

The Precise Synthesis of Phenylene-Extended Cyclic Hexa-*peri*-hexabenzocoronenes from Polyarylated [*n*]Cycloparaphenylenes by the Scholl Reaction**

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Abstract: The longitudinal extension of cycloparaphenylenes (CPP) towards ultrashort carbon nanotubes (CNTs) is essential for the solution based bottom-up synthesis of CNTs. Herein, the longitudinal extension of the CPP skeleton by the introduction of hexaphenylbenzene units towards polyarylated [*n*]CPPs is described. Further, the applicability of the Scholl reaction to selectively form graphenic sidewalls is demonstrated. The ring size and substitution patterns of the polyarylated [*n*]CPPs were varied to overcome strain-induced side reactions during the oxidative cyclodehydrogenation and cyclic *para*-hexa-*peri*-hexabenzocoronene trimers ([3]CHBCs) were selectively obtained. This concept is envisioned as an access to ultrashort carbon nanotubes subject to the condition that further benzene rings with the right connectivity will be inserted.

The synthesis of monodisperse, length- and diameter-defined carbon nanotube (CNT) sidewall segments, as possible seeds for CNT formation, poses a challenge in organic synthesis and materials science. The key point for the successful bottom-up synthesis

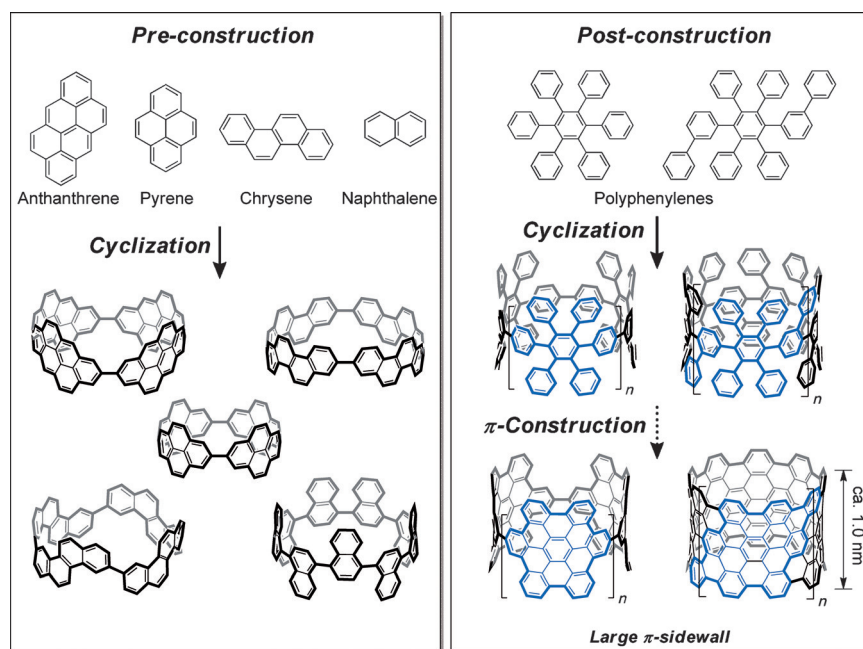


Figure 1. Concept of the pre-construction and post-construction methods for the synthesis of CNT segments with large π sidewalls.

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of CNT segments is the three-dimensional arrangement of polycyclic aromatic hydrocarbons (PAHs). The properties of PAHs strongly depend on the size and shape, being controlled by the bottom-up approach to access one-dimensional (1D) or 2D PAHs, such as graphene nanoribbons (GNRs)^[1–5] and nanographenes (NGs).^[6–10] Still, the bottom-up synthesis of CNTs remains challenging. Surface-mediated strategies, such as the recently reported growth of [6,6]-CNTs from singly capped precursors on a platinum surface^[11] or the longitudinal growth of cycloparaphenylene (CPP) precursors^[12,13] is supposed to be a promising route to structurally well-defined CNTs, since chirality and diameter are already predetermined. Regarding the precise structure control and processability, the solution-based bottom-up approach is more desirable. The pioneering work of Parekh and Guha in 1934^[14] and even more so the attempts of Vögtle and co-workers^[15] nearly sixty years later, led to the successful synthesis of a picotube in 1996^[16] and the CPPs in 2008,^[35] which are the smallest segments of armchair CNTs.^[17–35] A further extension of the π system, as an approach towards CNT segments, can be achieved by pre- and post-construction

methods (Figure 1). The incorporation of naphthalene,^[25] chrysene,^[24,29] anthanthrene,^[23] or pyrene^[18,20] building blocks into the carbon hoop are examples for the pre-construction method (Figure 1). However, longitudinal π extension and access to fully conjugated CNT segments seem to be limited, owing to the difficult functionalization of the different building blocks and the challenge to create a fully π -conjugated CNT sidewall segment.^[28,36]

As an alternative approach, we developed the post-construction method, similar to the synthesis of GNRs and NGs, in which, after obtaining the cyclic structure, the large π surface is formed by the Scholl reaction (Figure 1).^[37] This approach enables us to make variable CNT segments with large π sidewalls, such as hexa-*peri*-hexabenzocoronene (HBC). To obtain these CNT segments, the polyphenylene macrocycles and cylinders **1** to **4** were synthesized (Figure 2). However, the high ring strain in these macrocycles hampered a clean and selective cyclodehydrogenation towards CNT segments, and resulted in incompletely reacted, chlorinated, or 1,2-phenyl-shifted compounds.^[38] Therefore, we describe

herein the newly designed polyphenylene macrocycles **5a,b** and **6**, having a [15]- or [21]-CPP base with alkyl substitutions at the critical positions as a possible means to prevent a 1,2-phenyl shift (Scheme 1). In macrocycle **6**, 4,5,9,10-tetrahydropyrene units were incorporated to prevent rearrangements in the final step, since they resemble bis(ethylene)-bridged biphenyl units. Furthermore, we demonstrate the applicability of the Scholl reaction for the synthesis of [15,15]- and [21,21]-CNT sidewall segments **7** and **8** by the post-construction method.

The synthesis of the phenylene-extended and methyl-functionalized cyclic *para*-hexaphenylbenzene trimers ([3]CHPBs) **5a,b** started from the incorporation of chloro-1,3-dimethylbenzene into tetraarylbenzoquinone to yield the *syn*-diol adduct (for details see the Supporting Information). In the following steps, alkylation, arylene elongation by Suzuki cross coupling and iodination with iodine monochloride yielded the key kinked intermediates **10a,b** and **11**. These precursors were cyclized under Yamamoto conditions (Scheme 1) to primarily afford the cyclic trimers **9a,b**;

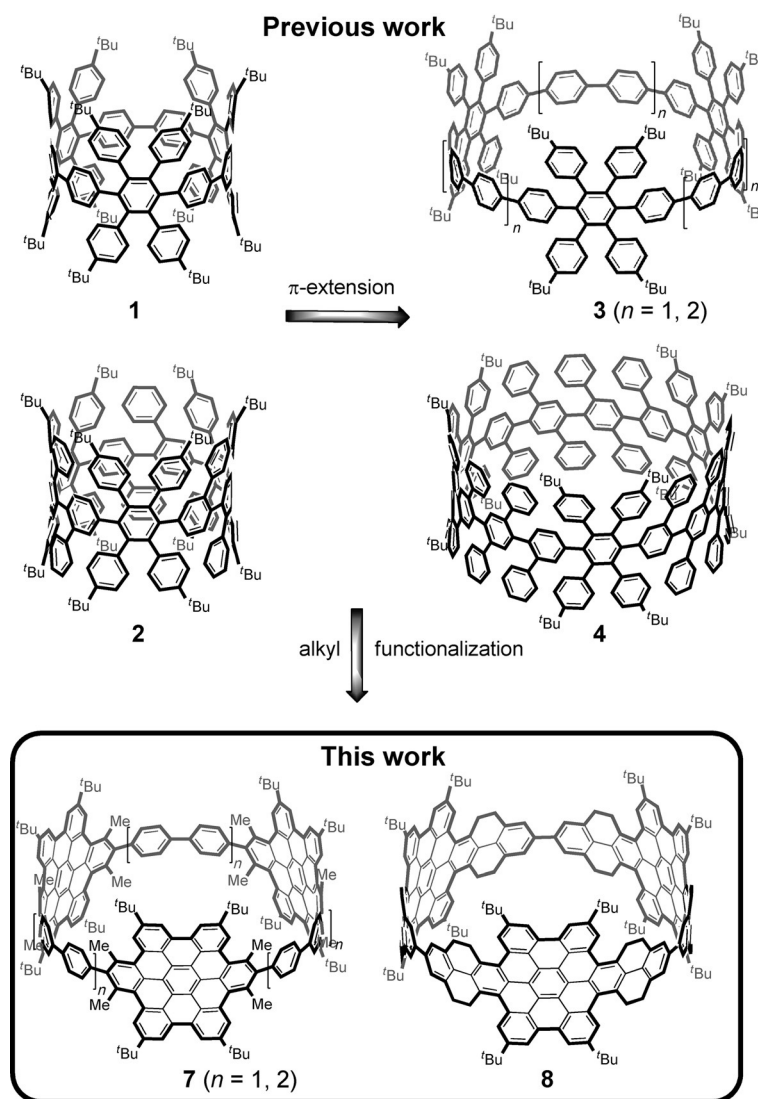
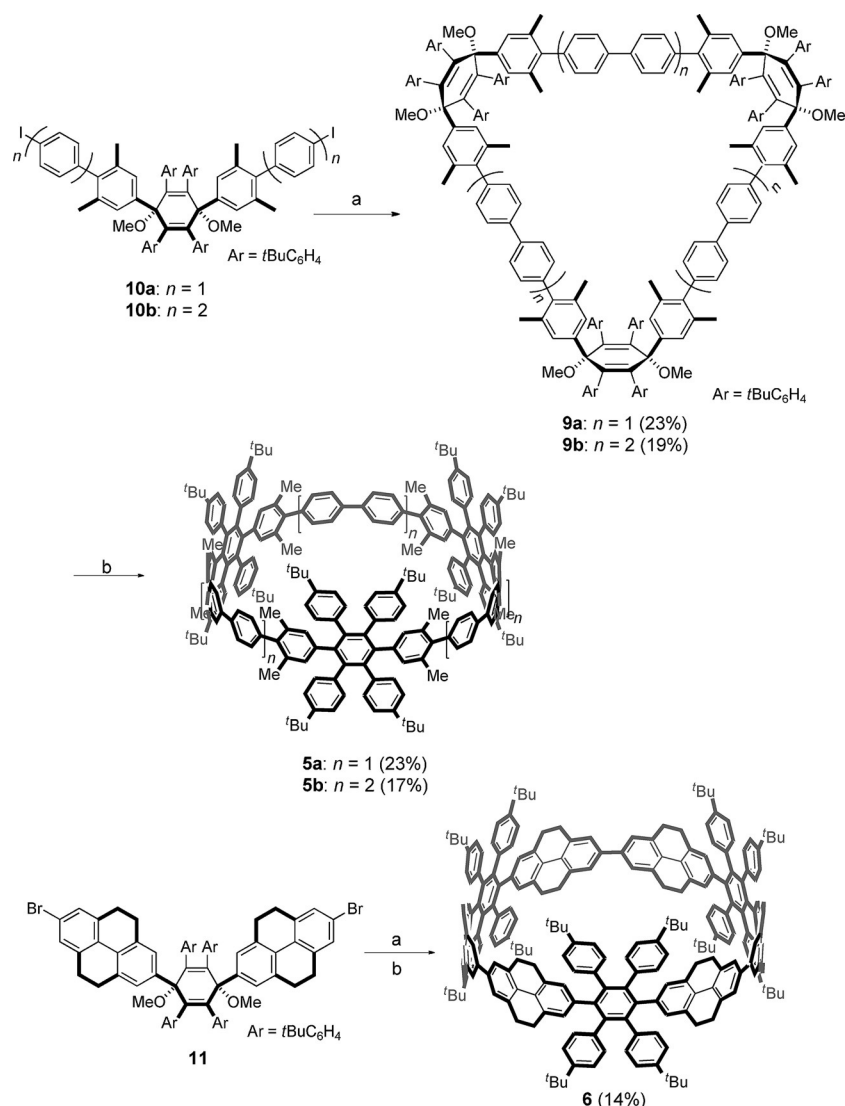


Figure 2. Polyphenylene macrocycles **1–4** and the alkyl functionalized [15,15]- and [21,21]-CNT segments **7** and **8**.



Scheme 1. Reagents and conditions: a) $[\text{Ni}(\text{cod})_2]$, cod, 2,2'-bipyridine, DMF, toluene, THF, 80°C , 16 h; b) sodium naphthalenide, THF, -78°C , 1 h or TiCl_4 , LiAlH_4 , THF, 80°C , 72 h; cod = 1,5-cyclooctadiene, DMF = *N,N*-dimethylformamide, THF = tetrahydrofuran.

linear side products and oligomers were separated by GPC. The phenylene-extended [3]CHPBs **5a, b** and **6** were obtained by the reductive aromatization with either sodium naphthalenide or low-valent titanium in THF.

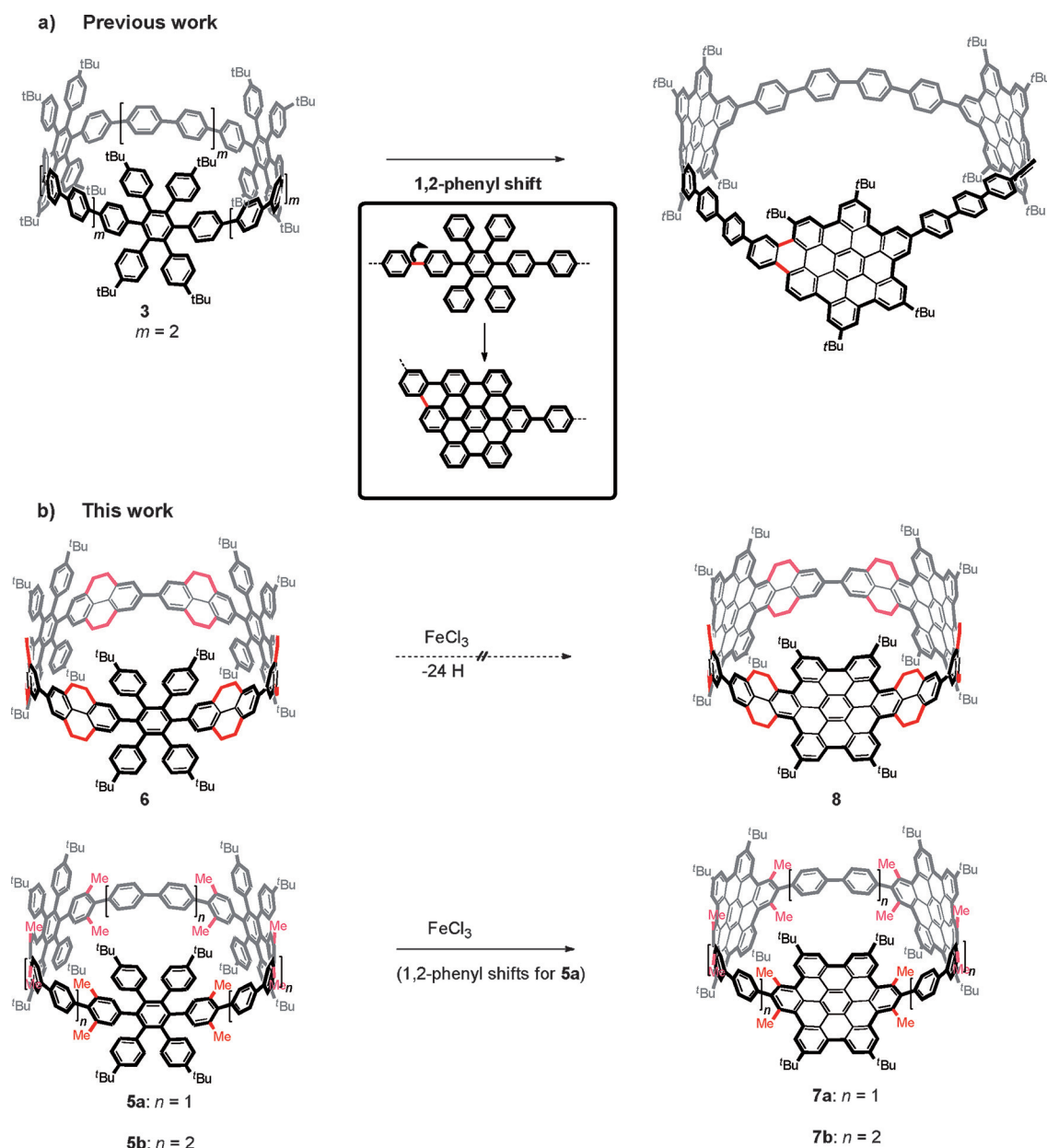
As a final step to form graphenic sidewalls, the macrocycles **5a, b** and **6** were subjected to cyclodehydrogenation with iron chloride at room temperature (Scheme 2).^[39–44] In previous studies a 1,2-phenyl shift was observed for the non-methylated [3]CHPBs **3** (Scheme 2a). Yet by having alkyl chains at these critical positions, the selective synthesis of phenylene extended cyclic hexa-*peri*-hexabenzocoronene trimers ([3]CHBCs) **7a, b** and **8** is expected, even if the ring strain and distortion were still high for **5a, b** and **6**.^[45]

The analysis of the cyclodehydrogenation products revealed an extra loss of two to six hydrogen atoms for **5a**. Two fractions with an additional loss of two hydrogen atoms (fraction 1) or four hydrogen atoms (fraction 2) were isolated by high-performance liquid chromatography purification and analyzed by MALDI-TOF mass spectrometry (Figure 3a, b), indicating strain-induced rearrangements.

The oxidative cyclodehydrogenation of **6** revealed that the reaction stopped after a loss of approximately 24 of the expected 36 hydrogen atoms (details see the Supporting Information). This implies that the strain in the 15-membered macrocycles is still too high to afford the desired [3]CHBCs **7a** and **8** without any strain-releasing side reactions.

In previous studies, we determined that an extension of the ring size from a 15- to a 21-membered CPP base significantly decreases the tendency toward side reactions.^[38] The oxidative cyclodehydrogenation of **5b** confirmed this trend and the desired [3]CHBC **7b** was selectively obtained in 80% yield (Scheme 2b). The isotopic mass peak pattern of **7b** in the high-resolution MALDI-TOF-MS is in good agreement with the simulated one (Figure 3c).

Further analysis by NMR spectroscopy confirmed the successful synthesis of **7b** (spectra are in the Supporting Information). Characteristic singlets at $\delta = 9.27$ ppm and 8.94 ppm in the ^1H NMR spectrum of **7b** confirmed the formation of HBC units during the cyclodehydrogenation of **5b**. Furthermore, sharp singlets at $\delta = 2.96$ ppm and $\delta =$



Scheme 2. Cyclodehydrogenation reactions.

1.74 ppm assigned to the methyl and *tert*-butyl substituents verified the highly symmetric character of the structure of **7b**. 2D-NMR techniques were used to elucidate the whole structure (see Supporting Information).

The electronic absorption and emission spectra also reflect the strain and distortion in the [3]CHPB macrocycles. In the UV/Vis spectra, significant differences could be observed for the absorption maxima of **5a**, **5b**, and **6** (Figure 4). The absorption maxima of CPPs appear at around 340 nm, independent of size, except for ring sizes below [8]CPP.^[46] For the phenyl- and alkyl-substituted [3]CHPBs, an absorption maximum at 280 nm was found for **5a**, whereas for **5b** the maximum was bathochromically shifted to approximately 300 nm, indicating a decrease in ring strain and the associated distortion.^[47] An even larger red-shift was observed for **6** with an absorption maximum at

350 nm because the rigid tetrahydropyrene units decrease the distortion of the CPP base, which enhances the π conjugation in comparison to **5a**.^[48]

The emission maxima of **5a**, **5b**, and **6** were found at 420 nm, 403 nm, and 420 nm, respectively. Compared with the Stokes shift of **5b** (8190 cm^{-1}), and **6** (4760 cm^{-1}), **5a** showed a quite large Stokes shift of 11 900 cm^{-1} . Since **5a** has a highly distorted CPP base in the ground state, the strain and distortion are released in the excited state, resulting in a large Stokes shift.^[38,46,49] After cyclodehydrogenation, the electronic absorption and emission spectra of **7b** showed distinctive patterns, which are observed in substituted HBCs, with weak α - and p -band absorptions at 421, 400, and 350 nm, respectively, and a strong β -band at 367 nm, as well as the emission maxima at 479, 508, and 545 nm.^[50,51]

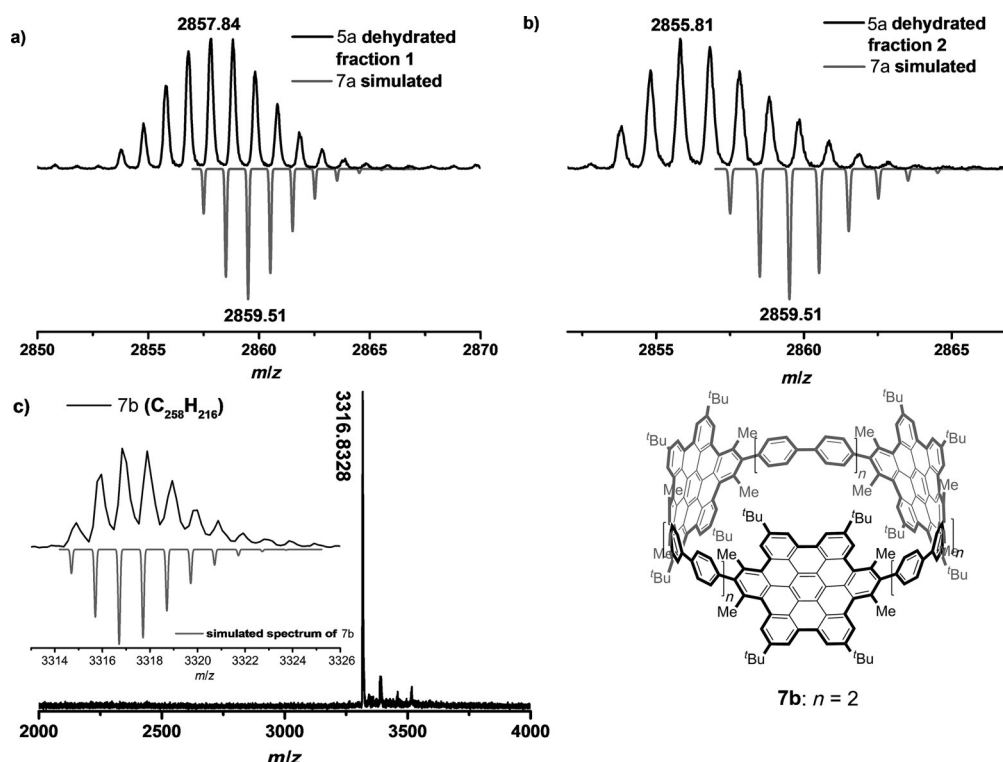


Figure 3. High-resolution MALDI-TOF MS spectra of **7b** and **5a** after cyclodehydrogenation and the simulated spectra, a) HPLC fraction 1 of **5a**; b) HPLC fraction 2 of **5a**; c) MALDI-TOF spectrum of **7b** and the corresponding structure.

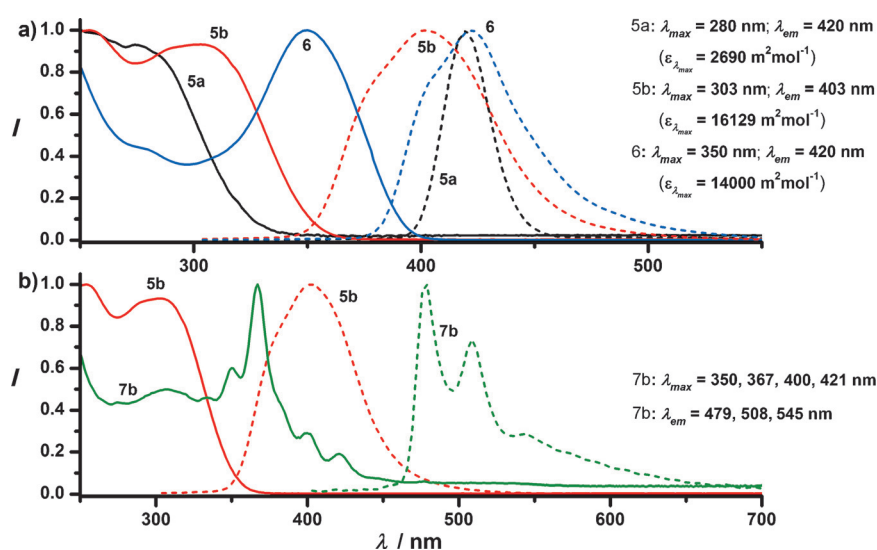


Figure 4. UV/Vis (solid line) and fluorescence spectra (dashed line) of a) **5a**, **5b** and **6** and b) **5b**, **7b** in CH_2Cl_2 .

In summary, we demonstrated the precise synthesis of the [3]CHBC macrocycle **7b**. The increase of the ring size combined with a blocking of the critical positions decreased the strain-releasing side reactions and selectively afforded [3]CHBCs. Furthermore, it was confirmed that the formation of graphenic sidewalls in strained cycles was possible by applying the Scholl reaction. Since a π extension of the [3]CHBC skeleton would lead to CNT sidewall segments, our post-construction method represents a promising way to the

bottom-up synthesis of CNTs. However, the ring-strain in the 15-membered macrocycles **5** and **6** was still too high to undergo a selective and complete dehydrogenation and the scale-up is limited. Therefore, the synthesis of polyphenylene macrocycles of sufficient size and structure to quantitatively form conjugated graphenic sidewalls is the future challenge for the efficient bottom-up synthesis of CNTs.

Keywords: carbon nanotubes · cycloparaphenylene · macrocycles · polycyclic aromatic hydrocarbons · Scholl reaction

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