Organic Nanotubes

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A Nanotube of Cyclic Porphyrin Dimers Connected by Nonclassical Hydrogen Bonds and Its Inclusion of C_{60} in a Linear Arrangement**

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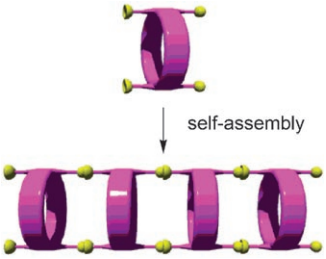
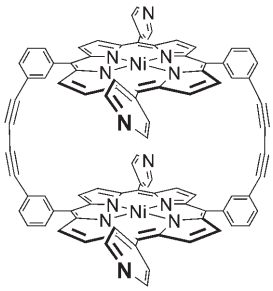
Recently, there has been great interest in the design and synthesis of nanotubular assemblies composed of porphyrin derivatives.[1] They are expected to offer tailored one-dimensional spaces and to be employed in technological applications, such as molecular-scale electronics, optical devices, sensors, light-energy conversion, and catalysis.[2,3] Moreover, supramolecular architectures consisting of porphyrin derivatives and fullerenes are currently attracting much attention as functional materials,[4,5] and a synthetic supramolecular peapod in which fullerenes are aligned within an organic nanotube has been of interest as an analogue to fullerenes included in carbon nanotubes.[1a,6,7] However, it has still been difficult to create the rationally predictable structure of a porphyrin nanotube, and there have been only a few examples of porphyrin nanotubes crystallographically analyzed at the atomic level.[1b–f] One method to construct organic nanotubes is to introduce self-assembling substituents into rigid cyclic molecules to stack them in one direction (Scheme 1).[8] We



Scheme 1. Schematic representation of the strategy for the formation of a tubular assembly with cyclic molecules.

have tried to build a new nanotube by applying this method to a rigid cyclic porphyrin dimer bearing self-assembling substituents. The resulting porphyrin nanotube was characterized by X-ray crystallography, and it can include C_{60} in its inner channel to produce a one-dimensional array.

A cyclic porphyrin dimer[9] linked by butadiyne moieties was chosen as the rigid ring, and the 4-pyridyl group was adopted as the self-assembling substituent vertical to the ring plane (Scheme 2). The designed dimer (Ni_2-CPD_{Py}) was



Ni_2-CPD_{Py}

Scheme 2.

predicted to construct a tubular assembly through complexation of the pyridyl groups with hydrogen-bonding donors or metal ions.[10–13] Ni_2-CPD_{Py} was synthesized from the corresponding nickel porphyrin monomer with two terminal C–C triple bonds by Glaser coupling catalyzed by copper(I) under air in 30% yield.[14]

Red single crystals of Ni_2-CPD_{Py} suitable for X-ray crystallography were obtained after slow evaporation of a $CHCl_3$/toluene solution. The Ni_2-CPD_{Py} molecule has a rectangular shape and a C_2 axis, which is parallel to the crystallographic *b* axis and bisects the axis through the two Ni ions (Figure 1a and Figure S1 in the Supporting Information).[15] The distances between the two Ni ions and the two midpoints of the butadiyne moieties are 11.635(1) Å and 13.585 Å, respectively. The porphyrin rings are ruffled, with alternating displacements of the *meso* carbon atoms above and below the plane formed by the four nitrogen atoms. The *meso* carbon atoms with pyridyl substituents are displaced outward by 0.503 and 0.553 Å, and the other *meso* carbon atoms are displaced inward by 0.473 and 0.603 Å. In comparison with the structure of the analogous porphyrin dimer,[9c] the most important differences are that the two porphyrin rings are rotated around the center-to-center axis by 26.4° with respect to each other and that the two butadiyne moieties are not coplanar; they display a torsion angle of 34.4° (Figure 1b,c and Figure S1 in the Supporting Information). Four solvent toluene molecules are incorporated into the structure per Ni_2-CPD_{Py} molecule, two inside the cavity and two outside.

Interestingly, a nanosized tubular assembly is observed in the crystal packing of Ni_2-CPD_{Py} without an additional hydrogen-bonding donor or metal ion. The tubular structure

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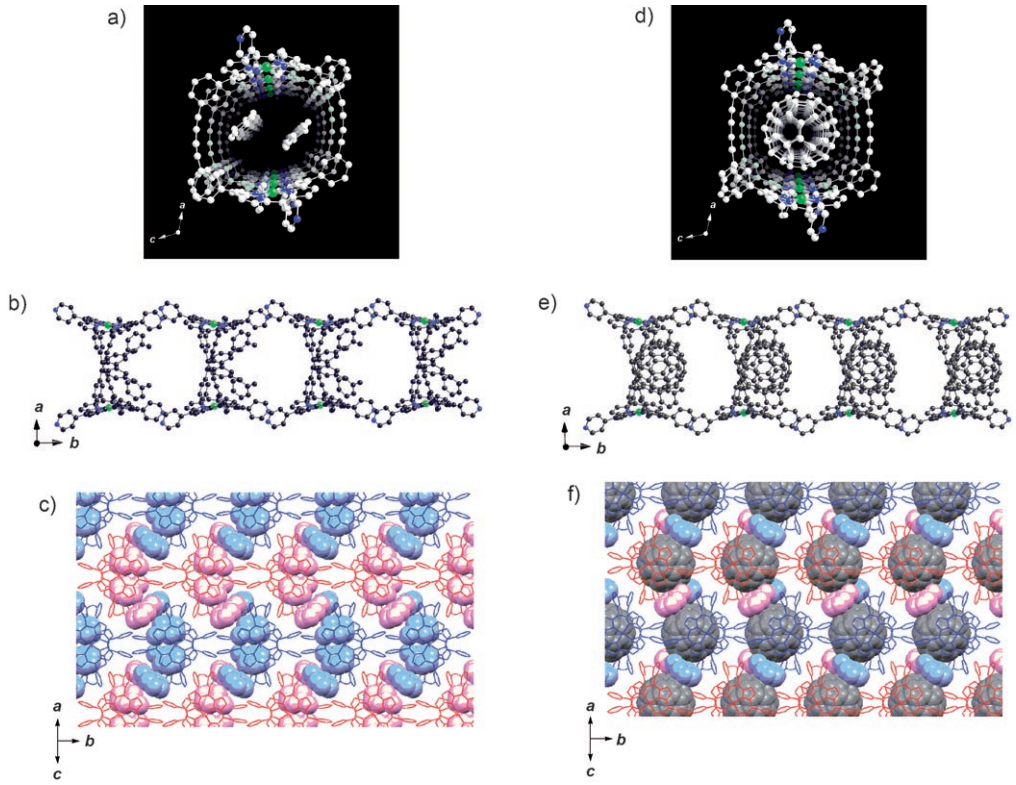

Figure 1. Crystal structures of tubular assemblies of a–c) Ni_2-CPD_{Py} and d–f) $C_{60}\subset Ni_2$-CPD_{Py}. Hydrogen atoms are omitted for clarity. a, d) front view; b, e) side view; c, f) top view. In (a, b, c, d), Ni green, N blue.

along the crystallographic *b* direction is formed by self-assembly through two kinds of cooperative noncovalent interactions between the cyclic molecules (Figure 2). One is a pair of complementary C–H···N hydrogen-bonding interactions between the pyrrole β-CH and the nitrogen atoms of the pyridyl groups with C···N distances of 3.328(5) and 4.020(6) Å, whereby the latter indicates a fairly weak bond. Such a nonclassical C–H···N hydrogen bond has rarely been observed for pyridyl groups in supramolecular structures,[16,17] in contrast to numerous examples of self-assembly through the coordination of pyridyl ligands to metal ions.[12,13] The other noncovalent interaction is a weak π–π interaction between the pyridyl groups. For this interaction, the shortest carbon–carbon distance is 3.478(7) Å and the dihedral angle of 13.04°. As a whole, the adjacent dimers along the *b* axis are linked by four hydrogen bonds and two π–π interactions. These noncovalent interactions construct a one-dimensional porphyrin array with a center-to-center distance of 14.537(1) Å, and the porphyrin planes and the butadiyne moieties form a rectangular channel along the *b* axis. The two toluene molecules outside the cavity also constitute part of the side wall of the tube. Ni_2-CPD_{Py} has an axial chirality stemming from the rotation of the two porphyrin molecules around the center-to-center axis. Each tube along the *b* axis is also chiral, because it comprises molecules of only one enantiomer. The tubes are aligned along the *c* direction with alternating enantiomers to make the crystal racemic.

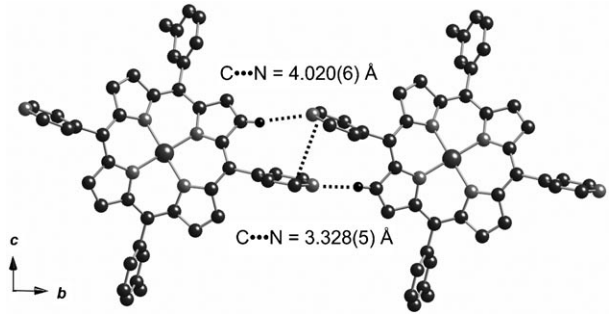

Figure 2. Details of the noncovalent interactions linking the cyclic porphyrin dimers in the crystal of Ni_2-CPD_{Py}. Hydrogen atoms are omitted except in the C–H···N moieties. N, Ni gray; C, H black.

Since Ni_2-CPD_{Py} has a suitable size for C_{60} inclusion, we investigated its potential as a host for C_{60}. The Job plot (415 nm) based on the UV/Vis absorption spectrum upon mixing of Ni_2-CPD_{Py} and C_{60} in $CHCl_3$/toluene at room temperature displayed a typical signature pattern for the formation of a 1:1 host–guest complex.[14] From the titration of Ni_2-CPD_{Py} with C_{60}, the association constant (K_{assoc}) was evaluated to be 2.0×10^5 M.[14] This value is nearly the same as that of the cyclic nickel porphyrin dimer linked by $-O(CH_2)_6O-$ spacers rather than by butadiyne.[18] Electrospray ionization mass spectrometry (ESI-MS) of a 1:1 mixture of Ni_2-CPD_{Py} and C_{60} in CH_2Cl_2/MeOH/CH_3COOH (50/50/0.2) revealed two peak clusters at *m*/*z* 2160.2 ($[Ni_2\text{-}CPD_{Py}+C_{60}]^+$) and 1080.3 ($[Ni_2\text{-}CPD_{Py}+C_{60}]^{2+}$).[14] The ^{13}C NMR spectrum of a 1:1 mixture of Ni_2-CPD_{Py} and ^{13}C-enriched

C_{60} in [D_8]toluene/$CDCl_3$ (1:1) showed a singlet signal arising from included C_{60} at $\delta = 141.7$ ppm, which is upfield from that of free C_{60} (143.4 ppm).[14]

One molar equivalent of C_{60} in toluene was added during the crystallization of Ni_2-CPD_{Py} in $CHCl_3$ to obtain reddish-black single crystals. X-ray crystallography revealed the 1:1 inclusion complex of C_{60} with Ni_2-CPD_{Py} ($C_{60}\subset Ni_2$-CPD_{Py}, see Figure S1 in the Supporting Information).[15] Both $C_{60}\subset Ni_2$-CPD_{Py} and Ni_2-CPD_{Py} crystallize in the same space group (*C*2/*c*) and have very similar lattice parameters. Therefore, the structure of Ni_2-CPD_{Py} with included C_{60} is similar; it displays C_2 symmetry and a slight increase of the ruffling distortion of the porphyrin rings.[19] In the crystal structure, two toluene molecules per $C_{60}\subset Ni_2$-CPD_{Py} molecule occupy almost the same positions outside the cavity as in the crystal of Ni_2-CPD_{Py}. A tubular assembly formed by the same C–H···N hydrogen bonds and π–π interactions is observed in the crystal packing of $C_{60}\subset Ni_2$-CPD_{Py} as in Ni_2-CPD_{Py} (Figure 1 d–f).[20] On the basis of the structural parameters of the C–H···N and pyridyl···pyridyl motifs, the weaker hydrogen bond and the π–π interaction appear to be enhanced in $C_{60}\subset Ni_2$-CPD_{Py}. The C_{60} molecules are linearly arranged in the inner channel to give a supramolecular peapod.[1a,6,7] The distance between the centers of the C_{60} molecules along the channel is 14.498(2) Å. There is a small difference in arrangement of the tubes between Ni_2-CPD_{Py} and $C_{60}\subset Ni_2$-CPD_{Py}. The molecular framework of Ni_2-CPD_{Py} changes from rectangular to square upon inclusion, as evidenced by the increased distance (12.596(2) Å) between the two Ni ions and the decreased distance (12.735 Å) between the midpoints of the butadiyne moieties. These results indicate that the inclusion takes place in an "induced fit" fashion. In most examples of inclusion complexes of C_{60} with porphyrins, the C_{60} molecule is situated above the center of porphyrin unit, and a 6:6 ring-juncture C–C bond of the fullerene is closest to the porphyrin, rather than a 6:5 junction.[4,18] However, in the present case (Figure 3), the C_{60} molecules are not located above the centers of the porphyrin units, because the cavity is slightly smaller than in the reported face-to-face porphyrin dimer with the $-O(CH_2)_6O-$ linkages.[18] The closest interaction in $C_{60}\subset Ni_2$-CPD_{Py} is a π–π stacking interaction between a six-membered ring of C_{60} and the six-membered ring composed of a pyridyl-substituted *meso* carbon atom, two α carbon atoms, two pyrrole nitrogen atoms, and the Ni ion. This interaction has a center-to-center distance of 3.459 Å and a dihedral angle of 11.46°. The nearest atoms of the Ni_2-CPD_{Py} molecule to C_{60} are two pairs of *ortho* hydrogen atoms of the pyridyl and phenyl groups, the C–H bonds of which are oriented towards C_{60} six-membered rings with separations between the carbon atoms and the ring centers of 3.525 and 3.796 Å, respectively, to realize multiple C–H···π interactions. It is likely that C_{60} is fixed by these noncovalent interactions with the Ni_2-CPD_{Py} molecule.

In conclusion, we have demonstrated the synthesis of a new porphyrin nanotube from the cyclic porphyrin dimer Ni_2-CPD_{Py} with self-assembling pyridyl substituents. The tube is constructed by the stacking of the cyclic molecules through unique C–H···N hydrogen bonds and π–π interactions of the pyridyl groups in the crystal. Furthermore, the formation of the 1:1 inclusion complex of C_{60} with Ni_2-CPD_{Py} ($C_{60}\subset Ni_2$-CPD_{Py}) was confirmed both in solution and in the crystal. C_{60} molecules are linearly arranged in the inner channel of the tubular assembly in the crystal. To the best our knowledge, this is the first example of an X-ray crystal structure determination for a supramolecular peapod.[1a,4–7] Some previous porphyrin nanotubes needed specific guest molecules for their formation and disassembled in the absence of the guests.[1a–d] In contrast, there are only small changes in the tubular structures between Ni_2-CPD_{Py} and $C_{60}\subset Ni_2$-CPD_{Py}, thus indicating the large tolerance of this porphyrin nanotube toward guest inclusion. Investigation of the inclusion properties of the present tubular assembly are in progress.

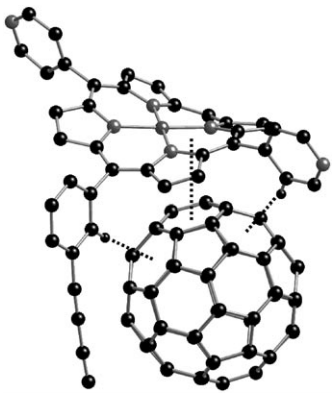

Figure 3. Details of the noncovalent interactions between Ni_2-CPD_{Py} and C_{60}. Hydrogen atoms are omitted except in the C–H···π motifs. N, Ni gray; C, H black.

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[14] For experimental details, see the Supporting Information.

[15] The X-ray experiments for Ni_2-CPD_{Py} and $C_{60}\subset Ni_2$-CPD_{Py} were carried out on a Rigaku RAXIS imaging plate area detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The crystals were mounted on a glass fiber. The data were collected for Ni_2-CPD_{Py} ($2\theta \le 54.86°$) and $C_{60}\subset Ni_2$-CPD_{Py} ($2\theta \le 54.92°$) at $-140\,°C$. To determine the cell constant and orientation matrix, three oscillation photographs were taken with an oscillation angle of 3.0° and exposure time of 60 s per degree for each frame. Intensity data were collected by taking 180 oscillation photographs with an oscillation angle of 5.0° and exposure time of 90 s per degree for each frame. Refraction data were corrected for both Lorentz and polarization effects. Ni_2-CPD_{Py}: $C_{120}H_{80}N_{12}Ni_2$, red crystal, crystal dimensions $0.21\times0.18\times0.12$ mm^3, monoclinic, space group $C2/c$, $a = 35.645(4)$, $b = 14.537(1)$, $c = 24.693(2)$ Å, $\beta = 118.835(5)°$, $V = 11208(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.071$ g cm^{-3}, 92256 reflections collected, 12752 reflections used and 793 parameters. $R_1 = 0.0706$ ($I > 2.0\sigma(I)$), $R_w = 0.2075$ (all data). $C_{60}\subset Ni_2$-CPD_{Py}: $C_{166}H_{64}N_{12}Ni_2$, reddish black crystal, crystal dimensions $0.31\times0.15\times0.10$ mm^3, monoclinic, space group $C2/c$, $a = 36.842(4)$, $b = 14.498(2)$, $c = 24.607(4)$ Å, $\beta = 115.396(5)°$, $V = 11837(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.311$ g cm^{-3}, 97678 reflections collected, 13545 reflections used and 839 parameters. $R_1 = 0.0767$ ($I > 2.0\sigma(I)$), $R_w = 0.2024$ (all data). CCDC-658588 and -658587 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[19] In the crystal of $C_{60}\subset Ni_2$-CPD_{Py}, the displacements of the *meso* carbon atoms from the four-nitrogen plane are 0.558, −0.418, 0.599, −0.658 Å, positive values meaning outward. The rotation angle of the two porphyrins around the center-to-center axis is 24.3°, and the torsion angle of the two butadiyne moieties is 31.1°.

[20] In the crystal of $C_{60}\subset Ni_2$-CPD_{Py}, the C···N distances between the pyrrole β carbon atoms and the nitrogen atoms of the pyridyl groups are 3.406(4) and 3.773(5) Å, the shortest carbon–carbon separation between the adjacent pyridyl groups is 3.414(7) Å, and the dihedral angle is 7.04°.

