

# Modular Synthesis of Monomers for On-Surface Polymerization to Graphene Architectures

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On the occasion of the 100<sup>th</sup> anniversary of the Scholl reaction.

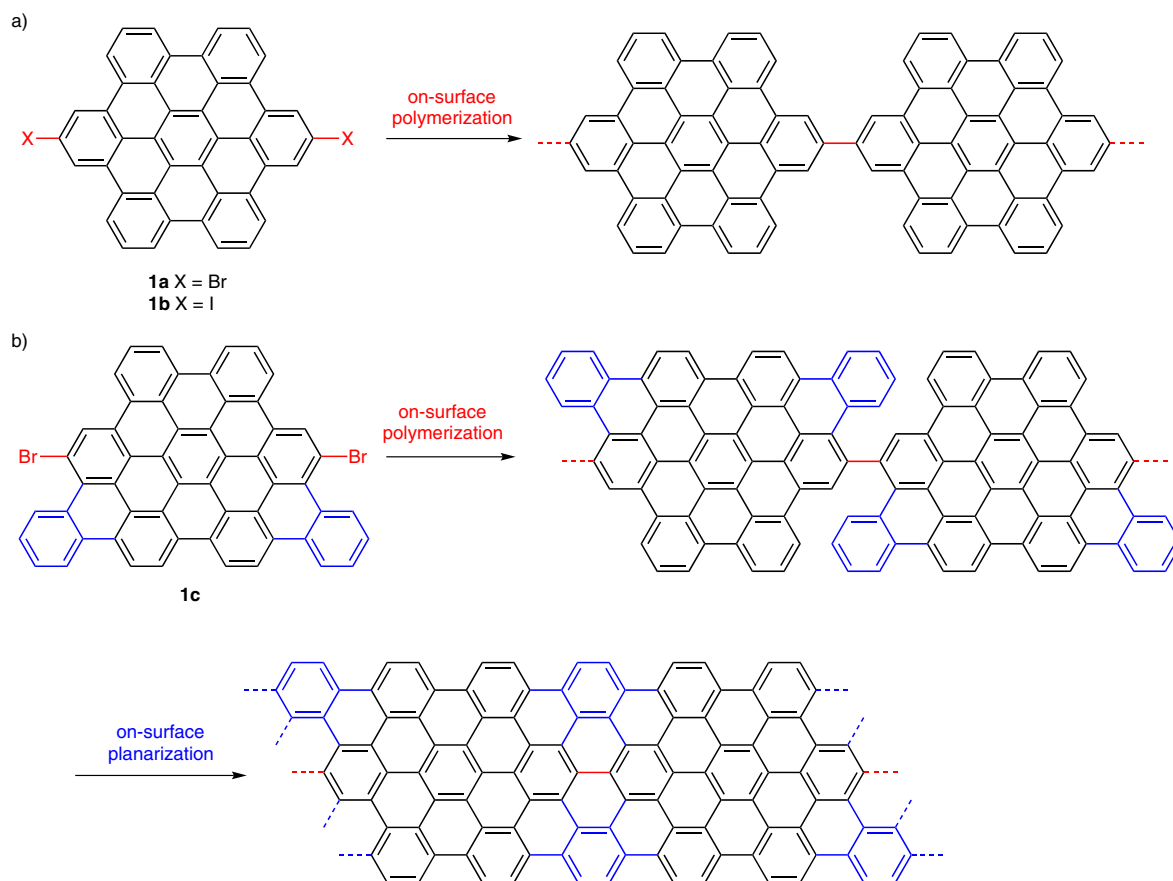
**Abstract:** We developed a modular synthesis of halogenated polycyclic aromatic monomers for on-surface polymerization to generate graphene wires, ribbons, and networks.

**Key words:** graphene monomers, graphene nanoribbons, functionalized graphene nanoribbons, graphene wires, hexabenzocoronene, on-surface polymerization

Graphene is one of the most promising materials for future electronic devices. It conducts electrons without heat dissipation, is transparent, strong yet flexible and very

light.<sup>1</sup> Several methods have been established for the synthesis of monolayers of graphene<sup>2</sup> although there are from the point of view of a chemist not thoroughly satisfying. Often they lack of means to entirely prevent the development of second and higher layers, they cannot control edge structures and still struggle with defects that have a strong influence on the behavior of graphene.<sup>3</sup>

Pure and defect-free graphene does not exhibit a band gap, which is strongly needed for application in electronic devices requiring semiconducting materials. This brings up the need for defined band gaps that can be created and



**Scheme 1** Concept of surface-supported fabrication of graphene architectures by use of a) conventional HBC monomers leading to graphene wires, and b) trapezoidal HBC monomers with two additional benzene rings to fill the gaps yielding graphene nanoribbons.

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tuned, for example, by doping graphene with other atoms and/or the use of graphene ribbons of defined width and edge structures. Graphene ribbons are made using either template-mediated growth<sup>4</sup> or longitudinal unzipping of carbon nanotubes.<sup>5</sup> None of these methods can provide uniform edge structures or exact tunable widths, and properties of functionalized graphene nanoribbons are so far treated mainly theoretically.<sup>6</sup> Therefore, a bottom-up approach with preorganized graphene monomers yielding defect-free graphene ribbons with a well-defined and (if needed) functionalized edge structure is required. For this purpose we envisioned to use Ullmann-type on-surface polymerization on gold surfaces.<sup>7,8</sup> In the following we describe a modular concept for the synthesis of potential monomers for graphene nanoribbons.

If one thinks of dibromo-substituted hexabenzocoronene (HBC) as basic monomer unit, providing 42 carbon atoms arranged already in the right way, one faces the problem of the formation of wires with gaps that need to be filled in order to generate ribbons (Scheme 1, a). Adding two more benzene units per monomer can solve this problem. We therefore decided to use trapezoidal monomers (Scheme 1, b).

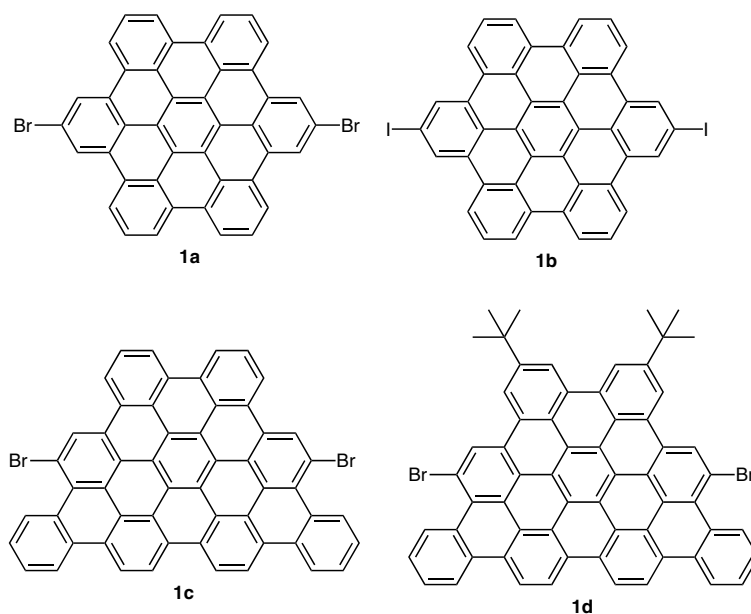
The underlying chemistry for the synthesis of these molecules has been pioneered mainly by Scholl et al. as early as in 1912<sup>9</sup> and Dilthey et al. in the 1930s<sup>10</sup> and was rediscovered and optimized by the Müllen group in the beginning of the 1990s.<sup>12</sup> Herein, we describe the synthesis of new derivatives (Figure 1) with original geometries and

reactive groups suitable for the synthesis of graphene ribbons.

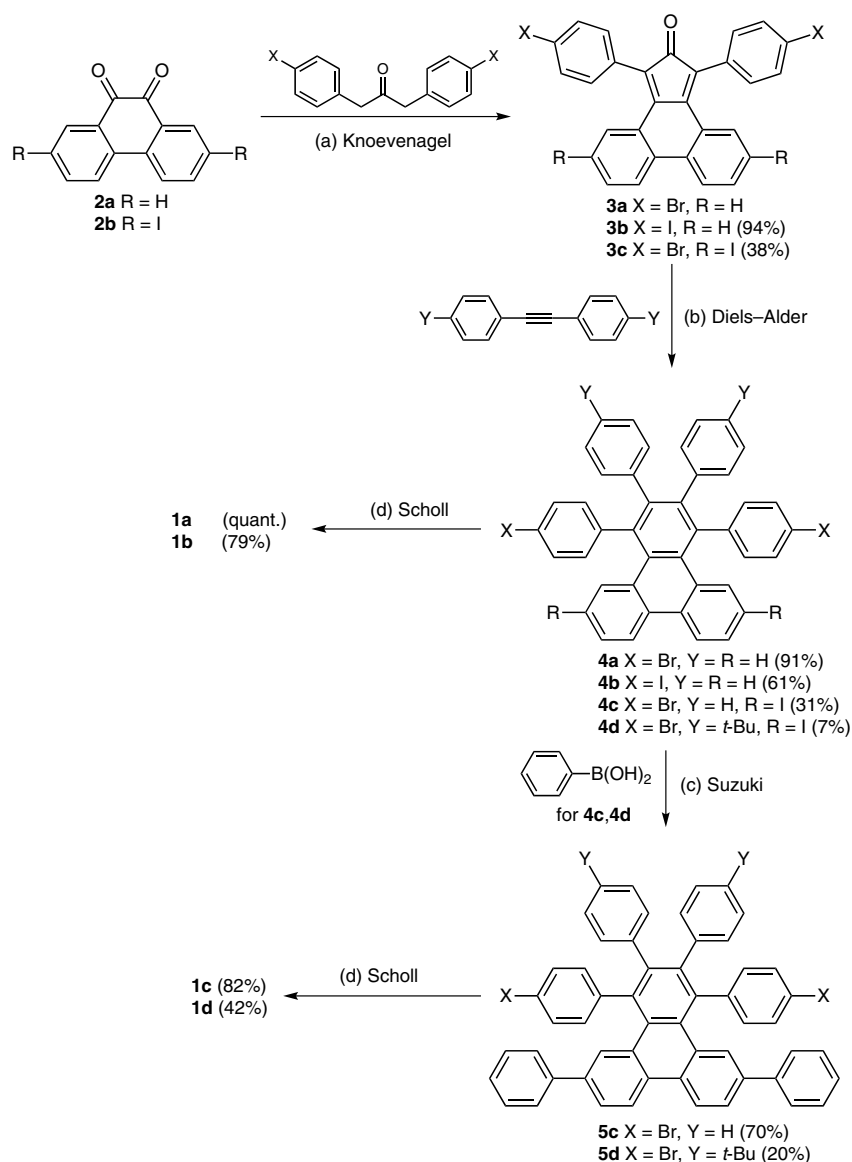
The synthetic route to compounds **1a–d** is summarized in Scheme 2. In a first step a twofold Knoevenagel condensation generates the cyclopentadienone<sup>13</sup> core that reacts as the diene in the subsequent Diels–Alder reaction with a (di)halogenated tolane derivative. Immediate aromatization by CO extrusion yields the corresponding hexaphenylbenzene derivatives **4a–d**.<sup>14</sup> In the case of **4c,d** the missing phenyl rings are introduced in an intermediate step via a Suzuki coupling to yield **5c,d**, which can be planarized, as well as **4a,b** to yield the desired HBC monomers **1a–d** using the Scholl protocol with anhydrous FeCl<sub>3</sub> as oxidizing agent.<sup>15,16</sup>

By applying our recently developed sequential growth approach<sup>17</sup> it should be possible to prepare graphene-type networks on gold surfaces. An appropriate HBC monomer would provide two iodo substituents for the initial 1D polymerization and four bromo substituents for the consecutive 2D cross-linking step (Scheme 3). Therefore the HBC derivative **9** was synthesized to deliver first information about the difficulties of this particular concept (Scheme 4).

To conclude, we accomplished the synthesis of possible monomers for graphene nanoribbons, wires, as well as graphene-type networks with predefined graphene structure in order to minimize the number of structural defects. Currently, we – in collaboration with surface physicists – test these monomers in on-surface polymerization reac-



**Figure 1** Synthesized monomers: monomers **1a,b** for graphene wires and trapezoidal monomers **1c,d** for graphene nanoribbons



**Scheme 2** Synthesis of monomers **1a–d**. *Reagents and conditions:* a) KOH, EtOH, reflux, 30 min; b) Ph<sub>2</sub>O, 1–14 h reflux; c) PhB(OH)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, [Pd(PPh<sub>3</sub>)<sub>4</sub>], toluene–H<sub>2</sub>O, reflux, 20 h; d) FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>–MeNO<sub>2</sub>, 14 h, r.t. Compound **3a** was synthesized according to literature.<sup>11</sup>

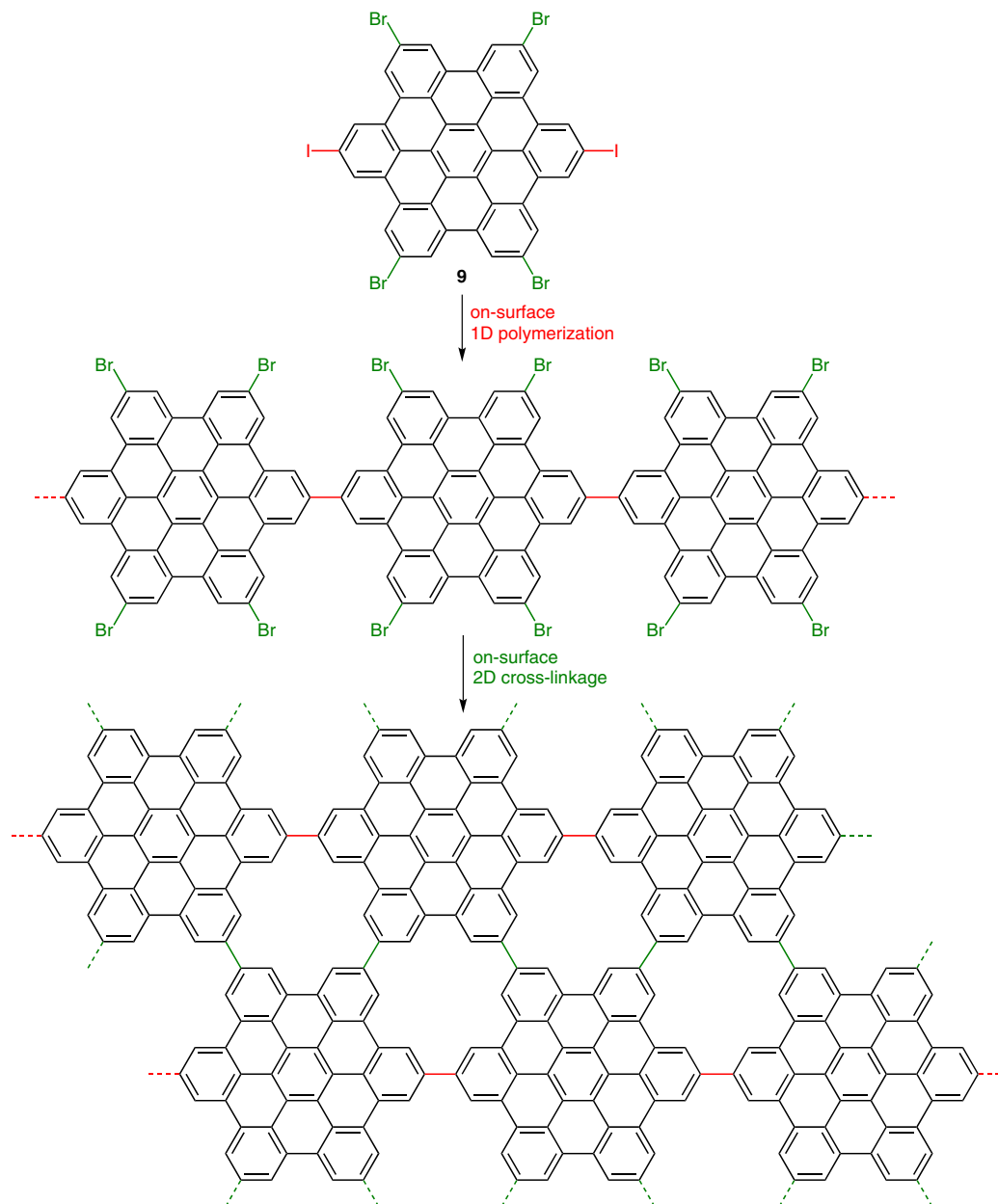
tions to identify suitable conditions (temperature, type of surface, coverage, etc.).<sup>18</sup> As the groups of Fasel and Müllen have already shown that similar (but not yet planarized) monomer structures do polymerize on Au(111) surfaces,<sup>19</sup> alternatively the precursor molecules **4a, b, 8**, and **5c, d** could be subjected to on-surface polymerization with subsequent planarization (in case the HBC derivatives turn out to be too sterically demanding for the on-surface polymerization). Using our synthetic approach it should also be possible to introduce doping atoms, such as pyridine-type nitrogen atoms via, for example, the respective diarylacetylene unit for further tuning of band gaps. So far established methods yield only statistically doped

graphene sheets and nanoribbons,<sup>20</sup> while our approach should provide graphene architectures with a defined number and position of the doping atoms.

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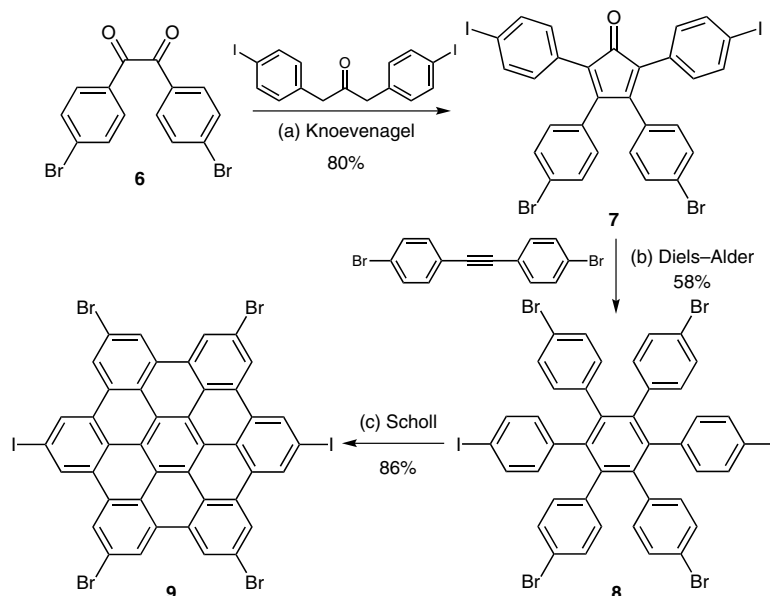
**Supporting Information** for this article is available online at <http://www.thieme-connect.com/ejournals/toc/synlett>.



**Scheme 3** Approach for the on-surface sequential growth of 2D graphene-type networks based on HBC monomer **9**

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**Scheme 4** Synthesis of HBC monomer **9**. *Reagents and conditions:* a) KOH, EtOH, reflux, 30 min; b) Ph<sub>2</sub>O, reflux, 14 h; c) FeCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>-MeNO<sub>2</sub>, 14 h, r.t.

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