

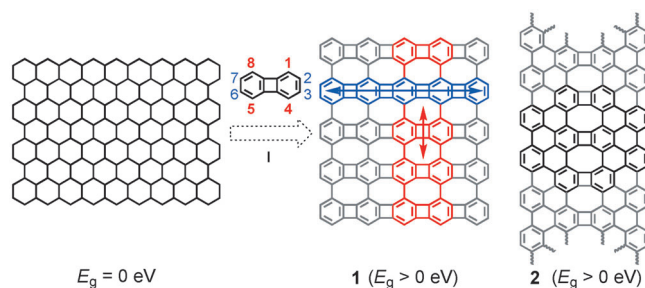
# Octafunctionalized Biphenylenes: Molecular Precursors for Isomeric Graphene Nanostructures\*\*

Florian Schlütter, Tomohiko Nishiuchi, Volker Enkelmann, and Klaus Müllen\*

**Abstract:** A straightforward method for the octafunctionalization of biphenylene based on the [2 + 2]-cycloaddition of an aryne intermediate has been developed. This enabled a “North–South” extension of biphenylene towards isomeric graphene nanoribbons composed of four-, six-, and eight-membered rings. This procedure furthermore allowed an “East–West” expansion to [n]phenylenes with different lengths. For the fabrication of isomeric nanographenes, octaarylbi-phenylenes decorated with phenyl, pyrenyl, and thieno substituents were prepared. The subsequent oxidative cyclodehydrogenation provided an expanded helicene as a model compound.

The unique binding properties of carbon can lead to different allotropes with exceptional structural and electronic properties.<sup>[1]</sup> In particular, the all-benzene family with different dimensionality, including fullerenes (sp<sup>2</sup>, 0D),<sup>[2]</sup> carbon nanotubes (sp<sup>2</sup>, 1D),<sup>[3]</sup> graphene (sp<sup>2</sup>, 2D),<sup>[4]</sup> and the elusive cubic graphite (sp<sup>2</sup>, 3D),<sup>[5]</sup> have sparked considerable attention. The vanishing band gap of graphene, however, hampers its utilization in organic electronics.<sup>[6]</sup> The lateral confinement towards graphene nanoribbons (GNRs),<sup>[7]</sup> and the introduction of different ring sizes,<sup>[1g,8]</sup> open the band gap, thus making these graphene materials application relevant. Biphenylene (I) can be viewed as an appealing subunit of novel carbon allotropes, such as isomeric graphenes **1** and **2** (Figure 1). The aromatic and antiaromatic character of biphenylene, and the resulting eight- and four-membered rings are thereby predicted to induce a band gap upon polymerization.<sup>[9]</sup>

The pioneering work of Vollhardt allowed for the functionalization of biphenylenes at the 2, 3, 6, and 7 positions along the so-called “East–West” direction (Figure 1, blue). This enabled further extension towards linear [n]phenylenes, whereas 1,2-functorialization allowed for the synthesis of angular systems.<sup>[10]</sup> However, the controlled functionalization of the 1, 4, 5, and 8 positions remained elusive; hence, apart from a dimer, the synthesis of “North–South” connected biphenylene ribbons has not been reported to date (Figure 1,



**Figure 1.** Overview of the connection between graphene and isomeric graphenes **1** and **2** with the smallest subunit, biphenylene (I). The arrows indicate the direction of expansion: along the 1, 4, 5, 8 positions (North–South, red), and the 2, 3, 6, 7 positions (East–West, blue).

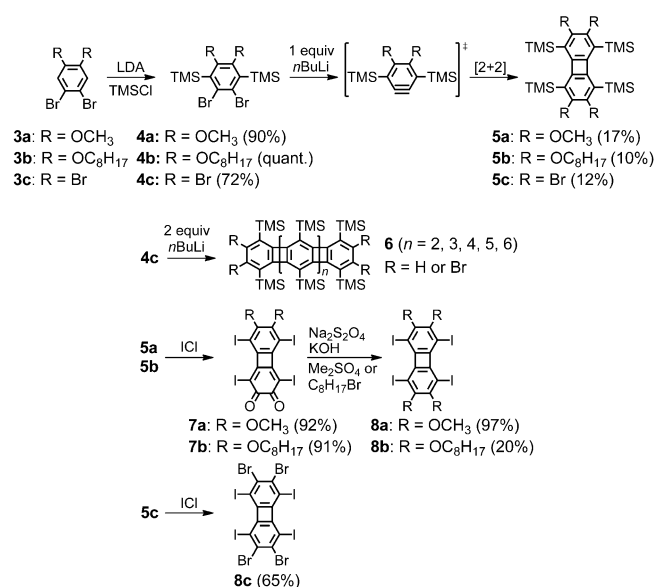
red).<sup>[9]</sup> To further expand biphenylene architectures, we present a novel functionalization strategy. This provides access to unique North–South extended isomeric GNRs and a one-step East–West expansion towards [n]phenylenes. Moreover, the procedure enables the preparation of isomeric nanographenes as model substances (**2**, Figure 1). The influence of the even-membered rings on the band gap of the resulting materials will be thereby emphasized.

Owing to the antiaromatic character and rehybridization of the bonds forming the strained four-membered ring, a direct halogenation of biphenylene at its 1, 4, 5, and 8 positions is impeded.<sup>[11]</sup> Therefore it was critical to attach the (masked) halogen functionalities prior to the formation of the biphenylene core. Among others, trimethylsilyl (TMS) groups can be introduced at alkoxydibromobenzenes (**3a/b**) by a deprotonation–silylation sequence using lithium di-*iso*-propylamide (LDA) and chlorotrimethylsilane (Scheme 1).<sup>[12]</sup> Subsequent lithiation of **4a/b** gave rise to an aryne intermediate, which underwent a [2+2]-cyclodimerization to afford 1,4,5,8-tetra(trimethylsilyl)-2,3,6,7-tetraalkoxybiphenylenes (**5a/b**). Owing to the steric hindrance of the TMS groups, the formation of the corresponding triphenylenes was not detected. Interestingly, by repeating the sequence with 1,2,4,5-tetrabromobenzene (**3c**) a similar silylation towards **4c** was observed. The subsequent [2+2]-cyclodimerization of the aryne intermediate allowed for the synthesis of 2,3,6,7-tetrabromo-1,4,5,8-tetra(trimethylsilyl)biphenylene (**5c**).<sup>[13]</sup> Moreover, using two equivalents of *n*-butyllithium led to the instantaneous formation of [n]phenylenes **6**, with *n* = 3, 4, 5, and 6. Unlike the multistep approach of Vollhardt,<sup>[10a–e,g]</sup> the described method enabled the synthesis of [n]phenylenes in one step, and thus allowed the anticipated East–West expansion. DFT calculations<sup>[14]</sup> confirmed the crucial influ-

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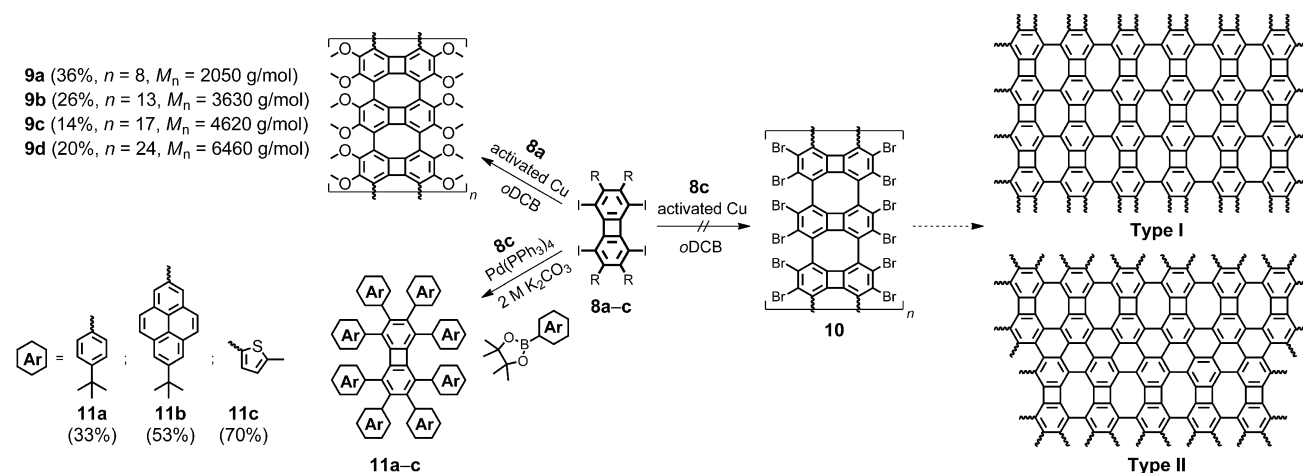
**Scheme 1.** Synthetic route towards polyphenylenes **6**, 1,4,5,8-tetraiodo-2,3,6,7-tetraalkoxybiphenylenes (**8a/b**), and 2,3,6,7-tetrabromo-1,4,5,8-tetraiodobiphenylene (**8c**). LDA = lithium di-*iso*-propylamide, TMS = trimethylsilyl.

ence of the TMS groups for the [2+2]-cycloaddition by a  $\pi$ -backbonding from the aryne to the d orbitals of the adjacent silicon atoms, which increased the electron density of the aryne intermediate (see the Supporting Information). The deprotective iodination of **5a/b** provided 1,2-diketones **7a/b**. This could be explained by the loss of the antiaromatic character of the four-membered ring as a driving force.<sup>[11c]</sup> Reductive alkylation<sup>[15]</sup> of **7a/b** led to fully soluble 1,4,5,8-tetraiodo-2,3,6,7-tetraalkoxybiphenylenes (**8a/b**)<sup>[16]</sup> with an overall yield of around 10–15% over four steps. Iodination of **5c** was conducted in a similar procedure, which afforded poorly soluble 2,3,6,7-tetrabromo-1,4,5,8-tetraiodobiphenylene (**8c**) in 65% yield.

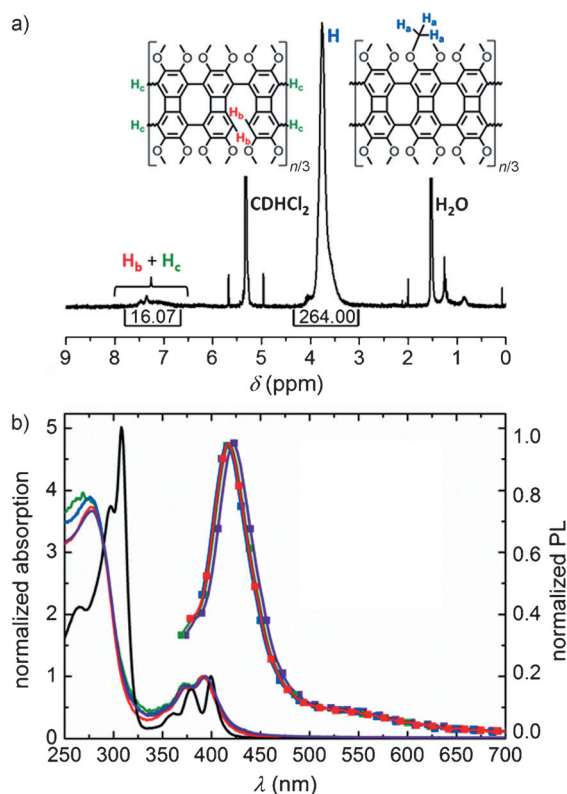
Having functionalized biphenylenes **8a–c** in hand, the polymerization along the North–South direction was targeted (Scheme 2). By screening different transition-metal-mediated polymerizations for **8a**, the Cu-mediated Ullmann coupling was found to be the most suitable.<sup>[17]</sup> Procedures such as the Yamamoto reaction resulted in a ring opening dimerization, owing to the reactivity of the central cyclobutadiene towards Ni<sup>0</sup> complexes (see the Supporting Information).<sup>[18]</sup> The Ullmann reaction conditions were optimized with activated copper in combination with 1,2-dichlorobenzene for seven days at 210°C. Size-exclusion chromatography (SEC) of the resulting polymer revealed a  $M_n = 2100 \text{ g mol}^{-1}$  (PDI = 1.40), which corresponds to seven biphenylene units (see the Supporting Information). MALDI-TOF MS confirmed the presence of defect-free dimers, trimers, and pentamers. Moreover, a tetramer with one non-fused eight-membered ring was observed (see the Supporting Information).

The obtained isomeric GNRs were separated into four polydisperse fractions **9a–d** (Scheme 2). This provided polymer **9d** with  $M_n = 6460 \text{ g mol}^{-1}$  (PDI = 1.21), which is composed of at least 22 connected biphenylenes. As MALDI-TOF MS has limitations for the detection of high-molecular-weight species with a high polydispersity, and SEC provides only approximate relative values, the number of defects were analyzed by <sup>1</sup>H NMR spectroscopy. Two sets of signals were observed, with an intensity ratio of two (aromatic, H<sub>b</sub> + H<sub>c</sub>) to 33 (aliphatic, H<sub>a</sub>) (Figure 2a). The obtained aromatic signals corresponded to approximately 16 protons related to eight non-fused eight-membered rings (iodine endgroup). However, taking (partial) protodehalogenation into account (four proton endgroups), six non-fused eight-membered rings were revealed. In other words, at least 13–15 eight-membered rings were expected for isomeric GNR **9d**.

Raman spectroscopy of **9a–d** revealed G- and 2G-bands at around 1601 and 3205 cm<sup>-1</sup>, which were similar to reported values for polyphenylene-based GNRs.<sup>[7h,i,19]</sup> The measurements were, however, accompanied by fluorescence (see the Supporting Information).



**Scheme 2.** Synthetic route for the North–South and East–West expansion attempts towards **9a–d**, and **10**, as well as towards model compounds **11a–c**. oDCB = 1,2-dichlorobenzene.



**Figure 2.** a)  $^1\text{H}$  NMR spectrum of isomeric GNR fraction **9d** in  $\text{CD}_2\text{Cl}_2$  at  $25^\circ\text{C}$  together with proton assignment. b) UV/Vis absorption (solid line) and emission (marked with squares) spectra of **8a** (black), **9a** (red), **9b** (blue), **9c** (green) and **9d** (violet). All spectra obtained in  $\text{CH}_2\text{Cl}_2$  ( $1 \times 10^{-6} \text{ M}$ ).

Isomeric GNRs **9a–d** and 1,4,5,8-tetraiodo-2,3,6,7-tetra-methoxybiphenylene (**8a**) were characterized by UV/Vis absorption and emission spectroscopy (Figure 2b and Table 1). By increasing the molecular weight towards ribbons **9a–d** small hypsochromic shifts for the longest wavelength transitions were revealed in comparison to monomer **8a**, reflecting large optical band gaps ( $E_g^{\text{opt}}$ ) of around 2.8 eV for

**Table 1:** Selected photophysical data for **8a**, **9a–d**, **11a–c** and **12**.

Compound	$\lambda_{\text{abs,max}}^{[a]}$ [nm]	$\lambda_{\text{PL,max}}^{[a,b]}$ [nm]	Stokes Shift [cm $^{-1}$ ]	$E_g^{\text{opt}[c]}$ [eV]
<b>8a</b>	265(s), 297(s), 308, 361(s), 380(s), 399	–	–	2.96
<b>9a</b>	277, 351(s), 373(s), 392	418	1590	2.87
<b>9b</b>	276, 353(s), 373(s), 391	417	1595	2.84
<b>9c</b>	269, 353(s), 372(s), 390	419	1775	2.83
<b>9d</b>	278, 353(s), 376(s), 394	423	1740	2.81
<b>11a</b>	309, 378, 394	433	2290	2.90
<b>11b</b>	276, 320(s), 333, 349, 393	538	6860	2.84
<b>11c</b>	320, 388,	538	7190	2.84
<b>12</b>	299, 395(s), 452	552	4010	2.74
HBC $^{[d]}$	362, 392, 465	490	1100	2.66

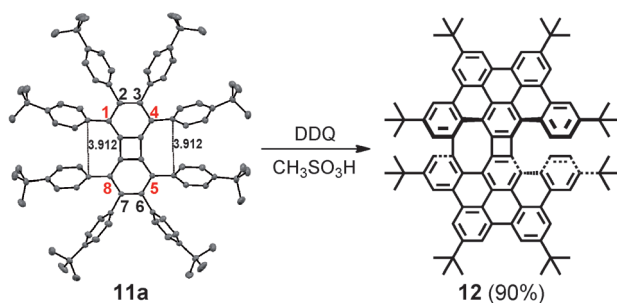
[a] All spectra obtained in  $\text{CH}_2\text{Cl}_2$  ( $1 \times 10^{-6} \text{ M}$ ). [b] Excited at the absorption maxima. [c]  $E_g^{\text{opt}} = hc/\lambda_{0.1\text{max}}$ . [d] Values were taken from Ref. [20]. (s) = shoulder.

the materials. Emissions at around 420 nm were detected for isomeric GNRs **9a–d**, in contrast to their monomer **8a**, which supported the increased  $\pi$ -conjugation upon North–South expansion. A moderate level of reorganization in the excited state was revealed by comparably low Stokes shifts of around  $1700 \text{ cm}^{-1}$ . DFT geometry optimizations (B3LYP/6-31G\*) on model oligomers were carried out, $^{[14]}$  which supported an out-of-plane distortion between the individual biphenylenes along the ribbon chains (see the Supporting Information). This was attributed to the steric repulsion between the methoxy groups of neighboring biphenylene subunits, which significantly decreased the  $\pi$ -conjugation of the isomeric GNRs, and thus increased their band gap in comparison to fully planar all-benzene GNRs (see the Supporting Information). $^{[7f,h-j]}$  The differences between the measured and calculated band gaps can be ascribed to the non-fused eight-membered rings, which were expected to further weaken the  $\pi$ -conjugation (see above). These results, however, verified the anticipated band-gap opening upon a selective introduction of eight- and four-membered rings to GNRs. $^{[1f,g]}$

Although the intrinsic properties of isomeric GNRs **9a–d** were mainly determined by the interplay between eight-, six- and four-membered rings, their lateral expansion was expected to govern their electronic characteristics. Thus, biphenylene **8c** was anticipated to initially polymerize along the 1,4,5, and 8 positions (North–South direction) towards **10** (Scheme 2), which could subsequently lead to the formation of two types of isomeric GNRs (types **I** and **II**; East–West direction) upon activation of the bromines. Even though multiple procedures were screened for the polymerization of **8c**, they were unsuccessful, most likely due to the sterically demanding bromines (see the Supporting Information).

Owing to the fact that the laterally extended isomeric GNRs were so far not accessible, octaarylbi(biphenylenes) **11a–c** were designed as model compounds for type **II** GNRs (Scheme 2). Comparing this type of isomeric nanographenes with well-studied polycyclic aromatic hydrocarbons (PAHs), such as hexa-*peri*-hexabenzocoronene (HBC), provides insights into the influence of selectively introduced non-hexagonal rings on the resulting properties. Precursors **11a–c** were easily accessed from **8c** by a one-step method utilizing the Suzuki–Miyaura reaction for sterically demanding eight-fold cross-coupling (Scheme 2). $^{[21]}$  The procedure provided octaphenyl- (**11a**), octapyrenyl- (**11b**) and octathienobiphenylene (**11c**) in 30–70 % yield. Single crystal X-ray analysis of **11a** and **11c** revealed two sets of different external aryl moieties, which are located at the 1, 4, 5, and 8 (equatorial), and the 2, 3, 6, and 7 (axial) positions. $^{[22]}$  Expectedly, they are significantly twisted for both molecules ( $54.1$ – $74.7^\circ$  and  $42.9$ – $68.8^\circ$  for **11a** and **11b**, respectively; hexaphenylbenzene = ca.  $82.5^\circ$ ), $^{[23]}$  whereas the biphenylene core remained almost planar (Scheme 3; see also the Supporting Information). With octaarylbi(biphenylenes) **11a–c** in hand, the subsequent intramolecular cyclodehydrogenation was targeted. Thus, **11a** was treated with dichlorodicyano-*p*-benzoquinone (DDQ) and methanesulfonic acid (Scheme 3). $^{[24]}$  Aside from the expected loss of 12 protons, MALDI-TOF MS confirmed the removal of two additional protons ( $m/z = 1218.72$ ), which was identified as the  $[M+\text{Na}]^+$  peak of **12** (see the Supporting





**Scheme 3.** X-ray crystal structure of **11a** with atom numbering and the synthetic route of its oxidative cyclodehydrogenation towards expanded helicene **12** (H atoms omitted for clarity).

Information). The formation of one eight-membered ring towards expanded helicene **12** is therefore very likely. Oxidative cyclodehydrogenation proved to be only successful in the case of phenyl-substituted **11a**, whereas identical reaction conditions resulted in no conversion and decomposition of the starting material for **11b** and **11c**, respectively.

UV/Vis absorption and emission spectroscopy confirmed optical band gaps ( $E_g^{\text{opt}}$ ) between 2.7 and 2.9 eV for **11a–c** and **12** (Table 1; see also the Supporting Information). The influence of the even-membered rings in a hexagonal lattice on the optical properties can be seen by comparing the absorption data of **12** versus that of HBC (Table 1; see also the Supporting Information).<sup>[20]</sup> The  $\alpha$ -band in the spectrum of the planar HBC ( $\lambda_{\text{abs,max}} = 465$  nm) was located at a longer wavelength than that of **12** ( $\lambda_{\text{abs,max}} = 452$  nm).<sup>[20,25]</sup> As expected, the distorted structure of **12** caused a larger  $E_g^{\text{opt}}$  and a bathochromically shifted emission ( $\lambda_{\text{PL,max}} = 552$  nm) compared to planar HBC. In the excited state, the distortion of expanded helicene **12** is released by partial planarization, which is displayed by a comparably large Stokes Shift of  $4000\text{ cm}^{-1}$ .

In conclusion, isomeric graphene nanostructures have been prepared having combinations of eight-, six- and four-membered rings. This was essentially based on a successful functionalization strategy of the 1, 4, 5, and 8 positions of biphenylene, which relied on a directed *ortho* silylation of tetrafunctionalized benzenes followed by a lithiation-induced [2+2]-cyclodimerization through an aryne intermediate. The procedure allowed for the successful synthesis of 1,4,5,8-tetraiodo-2,3,6,7-tetraalkoxybiphenylenes **8a/b**, 2,3,6,7-tetra-bromo-1,4,5,8-tetraiodobiphenylene (**8c**), and straightforward access to different [*n*]phenylenes **6** in one step. Polymerization of **8a** along its North–South direction resulted in the formation of isomeric GNRs. For the fabrication of isomeric nanographenes, octaaryl biphenylenes **11a–c** decorated with phenyl, pyrenyl, and thieno substituents were prepared from **8c**. The subsequent oxidative cyclodehydrogenation of **11a** provided expanded helicene **12**. The impact of the implemented even-membered rings on their electronic characteristics was reflected by large band gaps (ca. 2.8 eV) for the materials. The above concepts provide the capability to overcome the difficulties associated with semimetallic graphene in organic electronics and could thus open new perspectives for carbon-rich  $\pi$ -conjugated materials.

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