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Elements for a Rational Polymer Approach towards Carbon Nanostructures**

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graphene · nanotubes · polycycles · strained molecules · synthetic methods

Carbon nanostructures have prompted intense research efforts among scientists across various disciplines, as their unique mechanical, electronic, and optical properties promise to fuel progress in future technological applications.[1] Among the most interesting carbon nanostructures in terms of possible applications are one-dimensionally extended structures such as carbon nanotubes (CNTs) and graphene nanoribbons (GNRs).[1a,b] Their physical properties depend crucially upon their diameter and width, respectively, as well as structural details such as their edge topology.[1e–g] However, all available physical preparative methods typically produce mixtures of these materials, and considerable research efforts have focused on the development of sophisticated separation and purification processes.[1c–e] Hence, novel methods that allow the tailored preparation of carbon nanostructures need to be developed to not only provide a pathway toward structurally pure samples of the already known carbon nanostructures, but also to enable scientists to synthesize and investigate novel structures with tuneable properties.[2] In this context, multistep organic syntheses provide the highest degree of structural control, as showcased by Scott and co-workers in their seminal report on the total synthesis of the parent C_{60} fullerene.[3] More recently, the toolbox of classical organic synthetic methods has been complemented with new approaches inspired by the preparation of carbon materials. Thus, surface-catalyzed cyclodehydrogenation has emerged as a viable method for the conversion of polycyclic aromatic hydrocarbons into select types of fullerenes and heterofullerenes such as C_{60}, C_{84}, and $C_{57}N_3$.[4] Furthermore, significant steps towards the solution-phase synthesis of beltlike molecules as the shortest possible CNT segments have already been reported,[5] thus demonstrating the power of modern organic chemistry beyond natural product synthesis. However, the preparation of whole CNTs by stepwise syntheses will probably remain elusive. Instead, by analogy to how organic synthetic methods provided a sound foundation for polymer chemistry, the great challenge lying ahead is to develop a polymer synthetic approach which will allow the rational synthesis of one-dimensionally extended carbon nanostructures with a defined diameter and edge topology. A recent series of publications by Scott and co-workers[6] now places this goal within reach.

The approach, as also formulated by Bertozzi and Jasti,[7] envisions the synthesis of defined CNT segments (e.g. **1**–**3**; Figure 1) or caps in the first step. These fragments will then be utilized as templates (or initiators) for a growth reaction (or polymerization) of a suitable carbon precursor (or monomer). Scott and co-workers now contribute what seems to be the first truly suitable template for the envisioned strategy.[6a] Starting from the simple corannulene **4**,[8] they were able to synthesize an isomerically pure end cap of an armchair [5,5]-CNT in only three steps (Scheme 1). Thus, fivefold chlorination of **4** and subsequent Negishi coupling afforded the precursor **6**, which was converted into the desired $C_{50}H_{10}$ nanotube cap **7** by flash vacuum pyrolysis (FVP). It is

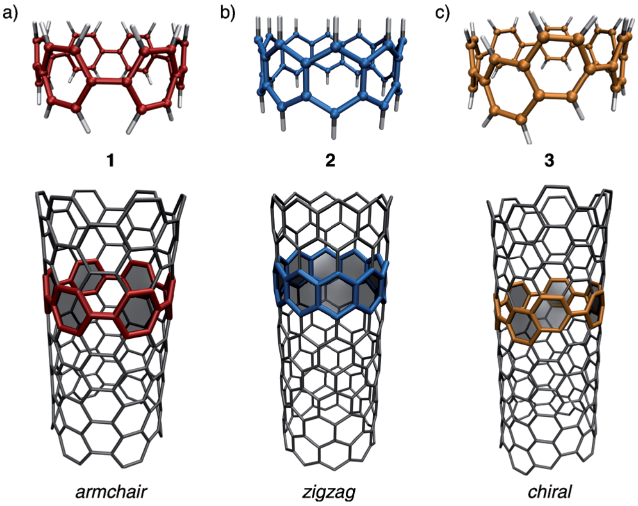

Figure 1. a) [6]cycloparaphenylene (**1**), b) [10]cyclacene (**2**), and c) cyclo[5]paraphenylene-2,6-naphtylene (**3**) represent the shortest segments of an armchair [6,6]-CNT, a zigzag [10,0]-CNT, and a chiral [7,6]-CNT, respectively, and may serve as templates for the synthesis of extended CNTs according to Bertozzi and Jasti.[7]

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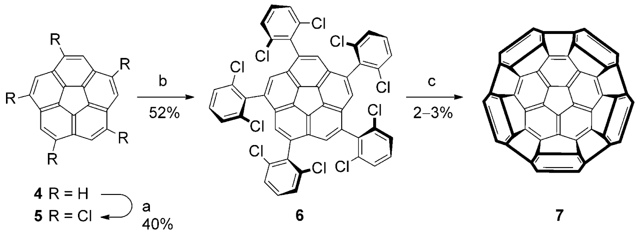
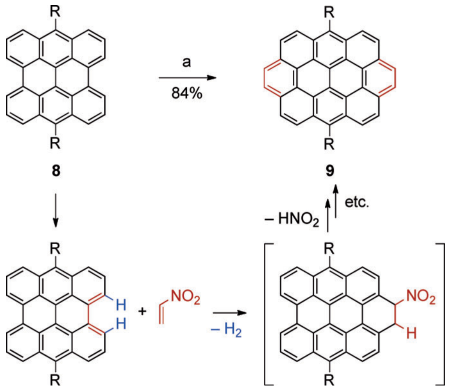
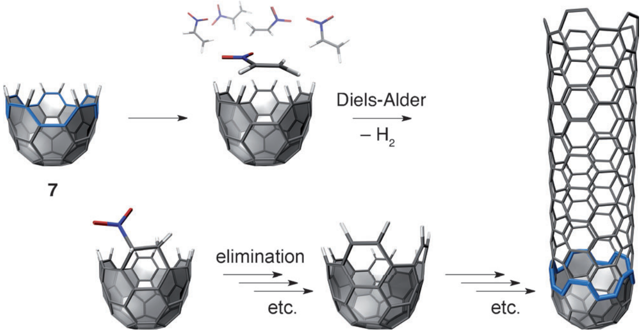


Scheme 1. Concise synthetic route toward the [5,5]-CNT end cap, which may be regarded as the shortest possible [5,5]-CNT. Reaction conditions: a) ICl, CH_2Cl_2; b) 2,6-dichlorophenylzinc, (RuPhos)Pd^{II}-($C_6H_4CH_2CH_2NH_2$)Cl·MTBE, THF, pressure vessel, 100°C; c) FVP, 1100°C/0.25 Torr. THF = tetrahydrofuran.



Scheme 2. Model reaction for the extension of an armchair rim by Diels–Alder addition of in situ generated nitroethylene. Reaction conditions: a) nitroethanol, phthalic anhydride, 135°C; R = mesityl.



Scheme 3. The polymer approach to armchair CNTs with defined diameters, starting from the nanotube end-cap **7** as an initiator and using nitroethylene as a masked acetylene replacement and "carbon monomer" for the growth of the CNT.

important to note that the reproducible but low overall yield of this concise synthetic route does not affect the overall efficiency of the proposed strategy because these caps will only serve as templates for the final polymerization reaction affording the pure CNT. In contrast to other synthetically accessible, beltlike CNT templates, these carbon nanotube end caps have no degree of conformational freedom. Therefore, the subsequent extension of this structure by polymerization of a carbon monomer does not require a planarization and should, hence, render the subsequent CNT growth thermodynamically more favorable.

In addition to caps as templates, a polymerization method for the subsequent CNT growth is required. Whereas Diels–Alder additions to the diene regions of the rims of armchair CNTs appear to be the natural choice for such an extension reaction, acetylene itself is not sufficiently reactive as a dienophile. Acetylene derivatives, however, would introduce substituents that would have to be removed in an intermittent step, thus rendering a continuous solution-phase polymerization process infeasible.[6b,d] To circumvent these problems, Scott and co-workers have now reported the Diels–Alder addition of nitroethylene as a masked acetylene replacement to be a viable approach.[6e] Simple nitroethanol served as the feedstock, and nitroethylene was generated in situ as a highly reactive, electron-poor dienophile. The rearomatization after the Diels–Alder addition provides a driving force for the subsequent elimination of hydrogen and nitrous acid, as conclusively shown in the reaction of nitroethylene with 7,14-dimesitylbisanthene **8** as a model compound with an aromatic armchair site (Scheme 2).

Transferred to the now available CNT end-caps **7**, as substrates for this Diels–Alder methodology, the pristine additional six-membered rings formed after addition of nitroethylene would then constitute part of a new armchair rim prone to undergoing additional Diels–Alder reactions and thus lead to the growth of the CNT (Scheme 3). Moreover, experimental evidence and theoretical results suggest that the Diels–Alder additions will successively become more favorable with an increasing length of the growing CNT, and templates with larger diameters will undergo the reaction more readily.[6b,d] Hence, while reports on its successful implementation are still pending, all required elements for a rational polymerization approach towards one-dimensionally extended carbon nanostructures are now in place.

This raises the question as to whether a similar strategy could also be applied to the synthesis of defined GNRs. Extensive research efforts have recently been devoted to their preparation by other approaches. Notably, Fasel and co-workers demonstrated the surface-assisted synthesis of well-defined armchair nanoribbons with lengths of up to 40 nm from halogenated polycyclic aromatic hydrocarbons (PAHs);[9] this is certainly a facile and elegant method utilizing synthetically easily accessible molecular precursors, but limited with respect to the accessible quantities and the processing of the obtained GNRs. Müllen and co-workers reported an alternative solution-based approach towards the synthesis of GNRs with similar lengths based on the $FeCl_3$-catalyzed cyclodehydrogenation of single-stranded poly(*o*-phenylene-*alt*-*p*-phenylene)s.[10] Thus, this approach provides processable material in tangible quantities but may encounter limitations when applied to GNRs with larger diameters. For this reason, a polymerization approach similar to the outlined synthesis of CNTs would be an attractive alternative pathway for the future preparation of GNRs, if only suitable templates and monomers can be found.

The examples presented herein serve to showcase that the organic synthesis of carbon nanostructures has moved on to the next frontier, that is, the preparation of one-dimensionally extended nanostructures. The approaches elegantly combine

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the stepwise synthesis of suitable precursors with polymerization reactions that eventually furnish the desired carbon nanostructures. This advance places the rational preparation of structurally uniform carbon nanostructures with tailored properties within reach, and the anxiously awaited implementation of carbon nanostructures into novel, carbon-based devices draws closer.

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