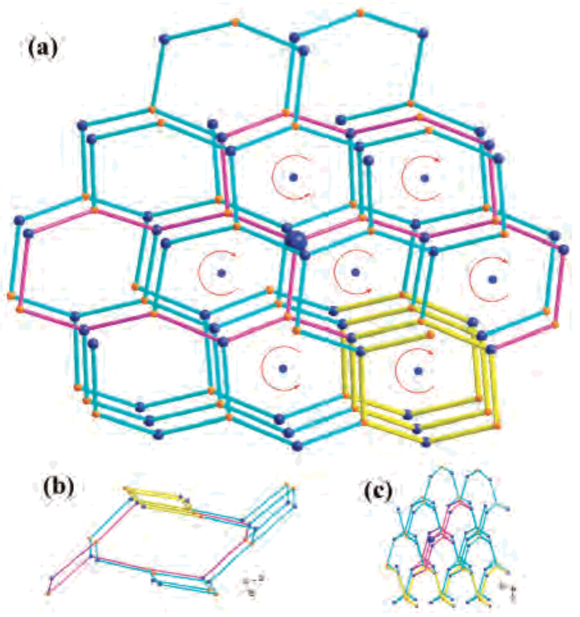

Figure 3. Schematic representation of the (10,3) net in **1** along the *a*, *b*, and *c* axes. Highlighted are a single helix (yellow) and three 10-membered shortest circuits (purple). The handedness of some helices is illustrated as red arrows, and the center dot defines the direction as out of the page.

thus be represented topologically by two types of three-coordinate nodes (triangular-pyramidal and trigonal-planar nodes, respectively). The whole structure can be extended to an unusual (10,3) net, as displayed in Figure 3. The extended Schläfli symbol of this net is $10_2.10_4.10_4$, which is assigned to the utp net. One triangular-pyramidal node links three planar nodes, and the angles between the three planes are 21.37°, 51.54°, and 56.41°, respectively. An interesting feature of this (10,3) net is the presence of parallel single helices running through the structure, as highlighted in Figure 3a. This net is constructed by hexagonal helices along the *b* axis. Each hexagonal helix connects to six adjacent helices by sharing a common edge. Because the right- and left-handed helices are alternatively arranged, the whole net is therefore racemic. The present net is strongly distorted. It differs from the regular utp net in the following three aspects: (i) It contains two type of nodes and cannot be classified as either a "regular" net [all vertexes, edges, and angles are equivalent (related by symmetry)] or a "quasi-regular" net [all vertexes and edges (but not angles) are equivalent]. (ii) Because of the presence of the triangular-pyramidal node, the 4_1 helical deposition in the regular utp net is lowered to 2_1 helical deposition. (iii) The space group of the most symmetrical configuration of the utp net is *Pnna*, which is different from the noncentrosymmetric space group $Pna2_1$ of complex **1**.

Thermogravimetric analysis (TGA) of **1** was performed in a N_2 atmosphere when it was heated to 800 °C at a rate of 10 °C min^{-1}. The TGA diagram of **1** indicates two main steps of weight losses (Figure S1 in the Supporting Information). The weight loss begins at 50 °C and is completed at 160 °C. The observed weight loss of 3.68% corresponds to the loss of the water molecules (calcd 3.67%). The framework $[Zn(BTC)(HBPP)]_n$ is stable up to 340 °C, and then decomposition starts.

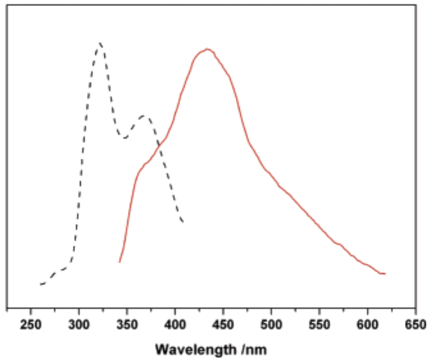

Figure 4. Fluorescent excitation (dashed line) and emission (red line) spectra of complex **1** in the solid state at room temperature.

Complex **1** is totally transparent in the visible region and insoluble in common solvents. The powder second-harmonic generation (SHG) measurements[18] of complex **1** (the powders were from crystals) were carried out in a manner similar to that described by Kurtz at $\lambda = 1064$ nm. It has a SHG of about 2 times as large as that of potassium dihydrogen phosphate, which confirms its nonlinear optical behavior and validates the noncentrosymmetric space group.

Preliminary fluorescence measurements in the solid state of **1** showed a broad band with a maximum at 440 nm when irradiated at 320 nm at room temperature (Figure 4). The intense emissions for the BTC ligands occur at 370 nm ($\lambda_{ex} = 334$ nm). A similar emission band at about 430 nm has also been observed previously for other zinc organic polymer compounds with either photoluminescent or nonphotoluminescent ligands. Therefore, this emission may not be related to the $\pi^* \rightarrow n$ transition of the ligands but simply arises from the charge-transfer transition.[19]

In summary, we have defined an unusual distorted noninterpenetrated utp net based on Zn coordination with the mixed ligands of BTC and BPP. The present results demonstrate that the template effect of the auxiliary ligand plays an important role in the construction of novel topological nets.

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Supporting Information Available: The TGA diagram of complex **1** and X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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