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Organic Nanotubes

Metal-Ion-Coated Graphitic Nanotubes: Controlled Self-Assembly of a Pyridyl-Appended Gemini-Shaped Hexabenzocoronene Amphiphile

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Metallic nanoclusters coated on electroactive materials,[1] such as carbon nanotubes, have attracted increasing attention in view of their potential utility for catalysis,[1b,2] sensing,[3] hydrogen/power storage,[4] and electronics.[5] In these applications, elaborate structural control of such composite materials in nanoscale regimes are considered very important for providing a wide and addressable interface toward substrates. From this point of view, nanotubular assemblies of π-conjugated molecules may serve as interesting scaffolds because of their large surface area. As the first step toward this goal, we herein report controlled assembly of platinum(II)-ligating hexabenzocoronene derivatives into graphitic nanotubes hybridized with metal-coordination layers, which are potential seeds for the formation of metallic nanoclusters.

Self-assembly of hexabenzocoronene derivatives has been extensively studied by Müllen and co-workers.[6] We previously reported a gemini-shaped hexa-*peri*-hexabenzocoronene (HBC) amphiphile (**1**) bearing triethylene glycol (TEG) side chains, that can self-assemble in THF to form nanotubes under heat–cool conditions (Figure 1).[7a] Further studies on a family of **1** with functional groups at the TEG termini allowed us to confirm that this basic molecular design is quite universal for the nanotubular assembly of HBC derivatives.[8] For the development of metal-ligating graphitic nanotubes, we synthesized HBC **2**[9] carrying pyridyl pendants at the TEG termini that allow complexation with a variety of transition-metal ions, such as platinum(II) and palladiu-

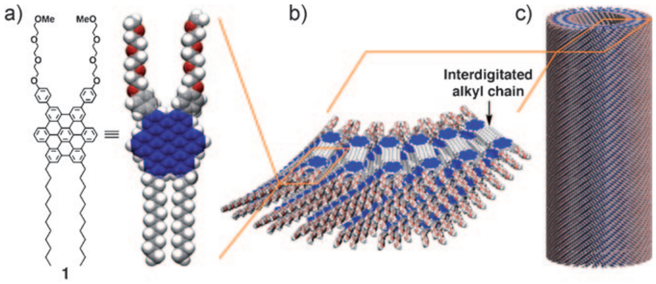

Figure 1. Illustrations of a) molecular structure and 3D model of HBC amphiphile **1** and b,c) the tubular assemblies of the hierarchical structure.

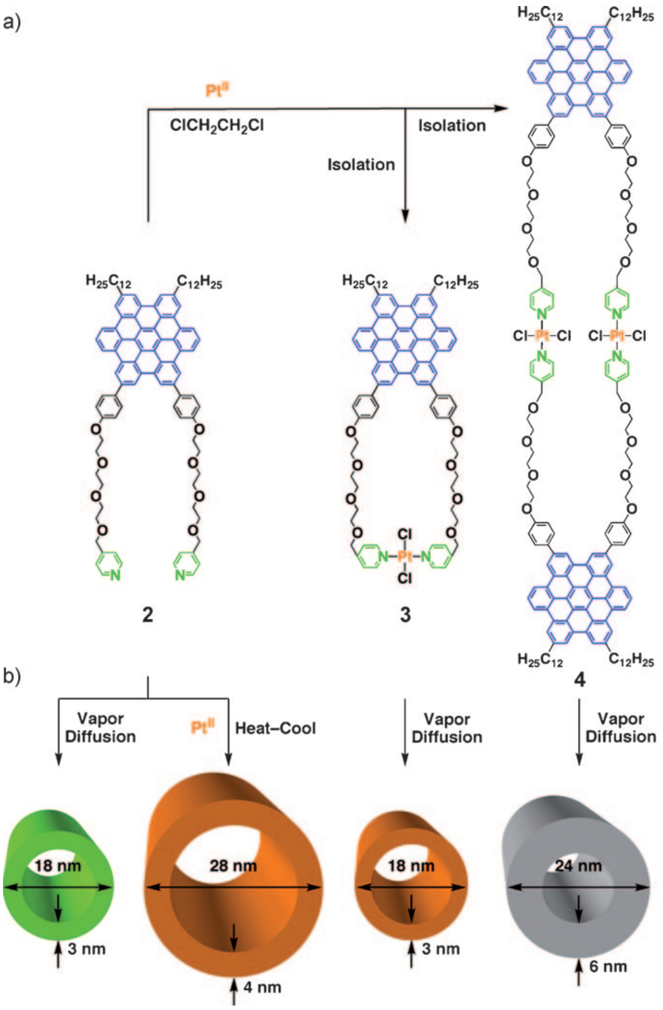

Figure 2. a) Derivatization of pyridyl-appended HBC **2** using platinum(II) coordination. b) Dimensional features of nanotubes from **2**–**4**, and **2** coassembled with *trans*-[Pt(PhCN)$_2$Cl$_2$].

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m(II).[10,11] However, under the conditions established for tubular assembly of **1**, HBC **2** was too soluble to undergo controlled assembly. Hence, we tried to optimize the conditions and found that compound **2**, when coassembled with *trans*-[Pt(PhCN)$_2$Cl$_2$] in toluene, gives a nanotubular structure under heat–cool conditions (Figure 2).

Typically, a suspension of a mixture of **2** (1.3×10^{-3} mmol, 2.0 mg) and *trans*-[Pt(PhCN)$_2$Cl$_2$] (1.3×10^{-3} mmol, 0.64 mg) in toluene (10.0 mL) was heated to 90 °C, whereupon the suspension became clear and then gradually turbid. After heating the solution overnight, the reaction mixture was allowed to cool to room temperature. The yellow-colored suspension thus formed displayed characteristic red-shifted absorption bands at 416 and 445 nm because of the formation of π-stacked HBC units upon *J*-aggregation (Figure 4, green curve).[7b] Scanning electron microscopy (SEM) showed the presence of cylindrical nanofibers (Figure 3b), which were confirmed by transmission electron microscopy (TEM) to be nanotubes having a uniform diameter of 28 nm and a wall thickness of 4 nm (Figure 3f). By means of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis, the nanotubes were found to contain platinum, whose content (10.8 %) was close to the value of 11.1 % as expected when all the pyridyl groups of **2** are bridged by PtCl$_2$. Hence, not only C–C bond-forming polymerization, as reported for the assembly of an olefin-appended HBC amphiphile,[12] but also metal-ligating supramolecular polymerization can assist selective tubular assembly of HBC even under very dynamic conditions. Meanwhile, when a palladium analogue of *trans*-[Pt(PhCN)$_2$Cl$_2$] with a much more dynamic coordination character (*trans*-[Pd(PhCN)$_2$Cl$_2$]) was used for the coassembly with **2**, only an irregular aggregate under identical heat–cool conditions was formed (Supporting Information, Figure S1).[9]

In the course of these studies, we noticed that metal-cyclized monomer **3** and dimer **4** are produced upon heating a mixture of **2** and *trans*-[Pt(PhCN)$_2$Cl$_2$] in appropriate solvents, such as 1,2-dichloroethane. Although insoluble oligomers formed concomitantly, **3** and **4** were isolated as soluble fractions in 21 and 9 % yield, respectively.[9] Interestingly, when Et$_2$O vapor was allowed to diffuse at 25 °C into a solution of **3** (1.4×10^{-3} mmol, 2.5 mg) in CH$_2$Cl$_2$ (5.0 mL),nanotubes were formed quantitatively (Figure 3c and g). Noteworthy are the assembly of the cyclic dimer **4** (Figure 3d and h) and the metal-free HBC **2** (Figure 3a and e) into nanotubes under the same vapor-diffusion conditions.[9] The electronic absorption spectra of these tubular assemblies displayed characteristic bands due to *J*-aggregated HBC units more explicitly than the nanotube of **2** coassembled with *trans*-[Pt(PhCN)$_2$Cl$_2$] (Figure 4). Furthermore, their infrared spectra showed CH$_2$ stretching vibrations owing to the dodecyl (C12) chains at 2918 (ν_{as}) and 2849 (ν_s) cm^{-1} (Supporting Information, Figure S4),[9] indicating that the paraffinic side chains adopt a stretched conformation upon interdigitation.[7b]

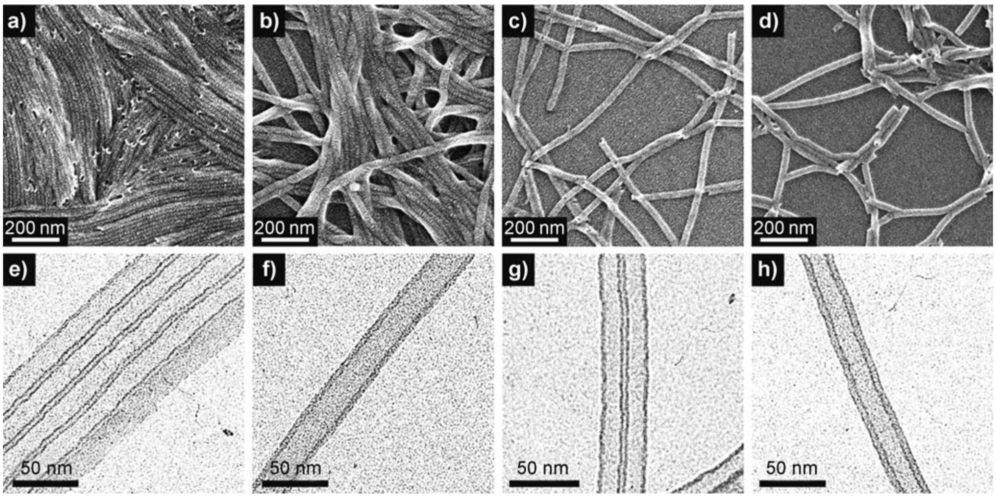

Figure 3. SEM (a–d) and TEM (e–h) micrographs of air-dried suspensions of nanotubes. Nanotubes derived from **2** under vapor-diffusion conditions (CH$_2$Cl$_2$/Et$_2$O) (a, e), **2** coassembled with *trans*-[Pt(PhCN)$_2$Cl$_2$] in toluene under heat–cool conditions (b, f), **3** under vapor-diffusion conditions (CH$_2$Cl$_2$/Et$_2$O) (c, g), and **4** under vapor-diffusion conditions (CH$_2$Cl$_2$/Et$_2$O) (d, h).

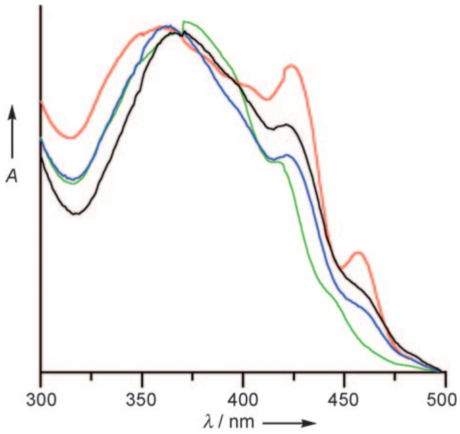

Figure 4. Electronic absorption spectra of air-dried suspensions of nanotubes from **2** (——), **3** (——), **4** (——), and **2** coassembled with *trans*-[Pt(PhCN)$_2$Cl$_2$] (——). Spectra are normalized at 370 nm.

In more detailed investigations, we found that the four types of nanotubes thus obtained possess some similarities and differences. First of all, when the nanotubes obtained from **2**–**4** were added to CH$_2$Cl$_2$, a good solvent for **2**, all of them disappeared immediately by dissociation into the corresponding monomers. In contrast, the nanotube, obtained by the coassembly of **2** with *trans*-[Pt(PhCN)$_2$Cl$_2$] under heat–cool conditions, was tolerant against dissociation in CH$_2$Cl$_2$ and retained its tubular morphology. Thus, HBCs **3** and **4** self-assemble without reshuffling their metal-coordination bonds (Figure 5). On the other hand, in the coassembly of **2** with *trans*-[Pt(PhCN)$_2$Cl$_2$], the metal coordination could take place both in an intermolecular and an intramolecular fashion. As observed in surface-polymerized nanotubes from olefin,[12,13] thiol,[14] and cumarine-appended HBC derivatives,[15] such an intermolecular metal coordination may effectively stabilize the π-stacked HBC array against dissociation. Secondly, the dimensions of the nanotubes are quite diverse. As summarized in Figure 2, the nanotubes from metal-free HBC **2** and the cyclic HBC **3** are identical to one another both in diameter (18 nm) and wall thickness (3 nm), and almost comparable to those obtained from HBC amphiphile **1** (Figure 1; diameter = 20 nm, wall thickness = 3 nm).[7a] In contrast, the nanotube of **2** coassembled with *trans*-[Pt(PhCN)$_2$Cl$_2$] has a slightly thicker wall (4 nm) and a much larger diameter (28 nm). Since the *J*-aggregate absorption bands are clearly less pronounced than those of the other nanotubes (Figure 4, green curve), such a dimensional feature of the coassembled nanotube may originate from the coexistence of intermolecular and intramolecular metal-coordination bonds on its surface (Figure 5). Note that the wall thickness of the nanotube from cyclic dimer **4** (6 nm) is almost twice as large as those of the nanotubes from metal-free HBC **2** and cyclic HBC **3**, although its tube diameter (24 nm) is not much larger (Figure 2). These observations indicate an interesting possibility that cyclic dimer **4** self-assembles most likely into a double bilayer wall (Figure 5). In contrast to the single bilayer structures observed for the coassembly of **2** with *trans*-[Pt(PhCN)$_2$Cl$_2$] and self-assembly of **3**, the double bilayer wall from **4** possesses pyridine–platinum(II) coordination layers that are embedded and, thus, unexposed to outer environments.

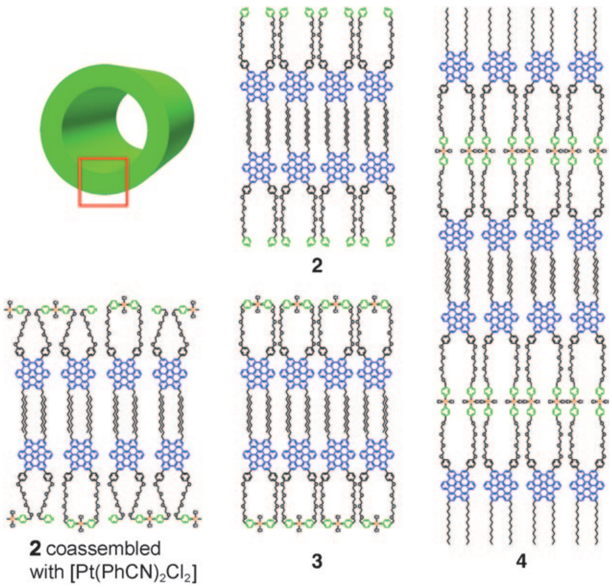

Figure 5. Proposed wall structures of nanotubes from **2**, **3**, **4**, and **2** coassembled with *trans*-[Pt(PhCN)$_2$Cl$_2$].

In connection with these structural features, the nanotube of self-assembled **4** displayed a marked difference in square-wave voltammetry (SWV) from the other three nanotubes. Figure 6 shows SWV characteristics of four nanotubes with respect to the oxidation of HBC units. The SWV profiles of the nanotubes of coassembled **2**/Pt^{II} (Figure 6, green curve) and self-assembled **3** (Figure 6, red curve) are virtually identical to one another, as expected from their structural analogy, whereas they are slightly but definitely different from the SWV profile of the nanotube obtained from metal-free HBC **2**. From these observations, it is apparent that the platinum-coordination layer most likely affects the oxidation profile of the HBC units in the tubular wall. Compared to these nanotubes, the tubular assembly of cyclic dimer HBC **4** (Figure 6, blue curve) exhibited a rather complicated SWV profile with at least two oxidation peaks below +1.2 V. Since the cyclic voltammetry profiles of non-assembled **3** and **4** in CH$_2$Cl$_2$ were not different from one another (Supporting Information, Figure S5), the clear difference in the electrochemical properties observed for their assembled states may support our claim that the nanotubular structure from **4** having a double bilayer wall essentially differs from the other three (Figure 5).

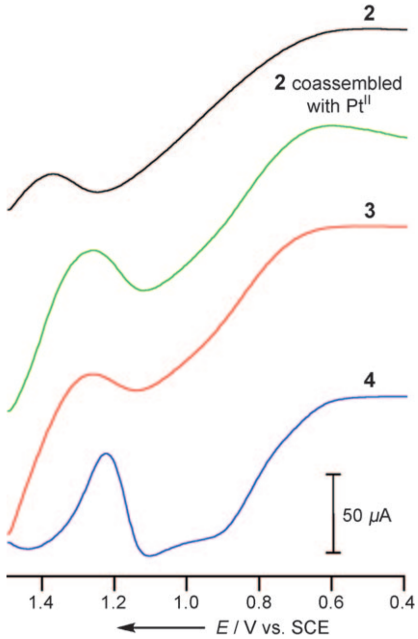

Figure 6. Square-wave voltammograms (SWV) of nanotubes from **2** (——), **3** (——), **4** (——), and **2** coassembled with *trans*-[Pt(PhCN)$_2$Cl$_2$] (——). The nanotube samples were coated on an ITO glass by drop casting and subjected to SWV at 25 °C in acetonitrile using tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$, 0.1 M) as a supporting electrolyte and ITO glass as a counter electrode. The arrow indicates the scanning direction.

In conclusion, by using pyridyl-appended hexabenzocoronene **2**, we successfully developed three different nanotubes that are molecularly hybridized with pyridine–platinum(II) coordination layers. To our surprise, even cyclic dimer HBC **4** with two HBC units can assemble into a nanotubular structure. For coordination chemistry, a wide variety of transition-metal ions are available which can be reduced to metallic clusters. Studies on seeding or templating the formation of metallic nanoclusters using metal-ion-coated hexabenzocoronene graphitic nanotubes is one of the subjects worthy of further investigation.

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