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# Stabilization of a Kinetically Favored Nanostructure: Surface ROMP of Self-Assembled Conductive Nanocoils from a Norbornene-Appended Hexa-*peri*-hexabenzocoronene

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***Abstract:*** Newly designed norbornene-appended hexabenzocoronene **1** self-assembles, upon diffusion of an $Et_2O$ vapor into its $CH_2Cl_2$ solution, to form either graphitic nanocoils or nanotubes, depending on the self-assembling conditions. The coiled assembly, selectively formed at 15 °C, is a kinetic intermediate for the tubular assembly and transforms into nanotubes on standing at 25 °C. However, post-ring-opening metathesis polymerization of the norbornene pendants of **1** enhances the thermal stability of the coiled assembly as well as the tubular one and disables a thermodynamic coil-to-tube transition. The polymerized nanocoils show an electroconductivity of $1 \times 10^{-4}$ S cm$^{-1}$ upon doping with $I_2$, while the nonpolymerized nanocoils are disrupted upon being doped.

## Introduction

In general, self-assembly is a thermodynamically controlled process[1] where a variety of temporarily formed kinetic intermediates eventually transform into a single organized structure with higher symmetry. However, in some cases, kinetic intermediates are more attractive than thermodynamic products. Here, we report selective formation and stabilization of a kinetically favored self-assembled conductive nanocoil,[2] a potential candidate for the realization of nanoscale solenoids.

Recently, we reported self-assembled nanotubular objects of hexabenzocoronene (HBC) amphiphiles (e.g., **3**) (Figure 1), which consist of helically rolled bilayer tapes composed of bilaterally coupled columns of $\pi$-stacked HBC units.[3] In the course of this study we noticed that under certain conditions coiled assemblies occasionally result together with the nanotubes. Although the nanocoil is highly attractive for its potential of helical electroconduction, such a less symmetric assembly likely exists only intermediately in the self-organization process. How does one select and stabilize this kinetic intermediate? This is a challenging issue in supramolecular chemistry.

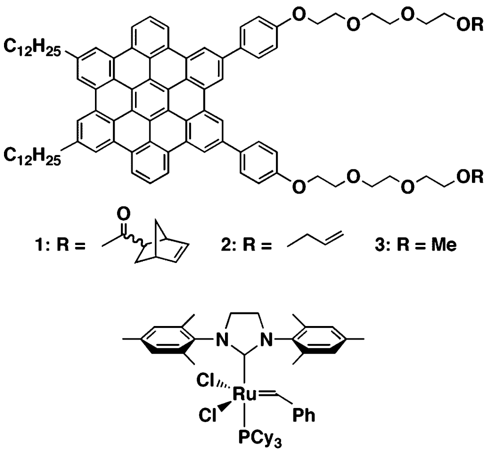

***Figure 1.*** Molecular structures of amphiphilic HBCs with polymerizable (**1** and **2**) and nonpolymerizable (**3**) end groups and ROMP catalyst **4**.

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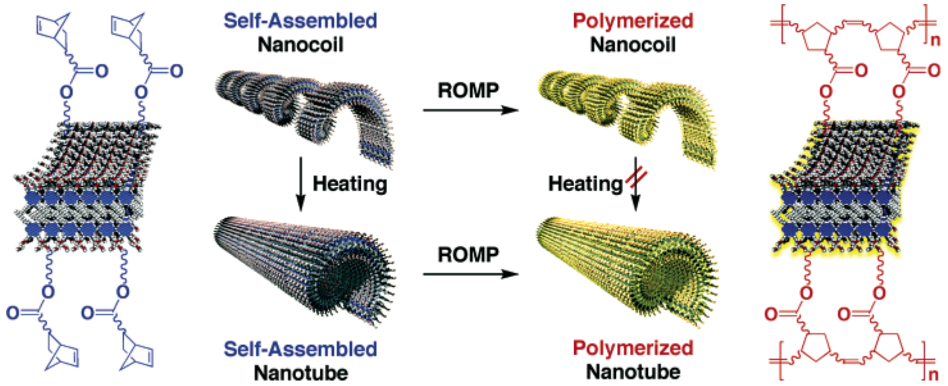
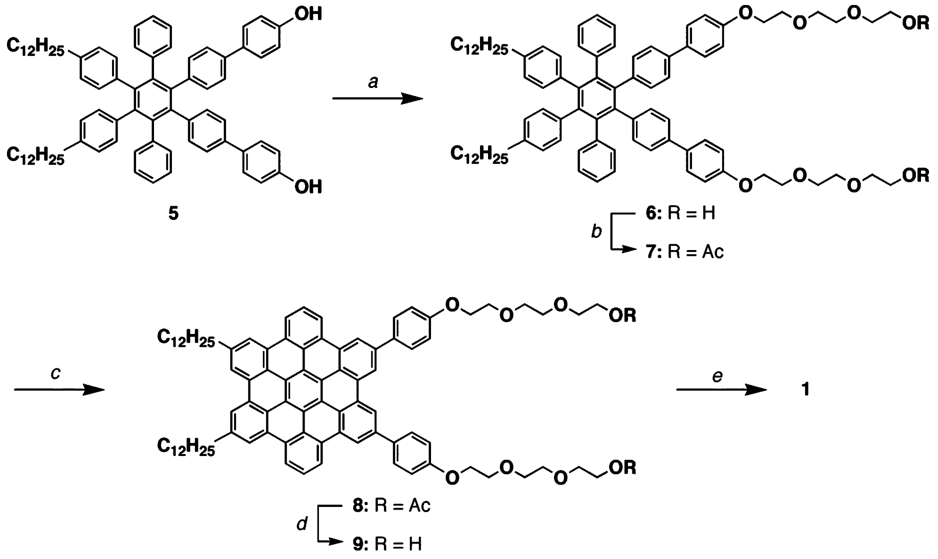


***Figure 2.*** Schematic representation of the concept of post-ROMP stabilization of self-assembled nanocoils and nanotubes from **1**.

***Scheme 1.*** Synthesis of Norbornene-Appended HBC **1**[a]



[a] (a) Triethylene glycol monochlorohydrin, $K_2CO_3$, KI, dry DMF, 80 °C, 72%; (b) $Ac_2O$, $Et_3N$, DMAP, dry $CH_2Cl_2$, 20 °C, 83%; (c) $FeCl_3$, $MeNO_2$, dry $CH_2Cl_2$, 20 °C, 61%; (d) aqueous KOH, THF; (e) 5-norbornene-2-carboxylic acid, DCC, DMAP, dry $CH_2Cl_2$, reflux, 28%.

Here, we highlight our serendipitous finding that self-assembly of norbornene-appended HBC **1** results in formation of either a coiled or a tubular object depending on the self-assembling conditions (Figure 2). Furthermore, a thermodynamic coil-to-tube transition, occurring eventually, can be disabled by subsequent ring-opening metathesis polymerization (ROMP)[4] of the norbornene pendants of **1**. Post-polymerization or cross-linking of self-assembled molecular building blocks is often utilized for enhancement of the structural robustness of non-covalent supramolecular architectures.[5] Prior to the present study we reported covalent stabilization of HBC graphitic nanotubes using reversible dimerization chemistry of coumarin and thiol functionalities incorporated into HBC as pendants.[6] To achieve permanent stitching of nanotubularly assembled HBC, we applied acyclic diene metathesis (ADMET)[4,7] to preformed nanotubes from allyl-group-appended HBC **2**.[8] However, post-polymerization with ADMET did not proceed under conditions suitable for controlled self-assembly. Alternatively, we later found that ADMET of nonassembled **2** in $CH_2Cl_2$ triggers spontaneous formation of surface-polymerized nanotubes with an enhanced thermal stability.[8] To accomplish post-polymerization that allows for stabilization of predetermined nanostructures, HBC **1** having more reactive norbornene functionalities was thus designed.

## Results and Discussion

Compound **1** was synthesized over five steps from hexaphenylbenzene derivative **5**[3b] (Scheme 1).[9] Triethylene glycol monochlorohydrin was allowed to react with **5** in DMF at 80 °C in the presence of $K_2CO_3$/KI, yielding **6** in 72%. The hydroxy groups of **6** were protected with acetyl groups using $Ac_2O/Et_3N$/DMAP in $CH_2Cl_2$ at 20 °C to afford **7** in 83% yield. Oxidative

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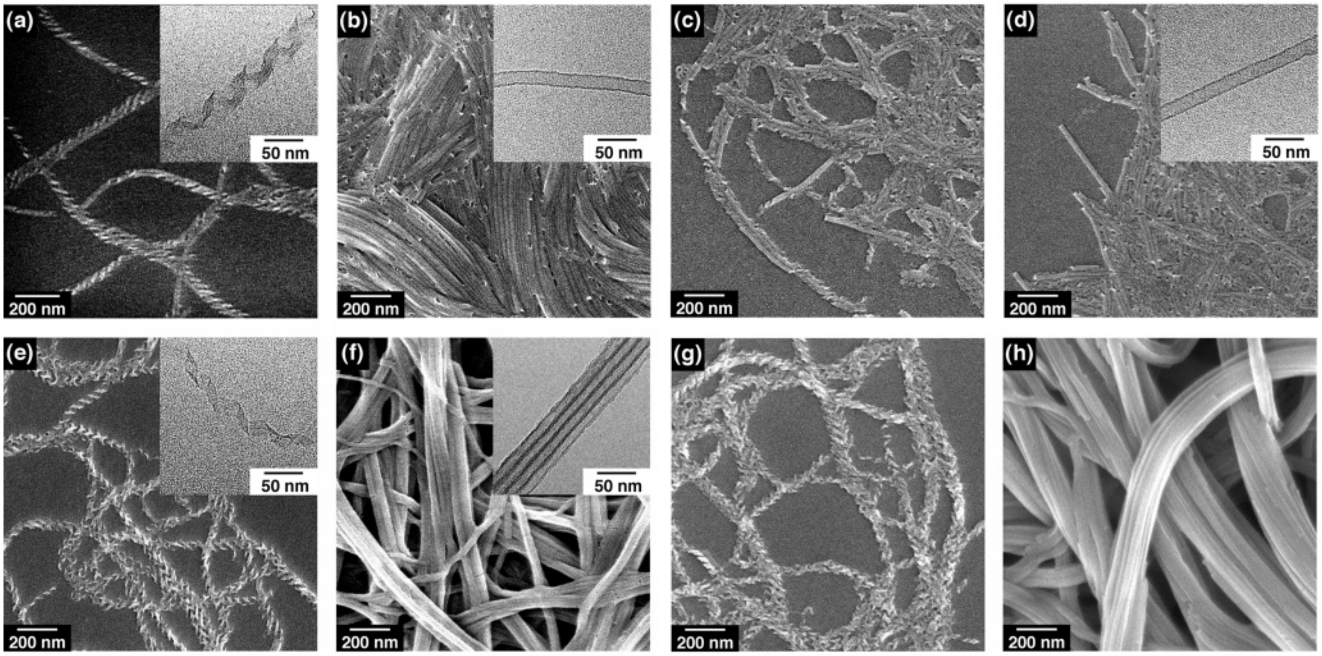

***Figure 3.*** SEM and TEM (inset) micrographs of air-dried suspensions of nanocoils and nanotubes. (a) Nanocoils and (b) nanotubes formed by $Et_2O$ vapor diffusion into $CH_2Cl_2$ solutions of **1**. Self-assembled nanocoils after being allowed to stand at 25 °C for (c) 3 and (d) 5 days. (e) Polymerized nanocoils and (f) polymerized nanotubes by post-ROMP. (g) Polymerized nanocoils after heating at 75 °C for 12 h, and (h) polymerized nanotubes after heating at 100 °C for 12 h.

cyclization of **7** by $FeCl_3/MeNO_2$ in $CH_2Cl_2$ at 20 °C resulted in formation of HBC derivative **8** in 61% yield. The acetyl groups were removed with aqueous KOH in THF to obtain hydroxy-group-terminated HBC derivative **9**. This substance was subjected to a condensation reaction with 5-norbornene-2-carboxylic acid using DCC/DMAP in $CH_2Cl_2$ under reflux, giving target norbornene-appended amphiphilic HBC **1** in 28% yield.

While HBC **2** self-assembles in THF to give nanotubes,[8] norbornene-appended HBC **1** was highly soluble in THF and hardly formed ordered assemblies. After many attempts, we noticed that, upon diffusion of an $Et_2O$ vapor into a $CH_2Cl_2$ solution of **1** (0.22 mM) at 25 °C,[9] controlled self-assembly of **1** took place quantitatively to give nanotubes having a uniform diameter of 20 nm and a wall thickness of 3 nm (Figure 3b). Interestingly, when the concentration of **1** in $CH_2Cl_2$ was higher (0.65 mM), vapor diffusion at 15 °C resulted in exclusive formation of a coiled assembly in quantitative yield.[9] As shown in Figure 3a, the diameter of the nanocoils (30 nm) is obviously greater than that of the nanotubes, while their wall thicknesses are nearly identical to one another. Each nanocoil consists of a helically rolled 20-nm-wide single bilayer tape with a pitch of 60 nm. Electronic absorption spectra of the nanocoils and nanotubes were quite analogous to one another, displaying red-shifted absorption bands, characteristic of $\pi$-stacked HBC, at 427 and 459 nm (Figure 4). A morphological similarity thus observed between the coiled and tubular assemblies suggests that the former is a kinetic precursor for the latter. In fact, when a suspension of the nanocoils, obtained at 15 °C by vapor diffusion, was warmed to 25 °C and allowed to stand, the nanocoils were gradually transformed into nanotubes. According to SEM microscopy, the self-assembled system after the initial 3 days still contained the nanocoils, which disappeared after 5 days to leave the nanotubes almost exclusively (Figure 3c and d). As confirmed by TEM, the diameter and wall thickness of the resulting nanotubes are identical to those formed at 25 °C by vapor diffusion (Figure 3b). Considering that the nanocoils are thus preferred only kinetically, their exclusive formation under slightly modified assembling conditions is remarkable.

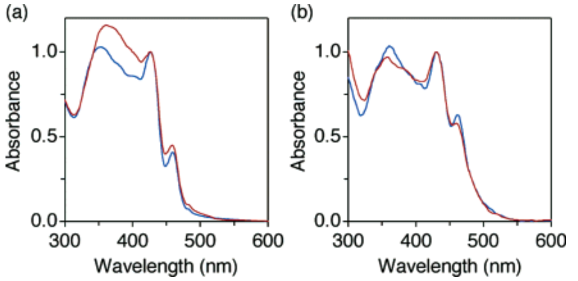

***Figure 4.*** Electronic absorption spectra of (a) nanocoils and (b) nanotubes from **1** in a range of 300−600 nm. Blue curves: before ROMP. Red curves: after ROMP. Spectra are normalized at 427 nm.

We found that post-ROMP of the norbornene pendants of **1** in the self-assembled nanocoils enables stabilization of their thermodynamically labile form. Thus, an $Et_2O$ solution of Grubbs catalyst **4**[4] (10 mol %) was added to an $Et_2O$ suspension of the nanocoils, and the mixture was stirred at 20 °C for 24 h.[9] Filtration of the reaction mixture allowed quantitative isolation of a yellow solid substance, which was completely insoluble in $CH_2Cl_2$, a good solvent for monomer **1**. In agreement with this observation, no molecular-ion peak due to monomeric **1** was detected by MALDI-TOF mass spectrometry of the filtrate (Figure S1).[9] Compared with the intact nanocoils before ROMP, the isolated product in the infrared spectroscopy displayed a large drop in intensity of a vibrational band at 1335 $cm^{-1}$ (Figure 5a), characteristic of norbornene (═C−H out-of-phase in-plane bending mode).[10] The relative integral value of this band suggested roughly 80% conversion of the cyclo-olefinic double

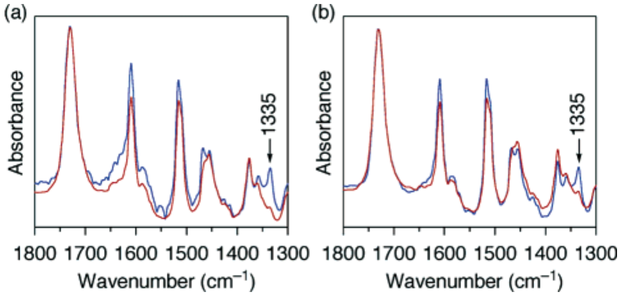

***Figure 5.*** Infrared spectra (KBr) of (a) nanocoils and (b) nanotubes from **1** in a range of 1800−1300 cm$^{-1}$. Blue curves: before ROMP. Red curves: after ROMP. Spectra are normalized at 1731 cm$^{-1}$.

bond into an acyclic one.[11] The absorption spectral profile of the assembly, characteristic of the $\pi$-stacked HBC units, hardly changed in this polymerization (Figure 4a), most likely due to the spatial separation of the norbornene and HBC units by the long oligoether chain. In relation to this observation, electron micrographs (Figure 3e) and AFM images (Figure S2)[9] showed that the nanocoils after ROMP preserve the helical structure and size regime. We also found that the polymerized nanocoils are thermally stable. For example, upon heating at 75 °C in a sealed ampule, the coiled structure, as observed by SEM (Figure 3g), survived even after 12 h in $Et_2O/CH_2Cl_2$ (100/1 v/v) whereas the nonpolymerized coil was disrupted completely.

Likewise, catalyst **4** was capable of metathesizing the norbornene pendants of the tubularly assembled **1** at 20 °C, affording thermally stable graphitic nanotubes, insoluble in $CH_2Cl_2$.[9] MALDI-TOF mass spectrometry of the polymerization mixture hardly detected monomeric **1** (Figure S1).[9] By means of infrared spectroscopy (Figure 5b), the conversion was determined as approximately 80%.[11] Since the norbornene pendants are located on both inner and outer surfaces of the tubular assembly, the rather high metathesis conversion suggests that **4** is able to go inside the nanotubes. As observed by electron microscopy (Figure 3f) and absorption spectroscopy (Figure 4b), the size regime of the nanotubes and the geometry of their $\pi$-stacked HBC units hardly changed in ROMP. The polymerized nanotubes thus obtained perfectly survived when a sealed ampule containing their suspension in $Et_2O/CH_2Cl_2$ (100/1 v/v) was heated at 100 °C for 12 h (Figure 3h). In contrast, the nonpolymerized version under similar conditions started to lose its morphological integrity even upon heating at 45 °C.

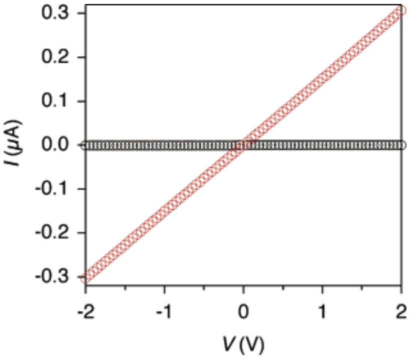

***Figure 6.*** $I-V$ profiles of polymerized nanocoils from **1** before (black circles) and after (red circles) being doped with $I_2$.

We investigated electroconductive properties of the graphitic objects using 3-$\mu$m-gap two-probe electrodes. Both nonpolymerized and polymerized nanocoils, on casting from their suspensions, gave uniform films. Upon exposure to $I_2$, the former was readily disrupted with a loss of the coiled structure (Figure S3).[9] In contrast, the latter was successfully doped with retention of the coiled morphology (Figure S3)[9] and displayed a linear $I-V$ profile (Figure 6), which allowed determination of the conductivity as $1 \times 10^{-4}$ S cm$^{-1}$. On the other hand, the nonpolymerized and polymerized nanotubes were heavily agglomerated and did not give films qualified for the measurement.

## Conclusions

For the covalent stabilization of HBC-based graphitic assemblies, we already reported an ADMET-triggered approach with allyl-group-appended HBC amphiphile **2**,[8] which however is hardly applicable to preassembled systems. In contrast, the new methodology based on ROMP of a norbornene analogue (**1**) may be referred to the ‘predetermined’ approach in which either a coiled or a tubular object fabricated beforehand can be post-polymerized (Figure 2). The polymerized graphitic nanocoils from **1**, thus obtained by taking advantage of this approach, are conductive upon being doped with $I_2$ and attractive for realization of nanoscale solenoids.

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**Supporting Information Available:** Details of synthesis and characterization of **1**, experimental procedures for self-assembly of **1** and post-ROMP, MALDI-TOF mass spectra, AFM images, and SEM micrographs (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) By reference to the intensity of the C═O stretching band at 1731 cm$^{-1}$, the extent of conversion of norbornene pendants was determined on the basis of the relative integral intensity of bands at 1335 cm$^{-1}$ before and after ROMP.