

## Ferrocene-based metal-organic nanotubes and nanorings with ultra-large dimensions: Redox-mediated modulation of noncovalent forces

Cleavage and formation of covalent bonds at desired positions are modern key technologies for the development of complicated organic molecules. However, when it comes to the synthesis of nanoarchitectures utilizing relatively weak attractive forces between molecules (i.e., noncovalent interactions), such nanoscale manipulations in which the self-assembled structures are deconstructed into modules and reassembled can be challenging due to difficulties in selectively modulating certain interactions among various attractive forces. Although a variety of beautiful nanostructures have been noncovalently synthesized, even more exotic or inaccessible selfassembled motifs may become available if methods to cut, paste, or merge assembled structures are realized. Some nanostructures have been shown to break into thermodynamically inaccessible low-symmetry pieces [1-3]. However, such selective cutting requires prior stabilization of the parent nanostructures by partial covalent crosslinking.

We have developed out-of-box supramolecular nanoarchitectures that can be cut and pasted without the aid of covalent crosslinking [4]. The nanoarchitecture is an ultralarge-diameter metal-organic nanotube, which can be preferentially 'cut' into its constituent coordination nanorings. Each nanoring has a 200-membered decagonal structure with an extra-large diameter of 7.5 nm. The key to successfully 'cut' the nanotube is the redox-active ferrocene motif employed in our metalligating units  $FcL_1$  and  $FcL_2$  (Fig. 1), which possess a metal-coordinating 4-pyridyl group at each terminus of the four aromatic arms. Since ferrocene derivatives thermally rotate their cyclopentadienyl rings freely in solution, both ligands change their tetratopic geometry dynamically. This 'geometrical uncertainty' should give rise to the formation of various types of metal-organic architectures, including fibers, macrocycles, sheets, porous networks, and ill-defined aggregates. To our surprise, an assembly of FcL1 with AgBF4 exclusively yields ultra-large-diameter nanotube FcNT<sub>1</sub>. To elucidate the structure of these unprecedented metal-organic nanotubes, we performed small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) analyses of the as-prepared dispersions and dried films of the nanotubes, respectively, using synchrotron radiation at **BL45XU** in collaboration with Dr. Takaaki Hikima and Prof. Dr. Masaki Takata (RIKEN).

Transmission electron microscopy (TEM) of an airdried acetonitrile (MeCN)/water dispersion of  $FcNT_1$  clearly displays hollow cylinders with a uniform 'wall



Fig. 1. Molecular structures of ferrocene-based tetratopic pyridyl ligands and schematic representation of the formation and transformation processes of ferrocene-based metal-organic architectures.

center-to-wall center' distance (nanotube diameter) of 7.5 nm [4]. SAXS analysis of FcNT<sub>1</sub> in MeCN provides detailed information about the assembly dimensions. The SAXS profile has a distinct oscillation lasting to a large scattering vector q, indicating that **FcNT**<sub>1</sub> has a uniform diameter (Fig. 2(a)). The observed SAXS pattern is nicely fitted by the form factor of a hollow cylinder model with a diameter of 7.5 nm. Considering the bending angle of FcL<sub>1</sub> (144°), this nanotube diameter allows a molecular model with a decagonal (10-mer) cross-section (vertex angle; 144°) composed of 10 bentshaped FcL1 ligands and 20 Ag(I) ions to be constructed (Fig. 2(c)). We also constructed nanotubular molecular models with nonagonal (9-mer) and undecagonal (11mer) cross-sections, and found that their calculated diameters of 6.8 and 8.2 nm, respectively, do not match the observed one. Furthermore, the SAXS patterns simulated for the corresponding hollow cylinder models clearly differ from that actually observed for FcNT1. These results are reasonable considering the fact that the ideal N-Ag(I)-N coordination angle of 180° can be realized only in the decagonal model. Analogous to FcL1, longer-armed FcL2 exclusively forms metalorganic nanotubes with large and uniform diameters. The theoretical fitting of the oscillatory SAXS pattern (Fig. 2(b)) using a hollow cylinder model indicates that this nanotube has a uniform diameter of 13.3 nm, which matches the predicted value from a 360-membered decagonal cross-section (Fig. 2(c)). This diameter is the largest among known metal-organic nanotubes.

Although SAXS analyses strongly suggested that the ferrocene nanotubes possess the decagonal crosssections, the wall structures of the tubular assemblies remain unclear. Thus, WAXD measurements of the oriented films were conducted to estimate how the

assembled components are arranged in the nanotube. We attempted several different methods to obtain such an oriented film from FcNT1, and finally found that FcNT<sub>1</sub> nanotubes align under a 10-T (tesla) magnetic field. This film displays a distinct WAXD pattern (Fig. 3(b)), which features a set of diffuse spots along the direction of the applied magnetic field. These spots agree well with those expected for a 2D hexagonal lattice with a lattice parameter a = 8.7 nm, indicating that the nanotubes are oriented perpendicular to the applied magnetic field and are hexagonally packed with an interpore distance of 8.7 nm (Fig. 3(a)). Meanwhile, along the longer axis of FcNT<sub>1</sub>, two distinct diffraction arcs (Fig. 3(b)) with d-spacings of 0.70 and 0.35 nm are observed. Taking into account the molecular structure and dimensions of bent-shaped FcL1, this diffraction pattern is attributed to the wall structure illustrated in Fig. 3(a), where **FcL**<sub>1</sub> with an eclipsed geometry stacks normally on top of each other in order to maximize the intermolecular  $\pi$ -stacking and metallophilic interactions.

The results of these analyses suggest that  $FcNT_1$  is likely composed of uniaxially stacked giant nanorings.



Fig. 2. (a, b) Experimental SAXS profiles (black broken curves) of MeCN dispersions of (a)  $FcNT_1$  and (b)  $FcNT_2$  at 25°C and their simulated scattering patterns (blue solid curves) for hollow cylinder models. (c) Computer-generated molecular (CPK) models for the cross sections of  $FcNT_1$  and  $FcNT_2$  using the optimized ligand structures from the molecular mechanics calculations.

The ferrocene units are located side-by-side along the longer axis of the nanotube, where stacking of the  $\pi$ -conjugated arrays, which include the ferrocene joint, together with the Ag(I)-Ag(I) metallophilic interaction, play crucial roles in the uniaxial connection of the coordination nanorings. This notion prompted us to envision that a one-electron oxidation/reduction of the ferrocene units in the nanotube may preferentially allow electrostatic modulation of the nanoring-nanoring interaction without breaking the Ag(I)-N coordination bond. In fact, we successfully (1) cut  $FcNT_1$  into the constituent nanorings by oxidation, (2) deposited the polycationic nanorings onto a negatively charged inorganic substrate, and (3) reconstructed FcNT<sub>1</sub> through uniaxial stacking of the reduced nanorings. This new approach of cutting and pasting on the nanoscale level should substantially contribute toward the science and technology of highly complex and functional nanoarchitectures.



Fig. 3. (a) Schematic representation of a onedimensionally oriented  $FcNT_1$  film sample and its proposed wall structure. (b) WAXD pattern of a one-dimensionally oriented  $FcNT_1$  film sample.

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