DOI: 10.1002/ange.200704747

Helical Nanocoils

Conductive One-Handed Nanocoils by Coassembly of Hexabenzocoronenes: Control of Morphology and Helical Chirality

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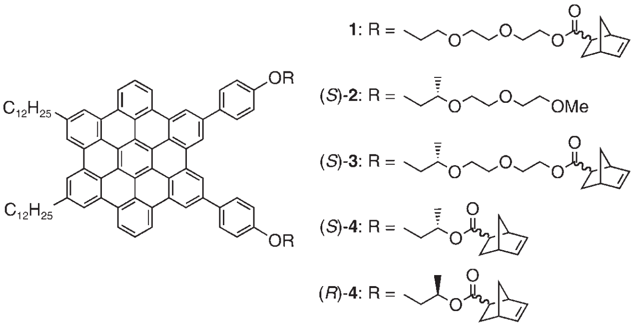
Electroconductive one-handed helical nanofibers are attractive in view of their potential for the realization of nanoscale solenoids. While there are many reported examples of the construction of helical nanofibers by self-assembly of π-electronic molecules,[1,2] most of these involve twisted ribbons,[3] which do not provide the coiled pathways essential for electromagnetic properties. Some coiled assemblies of aromatic molecules have been reported,[4] although they are still very rare and their conducting properties have not been investigated, mainly because of their insufficient morphological robustness for electrochemical doping. Thus, the design of nanostructures that satisfy the three requisites for electromagnetic properties—coiled pathways, one-handedness, and electroconductivity—is still a highly challenging research topic.

A few years ago we found that a Gemini-shaped hexabenzocoronene (HBC) bearing triethylene glycol and dodecyl chains self-assembles into a graphitic nanotube.[5] More recently, we have also found that the incorporation of pendant norbornene groups into the amphiphilic HBC (**1**) gives rise to a nanocoiled assembly with uniform diameter and helical pitch.[6] The metastable coiled structure exists for a sufficiently long time, probably because of a steric effect of the pendant norbornene groups, and therefore allows post ring-opening metathesis polymerization (ROMP) of the norbornene groups to covalently stabilize the kinetically selected assembly against a thermodynamic coil-to-tube transformation. The polymerized nanocoil consists of a π-stacked HBC array that exhibits conductivity upon oxidative doping.[6] However, the resultant nanocoils are a mixture of right- and left-handed ones, which means that further structural elaboration is needed to realize the one-handed helical graphitic array that is essential for the exploration of electromagnetic properties.



Herein we report the selective formation of covalently stabilized conductive nanocoils with a one-handed helical chirality by coassembly of norbornene-appended HBC derivatives **1** and **4** (Figure 1). This achievement is the result of a long-term effort to optimize the molecular structure and self-assembly conditions to suppress the concomitant formation of undesired structures, such as noncoiled fibers and nanotubes.

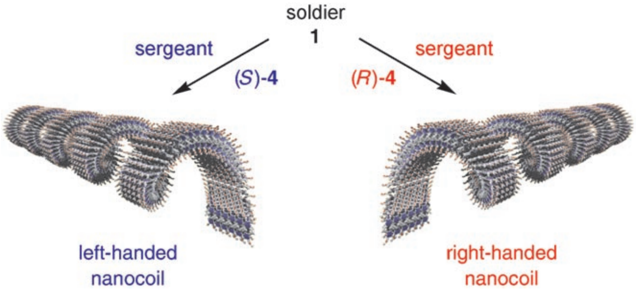


Figure 1. Formation of one-handed nanocoils through a sergeants-and-soldiers effect in the coassembly of **1** with **4**.

We have reported previously that HBC derivative (*S*)-**2**, which possesses a chiral handle in the hydrophilic chain, self-assembles into a nanotube containing a one-handed helical array of π-stacked HBC units.[3,7] This observation prompted us to investigate whether the self-assembly of (*S*)-**3** might lead to the formation of a one-handed nanocoil. However, only non-coiled fibrous assemblies and nanotubes were obtained[8]

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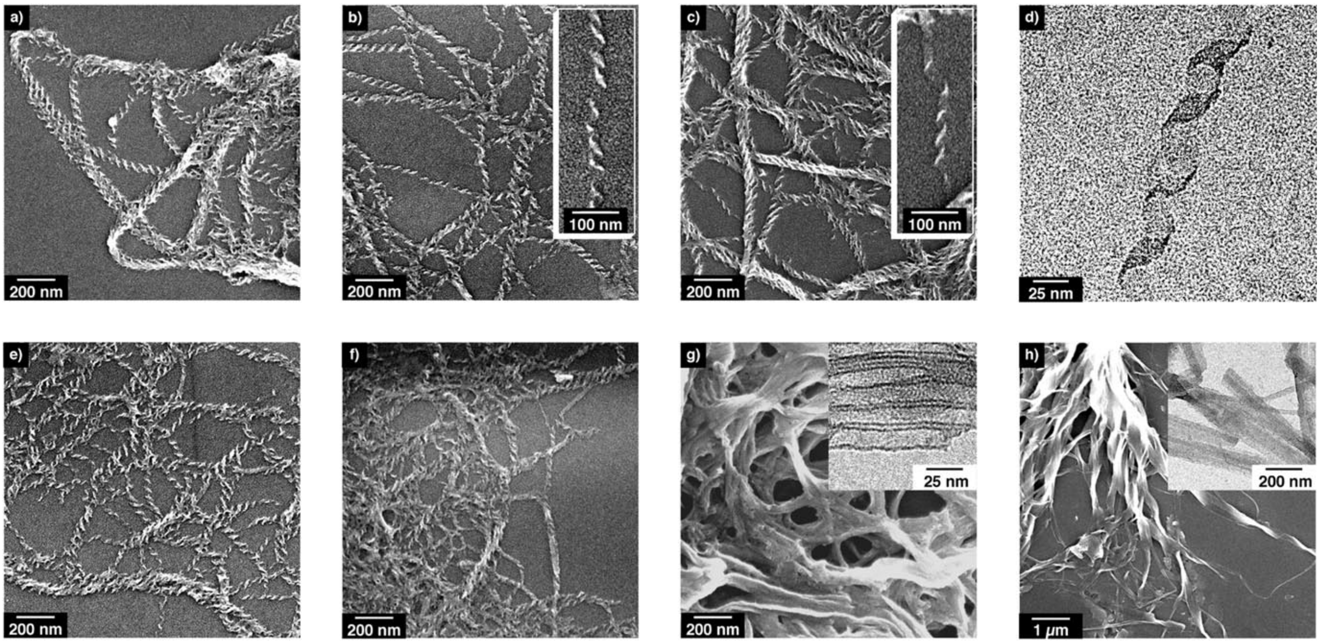

Figure 2. SEM and TEM images of air-dried suspensions of polymerized coassemblies of **1** and **4**. a–c) SEM images of the coassemblies formed from **1** with 1 mol% of (*S*)-4 (a), 20 mol% of (*S*)-**4** (b), or 20 mol% of (*R*)-**4** (c). d) TEM image of the sample prepared with 20 mol% of (*S*)-**4**. e–h) SEM images of the coassemblies formed with 50 (e), 60 (f), 80 (g; inset: TEM), and 95 mol% (h; inset: TEM) of (*S*)-**4**. The TEM images are not informative of the handedness.

despite thorough investigations under a variety of self-assembly conditions, including those optimized for the formation of the nanocoil from **1** and the one-handed nanotube from (*S*)-**2**. We then synthesized (*S*)-**4**, which has a shorter spacer between the norbornene and HBC moieties, with the expectation that a pronounced steric effect from the norbornene groups might facilitate nanocoil formation. However, as in the case of (*S*)-**3**, only nanotubular or fibrous assemblies were obtained from (*S*)-**4**.[8] These failures imply that the formation of nanocoils from Gemini-shaped HBC derivatives relies on a very delicate balance between the kinetic and thermodynamic parameters in the self-assembly process.

We found that the enantiomers of **4** can drive the stereoselective formation of nanocoils by coassembly with **1**. In a typical reaction, a 5-mL vial containing a mixture of **1** (0.52 μmol, 80 mol%) and (*S*)-**4** (0.13 μmol, 20 mol%) in CH_2Cl_2 (1 mL) was placed in a 50-mL vial containing 10 mL of Et_2O for vapor diffusion. The setup was kept at 15 °C in an incubator for 24 h to give a yellow precipitate quantitatively. Only left-handed nanocoils with a diameter of 30 nm and a pitch of 60 nm were observed by SEM microscopy. To enhance the morphological robustness, the coassembled nanocoils were surface-polymerized by ROMP according to a reported method.[6] Thus, the resulting vapor-diffusion mixture was diluted with Et_2O to a total volume of 20 mL (Et_2O/CH_2Cl_2 100:1 v/v) and the second-generation Grubbs catalyst **5** (0.065 μmol) was added to the resulting suspension. The mixture was stirred slowly at 20 °C for 24 h and the reaction was then quenched with a few drops of ethyl vinyl ether. The resultant solid was found to be insoluble in CH_2Cl_2, which is a good solvent for both **1** and (*S*)-**4**. The coiled structure of the coassembly was preserved during the polymerization, as confirmed by SEM and TEM micrographs (Figures 2b and 2d). The polymerized nanocoils were approximately 30 nm in diameter, 60 nm in pitch, and 20 nm in tape width. These dimensions are identical to those of the self-assembled nanocoils formed from **1** alone before and after ROMP of its pendant norbornene groups.[6] As expected, the use of (*R*)-**4** instead of (*S*)-**4** for coassembly with **1**, followed by surface ROMP under identical conditions to those described above, afforded nanocoils with the opposite helical sense (Figure 2c).

Analogous coiled nanofibers were obtained by the coassembly of **1** with (*S*)-**4** over a wide composition range (mol fraction of (*S*)-**4**: 1, 5, 10, 20, 30, 40, and 50%). However, undesired products began to form when the mol fraction of (*S*)-**4** exceeded 50% (60, 70, 80, 90, 95, and 99%). For example, both nanocoils and nanotubes were obtained at a mol fraction of (*S*)-**4** of 60 and 70% (Figure 2f), while only nanotubes with a diameter of 16 nm formed at 80 and 90% mol fractions of (*S*)-**4** (Figure 2g). A further increase of the mol fraction of (*S*)-**4** (95 and 99%) resulted in the formation of fibrous assemblies (Figure 2h). It should be noted that simultaneous morphology and handedness control requires much finer tuning of the self-assembly composition. As already described, the coassembly of **1** with 20 mol% of (*S*)- and (*R*)-**4** allows selective formation of the left- and right-handed nanocoils, respectively (Figures 2b and 2c). When the mol fraction of **4** was lower than 20% (10, 5, and 1%), however, the disfavored helical handedness was also obtained for the resulting nanocoils (Figure 2a), whereas when the mol fraction of **4** was higher than 50% (Figure 2e), the nanocoil remained one-handed despite the undesired formation of other assemblies such as nanotubes and fibers (see above and Figure 2 f).

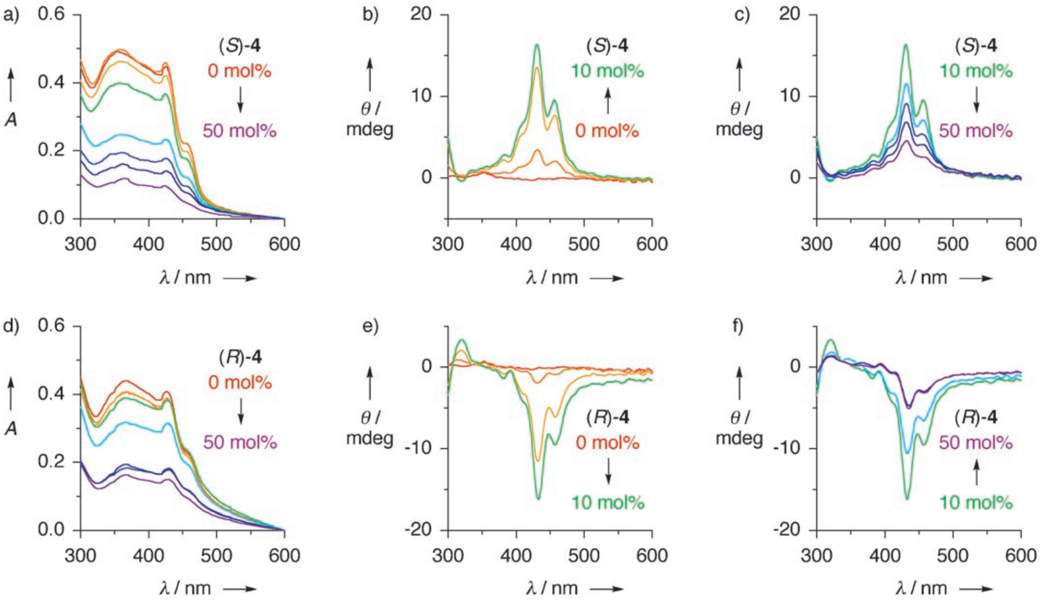

Figure 3. Electronic absorption and CD spectra of polymerized nanocoils obtained from **1** and (*S*)-**4** (a–c) or (*R*)-**4** (d–f) in Et_2O/CH_2Cl_2 (100:1 v/v; 30 μM) at 20°C, in a quartz cell with a path length of 10 mm.

The electronic absorption spectra of the coassembled nanocoils display red-shifted absorption bands at 426 and 459 nm due to the π-stacked HBC units (Figures 3 a and 3 d). Although the wavelengths of these absorption bands are unaffected by the mixing ratio of **1** and **4**, their intensities decrease notably with increasing mol fraction of **4**. Characteristic circular dichroism (CD) bands with positive and negative signs for (*S*)-**4** (Figures 3 b and 3 c) and (*R*)-**4** (Figures 3 e and 3 f), respectively, in accordance with the morphological inversion of the nanocoils in the SEM observations, were also observed in the region of these absorption bands. It should also be noted that the intensities of these CD bands change as a function of the mol fraction of **4**. Considering the hypochromic effect of **4** on the absorption spectral profile of the coassembly, the CD intensities at 431 and 457 nm were divided by the corresponding absorbances to approximate the net contribution of the π-stacked HBC array to the observed chiroptical activity. When plotted against the mol fraction of **4**, the ratio θ/A shows a saturation tendency with a monotonic increase up to 10 % (Figure 4), which suggests that the enhanced handedness of the coiled nanofibers formed by the coassembly of **1** with (*S*)- or (*R*)-**4** can be accounted for by the successful operation of the sergeants-and-soldiers effect (Figure 1).[9,10]

We also attempted the coassembly of **1** with (*S*)-**3** (1, 5, 10, and 50 mol %) but obtained a mixture of ill-defined structures and nanocoils with no particular helical selection.[8] This result suggests that it is difficult to coassemble **1** and (*S*)-**3** into a single object.

The electroconductive properties of the polymerized nanocoils were investigated by a two-probe method using 5 μm-gap electrodes, thereby taking advantage of their morphological robustness. Thus, an Et_2O suspension of the polymerized one-handed nanocoils obtained from **1** and (*S*)- or (*R*)-**4** (20 mol %) was cast onto the electrodes to give a uniform film. While the film before doping showed only a negligible electrical current, the doped film prepared upon exposure to an I_2 vapor was conductive and exhibited a linear *I*–*V* profile.[8] The average conductivity of the doped film composed of the polymerized nanocoils with a left-handed helical chirality was found to be $1.4\times10^{-4}\,S\,cm^{-1}$, which is comparable to those of the right-handed analogue and a racemic reference prepared from **1** alone.[6,8] In sharp contrast with the nonpolymerized nanocoils,[6] the polymerized nanocoils retain their morphological integrity throughout the oxidative doping with I_2.[8]

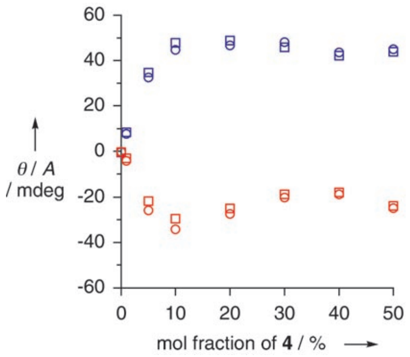

Figure 4. Plots of CD intensity/absorbance ratios at 431 (circles) and 457 nm (squares) versus the mol fraction of **4**. Blue: coassembly of **1** with (*S*)-**4**. Red: coassembly of **1** with (*R*)-**4**.

In conclusion, we have fabricated conductive nanocoils with a defined handedness by taking advantage of the sergeants-and-soldiers effect. One of the main difficulties encountered in this research was that the coiled assembly is a kinetically favored product and is therefore subject to transform into a tubular assembly thermodynamically. This situation meant that a coiled assembly with a sufficiently long lifetime to enable its covalent stabilization had to be designed. The other major difficulty arose from the fact that the morphological preference of the “sergeant” (**4**; fiber) is different from that of the “soldier” (**1**; coil). By overcoming these synthetic difficulties, we were able to fabricate the first

π-electronic nano-object that fulfils the three requisites for electromagnetic properties—morphologically robust coiled π-electronic pathways, single-handedness, and electroconductivity. Although supramolecular systems involving multiple assembling modules are hard to control, this work illustrates that the elaboration of such complex systems is essential for obtaining certain morphologies and properties.[11]

Received: October 13, 2007

Keywords: chirality · conducting materials · polymerization · self-assembly · supramolecular chemistry

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