

Concise Synthesis of 3D π -Extended Polyphenylene Cylinders**

Florian E. Golling, Martin Quernheim, Manfred Wagner, Tomohiko Nishiuchi,* and Klaus Müllen*

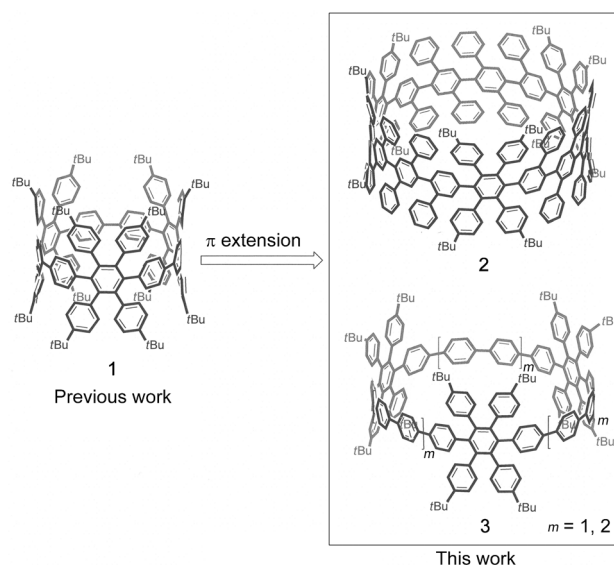
Abstract: The synthesis of structurally well-defined, mono-disperse carbon nanotube (CNT) sidewall segments poses a challenge in materials science. The synthesis of polyphenylene cylinders that comprise typical benzene connectivity to resemble precursors of [9,9] and [15,15] CNTs is now reported, and the products were characterized by X-ray crystallography. To investigate the oxidative cyclodehydrogenation of ring-strained molecules as a final step towards a bottom-up synthesis of CNT sidewall segments, phenylene-extended cyclic *p*-hexaphenylbenzene trimers ([3]CHPB) were prepared, and NMR studies revealed a strain-induced 1,2-phenyl shift. It was further shown that an increase in ring size leads to selectively dehydrogenated macrocycles. Larger homologues are envisioned to give smooth condensation reactions toward graphenic sidewalls and should be used in the future as seeds for CNT formation.

The extension of hexa-*peri*-benzocoronene (HBC) into the third dimension (3D) to form a cylindrical structure, is a key step towards the synthesis of size-defined carbon nanotube (CNT) segments. As one of the fundamental polycyclic aromatic hydrocarbons (PAHs), HBC^[1] has garnered increasing interest since the advent of graphene.^[2] Starting from polyphenylene precursors, the HBC motif has been widely used for the synthesis of one- (1D) and two-dimensional (2D) structures, such as nanoribbons^[3] and disc-shaped nanographenes (NGs).^[4] These graphenic structures are of great interest because of their electronic properties, which sensitively depend on the size and shape (armchair or zigzag) of the molecules. Oxidative cyclodehydrogenation is generally used to transform twisted polyphenylenes into fused and planar target structures.^[5] This approach allows the synthesis of compounds with different sizes and edge structures,^[6] and also affords five-,^[7] seven-,^[8] and eight-membered rings,^[9]

which lead to bent arenes, as they induce non-planarity.^[10] A different concept to obtain curvature, and thus 3D materials, is based on cyclic molecules, such as cyclo-*para*-phenylenes (CPPs).^[11] These macrocycles are envisioned as precursors for a 3D π extension towards length- and diameter-defined CNTs.^[12] Thus far, template-mediated growth of CNTs from opened C₆₀ and CPP precursors has been achieved on quartz and sapphire surfaces, yielding tubes with narrow diameter distributions.^[13] Still, the synthetic bottom-up 3D design that yields monodisperse, soluble, and short tubular CNT sidewall segments remains challenging.^[14]

To achieve a π extension of CPPs, a 3D-arranged cyclic *p*-hexaphenylbenzene trimer ([3]CHPB) was introduced by our group as a synthetic approach towards length-defined armchair CNTs. As oxidative cyclodehydrogenation is known to be a powerful reaction for the synthesis of linear, planar, and nonplanar structures (3D), its applicability to highly strained macrocycles was investigated.^[15] Nevertheless, the nine-membered [3]CHPB did not undergo clean and selective cyclodehydrogenation to give the corresponding cyclic *p*-hexa-*peri*-benzocoronene ([3]CHBC). For a bottom-up synthesis towards CNTs, two modes of extending the [3]CHPB are necessary: the extension of the circumference and the introduction of additional phenyl rings to form cylindrical CNT precursors (Scheme 1).

Herein, we describe the synthesis of the cylinders **2** and **4**, which are based on 9- and 15-membered *p*-phenylene rings, as precursors for [9,9] and [15,15] CNTs. To investigate the



Scheme 1. Concept of the size extension of **1**: cylinder **2** and extended [3]CHPB **3**.

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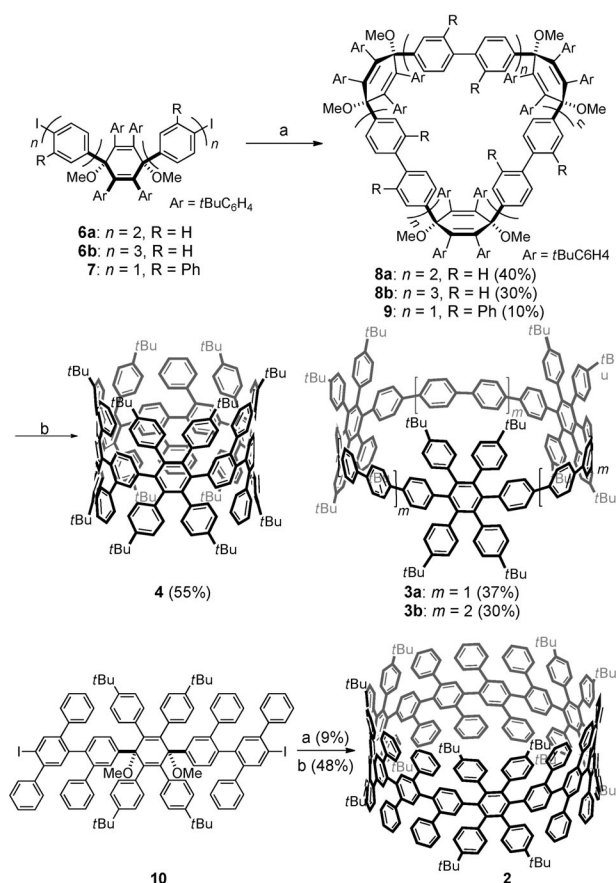
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Scheme 2. Reagents and conditions: a) $[Ni(cod)_2]$, 1,5-cyclooctadiene, 2,2'-bipyridine, DMF, toluene, THF, 80 °C, 16 h or $tBuLi$, $CuCN$, Et_2O -durequinone, -78 °C, 30 min $\rightarrow$ RT, 2 h; b) sodium naphthalide, THF, -78 °C, 1 h. $cod = 1,5$ -cyclooctadiene, DMF = N,N -dimethylformamide, THF = tetrahydrofuran.

oxidative cyclodehydrogenation of strained cycles in detail, the two less complex and extended [3]CHPB macrocycles **3a** and **3b** were synthesized, which consist of 15- and 21-membered CPPs.

For the synthesis of the π -extended [3]CHPBs **3a** and **3b**, the key intermediates **6a** and **6b** were subjected to the Yamamoto conditions (Scheme 2). The reactions primarily afforded the cyclic trimer **8a** and **8b**, owing to the kinking angle of the precursor.^[15] Linear tetramers and pentamers were also observed as side products. For **4**, however, Yamamoto coupling of **7** did not give the desired macrocycle **9**, but rather resulted in the dehalogenation of the kinked starting material **7**, which was caused by the steric demand of the *ortho*-phenyl substituents. The synthetic challenge was overcome with an oxidative coupling via a Lipshutz cuprate intermediate that gave macrocycle **9**, which contains a 15-membered phenylene ring.^[16] As mentioned before, the kinking angle of substrate **7** leads to the preferred formation of a cyclic trimer. A subsequent reductive aromatization with sodium naphthalide in THF furnished the macrocycles **3a** and **3b** and the sterically demanding cylinder **4**, which resembles a phenylene-based [9,9] CNT precursor segment.

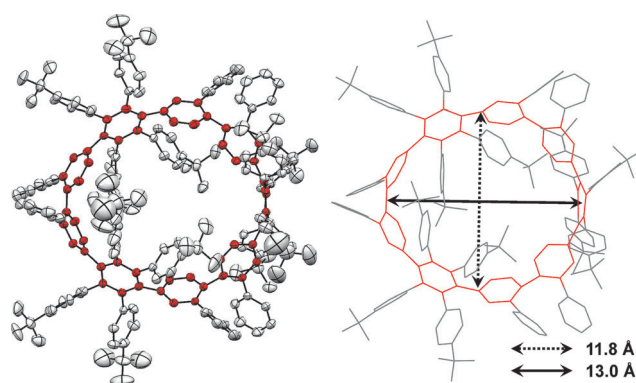


Figure 1. X-ray crystal structure of **4**. ORTEP drawing (left) and wire-frame model (right). Ellipsoids set at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity (see the Supporting Information). The CPP rings are depicted in red.

To extend cylinder **4** from a 9- to the 15-membered ring **2**, six additional terphenyl units were introduced (Scheme 2). Therefore, **7** was terphenylated through a Suzuki coupling to give the kinked precursor **10** in two steps (see the Supporting Information). Analogous to the synthesis of **4**, oxidative coupling and subsequent reductive aromatization afforded the trimeric macrocycle **2** in similar yields.

Single crystals of **4** were grown from a CH_2Cl_2 /acetonitrile solution. X-ray analysis^[17] revealed an ellipsoid structure with a length of 13.0 Å and a width of 11.8 Å (Figure 1). The dihedral angles vary between 42° and an astonishing 84°. To the best of our knowledge, these values are unprecedented, as the maximum dihedral angles for [9]CPP^[11g] and [3]CHPB trimer **1** are 44° and 67°, respectively. These large dihedral angles induce, either directly or in neighboring positions, strong twists of single phenyl units with a maximum internal dihedral angle ($C_{ipso}-C_{ortho}-C_{ortho}-C_{ipso}$) of 8.2° (see the Supporting Information). A quinoidal character, as reported for [9]CPP, was not observed for compound **4**, owing to the previously described large dihedral angles between adjacent phenyl rings. The outlined physical properties support the presence of a highly strained macrocycle.

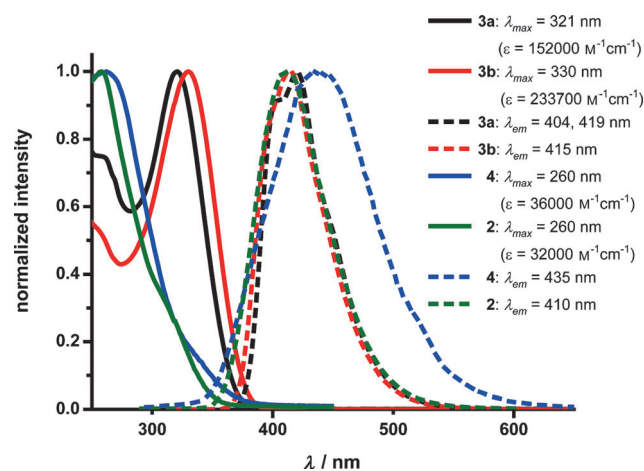


Figure 2. UV/Vis (—) and fluorescence (---) spectra for **3a**, **b** (CH_2Cl_2), **2**, and **4** (hexanes).

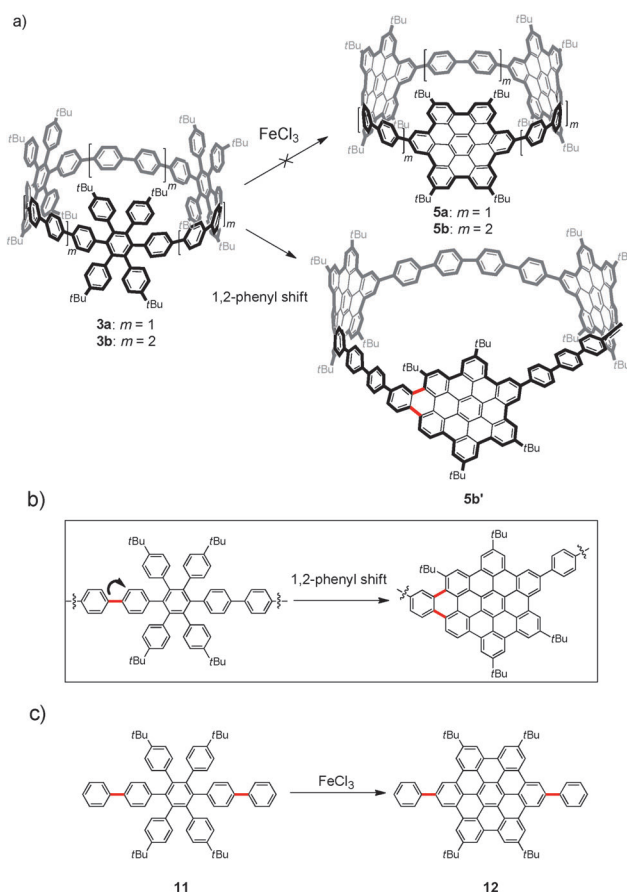
The strain of the cylinders can also be deduced from the UV/Vis spectra (Figure 2). The absorption maxima of **2** and **4** are hypsochromically shifted to 260 nm, whereas the absorption maxima of [3]CHPB macrocycles and CPPs are found at 320 nm and 340 nm, respectively.^[11a] This can be explained by the distortion between phenyl rings in the CPP base, which leads to a reduction in π conjugation.^[18] The emission maxima of **2**, **3a**, and **3b** appeared at 410–420 nm, the emission maximum of **4** was bathochromically shifted to 435 nm. In the excited state, however, the large ring strain and the distortion of these CPP scaffolds are released by partial planarization of neighboring phenyl rings, which results in large Stokes shifts.^[19] This effect was especially pronounced for the small cylinder **4**.

Cyclodehydrogenation of cylinders **2** and **4** under oxidative conditions resulted in mixtures of dehydrogenated products, which indicates partial formation of cyclic graphenoid structures. To investigate the oxidative dehydrogenation for molecules with different degrees of ring strain, we designed structures **3a** and **3b**. Circumferences that are larger than that of compound **1** were obtained by introducing six and twelve additional phenylene rings, respectively, to obtain HPB units that are embedded into a CPP with reduced ring strain.

The less distorted and less strained macrocycles **3a** and **3b** were subjected to cyclodehydrogenation with different oxidants, such as $\text{CF}_3\text{SO}_3\text{H}$ with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), $\text{Sc}(\text{OTf})_3/\text{DDQ}$ (Tf = trifluoromethanesulfonyl), phenyliodonium bis(trifluoroacetate) (PIFA) with $\text{BF}_3 \cdot \text{Et}_2\text{O}$, or FeCl_3 .^[20] The addition of FeCl_3 at room temperature gave the best results and led to highly dehydrogenated compounds without any chlorinated side products. Rather than the expected [3]CHBCs **5a** and **5b**, we obtained compounds with an extra loss of two (**5b'**), four, and six (**5a'**; see the Supporting Information) hydrogen atoms (Scheme 3a,b). For a better understanding of these findings, the model compound **11** was synthesized, which could be selectively converted into the expected target compound **12** by oxidative cyclodehydrogenation (Scheme 3c). In previous studies, a 1,2-phenyl shift was observed for the cyclodehydrogenation of PAHs toward NGs, which resulted in a higher degree of dehydrogenation.^[21]

In the following discussion we focus on **5b'**, as several structural isomers were found in the product mixture of **5a'**. The ion peak at m/z 3143.4757 that was obtained by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry revealed an additional loss of two hydrogen atoms for **5b'**, compared to the expected compound **5b**, which suggests that a 1,2-phenyl shift has occurred (Scheme 3). Detailed NMR studies confirmed the 1,2-phenyl shift for **5b'**. The appearance of two AB systems at 9.79 ppm and 9.62 ppm in the ^1H NMR spectrum, supported by further 2D NMR studies, is consistent with the structure of **5b'** (see the Supporting Information).

These results suggest that ring strain was relieved upon cyclodehydrogenation by a 1,2-phenyl shift to give the rearranged macrocycle **5b'**. Furthermore, we could demonstrate that the increase of the CPP circumference from a 15- to a 21-membered ring afforded **5b'** as a single compound.



Scheme 3. a) Cyclodehydrogenation reaction of **3b**; b) 1,2-phenyl shift; c) cyclodehydrogenation of model compound **11**.

These findings show that an increase in ring size can lead to selectively dehydrogenated macrocycles.

In summary, we have presented the bottom-up synthesis of the two polyphenylene cylinders **2** and **4**. As the sidewalls are comprised of accordingly joined benzene rings, they represent precursors of [9,9] and [15,15] CNTs. For macrocycle **4**, a single-crystal structure could be obtained, which revealed a strongly bent cycle. To investigate the oxidative cyclodehydrogenation in the presence of ring strain, the less complex 3D-arranged [3]CHPBs **3a** and **3b** were designed. Detailed NMR studies revealed that a 1,2-phenyl shift had occurred during the reaction to give **5'**. These results show that strained macrocycles can undergo oxidative cyclodehydrogenation to potentially access defined CNT segments. Future challenges include the synthesis of larger homologues with smooth condensation reactions towards graphenic walls and the use of the products as seeds for carbon-nanotube formation.

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