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# A New Metal–Organic Open Framework Consisting of Threefold Parallel Interwoven (6,3) Nets

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Threefold parallel interwoven (6,3) nets were assembled from Ni(II) cyclam complex and 1,3,5-tris[2-(4-carboxyphenyl)-1-ethynyl]benzene. The network generates triangular voids of effective size ca. 18.4 × 14.7 × 9.5 Å. It contains 35% free volume of the crystal volume and is stable up to 300 °C.

Although interpenetration is a major impediment in the achievement of a large size of channels or cavities in the metal−organic open framework,[1−5] it can occasionally provide permanent porosity in the structure.[6,7] To obtain metal−organic open frameworks without interpenetration, we have utilized macrocyclic complexes as metal building blocks.[8−12] When 1,3,5-tricarboxybenzene was used as an organic building block, the frameworks generated cavities or channels of effective size ca. 10 Å and their thermal stabilities ranged up to 200 °C.[8−11] They showed selective binding of guest molecules such as D-glucose, metal complexes, alcohols, and aromatic compounds. To create much larger cavities in the 2D networks, which possibly interpenetrate or interweave one another, we now employed a big organic building block, 1,3,5-tris[2-(4-carboxyphenyl)-1-ethynyl]benzene (TCPEB).[13]

The self-assembly of TCPEB with Ni(II) cyclam complex in a mixture of DMF/water/pyridine (1.5/2/3, v/v) results in $[Ni(C_{10}H_{24}N_4)]_3[C_{33}H_{15}O_6]_2\cdot 6C_5H_5N\cdot 4H_2O$ (**1**).[14,15] **1** is insoluble in water and common organic solvents, and slightly soluble in a pyridine−$H_2O$ mixture. The **1** crystal retains transparency upon exposure to the atmosphere, but it loses guest molecules in air as evidenced by elemental analyses.

In **1**, 2D (6,3) networks with honeycomb cavities of ca. 50 Å size are built but they are triply parallel interwoven[16,17] to give rise to a thick 2D layer that generates smaller triangular voids of dimensions 23.6 × 23.5 × 23.7 Å with an effective cavity size ca. 18.4 × 14.7 × 9.5 Å. **1** contains 35% free volume of the crystal volume and shows thermal stability up to 300 °C. To the best of our knowledge, this is the first example of the interwoven nets assembled from macrocyclic complexes. In addition, it is quite unusual that the 3-fold parallel interwoven structure contains free volume. There exist many parallel interpenetrating 2D networks, but their free spaces are blocked by the interpenetrating nets.[18−20]

An ORTEP view of the fundamental unit of **1** is shown in Figure 1. In **1**, each Ni(II) macrocyclic complex is

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(14) Synthesis of **1**. To an aqueous solution (2.0 mL) of $[Ni(C_{10}H_{24}N_4)](ClO_4)_2$ (30 mg, 0.086 mmol) was slowly added a DMF/pyridine solution (1:2 v/v, 4.5 mL) of TCPEB (19 mg, 0.18 mmol). The solution was heated to 60 °C and then hot-filtered. The filtrate was allowed to stand at room temperature for several days until yellowish-pink crystals formed, which were filtered off, washed with water and EtOH, and dried in air. (When more water or DMF was used, only insoluble precipitates formed instead of crystals.) Yield: 48%. FT-IR for **1**: $\nu_{O-H}$, 3372 cm$^{-1}$; $\nu_{N-H}$, 3266, 3159 cm$^{-1}$; $\nu_{C=O}$, 1584, 1377 cm$^{-1}$; $\nu_{C=C}$, 1544 cm$^{-1}$. UV/vis (diffuse reflectance): $\lambda_{max}$ = 513 nm. Since the original crystal loses guest molecules upon exposure to air, we cannot obtain consistent elemental analysis data for the original crystal. Therefore, we provide the data for the dried crystal. Anal. Calcd for the solid dried at 100 °C under vacuum for 2 h, $[Ni(C_{10}H_{24}N_4)]_3[C_{33}H_{15}O_6]_2\cdot 2.5H_2O$ ($Ni_3C_{96}H_{110}N_{12}O_{16}$): C, 62.80; H, 5.87; N, 9.15. Found: C, 62.80; H, 6.16; N, 9.13.

(15) For X-ray crystallography, see Supporting Information. Crystal data of **1**: $Ni_3C_{126}H_{140}N_{18}O_{16}$, fw = 2338.68, monoclinic, space group $P2_1/C$, $a$ = 9.424(5) Å, $b$ = 40.582(5) Å, $c$ = 15.819(5) Å, $\beta$ = 96.183(5)°, $V$ = 6014.7(38) Å$^3$, $Z$ = 2, $T$ = 293 K, R1 = 0.0534 ($I > 2\sigma(I)$), wR2($F^2$) = 0.1235 ($I > 2\sigma(I)$). GOF = 0.928, the largest peak and hole = 0.8532/−0.257.

(16) "Interpenetrating" is widely used, but "interwoven" is used specifically to illustrate the parallel interpenetration of wavy 2D layers.[17]

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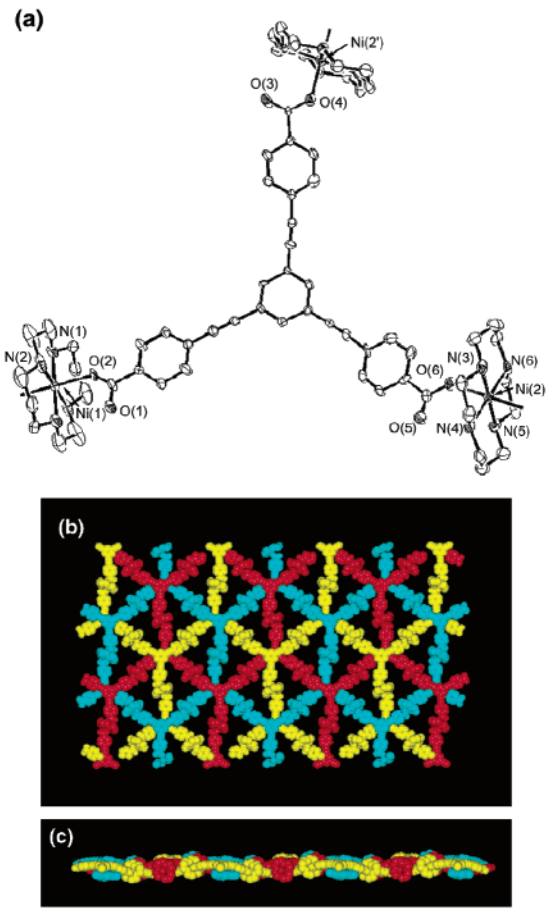
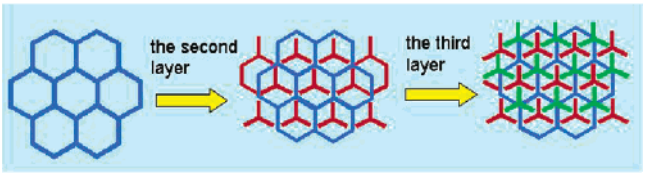



**Figure 1.** (a) An ORTEP drawing of the building block unit of **1** with selected atomic numbering scheme. Thermal ellipsoids are drawn with 30% probability. Symmetry code: (′) $-x + 1, y + {}^1/_2, -z + {}^1/_2$. CPK representations for top view (b) and side view (c) of **1**, showing 3-fold parallel interwoven (6,3) nets. **1** contains 35% free volume of the crystal volume.

**Scheme 1.** Schematic Representation of Interwoven Structure




coordinated with two carboxylate oxygen atoms of $TCPEB^{3-}$ at the axial sites to display a distorted octahedral coordination geometry, and each $TCPEB^{3-}$ ion binds three Ni(II) complexes, which gives rise to a 2D (6,3) net (Figure 1). The Ni−O(carboxylate) and Ni−N(macrocycle) bond distances are average 2.119(3) and 2.052(5) Å, respectively. The four benzene rings in the $TCPEB^{3-}$ ligand are relatively coplanar (dihedral angles between central benzene and the three terminal phenyl rings are 4.19°, 20.50°, and 17.90°), but the whole ligand is slightly bowl-shaped, which makes the 2D layers undulate. The undulating (6,3) net contains honeycomb-like cavities, each of which is made up of six Ni(II) macrocyclic complexes and six $TCPEB^{3-}$ ligands. The corner-to-corner distance of the cavity is 48.9−53.1 Å (Ni···Ni distance between opposite sides of the cavity, ca. 40.6 Å). In the structure, any two (6,3) undulating nets are

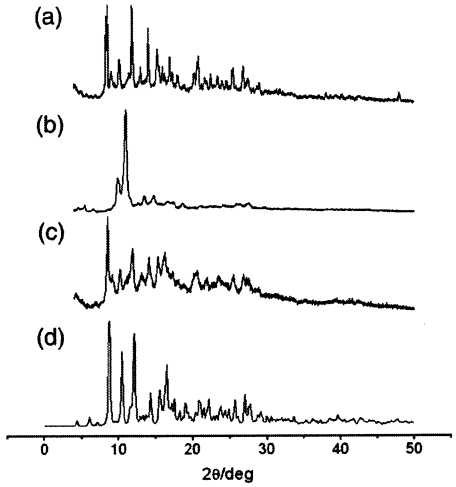



**Figure 2.** XRPD patterns for (a) original host solid **1**, (b) evacuated solid at 78 °C for 2.5 h, (c) sample in b immersed in pyridine/$H_2O$ (v/v, 3/2) for 50 min, and (d) simulated pattern based on single-crystal X-ray data of **1**.

parallel but the third layer weaves them to construct a thick triply interwoven 2D structure as described in Scheme 1. Within the triply interwoven nets, the central benzene units of $TCPEB^{3-}$ in a layer exhibit offset $\pi-\pi$ interactions with those of the other layers (shortest C···C distance, 3.470 Å). Between the thick 2D layers, there exist offset $\pi-\pi$ interactions between the central benzene rings of $TCPEB^{3-}$ ions in a layer and the 4-carboxyphenyl rings belonging to the adjacent layers (shortest C···C distance, 3.535 Å).

Due to the interwoven phenomena, each honeycomb cavity (48.9−53.1 Å size) in the (6,3) net is divided into six smaller triangular voids of dimensions 23.6 × 23.5 × 23.7 Å (effective cavity size ca. 18.4 × 14.7 × 9.5 Å). The cavities are filled with six pyridine and four water guest molecules per unit formula. Some pyridine guest molecules show $\pi-\pi$ interactions with 4-carboxyphenyl rings of the host (centroid distances, 4.386 and 4.669 Å; dihedral angles, 48.12° and 55.31°, respectively). Some water guest molecules are hydrogen bonded with the free carbonyl oxygen atoms of the $TCPEB^{3-}$ molecule (O3···Ow2, 2.752 Å), secondary amines of the macrocycle (N3···Ow1, 3.064 Å), and pyridine guest molecules (N8···Ow2 ($x, -y + {}^1/_2, z + {}^1/_2$), 2.892 Å). The free volume of a unit cell is 2127.2 $Å^3$ (35.4%) as estimated by PLATON.[21]

Thermal gravimetric analysis for the crystalline sample **1** indicates that all guest molecules are continuously removed at 23−205 °C. The remaining compound can be heated to 300 °C without any additional weight loss. Compared with other noninterwoven open frameworks built with Ni(II) macrocyclic complexes,[8−12] **1** shows better thermal stability presumably due to the interwoven structure.

In Figure 2, the XRPD pattern of **1** as prepared is compared with that of the evacuated solid as well as that of the simulated pattern obtained from the single-crystal X-ray data. The dried solid prepared at 78 °C under vacuum shows broad peaks at different positions, as compared with the pattern of **1** as synthesized. This indicates that the structure

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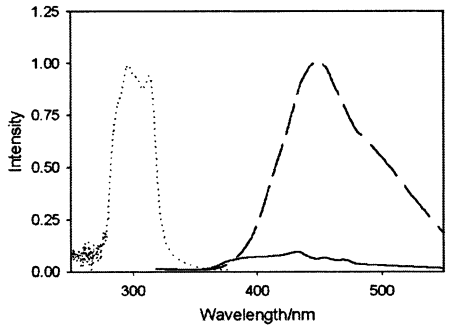


**Figure 3.** Solid fluorescent emission spectra for **1** (—) and TCPEB (– –) and absorption spectrum for TCPEB in 0.1 M NaOH aqueous solution (···), respectively.

of the dried solid is altered. The gas sorption study on the dried solid gave a Langmuir surface area of 6.07 $m^2/g$, which indicates the poor porosity of the dried solid. (It has been frequently observed in our laboratory that 2D layers slide relative to one another to block the pores when a vacuum was applied to the solid for the gas sorption measurement.) However, when the dried solid was immersed in the mixture of $H_2O$/pyridine (2:3, v/v) for 50 min, an XRPD pattern similar to that of the original solid was regenerated (Figure 2c). This indicates that the structure of 3-fold interwoven nets is maintained throughout the processes of removal and rebinding of the guest molecules.

The solid fluorescent emission spectra of free ligand TCPEB and **1** are presented in Figure 3. The free ligand TCPEB emits fluorescent light at $\lambda_{max} = 447$ nm in the solid state when it is irradiated at 300 nm. However, the fluorescence is effectively quenched in the solid **1**. The fluorescent quenching in **1** occurs probably because the Ni(II) ion possesses low-energy half-filled d levels suitable for a double exchange energy (or electron) transfer process with TCPEB ligand.[22]

In conclusion, we have constructed 3-fold parallel interwoven nets by the self-assembly of a Ni(II) macrocyclic complex and a big rigid tricarboxylate ligand. In the structure, three independent (6,3) nets with honeycomb-like cavities (49−53 Å size) interweave to give rise to the 2D open framework generating smaller triangular voids, which provides 35% free volume. Although free TCPEB ligand emits fluorescent light, the emission was quenched in the solid **1**.

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**Note Added after ASAP:** Due to a production error, the Supporting Information paragraph in the version of this paper posted ASAP on January 7, 2003, incorrectly lists an ORTEP view. The correct description of the Supporting Information is present in the version posted on January 10, 2003.

**Supporting Information Available:** FT-IR spectrum of the dried solid, TGA and DSC plots, crystallographic tables, and an X-ray crystallographic file in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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