Self-Assembled Arrays of Organic Nanotubes with Infinitely Long One-Dimensional H-Bond Chains

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Recent interest in nanotechnology leads to a dramatic upsurge in the quest for tubular organic/inorganic nanotubes.[1] However, few organic nanotubes exhibit interesting useful electrochemical/photochemical properties. Therefore, we have designed, synthesized, and characterized self-assembled organic nanotube arrays composed of nontubular subunits of electrochemically/photochemically active calix[4]hydroquinones (CHQ). The nanotubes have infinitely long one-dimensional (1D) H-bond arrays which have been observed for the first time. This 1D H-bond is quite interesting in that 2D and 3D H-bonds have been reported recently.[2] The 1D H-bond arrays help form a linear tubular polymer structure which can be suspended in aqueous solution and also be grown to very thin tubes as well as well-ordered arrays of tube bundles under aqueous environment. The strong reducing power of the nanotube is found to be of great use in designing nanoscale metal architecture.

CHQ is a reduced form of calix[4]quinone (CQ) (Figure 1A).[3] It has four hydroquinone moieties with eight −OH groups. Four inner −OH groups form a circular proton-tunneling resonance of H-bonds,[4] which stabilize the "cone" structures. The four other free −OH groups can lead to self-assembled structures with intermolecular H-bonds. Thus, using the computer-aided-molecular design approach based on intermolecular interaction forces,[5] we investigated the assembling phenomena of CHQs with density functional calculations of various possible combinations of assembled structures derived from previously reported calixarene-based dimers, trimers, tertramers, hexamers, and polymers[6] (Figure 1B−F). The results suggest that in the presence of bridging water molecules, a linear tubular polymeric structure is highly stabilized by the formation of H-bonded bridges between repeating tubular octamer units.[7]

Indeed, in experiments, addition of water molecules into CHQ in acetone resulted in stable self-assembling thin needlelike nanotube bundles.[8] The size varies, depending on the evaporation rate and temperature. Small samples were analyzed with high-resolution electron microscopy (HREM). The images in Figure 2A show a single-channel nanotube of 2 nm width and a thin bundle (20 nm wide and 750 nm long). In the presence of cesium sulfate, the bundles grow into large needlelike black crystals (more than 5 mm long and 0.5 mm wide) in a week.

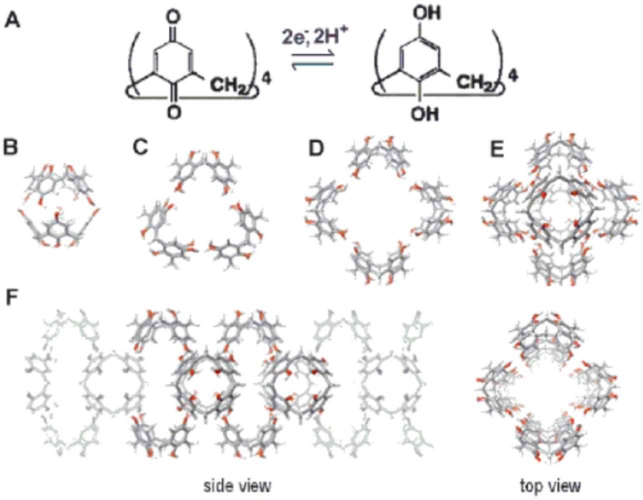

Figure 1. Scheme of calix[4]quinone(CQ)/calix[4]hydroquinone (CHQ) redox reaction (A), and the self-assembled structures [dimer (B), trimer (C), tetramer (D), octahedral hexamer (E), and tubular octamer as a repeating unit of the tubular polymer (F)] of CHQs.

The crystal structure characterized by X-ray crystallography shows that the bundles of CHQ nanotubes form novel chessboard-like rectangular structures (Figure 2B).[8] Each nanotube has a 17 Å × 17 Å cross section with 6 Å × 6 Å square pore (with the van der Waals volume excluded). The structure of the 1D tubular polymer based on the above X-ray structure along with ab initio calculations for the −OH orientations is shown in Figure 2C. The scanning electron microscope (SEM) images of the nano- and microscale nanotube bundles are shown in Figure 2D,E.

The X-ray structure shows infinitely long 1D H-bond[10] arrays composed of −OH groups of CHQs and water molecules (Figure 3A,C) and well-ordered intertubular $\pi-\pi$ stacking[11] pairs (Figure 3B).[12]

In the 1D H-bond array, the H-bond length (O−O distance is 2.675 Å for CHQ-water; 2.643 Å for CHQ−CHQ based on the X-ray data) is particularly short (despite the absence of charged

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[7] The capsule-like dimer, cyclic trimer, cyclic tetramer, octahedral hexamer, and tubular octamer are connected by 4, 6, 8, 24, and 20 intermolecular H-bonds, respectively. Thus, the hexamer has the largest assembling energy per monomer (51 kcal/mol at the B3LYP/3-21G level calculation). However, in the presence of bridging water molecules, the tubular octamer with hydroquinone−water H-bonds has the largest assembling energy (114 kcal/mol). When the tubular octamer forms a linear tubular polymer with repeating units, the stability is further enhanced by the formation of H-bonded bridges between repeating units.

[8] CHQ monomer (0.1 g) dissolved in 50 mL of 1:1 water−acetone solution in ambient conditions leads to the formation of tubular polymers in solution. As acetone slowly vaporizes through the ∼2 mm diameter hole of the sealing cap, the bundles grow from the surface of solution.

[9] Crystal data for the structure have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161593. Crystal data: orthorhombic, space group C_{mmm} with $a = 25.03560(10)$ Å, $b = 23.3007(5)$ Å, $c = 11.6313(2)$ Å and $\alpha = \beta = \gamma = 90°$ for empirical formula $C_{28}H_{32}O_{12}$; $V = 6785.08(19)$ Å^3, $Z = 8$, $T = 223(2)$ K. Final full-matrix least squares refinement on F^2 with all 2988 reflections and 202 variables converged to $R1(I > 2\sigma(I)) = 0.0866$, $wR2(\text{all data}) = 0.3146$, and $GOF = 1.206$.

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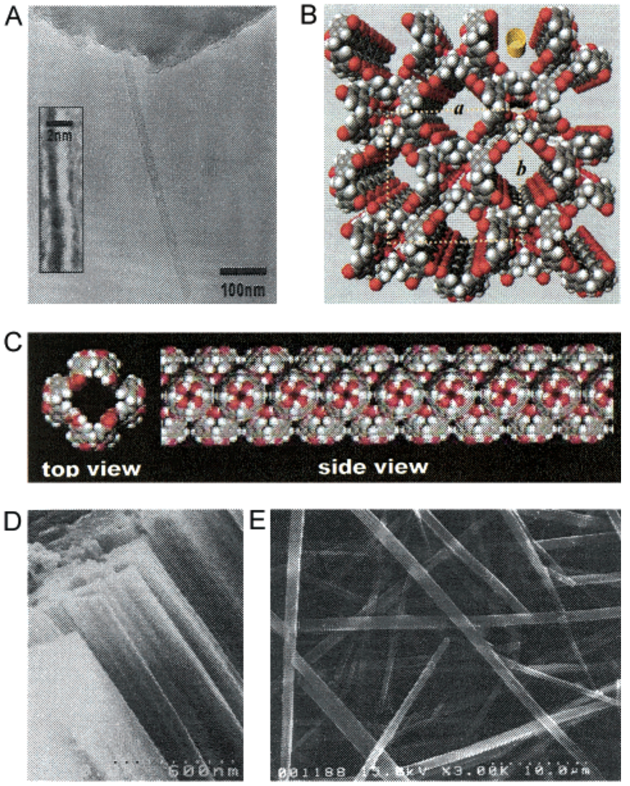

Figure 2. HREM image (200 kV) of a ∼10 × 10 nanotube bundle (∼20 nm wide, ∼750 nm long) and a single nanotube (∼2 nm wide) which is loosely attached to the main bundle (A), cross-sectional view of a CHQ nanotube crystal structure (with the unit cell represented by dotted lines) (B), tubular polymer structure of the single nanotube obtained with X-ray analysis and ab initio calculations for the H orientations (top and side views) (C), and the SEM images of the nano- and microscale bundles (D,E).

species), which is somewhat comparable to that of the short, strong H-bond.[13] FT-IR spectra of CHQ nanotubes show evidences of the H-bond arrays (Figure 3D). The −OH stretch vibration modes of the CHQ monomer consist of free −OH vibrations (3422 cm^{-1}) and circular H-bonded OH vibrations in the cone of four-membered H-bonded ring (3204 cm^{-1}). In the tubular structures, the free OH groups in the monomers form intermolecular H-bonds with those of the adjacent monomers and water molecules. Consequently, the intensity of the free −OH stretch peak decreases, and the intensity of H-bonded −OH stretch peak increases. Furthermore, this H-bonded −OH stretch vibration peak red-shifts to 3189 cm^{-1}, indicating the formation of the 1D array of short H-bonds. In addition, we note that the concerted −OH-bending mode in the cone shows a sharp peak around 1649 cm^{-1} for the monomer, but is blue-shifted to 1692 cm^{-1} in the tubular structure.[14] These infinitely long 1D H-bond arrays would have interesting features in proton/electron tunneling phenomena[4] and other physical/ chemical properties.

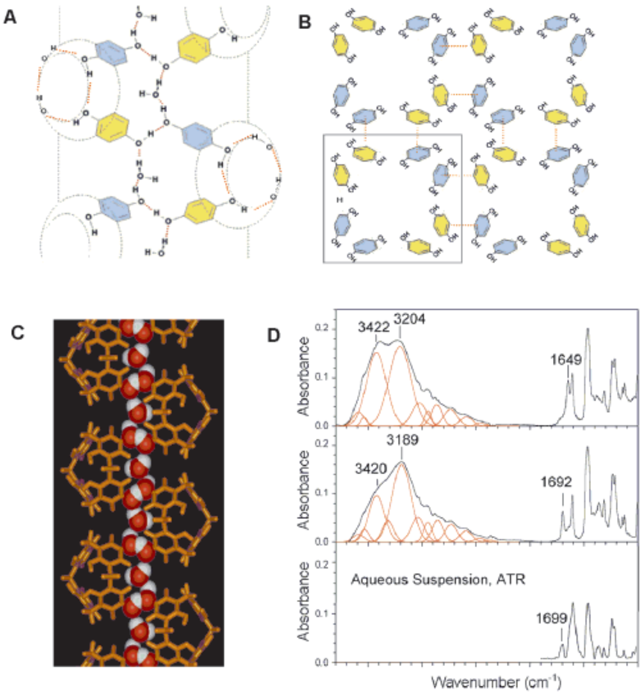

Figure 3. Schematic views of a longitudinal H-bonded relay (A) and intertubular $\pi-\pi$ stacking interactions with upper and lower parts of CHQ represented in blue and yellow (B), the H-bonds in the CHQ nanotube and their FT-IR spectra: a model for a longitudinal H-bonded relay by OH groups of CHQs and water molecules (C), and the FT-IR spectra (black) and the deconvoluted spectra (red) of CHQ monomers (top) and nanotube bundles (middle) in KBr pellet in solid state, and the FT-IR spectra (attenuated total reflectance) of the aqueous suspension of nanotube bundles (bottom) (D).

To see whether the nanotube structure can be characterized in solution, we investigated the FT-IR spectra (bottom inset of Figure 3D) of the nanotubes suspended in aqueous solution wherein the crystals were growing. In the solution spectrum, the sharp OH characteristic peak of the nanotube was observed at 1699 cm^{-1}, implying the existence of nanotublar structures in the aqueous solution.

The nanotube arrays can be utilized in many interesting nanosystems. Utilizing the redox reaction of the nanotube with novel metal ions, we have made silver nanowire arrays, which would be useful for molecular electronic devices.[15] The interesting structures and functions of CHQ nanotubes should find numerous applications, which are in progress in our laboratory.[16]

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Supporting Information Available: A crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) The number of H-bonds in the 1D H-bond arrays is twice that of $\pi-\pi$ stacking pairs, and the calculated average binding energy of a short H-bond in the array is larger than that of an aromatic $\pi-\pi$ stacking pair. Therefore, the growth along the tubular axis is much more favorable, and thus CHQs can be assembled to form long tubular structures, each of which is framed with four (infinitely long) 1D H-bonds. Then, these long nanotubes form well-ordered arrays of nanotube bundles with inter-tubular weak $\pi-\pi$ stacking interactions. The distance between two hydroquinone centroids is 3.613 Å, and the angle between two π-ring planes is only 3.3°.

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(14) This blue-shift arises from shrinking of the cone (which restricts the −OH-bending) along the 1D H-bond array direction. It is evidenced from the X-ray structure of the cone where the inter-oxygen distances along the tubular axis are slightly shortened (2.650 Å), as compared to those perpendicular to the tubular axis (2.679 Å). The modes of experimental frequencies were characterized by ab initio calculations (B3LYP/6-31G*). The average binding energies for the H-bonding pairs (∼8 kcal/mol) and stacking aromatic pairs (∼5 kcal/mol) were calculated at the MP2/6-31G* level.

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(16) The organic nanotubes could also be used as a model for selective water/ion channels in biological systems and a nanohost to include size-specific guest molecules.