Nanoribbon Synthesis

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Graphene Nanoribbons by Chemists: Nanometer-Sized, Soluble, and Defect-Free**

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Dedicated to Professor Henning Hopf on the occasion of his 70th birthday

Structural perfection is of key importance in the synthesis of graphene nanoribbons (GNRs), since there is a fundamental connection between the electrical properties and the width, the edge periphery, and the occurrence of defects.[1] Graphene itself is a zero-band-gap semimetal, whereas GNRs with a width smaller than 10 nm show semiconducting behavior that renders them suitable active materials for electronic devices.[2] A considerable longitudinal extension would enable ready processing and device fabrication with single ribbons. The synthetic challenge is the preparation of such defined graphene structures with high aspect ratios (length/width) that until now could not be attained by physical methods. Top-down approaches (Figure 1), such as the reduction of graphite oxide,[3] lithography,[4] the unzipping of carbon nanotubes,[5] or the mechanical exfoliation[2] of graphene, have so far lacked any means of control over the size and edge structure of the resulting products and have thus led to poorly defined graphene materials.

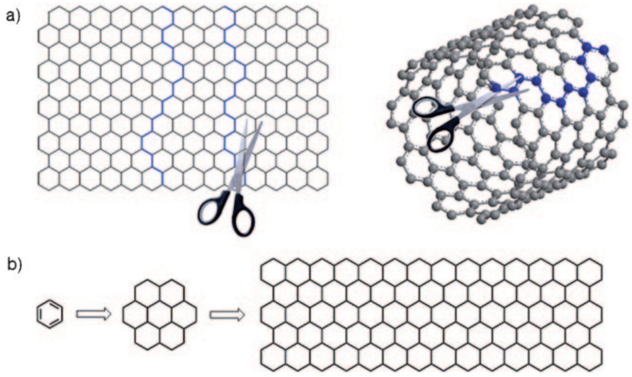

Figure 1. Schematic overview of the a) top-down and b) bottom-up fabrication of GNRs.

Bottom-up organic synthesis enables structural control on the atomic scale and thus enables chemists to reach their goal of synthesizing defined carbon materials, such as carbon nanotubes (CNTs)[6] or nanographenes, with different aspect ratios.[7] Recently, we fabricated atomically precise GNRs by employing a surface-assisted coupling reaction followed by a thermally induced intramolecular cyclodehydrogenation step to yield nanoribbons with different widths and edges.[8] However, at present this method is limited to the production of sub-monolayers on conductive surfaces, and thus processing can only rely on physical methods. In contrast, methods for the solution synthesis of GNRs have been developed in the last few years which have enabled the preparation of nanoribbons with a width of about 1 nm and a length of up to 10 nm.[7c] This route was based on the preparation of tailored polyphenylene precursors, which were converted into the corresponding polycyclic aromatic hydrocarbons (PAHs) by a Scholl reaction (oxidative cyclodehydrogenation). Nevertheless, it was found that perfectly shape-defined GNRs could still not be synthesized. Owing to defects caused by incomplete cyclodehydrogenation and side reactions that occurred during the final reaction step, careful optimization of the reaction procedure was required.[9] Attempts to extend the systems in length were hampered by the already low solubility of the precursors. To further broaden the scope of application of graphene-type materials produced by bottom-up organic synthesis, the challenge is to overcome these limitations. In this study, we investigated whether the Scholl reaction would enable the synthesis of structurally perfect GNRs.

Herein we present a series of nanoribbons **4**, **5**, and **6** (Scheme 1) that were synthesized from polyphenylene precursors with a unique nonrigid kinked backbone to introduce higher solubility in comparison to that of strictly linear poly(*para*-phenylene) systems.[10] We also prepared corresponding model compounds to gain better understanding of the cyclodehydrogenation in the synthesis of extended conjugated nanoribbon systems with a special focus on the degree of dehydrogenation and the occurrence of rearrangements within the ribbon backbone. Indeed, full dehydrogenation of linear polyphenylenes with a length of more than 40 nm is possible without rearrangement and yields perfectly defined conjugated nanoribbons that are still soluble in common organic solvents. The nanoribbons were characterized by different methods to prove the structural perfection, including infrared and Raman spectroscopy, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry (MS), and solution techniques, such as UV/Vis

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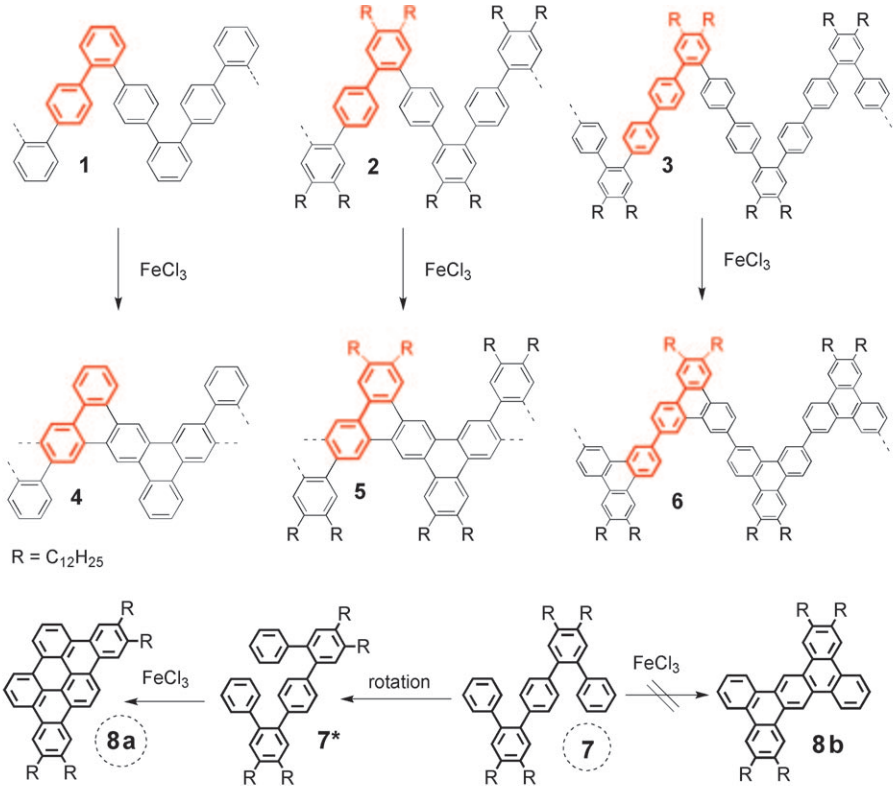

Scheme 1. Polyphenylene precursors **1**–**3**, conjugated ribbons **4**–**6**, and model compounds **7** and **8**; repeat units are highlighted in red.

The polymer precursors **1**–**3** were synthesized by a microwave-assisted Suzuki polycondensation of an equimolar mixture of *ortho*-dibromobenzenes and benzene-1,4-diboronic esters (see the Supporting Information) and subsequent end capping of the bromo end with a phenylboronic ester and of the boron end with bromobenzene. Finally, the polymers were converted into the corresponding ribbons **4**–**6** through an intramolecular cyclodehydrogenation reaction with FeCl$_3$ as an oxidant in dichloromethane at room temperature for 3 days. In contrast to previous approaches in which limited solubility and steric hindrance provided problems during the polymerization step to form polyphenylene precursors,[7] it was found that the kinked backbone enabled ready synthesis of polymers **1**–**3** with high molecular weights. Molar masses of up to 16000 g mol^{-1} for polymer **1** were found by MALDI-TOF MS with a signal pattern typical for A–B-type polymerization (see the Supporting absorption, photoluminescence, and gel permeation chromatography (GPC) analysis.

Oligomer **7**, a defined segment of polymer precursor **2** with a kinked backbone, can have two conformational isomers, **7** and **7*** (Scheme 1). If rearrangement reactions are suppressed, full cyclodehydrogenation of these isomers would lead to the symmetrical products **8a** and **8b**. Cyclodehydrogenation of **7** was carried out with FeCl$_3$ as an oxidant in dichloromethane at room temperature for 1 h to yield solely PAH **8a** as a waxy material. The solubility of **8a** in common organic solvents enabled full structural characterization. ^{1}H NMR spectroscopy of PAH **8a** in [D$_8$]THF clearly confirmed that **8a** rather than **8b** was formed with high specificity (Figure 2a). High-resolution MALDI-TOF MS gave further proof, as the main peak found corresponded to **8a** with a calculated mass of 1048.88 g mol^{-1} (Figure 2b)—any other product would have a different mass as a result of a different number of newly formed bonds. The factors controlling this reaction are still undetermined.

On the basis of the concept of a kinked backbone, we further enlarged our system towards polymeric model compounds **1**–**3** (Scheme 1) with the aim of synthesizing ribbon-type compounds **4**–**6** with extended conjugation. Polymer **1** is a linear polyphenylene precursor that can be subjected to cyclodehydrogenation to yield conjugated nanoribbon **4**. For comparison, model systems **2** and **3** were developed with a large number of dodecyl alkyl chains for better solubility. The synthesis of polymer **3** demonstrates how easily the width of the resulting system can be extended.

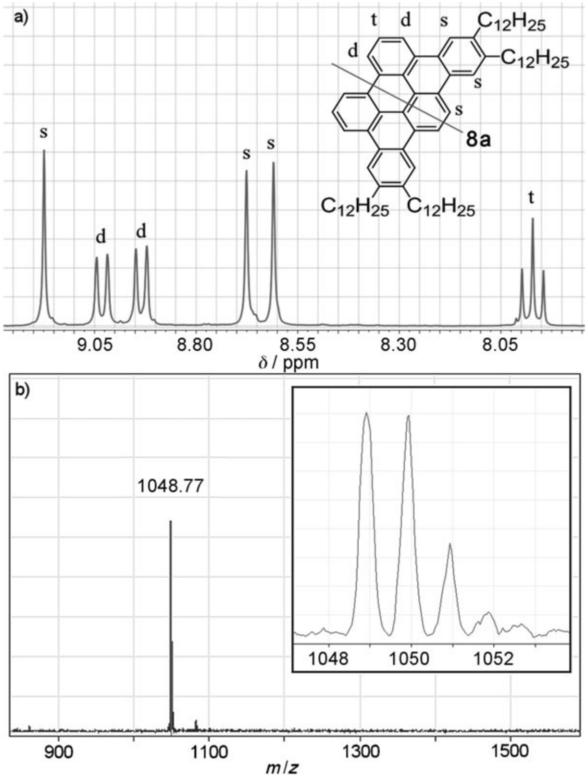

Figure 2. Structural elucidation of the dehydrogenated model compound **8a** by a) H NMR spectroscopy ([D$_8$]THF, room temperature) and b) MALDI-TOF MS.

Information). This molecular weight corresponds to approximately 105 repeat units, and a polymer-chain length of more than 40 nm was calculated. As MALDI-TOF MS has significant limitations for the detection of high-molecular-weight species with a high polydispersity, it cannot be used to determine the actual maximum molecular weights reached.[11] Also, GPC analysis can only give approximate relative values, which are calculated by using a polystyrene (PS) standard. For this reason, we only discuss a few characteristic results herein.[12] For polymer **2**, a molecular weight of up to 20000 $\text{g}\,\text{mol}^{-1}$ was detected by MALDI-TOF MS, and GPC analysis with PS standards indicated an average molecular weight of $M_n = 9900\ \text{g}\,\text{mol}^{-1}$ and a polydispersity index as low as 1.40. After dehydrogenation, $M_n = 20000\ \text{g}\,\text{mol}^{-1}$ was found for **5** by GPC analysis, in full agreement with our expectations, owing to a considerable increase in the stiffness during the conversion from a flexible polymer into a ribbon with a higher hydrodynamic radius. Ribbon **4** was obtained as an insoluble powder, whereas the cyclodehydrogenation of alkyl-substituted polymers **2** and **3** yielded **5** and **6** as waxy materials that could be dissolved in common organic solvents, such as toluene, THF, and dichloromethane. This solubility enabled detailed structural characterization in solution. The good solubility of more than 40 $\text{mg}\,\text{mL}^{-1}$ at room temperature can be attributed to the steric demand of the peripheral alkyl chains, which hinder aggregation in solution.

For the first time, ribbons **5** and **6** enabled characterization by UV/Vis and photoluminescence spectroscopy in solution. Strong broadening of the peaks in the absorption spectra hindered analysis. However, in the photoluminescence spectra, a red-shift of the emission maximum of almost 200 nm between polymer **2** and ribbon **5** clearly indicated an expanded chromophore, which leads to a smaller band gap (see the Supporting Information).

By way of example, an oligomer **1*** of polymer precursor **1** with seven repeat units ($n = 6$ with end capping at both ends) was isolated and dehydrogenated (Figure 3 a). It was possible to monitor the loss of hydrogen atoms during the cyclodehydrogenation by MALDI-TOF mass spectrometry and compare this experimental result with a calculated result. Figure 3 a presents an enlarged segment of superimposed mass spectra of the oligomeric precursor **1*** and the corresponding dehydrogenated ribbon **4***. It could be expected that the terminal *ortho*-biphenyl group in the polymer would rotate freely (see the red arrow in Figure 3 a) and enable the formation of two isomers after dehydrogenation. However, as shown for model compound **7** (Figure 2 a), only one specific ribbon **4*** was formed. The mass spectrum clearly shows that exactly 16 hydrogen atoms were removed, in full accordance with the expected result presented in the reaction scheme, to yield the desired GNR with predictable structural perfection.

This result was further validated by Raman spectroscopy, which provided relevant information about the extended π conjugation of ribbon **4***.[13] The sample was subjected to Raman spectroscopy in a KBr pellet with laser excitation at a wavelength of 532 nm. The resulting first-order Raman spectrum shows two important lines: a first band located at 1335 cm^{-1} with a shoulder at 1248 cm^{-1} and a second band located at 1605 cm^{-1} (Figure 3 b). This pattern is characteristic for all-benzenoid PAHs, with a unique fine structure at 1300 cm^{-1}. The relative intensities and positions of the signals correlate to the size and symmetry of the molecules. On the

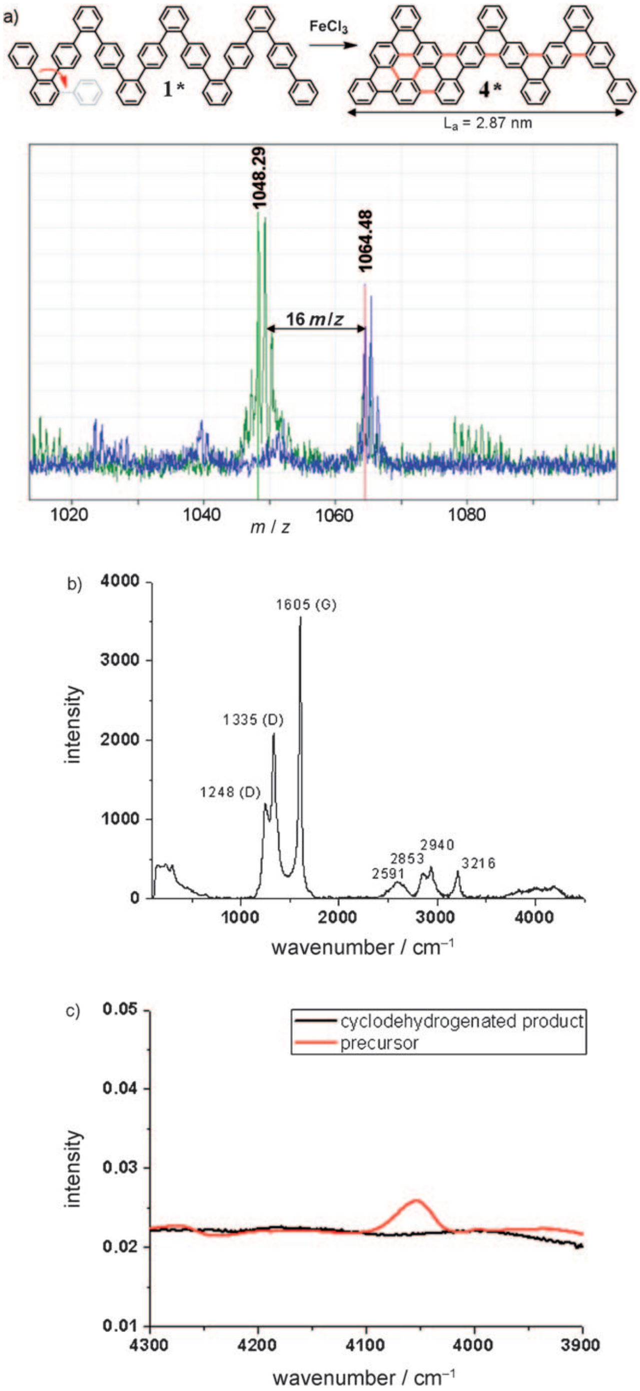

Figure 3. a) Superimposed MALDI-TOF mass spectra of an oligomer **1*** (7 repeat units, $n = 7$) of polymer **1** (blue) and the corresponding ribbon **4*** (green). The spectra show the loss of exactly 16 hydrogen atoms during cyclodehydrogenation. b) Raman spectrum of the dehydrogenated oligomer **4*** showing that it is a ribbon with a length of approximately 2.9 nm. c) Relevant spectral region of the IR spectra of polymer **1*** (red) and ribbon **4*** (black) showing full disappearance of the band at 4050 cm^{-1} (free phenyl rotation) upon cyclodehydrogenation.

basis of the model of so-called disordered graphite, it was possible to calculate the L_a dimension of the conjugated nanoribbon **4*** to be on the order of 2.8–2.9 nm.[14] This value shows remarkable agreement with the dimensions of 2.9 nm computed on the basis of theoretical calculations (Spartan '04, minimized energy) of the heptamer shown in Figure 3a. These results unambiguously validate that all possible bonds within polymer **1*** were constructed as indicated, and conjugation is extended over the whole molecule. They are further supported by comparison of the IR spectra of precursor **1*** and dehydrogenated ribbon **4*** (Figure 3c). Of particular diagnostic importance is the combination peak at 4050 cm^{-1}. This band can be taken as a "marker" of the presence of free rotating phenyl rings in the molecule and is clearly observed in the spectrum of **1***. The disappearance of this peak in the spectra of **4*** and **4**–**6** indicates the absence of noncondensed benzene rings in the molecule,[15] and thus confirms the full cyclodehydrogenation of polymers **1**–**3**.

In conclusion, it has been shown for the first time that structural perfection in the classical bottom-up synthesis of defined graphene nanoribbons **4** and **5** is possible through the use of an oxidative cyclodehydrogenation with $FeCl_3$. Ribbons with lengths of 40 nm were synthesized from polyphenylene precursors **1** and **3** with a flexible kinked backbone. The straightforward introduction of alkyl chains made the resulting ribbons soluble and thus enabled solution processability: an important requirement for the large-scale preparation of electronic devices. By following the above concept, one can readily design other oligophenylene building blocks, which upon (Suzuki- or Yamamoto-type) polymerization should afford suitable precursor polymers for the fabrication of GNRs with different aspect ratios and edge structures. Examples documenting the power of chemical GNR synthesis will follow.

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