Nanotube Self-Assembly

DOI: 10.1002/ange.200801404

Hierarchical Supramolecular Self-Assembly of Nanotubes and Layered Sheets**

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Interest in tubular nanostructures has been continuously growing since the discovery of carbon nanotubes in 1991. Tubular nano-objects have displayed unique optical, electronic, and magnetic properties and have found potential use in such applications as nanodevices, catalysis, biomimetics, and energy storage.[1–5] The preparation of novel high-quality nanotubes is still a challenging field of research. In contrast to inorganic[6,7] and macromolecular tubules,[8,9] which have been explored extensively over the last decade, low-molecular-weight organic compounds with their intrinsic merits of diversity, tailorability, and multifunctionality are good candidates for the construction of nanotubes.[10–12] The supramolecular self-assembly process of mimicking nature to construct biologically active structures can generate ordered complex structures from simple building blocks.[13,14] Thus, the self-assembly of nanotubes from well-defined, simple building blocks would be fascinating and practically useful. However, progress on the self-assembly of organic nanotubes from nonamphiphiles to date lags behind that of their amphiphilic counterparts,[1,15–19] which usually follows a twisted-belt mechanism.[20–22]

Herein, we report the hierarchical supramolecular self-assembly of a small organic nonamphiphilic molecule, *para*-terphenylen-1,4″-ylenebis(dodecanamide) (**TB**), to form a new kind of rolled-up organic nanotube from its nanosheet precursor. We also highlight the use of these rolled-up nanostructures as a template to fabricate composite nanotubes with C_{60} inside. The formation of the self-assembled nanotubes follows a similar mechanism to that proposed for the formation of multiwalled carbon nanotubes.

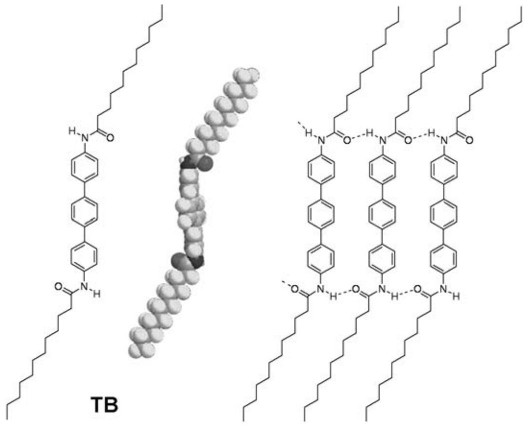

Figure 1. Chemical structure of **TB** and the possible intermolecular translation-related hydrogen bonding.

As shown in Figure 1, **TB** has a central rigid terphenylene segment, two secondary amido functional groups, and two flexible alkyl chains. The unique structural feature of **TB** makes it an ideal candidate for self-assembling through π–π stacking and directed intermolecular hydrogen bonding. The terphenylene segment has a strong tendency to aggregate through π–π overlap. The structural feature allows **TB** to form a supramolecular ladder structure through intermolecular translation-related hydrogen bonding.[23,24] The π–π interaction and the intermolecular hydrogen bonding have a synergistic effect on the formation of extremely stable aggregations.

TB was synthesized by Suzuki cross-coupling (Figure S1 in the Supporting Information). The strong synergistic effect of the π–π stacking and directed intermolecular hydrogen bonding made **TB** almost insoluble in any solvent at room temperature, thus making routine characterization impossible. **TB** precipitated from the solvent mixture during the reaction, but it could be completely redissolved in hot THF and precipitated after cooling, which made purification convenient. The high purity of **TB** was confirmed by combustion analysis.

The self-assembly of **TB** is a solvent-mediated process. The concentration of **TB** in the THF solution determined the formation of the self-assembled nanotubes and/or layered sheets. A suspension of **TB** in THF (concentration: 0.1 $mg\,mL^{-1}$) was heated to reflux until all the solids were completely dissolved to form a colorless, clear solution. The solution was allowed to cool gradually to room temperature; it turned cloudy after about 1 h. A scanning electron microscopy (SEM) study of an air-dried suspension of **TB** on a silicon substrate showed the formation of fibril assemblies with a high aspect ratio (Figure 2a and Figure S3a in the Supporting Information). The open-ended feature of these fibers revealed a tubular structure (Figure 2b). Transmission electron microscopy (TEM) images showed the presence of tubes several tens of micrometers in length with an average

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[**] We thank X. Zhang and C. C. Han for discussions, W. Wang for the low-angle powder X-ray diffraction measurements, and Y. Geng for assistance in cross-linking of the nanotubes. This work is supported by Natural Science Foundation of China grants 20574075, 20423003, and 50521302.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200801404.

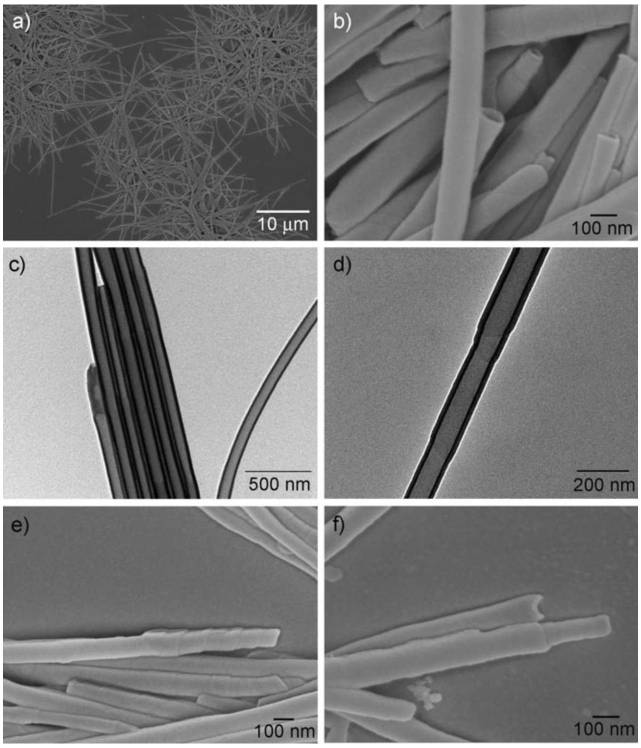

Figure 2. Morphology of self-assembled **TB**. a) SEM image of a sample prepared by dropping a THF suspension of self-assembled **TB** (0.1 mg mL^{-1}) onto a silicon substrate followed by air drying and coating with Pt; b) high-magnification SEM image of self-assembled **TB** with an open-ended cross section; c) TEM image of self-assembled **TB**; d) high-magnification TEM image of self-assembled **TB**; e) high-magnification SEM image of self-assembled **TB**; f) internal and external screw ends of the self-assembled tubes.

diameter of 100 nm and a wall thickness of 20 nm (Figure 2c and d).

Magnified SEM images revealed a novel rolled-up style of nanotube. In contrast to multiwalled carbon nanotubes, which can be formed by rolling up graphite sheets around the edges both seamlessly and concentrically,[25] or most of the lipid nanotubes that involve a helically coiled ribbon structure as an intermediate,[20–22,26] the nanotubes derived from **TB** were of a scrolling structure formed by rolling up sheets (Figure 2e).[27] Two terminal types of tubes are shown in Figure 2f. High-quality SEM images of nanotubes self-assembled by the bis(stearamide) analogue of **TB**, which was synthesized by a similar method, clearly revealed that the nanotubes have a rolled-up structure (Figure S2 in the Supporting Information). We also found that the nanotubes were thermally stable, as confirmed by SEM observation after heating the nanotubes at 100 °C for several hours under ambient conditions (Figure S3b in the Supporting Information).

Increasing the concentration of **TB** to 1.0 mg mL^{-1} resulted in the exclusive formation of layered sheets several tens of micrometers in length, several micrometers in width, and several hundred nanometers in thickness (Figure 3a and Figures S3c, S3d, and S4 in the Supporting Information).

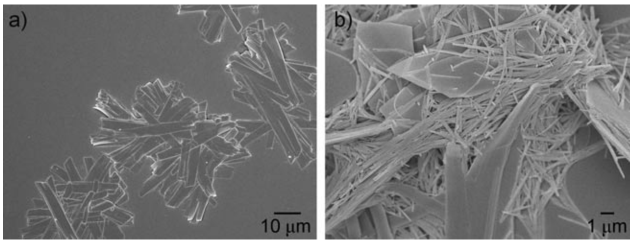

Figure 3. SEM images of self-assembled **TB** at concentrations of a) 1.0 and b) 0.5 mg mL^{-1}.

The FTIR spectra of the nanotubes and layered sheets on KBr plates (Figure S5 in the Supporting Information) showed CH_2 stretching vibrations at lower frequencies (ν_{anti}: 2917 cm^{-1}; ν_{sym}: 2847 cm^{-1}), which were ascribable to an all-*trans* conformation, thus indicating that the alkyl chains were closely packed to form a crystalline domain.[28] The absorption frequencies of the $C=O$ bond stretching (amide I) for the rolled-type nanotubes and the layered sheets are 1657 and 1656 cm^{-1}, respectively. The absorption frequencies of the N–H deformation band (amide II) for the nanotubes and layered sheets are 1541 and 1544 cm^{-1}, respectively. The IR results indicate that a translation-related hydrogen bond was formed in both the nanotubes and layered sheets.[28,29]

Low- and wide-angle powder X-ray diffraction experiments were performed on the nanotube and layered sheet samples to determine their structures. The low-angle powder X-ray diffraction patterns (Figure S6 in the Supporting Information) showed two ordered reflection peaks with a long-range ordering of 4.63 and 4.34 nm, respectively. These values are consistent with the length of **TB** (4.5 nm in its fully stretched conformation) calculated by Corey–Pauling–Koltun (CPK) molecular modeling. The wide-angle X-ray powder diffraction patterns (Figure S7 in the Supporting Information) of both layered sheets and nanotubes displayed several strong, sharp peaks in the range of 19 to 24° because of the packing of the alkyl chains and π–π stacking of the terphenylene segments. The observed *d* spacing of 0.39 nm is probably a result of the center-to-center distance between the terphenylene units, whereas the *d* spacing of 0.44 nm is possibly caused by the ordered packing of the alkyl chains.[30,31]

Both the nanotubes and layered sheets exhibited a strong fluorescence under illumination by UV light (Figure S8 in the Supporting Information), and the photoluminescence spectra of the nanotubes excited at different wavelengths are shown in Figure S9 in the Supporting Information. The spectra displayed an expected exciton-like character[23,30] following the increase of the excitation wavelength to the red edge of the absorption band (390 nm; Figure S10 in the Supporting Information), thereby resulting in a red-shifted fluorescence emission.

To understand the mechanism for the formation of layered sheets and rolled-up-type nanotubes,[32] we performed contrast experiments: reducing the concentration of **TB** in THF from 1.0 to 0.5 mg mL^{-1} resulted in the coexistence of nanotubes and nanosheets in the precipitate (Figure 3b). The formation of layered sheets or nanotubes clearly depends on the concentration of **TB** in THF. Therefore, we proposed the following formation mechanism (Figure 4). First, the synergistic effects of π–π stacking and directed intermolecular hydrogen bonding conducted the hierarchical self-assembly of thin layers. The π–π overlaps of the terphenylene segments and the translation-related hydrogen bonding of the secondary amides are extremely strong attractive forces, and are both capable of making **TB** self-assemble to form one-layer nanosheets (routes A and B, Figure 4). The one-layer nanosheets, which have very high surface areas, are unstable and have a strong tendency to either stack to form layered sheets with lamellar structures (route C) or to form rolled-up-type nanotubes (route D). Both of these procedures can lower the energies through reducing the surface areas.

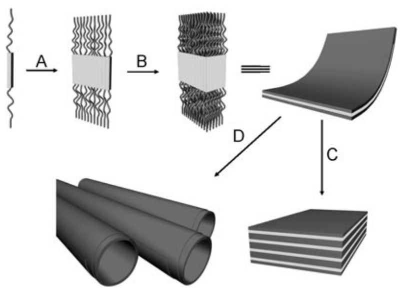

Figure 4. Possible mechanism for the formation of self-assembled rolled-up nanotubes and layered sheets. A) Primary self-assembly of **TB** by π–π stacking of terphenylene units and intermolecular hydrogen bonding between amido functional groups affords supramolecular ladder structures. B) Secondary assembly of the ladder structures by stacking them together leads to a supramolecular sheet. C) Tertiary assembly is the stacking of the resulting supramolecular single-layer sheets to form layered sheets. D) The alternative tertiary assembly is the rolling up of the resulting supramolecular single-layer sheets to form nanotubes.

At high concentration, the primarily self-assembled one-layer sheets have a greater possibility to stack to form layered sheets, whereas at low concentration, the single-layer nanosheets are too far from each other, and thus have little opportunity to stack to form layered sheets. As a result, the one-layer nanosheets probably tend to curl up to form rolled-up-type nanotubes. We quenched the hot THF solution of **TB** ($0.5\,\mathrm{mg\,mL^{-1}}$) with liquid nitrogen in the presence of a silicon substrate, which may capture the very thin nanosheets and stabilize them. As expected, relatively thin and flexible nanosheets were frozen onto the silicon substrate (Figure S3e in the Supporting Information). This result clearly demonstrates that in the early stages of self-assembly, relatively thin nanosheets are formed. Because thin nanosheets have a relatively high surface area, they further self-assemble to form layered sheets or rolled-up nanotubes depending on the conditions used.

The self-assembled nanotubes are in the metastable state, which could convert to the more thermodynamically stable layered-sheet form through solvent-mediated deconvolution. If the self-assembled nanotubes were deposited in THF for two days, most of the nanotubes could unwind to form layered sheets (Figure S3f in the Supporting Information). On the other hand, the tubular structure could be re-formed by first refluxing this suspension to form a clear solution and then subsequently cooling it. The centrifugation of the suspension, the dispersion of the remaining wet solid in a small amount of 1,4-dioxane, and finally freeze-drying exclusively led to nanotubes. In dry form, the self-assembled nanotubes are stable and can be kept in air for at least six months without unwinding (Figure S3g in the Supporting Information).

This reversible transformation between tubules and thick layers motivated us to investigate the loading and release of C_{60} fullerene during this cycle. C_{60}-filled nanotubes were successfully fabricated by co-assembly of **TB** and C_{60}. A TEM image of the air-dried suspension revealed the formation of C_{60}-filled nanotubes (Figure 5 a). In particular, there is a clear enlargement of the tube size and the width of the wall.

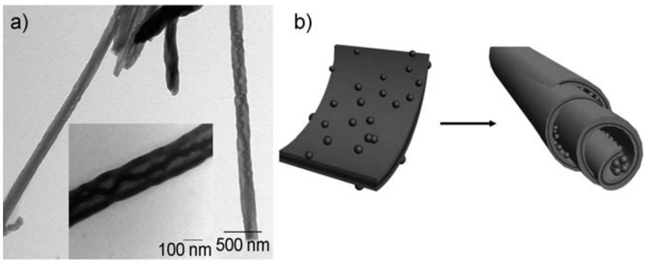

Figure 5. a) TEM image of C_{60}-filled nanotubes (inset: higher-magnification TEM image). b) The formation of a C_{60}-filled nanotube.

The alkyl chains can be cross-linked by irradiation with γ-rays, and the cross-linked nanotubes were used to study the driving force of this co-assembly process. 1) Deposition of the cross-linked nanotubes[33] was carried out in a supersaturated toluene suspension of C_{60}. We expected that the C_{60}, if driven by capillary forces or other host–guest interactions, would diffuse into the hollow space.[34] 2) The same co-assembly conditions were also applied to the cross-linked nanotubes. In both cases, no C_{60}-filled nanotubes were formed.[33] Based on the above experimental results, we deduce that the C_{60}-filled nanotubes were formed during the rolling-up process.

A possible co-assembly mechanism is shown in Figure 5 b. THF is a bad solvent for C_{60} and the surface of the nanosheets is hydrophobic, so C_{60} has a tendency to deposit on the nanosheets. Rolling up of these hybrid nanostructures provides a confined environment for further aggregation of C_{60}, thus inducing concomitant self-assembly of a C_{60} nanowire.[34a] Also, compared to the "naked nanosheets", the presence of C_{60} seemingly influences the rolling-up process and finally enlarges the dimension of the hybrid tubes: the deposition of C_{60} might cause looser rolling up, and the possibility that C_{60} is sandwiched between the multiwalls should also be considered as a reason for this enlargement. This unique quasi-cable-like structure is very appealing, because the inner fullerene wire is semiconducting and the outer surface of the nanotube is an insulating material. The C_{60}-filled nanotubes unwound and released C_{60} clusters when suspended in THF for two days (Figure S11 in the Supporting Information). One can expect that this new type of fullerene-embedded hybrid tubular structure and such controlled release would be promising in a variety of potential applications, such as optoelectronic nanodevices.

In conclusion, the self-assembly of **TB** in THF formed distinct fluorescent, multiwalled, rolled-up organic nanotubes and/or layered sheets. The nanotubes are micrometers in length and have diameters in the range of 90 to 120 nm, with approximately 20-nm-thick walls and an aspect ratio up to 300 with a novel scrolling pattern. The possible self-assembly mechanism was discussed. The nanotubes, which have a hydrophobic inner surface, can be used as nanotubular containers to incorporate C_{60}. Therefore, quasi-cable-like structures with C_{60} nanowires inside the self-assembled nanotubes have been fabricated. The reversible transformation between nanotubes and layered sheets can be used to control the loading and release of C_{60}.

Received: March 24, 2008

Keywords: fullerenes · layered sheets · nanotubes · self-assembly · supramolecular chemistry

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