Nanomaterials

A Porphyrin Nanotube: Size-Selective Inclusion of Tetranuclear Molybdenum–Oxo Clusters[**]

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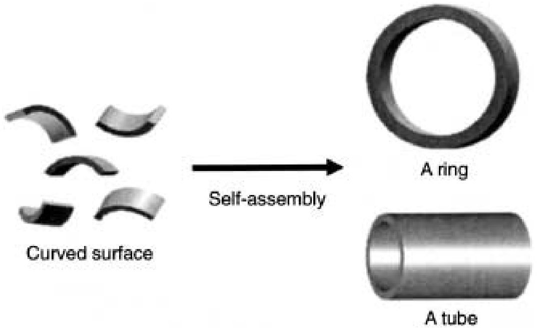
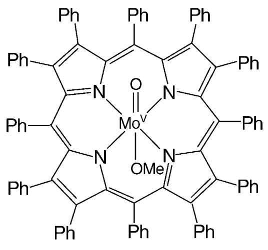
Nanotubes, and in particular carbon nanotubes, are important functional materials for technological innovations.[1] Nanotubular structures can be formed by the self-assembly of organic compounds[2] and biological materials such as the tobacco mosaic virus coat protein,[3] and cyclic D,L-peptides such as gramicidin A and its analogues.[4] Inorganic coordination compounds have also been known to generate tubular supramolecules by self-assembly through the coordination of bridging ligands to metal complexes as building blocks.[5] The inclusion of atoms and molecules into nanotubes has been an important issue in adding certain functionalities, such as the modulation of bandgaps in carbon nanotubes.[6]

As a molecular segment of those nanoscaled assemblies, porphyrins and metalloporphyrins have been attractive candidates for light-harvesting complexes in bacteriochlorophylls.[7] Porphyrins are known to be useful and robust molecules with many chemical and physical properties that exhibit functionality by virtue of their photochemical and optical properties.[8] The aggregation and self-assembly of porphyrins and their metal complexes has gained much attention and many assemblies have been reported. Representative strategies for those assemblies of porphyrin complexes include: 1) Utilization of intermolecular π–π interactions between planar porphyrin surfaces,[9] 2) axial coordination of bridging ligands to link metal components,[10] 3) introduction of functional groups to form intermolecular hydrogen bonds,[11] and 4) hydrogen bonding of axial ligands with each other or other bridging entities.[12] In the development of synthetic materials, porphyrin aggregates have been utilized to perform electron/lithium-ion transport in the solid state.[13] However, these aggregates consist of planar porphyrin arrays, which limit the shape of the porphyrin assemblies obtained. The use of highly distorted porphyrins as building blocks to construct self-assembled supramolecular structures will provide a novel category of porphyrin aggregates (Scheme 1) as a result of their curved surfaces; such aggregates cannot be prepared from planar porphyrins. We adopted dodecaphenylporphyrin (H_2DPP) as a ligand[14] and succeeded in the formation of a novel porphyrin nanotube by the self-assembly of its Mo^V complex. The nanotube was found to include three kinds of tetranuclear Mo^{VI}–oxo clusters that have unprecedented structures.



Scheme 1. Conceptual description of the self-assembly of molecules with curved surfaces.

Crystals of the tubular assembly were obtained by recrystallization from a solution of the precursor complex [Mo(DPP)(O)(OCH_3)] (**1**) in toluene by the diffusion of methanol vapor. The composition of the crystals was revealed



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to be $[\{Mo(O)(OH_2)(DPP)\}\{Mo_4O_{14}H_2\}_{0.4}\{Mo_4O_{13}H_2\}_{0.1}]\cdot H_2O\cdot 0.5\,C_6H_5CH_3$ (**2**), which included dianions of Mo–oxo clusters as counterions.[15] X-ray crystallography of **2** revealed a tubular structure for the crystalline assembly.

The molecular structure of the $[Mo(DPP)(O)(H_2O)]^+$ ion in **2** is depicted in Figure 1. The ion exhibits a severely distorted structure, which results in a curved surface. The Mo=O bond length (Mo1-O1) was 1.672(2) Å and that of the Mo-OH_2 bond (Mo1-O2) was 2.340(2) Å. The displacement of each atom in the equatorial mean plane of $[Mo(DPP)(O)(H_2O)]^+$ suggested a saddle distortion of the DPP^{2-} ligand, in which four pyrrole rings are directed upward and downward alternatively (Supporting Information). The distortion of the porphyrin ring was also reflected in its EPR spectrum in CH_2Cl_2, which exhibits a reduced superhyperfine coupling constant ($g = 1.966$, $A_N = 1.910 \times 10^{-4}\,cm^{-1}$) for the four nitrogen atoms of the DPP^{2-} ligand.[16] This is due to a weakened σ interaction between the Mo^V center and the four nitrogen atoms through their sp^2-hybridized lone-pair orbitals.

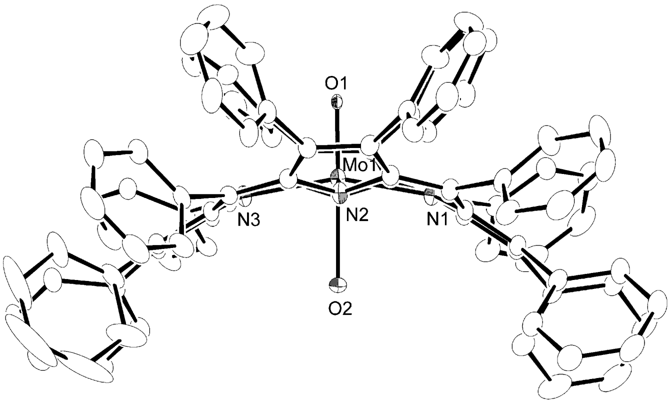

Figure 1. An ORTEP drawing of the $[Mo(DPP)(O)(OH_2)]^+$ ion in **2** with 50% probability thermal ellipsoids. Selected bond lengths [Å] and angles [°]: Mo1-O1 1.672(2), Mo1-O2 2.340(2), Mo1-N1 2.092(3), Mo1-N2 2.087(3), Mo1-N3 2.101(3), Mo1-N4 2.078(3); O1-Mo1-O2 179.0(1), O1-Mo1-N1 101.0(1), O1-Mo1-N2 99.6 (1), O1-Mo1-N3 99.9(1), O1-Mo1-N4 100.4(1).

In the crystal of **2**, $[Mo(DPP)(O)(H_2O)]^+$ ions were shown to form a novel tubular assembly having an inner space of 1 nm diameter, by the virtue of intermolecular π–π interactions of alternately inserted peripheral phenyl groups. The ring–ring distances are in the range of 3.46–3.74 Å. Figure 2a shows a side view of the tube with tetranuclear Mo clusters included, which are clearly derived from the decomposition of **1** during crystallization (see Supporting Information). The figure shows that a hydrophilic nanosized space exists between the hydrophobic porphyrin surfaces, which can include the Mo–oxo along the crystallographic *c* direction. Figure 2b displays a view along the nanotube, which shows the included tetranuclear Mo–oxo clusters and water molecules of crystallization (peripheral phenyl groups are omitted for clarity). The Mo–oxo clusters interact through hydrogen bonding with the $[Mo(DPP)(O)(OH_2)]^+$ ions and with water molecules of crystallization to form a network inside the tube. A top view of the nanotube without the included species is depicted in Figure 2c to clarify the size and the hydrophilic environment in the tube. Direct interactions between the nanotubes were not observed, however, toluene molecules of crystallization served to associate the tubes through π–π and CH/π interactions. The tubes aligned to be perpendicular to the *b* axis and formed an ordered channel structure in the

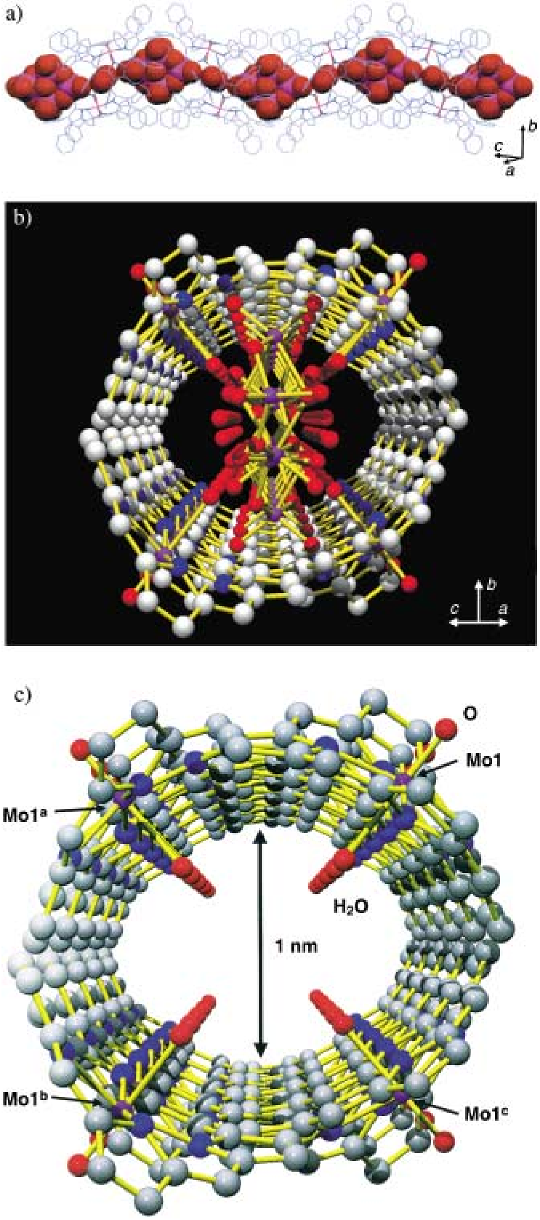

Figure 2. Structure of tubular assembly of **2** in the crystal (toluene molecules of crystallization were omitted for clarity): a) Side view of the $[Mo(DPP)(O)(OH_2)]^+$ nanotube (wire frame) with tetranuclear Mo–oxo clusters inside(O red, Mo purple); b) view along the nanotube showing the Mo–oxo clusters and the water molecules of crystallization (peripheral phenyl groups are removed for clarity; Mo purple, O red, N blue, C gray); c) Top view of the nanotube surface (peripheral phenyl groups and included species are omitted for clarity; colors for atoms are the same as in b). Crystallographic symmetry elements: $Mo1^a$ ($1-x$, y, $1/2-z$); $Mo1^b$ ($1/2-x$, $1/2-y$, $-z$); $Mo1^c$ ($1/2+x$, $1/2-y$, $1/2+z$).

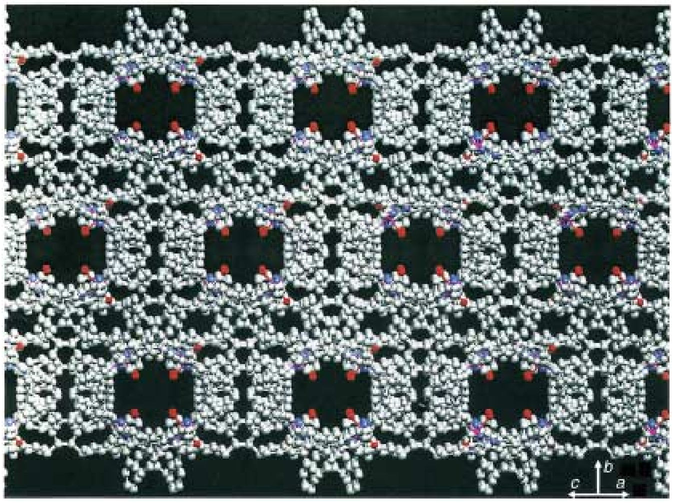

Figure 3. The crystal packing of **2**.

crystal (Figure 3), similar to those observed for inorganic zeolites.[17]

Three kinds of tetranuclear Mo–oxo cluster were found in the tube (Figure 4; see also Supporting Information). The estimated occupancies of those clusters were 0.8 for C1, 0.1 for C2, and 0.1 for C2′, respectively. All the clusters possess unprecedented discrete structural motifs with only oxo and hydroxo bridges and terminal oxo groups without any organic moieties. In the case of C1, two μ-hydroxo and four μ-oxo bridges link two octahedral and two tetrahedral Mo^{VI} centers. No metal–metal interaction was recognized based on interatomic distances (> 3 Å). This structural motif has been found in Mo–oxo clusters with hydrazido and diazenido groups instead of the terminal oxo moieties, as reported by Zubieta and co-workers.[18] Clusters C2 and C2′ were revealed to have two terminal hydroxo and one μ-oxo groups. Short Mo=O and Mo−OH bond lengths and the lack of a Mo···Mo bonding interaction suggests that all the four Mo centers are Mo^{VI}, as in C1, rather than in a mixed-valent state. In sharp contrast to C1, two tetrahedral and two pseudo-square-pyramidal geometries were observed for the C2 and C2′ clusters. Thus, the clusters C2 and C2′ are probably neutral species and one of two water molecules of crystallization shown in Figure S2 of the Supporting Information could be formally a hydroxide ion. C2 and C2′ can be intermediates for larger Mo–oxo aggregates but they are stabilized and protected by shielding of the hydrophobic porphyrin nanotube. The included Mo^{VI}–oxo clusters are all tetranuclear because they are favorable in size so as to be included within the tube of 1 nm diameter. We assume that those tetranuclear clusters could be formed in accordance with the porphyrin aggregation in the hydrophilic cavity and they could also act as templates for the tube to be stabilized.

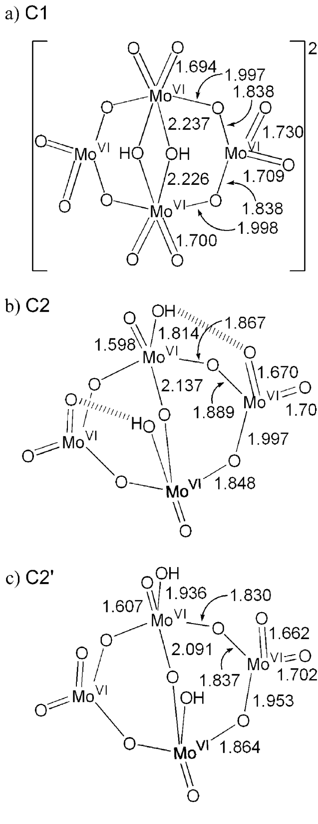

Figure 4. Schematic descriptions of Mo–oxo clusters: a) C1; b) C2; c) C2′, with selected bond lengths [Å].

In conclusion, we have demonstrated a new strategy to form a porphyrin nanotube with a saddle-distorted metalloporphyrin complex by virtue of ensemble of noncovalent interactions, such as π–π interactions and hydrogen bonding. The hydrophobic porphyrin nanotube runs along one direction (perpendicular to the *b* axis) and a hydrophilic inner space can include fairly large molecules such as tetranuclear Mo–oxo clusters. The distorted and curved porphyrin surfaces can allow us to access new frontiers in functional materials.

Experimental Section

1: H_2DPP (0.100 g, 0.082 mmol) was heated with $[Mo(O)_2(acac)_2]$ (0.134 g, 0.410 mmol) in PhOH (0.5 g) at 240 °C under nitrogen for 2 h. After the removal of PhOH under reduced pressure, the residue was purified by chromatography on an alumina column using CH_2Cl_2/MeOH (10:1) and a silica gel column using CH_2Cl_2/MeOH (1:1) as the eluent. A green fraction was collected from which a green powder (0.047 g, 41 %) was obtained. Elemental analysis (%) calcd for $C_{93}H_{63}MoN_4O_2{\cdot}CH_3OH$: C 80.85, H 4.84, N 4.01; found: C 80.45, H 4.67, N 4.00. Green crystals of the porphyrin nanotube ($[Mo(O)(OH_2)(DPP)][(Mo_4O_{14}H_2)]_{0.5}{\cdot}H_2O{\cdot}0.5\,C_7H_8$; **2′**) were prepared by the diffusion of methanol vapor into a solution of **1** in toluene for one week. Elemental analysis (%) calcd for $C_{102.5}H_{77}N_4O_{10}Mo_3$: C 67.92, H 4.28, N 3.09; found: C 68.36, H 4.44, N 3.38.

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[15] X-ray data for **2**: monoclinic, space group $C2/c$, $a = 21.496(4)$, $b = 30.230(6)$, $c = 25.858(5)$ Å, $\beta = 104.85(3)°$, $V = 16242(6)$ Å^3, $T = 123(2)$ K, $Z = 8$, $R = 0.061$ ($I > 2\sigma(I)$), $R(Rw) = 0.064$ (0.130) (all data), GOF = 1.18. CCDC-221027 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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