

6 Crystallography

6-1 A 3.5 nm Self-assembled Coordination Nanotube

Well-defined tubular structures attract considerable current interest over a broad range of scientific areas [1,2]. Although various aspects of carbon nanotubes have been extensively investigated, there have been few reports on giant discrete molecular-based tubes. One of the most efficient approaches for creating giant tubular structures is the use of self-assembly of tape-like molecules into cylindrical shapes (Fig. 1). Using this strategy, we have previously synthesized 2-nm-sized coordination nanotubes from pentapyridine, Py-Py'-Py'-Py'-Py (Py = 3-pyridyl, Py' = 3,5-pyridylene), and $\text{enPd}(\text{NO}_3)_2$ [3]. A flexible molecular tape **1** was designed in which two Py-Py'-Py units are connected by a biphenyl linker. The length of this ligand is 3.5 nm, which should be directly transferred to the length of the tube. We report here the crystal structure of a 3.5 nm coordination nanotube $\mathbf{2}^{24+}$ self-assembled with a 3.0 nm strand template molecule [4].

The key to the successful assembly of a long coordination tube is the selection of a linker for connecting two tape-shaped units. We designed a ligand **1** that possesses a rigid biphenylene spacer. For the assembly of **1** into a 3.5 nm coordination tube $\mathbf{2}^{24+}$, we also designed the ca. 3.0 nm strand template molecule **3**. In **3**, two anthracenecarbonyl moieties are linked by a diethylene glycol unit, making an ideal fit for the $\mathbf{2}^{24+}$ tube. We have observed the remarkable template effect of **3** for the smooth assembly of $\mathbf{2}^{24+}$ by NMR spectroscopy. In addition to the NMR spectroscopic results, the formula of $\mathbf{2} \cdot \mathbf{3} \cdot (\text{NO}_3)_{24}$ was confirmed by cold-spray ionization mass spectrometry, where a series of prominent peaks of $[\text{M} - (\text{NO}_3^-)_n]^{n+}$ was observed.

The structure of the $\mathbf{3} \subset \mathbf{2}^{24+}$ complex was unambiguously determined by single crystal X-ray analysis at beamline NW2A of PF-AR. Twisted prism-like single crystals were obtained by the slow evaporation of a solution of $\mathbf{3} \subset \mathbf{2}^{24+}$ over a period of one month. It was not possible to determine the crystal structure of $\mathbf{3} \subset \mathbf{2}^{24+}$ using a conventional X-ray source. However, despite the severe disorder of the solvent molecules and the poor spot resolution due to an extraordinarily long *b* axis (122 Å), synchrotron radiation ($\lambda = 0.6890$ Å) with high flux and low divergence afforded high quality diffraction data.

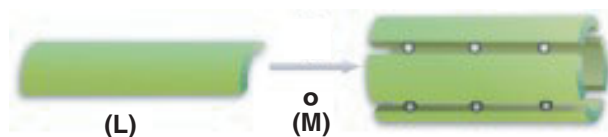


Figure 1
The scheme for creating molecular-based tube is to link tape-like molecules into cylindrical shape.

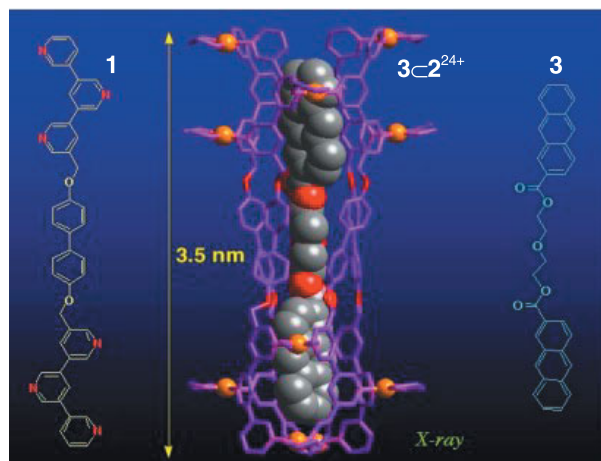


Figure 2
Molecular structure of $\mathbf{3} \subset \mathbf{2}^{24+}$. For clarity, H atoms, solvent molecules, and anions are omitted.

The observed crystal data for $\mathbf{3} \subset \mathbf{2}^{24+}$ was: orthorhombic, space group *Fdd2*, $a = 49.2540(12)$ Å, $b = 122.86(4)$ Å, $c = 27.6620(5)$ Å, $V = 167395(55)$ Å³, $Z = 16$. The tubular structure of $\mathbf{2}^{24+}$ with the length of 3.5 nm (shown in Fig. 2) is, to our knowledge, the longest tubular host compound to be crystallographically defined. As expected, each ligand adopted the most extended conformation while the tube framework was slightly helicated. The packing diagram in Fig. 3 shows that the nanotubes are aligned in parallel along the *b* axis where channels of molecular tubes exist. The results of the X-ray analysis indicate that the principle intermolecular interactions for encapsulation of the strand guest molecule in the nanotube are π - π stacking and CH- π interactions between host and guest. Within the cavity of $\mathbf{2}^{24+}$, two anthracene moieties of **3** are gripped by four tris(3,5-pyridine) units that are held together by six Pd(II) ions. 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 $\mathbf{2}^{24+}$ are simultaneously assembled by dual templating at the two anthracene moieties of **3**.

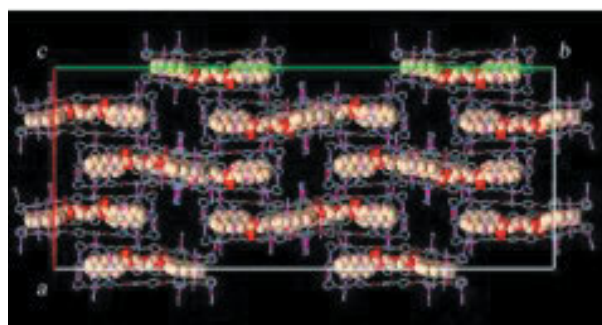


Figure 3
Packing diagram of $\mathbf{3} \subset \mathbf{2}^{24+}$. For clarity, H atoms, solvent molecules, and anions are omitted.

After extraction of the guest, the framework remained unchanged at room temperature, in sharp contrast to the behavior of previously reported shorter tubes that immediately collapsed when the template was removed. This fact indicates that, being cooperatively sustained by 24 Pd(II)-pyridine interactions, empty tube 2^{24+} possesses considerable kinetic stability and is capable of binding other molecules in the cavity.

Facile preparation as well as the stability of the tube even after template removal provides a new approach for making transportation channels in biological membranes with thicknesses comparable to the length of the present coordination nanotube.

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6-2 Open-mouthed C₆₀ Swallows a Hydrogen Molecule

In order to carry out research into the use of molecular capsules as hydrogen storage materials or for medicinal applications, techniques to insert gas or unstable molecules into a molecular cage must be developed. Fullerene, C₆₀ is a typical soccer-ball-shape cage molecule, and the organic synthesis of endohedral C₆₀ at will is a challenging task. Prof. Komatsu's group recently succeeded in the 100% incorporation of H₂ molecules into derivatives of aza-thia open-cage fullerenes (ATOCF), as shown in Fig. 4 [1]. This compound can be regarded as a nano-sized container for a single hydrogen molecule, with which we can store hydrogen at controlled pressure and temperature. The extraordinary high-field shift of the ¹H NMR signal of the H₂ molecule reported in Ref. 1 surely indicates that H₂ is encapsulated *somewhere* inside the fullerene cage. However, more substantial information is needed concerning the location of the H₂ molecule within the cage of ATOCF, and this information can be obtained only through the direct observation of the molecule. X-ray diffraction analysis using synchrotron radiation appeared most suitable for this purpose, and we have obtained accurate X-ray diffraction data using a Weissenberg type

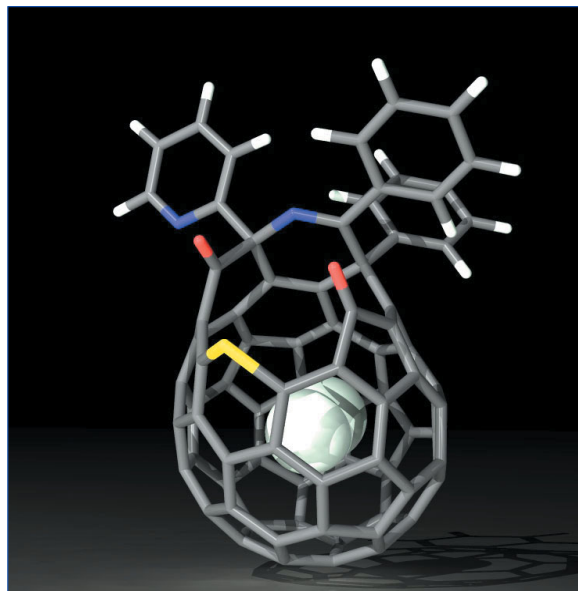


Figure 4
Molecular structure of H₂@ATOCF. The encapsulated H₂ molecule is shown as a space-filled model.

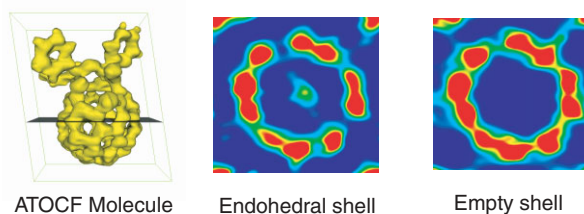


Figure 5
Maximum Entropy Method electron densities of H₂@ATOCF (center) and empty ATOCF (right), shown as equal-density contour surfaces. The contour maps are drawn over the range 0.01e/Å³ to 0.11e/Å³, as indicated in the left-hand panel.

imaging-plate detector at BL-1A. From X-ray diffraction analysis of a single crystal, we have succeeded in the direct observation of a single floating H₂ molecule inside of the hollow cavity of this fully H₂-encapsulating ATOCF molecule (Fig. 5) [2]. The number of electrons belonging to encapsulated H₂, estimated by integration from the center of the cage to the point of minimum electron density, turned out to be 2.0±0.1. This result exactly corresponds to the presence of one H₂ molecule at the center of the hollow cage of the ATOCF molecule, in excellent agreement with the ¹H NMR result [1], demonstrating that this H₂-encapsulating compound is the first material which can allow us to determine the physical properties of single floating H₂ molecule.

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6-3 Design, Fabrication and Performance of a New Furnace for High-resolution Synchrotron Radiation Powder Diffraction Studies up to 1900 K – An Application to Determine the Electron-density Distribution of Cubic CaTiO_3 Perovskite at 1674 K

It is an important challenge to carry out accurate structural analysis using *in situ* diffraction data obtained from materials at high temperatures. Laboratory-based X-ray powder diffractometry using Bragg-Brentano geometry encounters some serious difficulties for high-temperature structural analysis. Synchrotron radiation powder diffraction can overcome these difficulties. Some research groups have previously performed *in situ* synchrotron radiation powder diffraction experiments above 1000 K, however there has been very little work on precise analysis leading to electron-density distributions above 1000 K.

A new electric furnace to measure high-resolution synchrotron radiation powder diffraction profiles from materials at high temperatures up to 1900 K in air has been designed and fabricated (Figs. 6 and 7) [1, 2]. The furnace consists of a ceramic refractory with MoSi_2 heaters, a water-cooled aluminium body and an automatic sample stage (Fig. 6). We have carried out synchrotron radiation powder diffraction experiments with X-rays of wavelength 0.99945 Å at BL-3A. Diffraction data for a CaTiO_3 powder sample at 1674 K in air were collected in the asymmetric flat-type reflection geometry. This method has the follow-

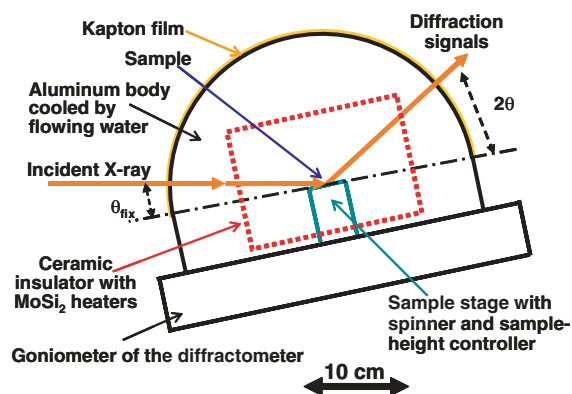


Figure 6
Schematic diagram of the new furnace designed and fabricated in the present work [1].

ing merits: (i) correction for the absorption effect is not necessary in the structural refinement, (ii) the sample temperature does not change during the 2θ scanning, in contrast to the the symmetric $2\theta/\theta$ scanning technique (the temperature was maintained with stability ± 0.1 K using a thermocouple temperature control), and (iii) there is little reaction between the specimen and its holder at high temperatures.

In the synchrotron-radiation-diffraction data of CaTiO_3 obtained at 1674 K, the background intensity was extremely low (7-24 counts) compared to the strongest peak intensity (30127 counts). Thus, the present furnace is useful to investigate accurately the intensity data of very weak peaks near a phase transition or due to significant temperature factors at high temperatures. The full-widths at half-maximum of the diffraction peaks at 1674 K ranged from 0.0087 deg. to 0.0197 deg, indicating a high angular resolution. The corresponding $\delta d/d$ values range from 0.041 to 0.118 %, where d and δd are the lattice spacing and peak width in the d scale. Rietveld refinement for the diffraction data of the CaTiO_3

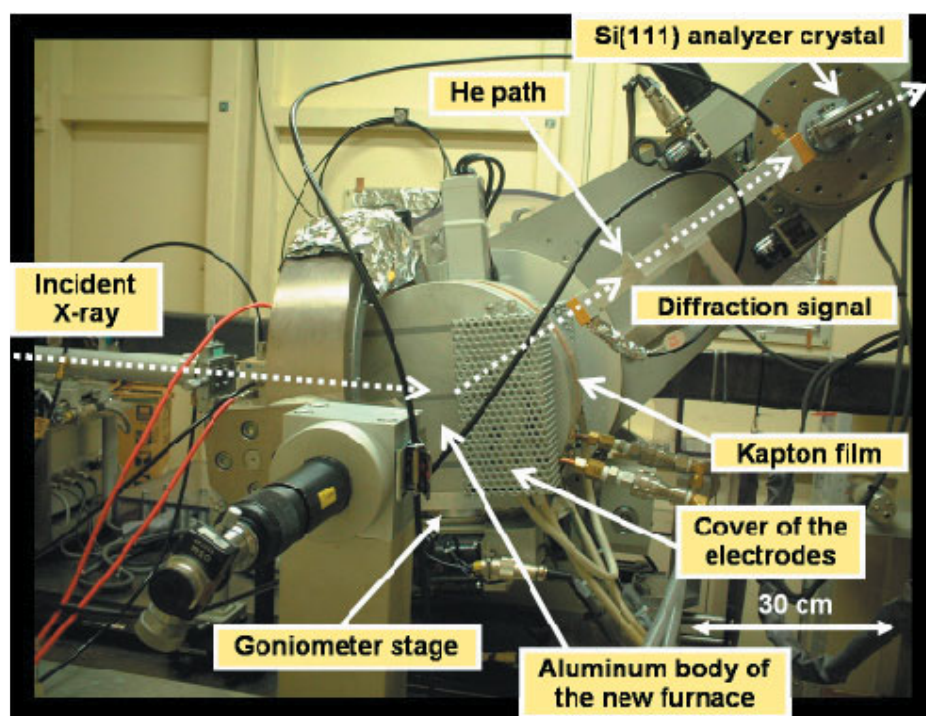


Figure 7
Photo of the new furnace installed at BL-3A [1]. White dashed lines with arrows denote the incident X-ray beam and diffracted signals.

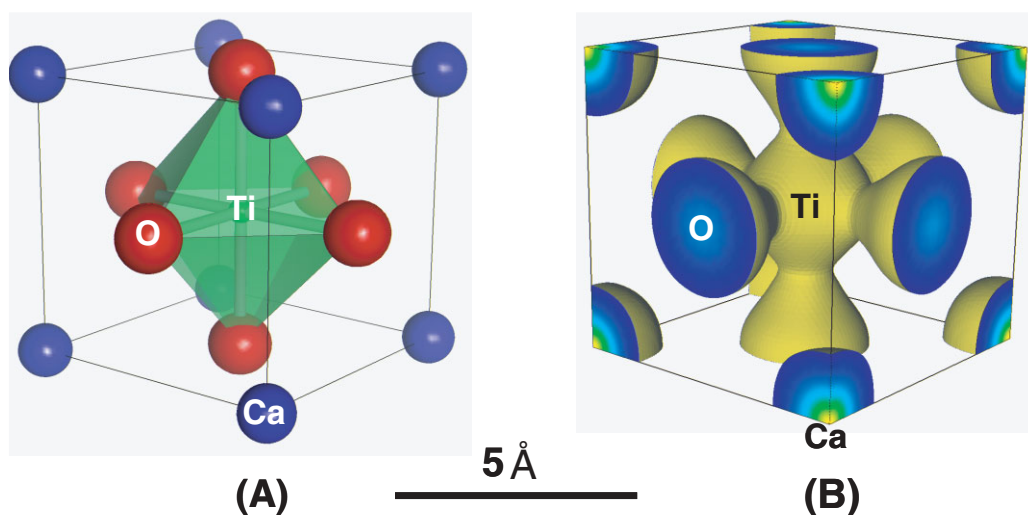


Figure 8
 (A) Refined crystal structure of cubic CaTiO_3 perovskite at 1674 K in air [1]. (B) Electron-density distribution with equicontour surface at $1.0 \text{ e}/\text{\AA}^3$ of the cubic CaTiO_3 at 1674 K [1]. These figures were made using the computer program *VENUS* developed by Dilanian and Izumi [3].

perovskite was successfully refined by the ideal cubic $Pm\bar{3}m$ perovskite-type structure (Fig. 8(A)). The goodness of fit was 1.05, indicating extremely good fitting. The refined unit-cell parameter was $3.89846(1) \text{ \AA}$ at 1674 K. We could also refine the anisotropic thermal parameters: $\beta_{11}=0.117(3)$, $\beta_{22}=\beta_{33}=0.106(2)$ and $\beta_{12}=\beta_{23}=\beta_{31}=0$. The electron-density distribution of this sample was successfully obtained by the maximum-entropy method (MEM) and MEM-based pattern fitting. The R -factor R_B was improved from 8.27% (Rietveld refinement) to 7.45% (whole pattern fitting with the MEM structure factors). Also R_F was improved from 6.57% to 5.38%. The electron density between the Ti and O atoms shows features characteristic of covalent bonding (Fig. 8(B)), which might be formed by the hybridization of the Ti-3d and O-2p electrons. There was much less electron density between the Ca and O atoms, indicating that the Ca atoms are isolated

and more ionic. These results clearly show that the present high-temperature synchrotron radiation powder diffraction system yields high-quality data for Rietveld and MEM analyses.

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