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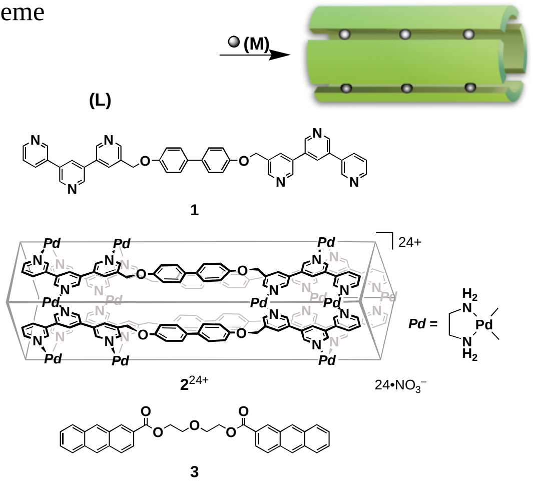
A 3.5 nm Coordination Nanotube

Takumi Yamaguchi,[1] Shohei Tashiro,[1] Masahide Tominaga,[1] Masaki Kawano,[1] Tomoji Ozeki,[2] and Makoto Fujita*[,1]
[1] Department of Applied Chemistry, The University of Tokyo, CREST, Japan Science and Technology Corporation (JST), Bunkyo-ku, Tokyo 113-8656, Japan
[2] Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan

Introduction

Molecular self-assembly has been providing quite efficient approaches to well-defined tubular structures, which attract considerable current interest in broad scientific areas [1, 2]. One of the most efficient approaches to molecular-based tubes is to link tape-like molecules into cylindrical shapes (Scheme). We report here a successful structural determination of the self-assembly of a 3.5 nm coordination nanotube **2**$^{24+}$ accomplished by using a 3.0 nm strand molecule as a template. Facile preparation as well as the stability of the tube even after the template removal makes possible the discrete assembly of tubes that potentially interpenetrate biological membranes whose thickness is comparable to the length of the present coordination nanotube.

Scheme



Results

Single crystals of **3**⊂**2**$^{24+}$ complex were obtained by the slow evaporation of the solution of **3**⊂**2**$^{24+}$ over one month. X-ray crystallographic measurement was performed on PF–AR NW2 beamline with a crystal cooled at 88 K. Crystal data for **3**⊂**2**$^{24+}$ is as follows: orthorhombic, space group *Fdd*2, λ = 0.68900 Å, a = 49.2540(12) Å, b = 122.86(4) Å, c = 27.6620(5) Å, V = 167395(55) Å^3, Z = 16, $R_1(F)$ = 15.8%. Despite the severe disorder of solvent molecules and the poor resolution of spots due to an extraordinarily long b axis (122 Å), synchrotron X-ray irradiation with high flux and low divergence afforded high quality diffraction data, from which the tubular structure of **2**$^{24+}$ with the length of 3.5 nm was revealed. That is, to our knowledge, the longest tubular host compound among those crystallographically defined. Each ligand adopted the most extended conformation while the tube framework was slightly helicated.

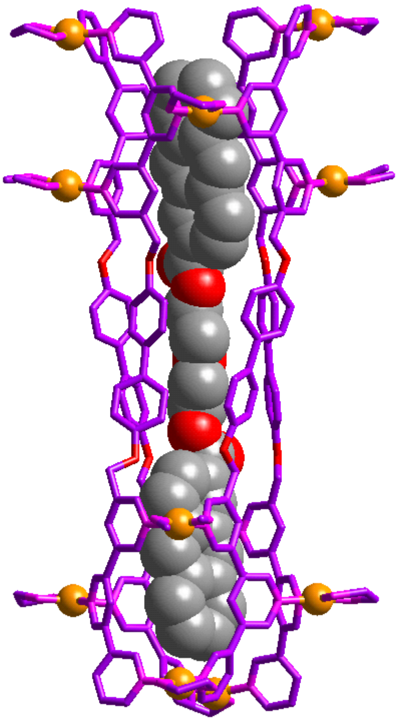


Figure 1. Crystal structure of **3**⊂**2**$^{24+}$. For clarity, H atoms, solvent molecules, and anions are omitted.

Guest **3** is also the longest among those revealed so far by an X-ray analysis. Within the cavity of **2**$^{24+}$, two anthracene moieties of **3** are gripped by four tris(3,5-pyridine) units that are held together by six Pd(II) ions via π-π stacking and CH-π contact. The diethylene glycol linker is essential because the tube did not assemble efficiently when anthracene or anthracenecarboxylate was employed as a template. Probably, Pd(II)-linked frameworks at the both ends of **2**$^{24+}$ are simultaneously assembled by dual templating at the two anthracene moieties of **3**.

References

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*mfujita@appchem.t.u-tokyo.ac.jp