

Phenyl Substituted Cyclo(meta)polyphenylenes: One More Step Towards the Total Synthesis of Diameter-Controlled Zig-Zag Carbon Nanotubes

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The calixarene-templated synthesis of new cyclo(meta)-polyphenylenes (CMPs) is described. These compounds are functionalized with added aromatic units, that are suitably oriented for

oxidative aromatization to be envisioned. This could pave the way towards the synthesis of elongated segments of zigzag-type single-walled carbon nanotubes (SWCNTs).

Introduction

The total synthesis of carbon nanotubes and related nanocarbons is currently a hot topic, actively pursued by several groups around the world.^[1–3] Since the pioneering work of Jasti and Bertozzi in 2008,^[4] most proposed approaches are based on Cycloparaphenylenes (CPPs), as these CPPs can be considered short segments of armchair-type SWCNTs. Indeed, these CPPs have been used as seeds for the growth of carbon nanotubes under Chemical Vapor Deposition (CVD) conditions.^[5,6] On the other hand, the synthesis of zigzag-type SWCNT short segments is less documented.^[7]

In recent years, the synthesis of strained cyclo-phenylenes has been considerably expanded by the groups of Itami,^[8–11] Yamago,^[12–19] Mullen,^[20,21] Jasti,^[22,23,32–35,24–31] Isobe^[36–40] among others.^[41,42] The total synthesis of lengthened SWCNT segments from these CPPs is being explored by inserting extra aromatic units on their sides. This should allow for the formation of expanded aromatic structures through conjugative aromatization.^[20,21,34,43–47] It should be noted that most of the previously mentioned approaches will only lead to metallic, armchair-type SWCNTs.^[48,49] However, semiconducting ones are

far more interesting for the realization of electronic devices.^[50–53] For this reason, the synthesis of zigzag-type SWCNTs appears as an interesting target, as the electronic properties of these nanotubes are only diameter-dependent.^[48,49] Indeed, a diameter-controlled synthesis of such nanotubes will selectively result in semiconducting or metallic nanotubes at will. Within this framework, the group of Isobe synthesized different topologies of carbon nanorings, equivalent to zig-zag type SWCNT short segments.^[54–58]

The next step is the synthesis of lengthened segments. This could be envisioned from intermediates **8** and **10** shown in Figure 1, derived from the previous CMPs by introducing extra

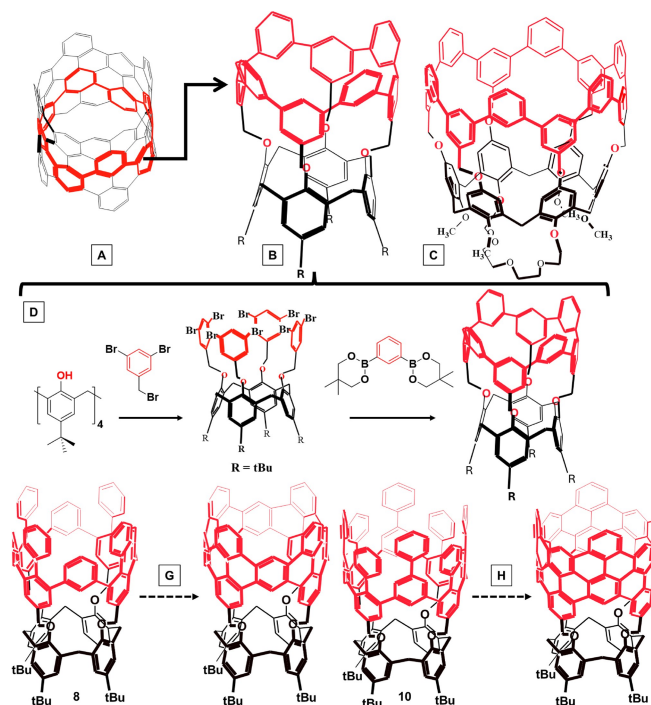


Figure 1. A) CMPs as repeating units for SWCNTs construction; B → C) examples of previously described zigzag SWCNT short segments of different diameters, obtained using calixarenes as templates;^[11] D) synthetic strategy; **8** and **10**) calixarene-supported CMPs bearing extra aromatic units; G and H) expected aromatization towards lengthened SWCNT short segments.

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aromatic units. An oxidative aromatization of these intermediates should result in the formation of the expected lengthened segments (Figures 1G and 1H).

Within this framework, our group reported a very simple synthesis of zigzag-type carbon nanotubes short segments (Figure 1D).^[1] Our approach considers this family of nanotubes as derived from a CMP repeating unit^[57,59,60] (Figure 1A, red). Diameter-controlled CMPs were then obtained using calixarenes as templates (two examples shown on Figures 1B and C). Dibromophenyl units are organized using calixarenes as templates, and subsequently linked together using successive Suzuki couplings with bis(boronic)acid derivatives (Figure 1D).

Results and Discussion

We report here on the synthesis of the two CMPs key intermediates **A** and **B** shown in Figures 1E and F. Their synthesis is described in Figure 2 (see supporting Information, S7 and S8 for details). Starting from the commercially available dibromoaniline **1**, a Sandmeyer diazotation/iodine exchange sequence leads nearly quantitatively to the aromatic iodide **2**. The reaction of **2** with phenylboronic acid, followed by NBS, results in the formation of the benzylic tribromide **4** (S3). This compound is then clipped onto a calix[4]arene template, resulting in the formation of the platform **6**. From this

compound, segments **8** and **10** were obtained upon reaction with bis(boronic)esters **7** and **9** respectively, using the same pre-catalyst. The synthesis of the boronic ester **9** is detailed in the Supporting information (S5). Surprisingly, the reaction between the calix-scaffold **6** and **9** to get the SWCNT segment **10** was favored by microwave irradiation, whereas the reaction between **6** and **7** proceeded under normal conditions. This reactivity difference may be related to increased crowding effects in the former case. Compound **10** proved to be not very stable (in contrast with **8**), making its purification quite difficult, despite the fact that the MALDI-MS mass spectrometry of the crude may appear encouraging at first sight (see S8, p. 33).

Compounds **8** and **10** were characterized by 1D/2D NMR experiments and MALDI-TOF MS mass spectrometry. For both segments, the most characteristic feature of the ¹H NMR spectra is the presence of a very similar set of doublets from the bridging methylene protons of the calix[4]arene template (Figure 3, green hydrogens/green arrows, see also Supporting information, S7 and S8). This evidences the high symmetry of these molecules.

Interestingly, the chemical shifts of these bridging methylene protons are increased by about 1 ppm compared with the values typically observed for calix[4]arenes (Figure 3).^[61]

This downfield shift is characteristic of this family of calixarene-supported zigzag SWCNT short segments. It is due to the magnetic influence of the upper SWCNT short segment on the calixarene bottom stage. A sharp singlet is also observed in the same area, attributed to the protons of the benzylic link between the calixarene stage and the SWCNT short segment. The chemical shift of these benzylic protons appears as upfield shifted by nearly 1 ppm compared to commonly encountered values. This phenomenon is attributed to the location of these benzylic protons just above the aromatics from the calixarenic template and is also characteristic of this family of compounds. Interestingly, some signals associated with aromatic units show an unexpected symmetry-lowering effect (see S7 and S8). This effect is more evident at low temperature (S7, p. 20) indicating that the rotation of some of the aromatic units is hindered (Figure 4).

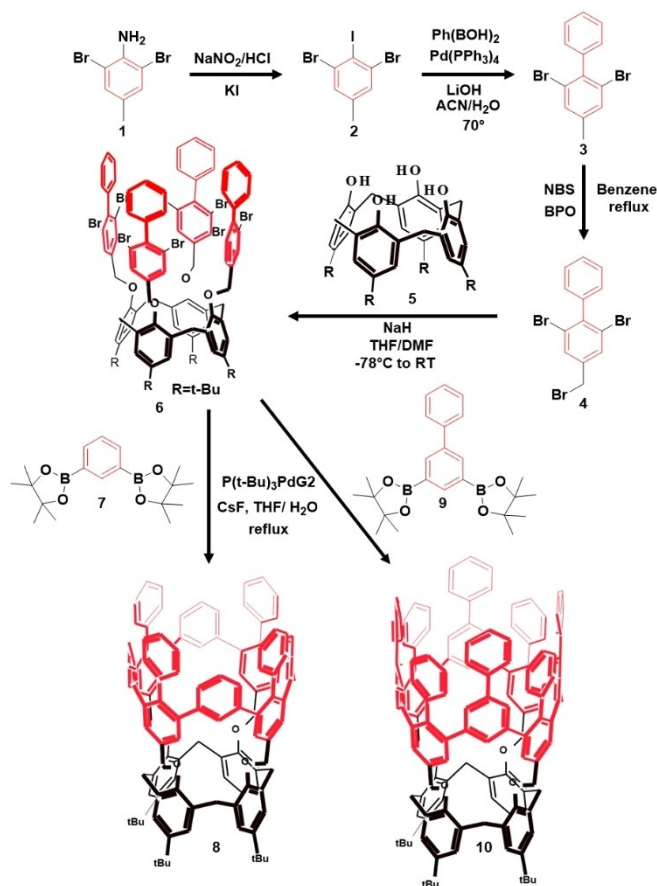


Figure 2. Synthesis of the SWCNT short segments **8** and **10**.

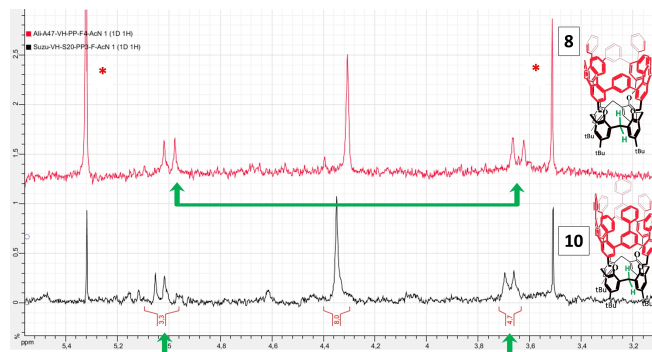


Figure 3. Zoom over the ¹H NMR spectra of the bridging methylene protons of the calixarene stages of segments **8** and **10** (green arrows highlighting the pair of doublets).

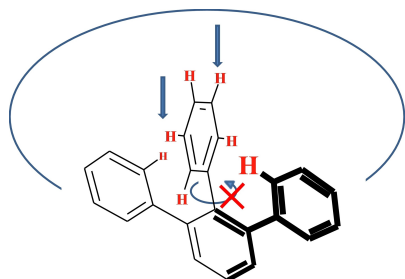


Figure 4. Hindered rotation of an aromatic unit, resulting in different chemical shifts for the protons on each of its sides (arrows).

As mentioned earlier, compound **10** shows a lower stability compared with **8**. DFT optimizations were undertaken to gain a better understanding of this phenomenon as shown in Figure 5. The result fully confirms the structural assignments deduced from the NMR analysis and clearly evidences the compact arrangement of the upper aromatic units. This may increase the overall strain associated with **10** and/or facilitate the occurrence of uncontrolled photocyclizations.

Regarding this latter point, a photocyclization experiment was conducted under oxidizing conditions (S9) and analyzed by MALDI-MS mass spectrometry. Along with the complete disappearance of **10**, the experiment resulted in a complex mixture of products, some of which possibly correspond to partially aromatized compounds (as indicated by successive losses of hydrogen). A peak appears in the expected range for the fully aromatized product, but the S/N ratio is too low to draw definite conclusions.

Conclusions

Two new zigzag SWCNT short segments were synthesized. They include extra aromatic units favorably oriented to enable oxidative conjugation. Moreover, the benzylic bonds linking the SWCNT short segment and the calixarene may be cleaved (e.g. hydrogenolysis over Pd catalysts), thus allowing the recovery of the segment alone. We also show that two different positions of the CMPs can be independently functionalized by extra aromatic units, opening the way to the controlled introduction of new patterns of dopants in the final lengthened SWCNT

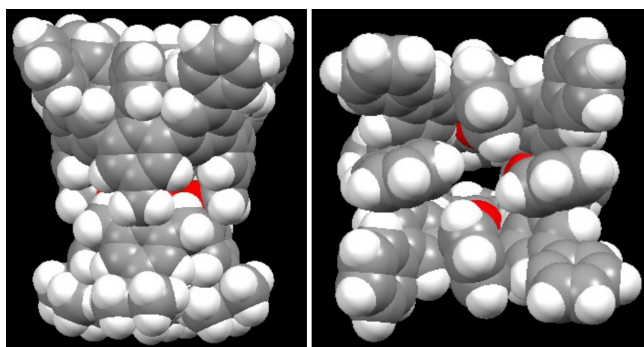


Figure 5. DFT optimized structure of compound **10** (side view/top view).

segments. Preliminary photochemical aromatization experiments are reported, but extensive optimizations are still needed to control the course of these reactions. However, this paves the way towards the synthesis of fully conjugated structures.

Supporting Information Summary

Supporting information are associated with this manuscript.

Additional references cited within the Supporting Information.^[62–64]

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Carbon nanotubes · Organic synthesis · CPP · Calixarenes · CMP

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