Polycyclic Aromatic Hydrocarbons

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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.*

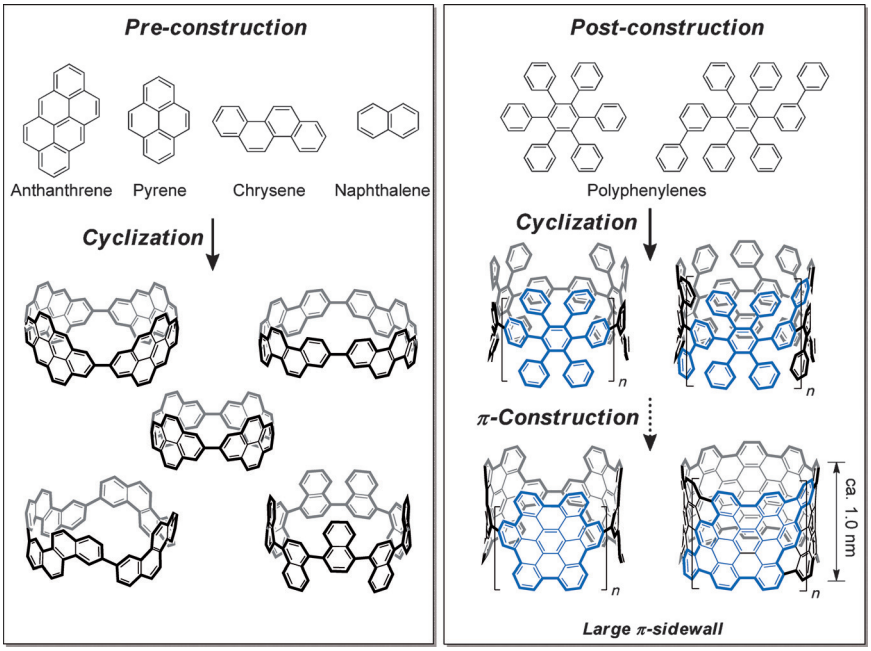

Figure 1. Concept of the pre-construction and post-construction methods for the synthesis of CNT segments with large π sidewalls.

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 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 coworkers[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

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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**;

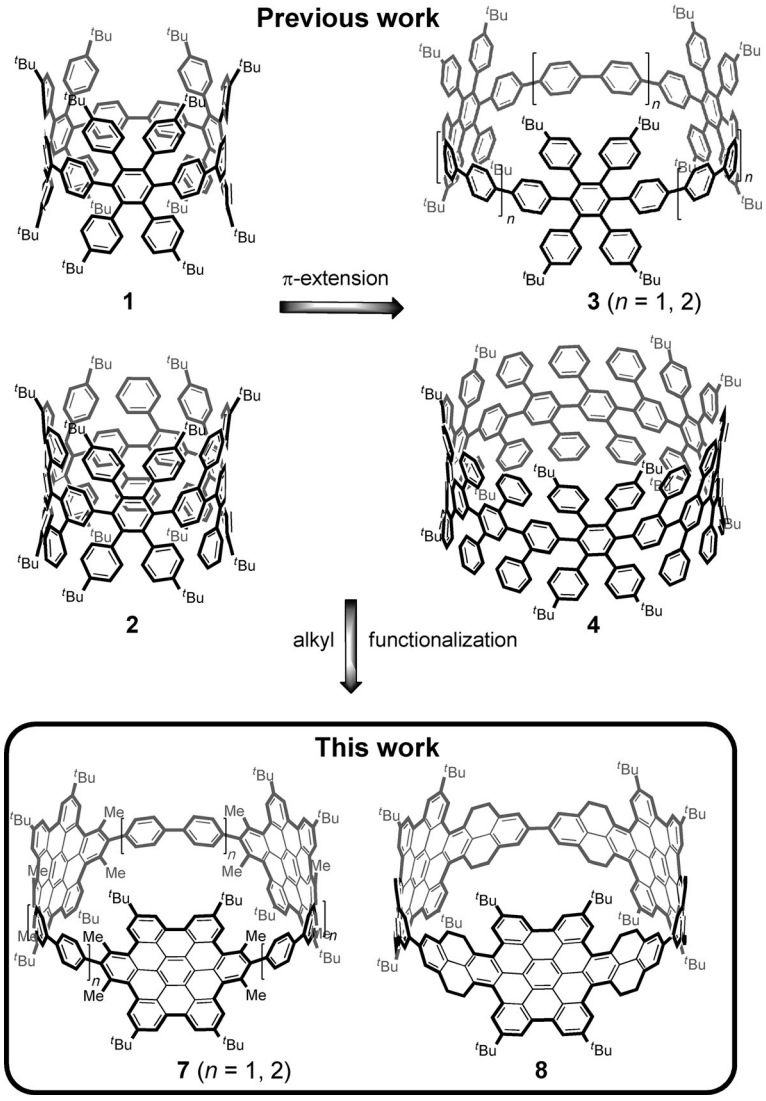
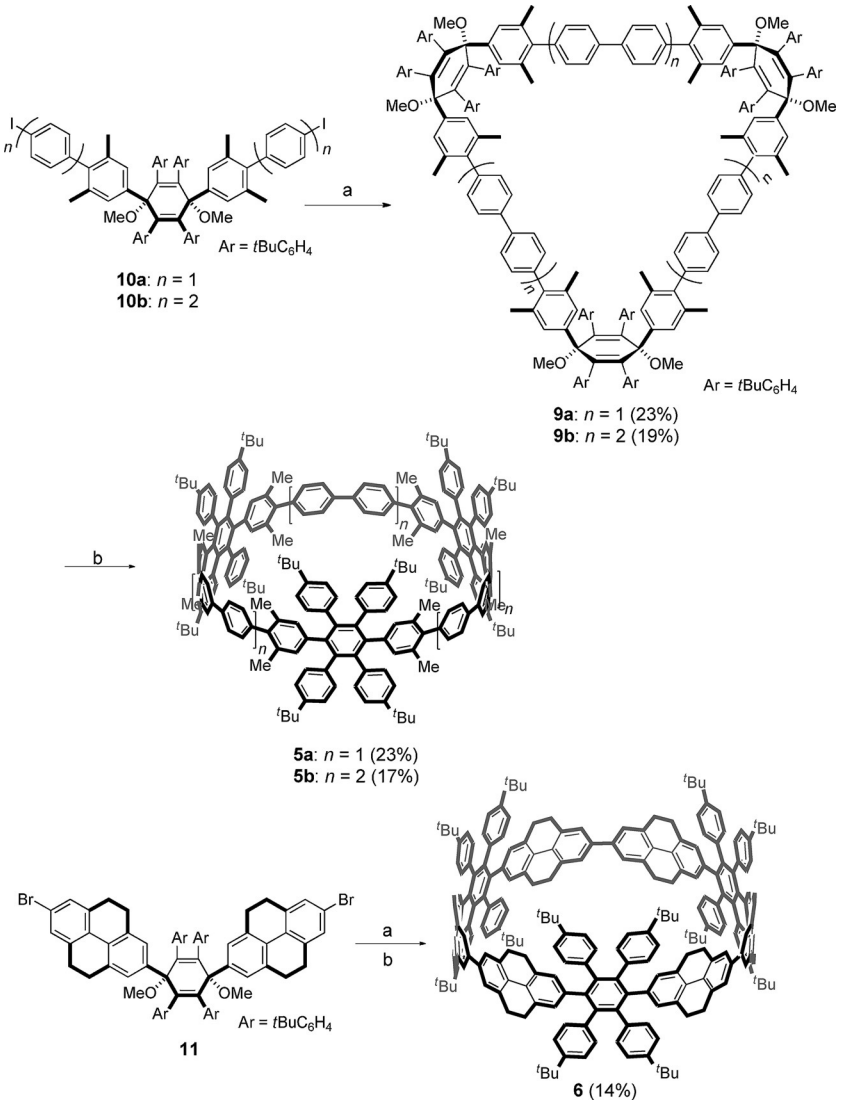


Figure 2. Polyphenylene macrocycles **1**–**4** and the alkyl functionalized [15,15]- and [21,21]-CNT segments **7** and **8**.



Scheme 1. Reagents and conditions: a) $[Ni(cod)_2]$, 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.

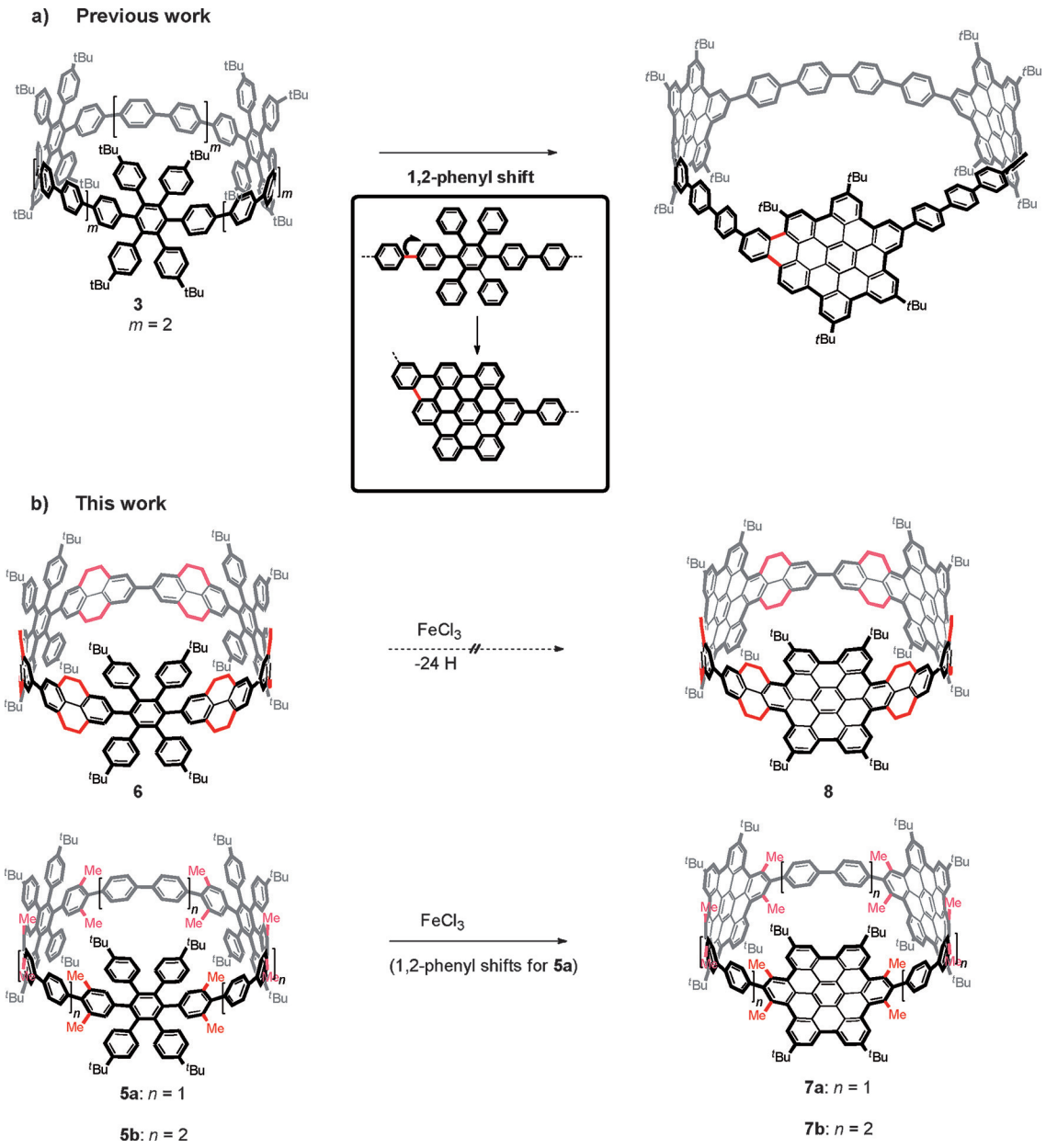
As a final step to form graphenic sidewalls, the macrocycles **5a**,**b** and **6** were subjected to cyclodehydrogenation with iron chloride at room temperature (Scheme 2).[39–44] In previous studies a 1,2-phenyl shift was observed for the non-methylated [3]CHPBs **3** (Scheme 2a). Yet by having alkyl 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 ^{1}H 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 cyclodeydrogenation, 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]

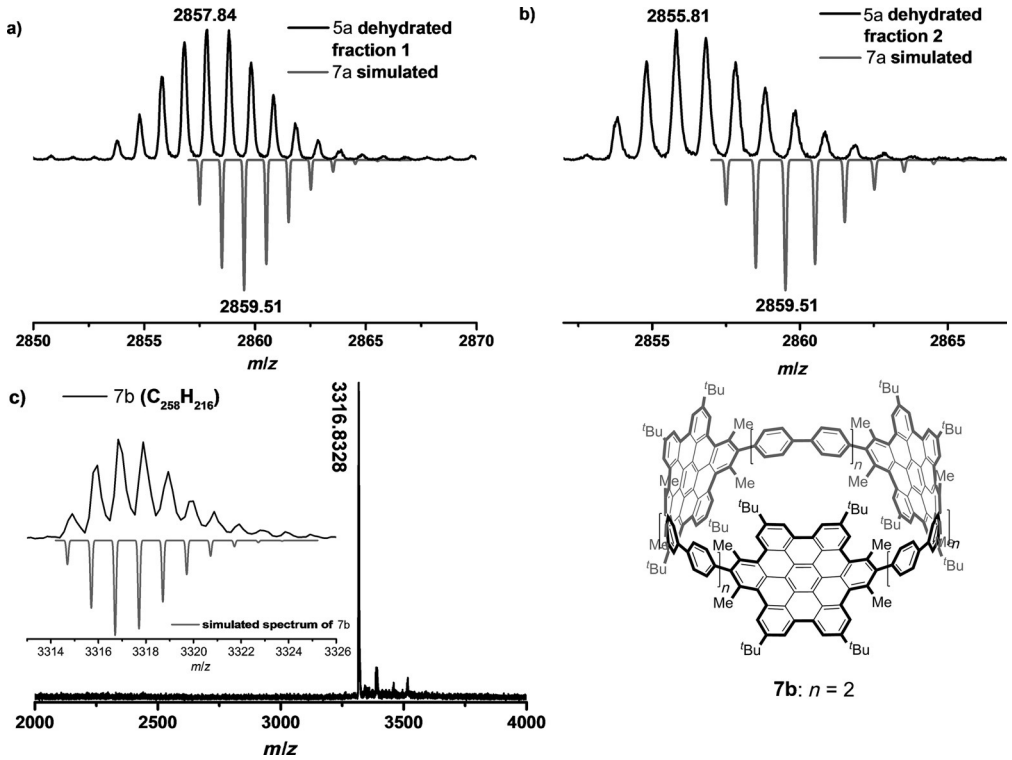


Figure 3. High-resolution MALDI-TOF MS spectra of **7b** and **5a** after cyclodehydrogenation and the simulated spectra, a) HPLC fraction 1 of **5a**; b) HPLC fraction 2 of **5a**; c) MALDI-TOF spectrum of **7b** and the corresponding structure.

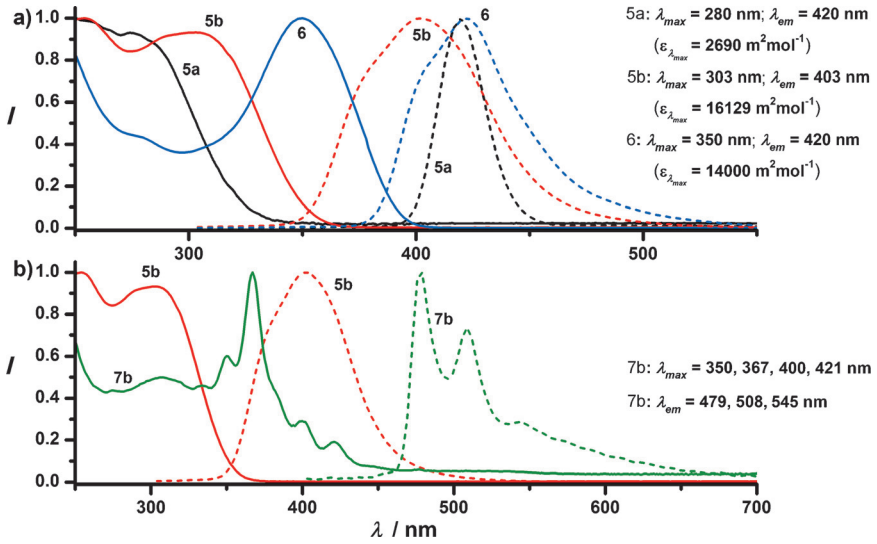


Figure 4. UV/Vis (solid line) and fluorescence spectra (dashed line) of a) **5a**,**b** and **6** and b) **5b**, **7b** in CH_2Cl_2.

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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