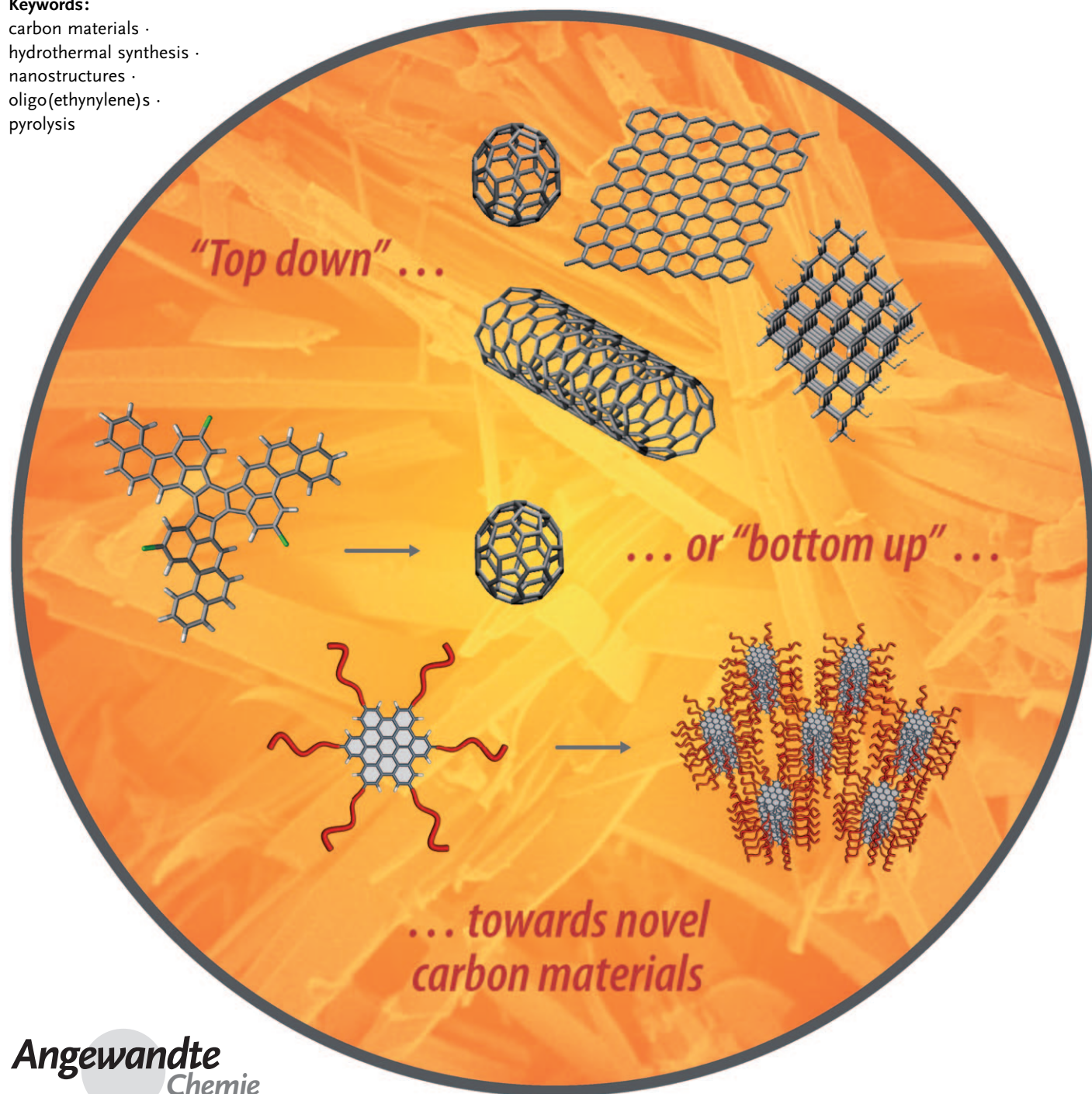


Nanostructured Carbonaceous Materials from Molecular Precursors

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Nanostructured carbonaceous materials, that is, carbon materials with a feature size on the nanometer scale and, in some cases, functionalized surfaces, already play an important role in a wide range of emerging fields, such as the search for novel energy sources, efficient energy storage, sustainable chemical technology, as well as organic electronic materials. Furthermore, such materials might offer solutions to the challenges associated with the on-going depletion of non-renewable energy resources or climate change, and they may promote further breakthroughs in the field of microelectronics. However, novel methods for their preparation will be required that afford functional carbon materials with controlled surface chemistry, mesoscopic morphology, and microstructure. A highly promising approach for the synthesis of such materials is based on the use of well-defined molecular precursors.

1. Introduction

The high natural abundance of carbon, its low specific weight, as well as the chemical and thermal robustness of the different carbon allotropes have resulted in carbon components being increasingly utilized in cheap, lightweight, and durable high-performance materials over the past two decades.^[1] In particular, carbon nanostructures such as fullerenes, carbon nanotubes (CNTs), and carbon fibers have been used in a broad range of technological applications, such as novel energy sources, efficient energy storage, sustainable chemical technology, high-performance construction materials, and organic electronic materials.^[2,3]

The various nanostructured carbon materials that are accessible synthetically cover the entire range of dimensionalities, from “zero-dimensional” (fullerenes, diamond clusters), over one-dimensional (carbon nanotubes (CNTs), diamond nanorods), to two-dimensional (graphene sheets, diamond nanoplatelets) and three-dimensional structures (nanocrystalline diamond films, fullerite, CNT ropes).^[4] “Inverted” carbon nanostructures in the form of mesoporous carbon materials can also be formed.^[5] This diversity of carbonaceous materials on the nanometer scale constitutes the basis for their use as functional components in various applications. For example, activated carbon has been proven experimentally to be a promising storage medium for hydrogen.^[6] A recent theoretical study has suggested that graphite derivatives with an increased interlayer spacing (such as graphite intercalation compounds) might exhibit hydrogen storage capacities of up to 6.5% (w/w), thereby meeting the requirements for industrial application.^[7] Carbon materials are also used as insertion electrode materials, for example, in rechargeable lithium batteries.^[8] As the insertion of lithium ions into carbon materials relies on the reversible formation of lithium–carbon intercalation compounds, lithium uptake strongly depends on the crystallinity, the microstructure, and the micromorphology of the carbonaceous material.^[9–13] Moreover, carbon nanostructures could be used as the active catalyst component for certain chemical reactions. Such “carbon-only” catalysts may be an elegant way to

develop cost-efficient, sustainable, and environmentally friendly catalyst systems.^[14–16] Furthermore, nanostructured carbon materials have already found widespread use in high-performance, fiber-reinforced composites with applications, for example, in the automotive and aerospace industries.^[17] Fullerenes and carbon nanotubes have also been investigated as active components in organic electronic devices as well as nonlinear optical materials.^[18] Finally, carbon–inorganic nanocomposite materials have been used successfully in the development of electronic devices, sensors, and catalysts.^[19–31]

The preceding examples all highlight the impact carbon materials could have in materials science and technology. However, an improved and detailed understanding of the interaction of gases, ions, or reactants with carbon surfaces, as well as electron transport in carbon-based organic semiconductors is needed. For this purpose, novel preparative methods need to be developed to provide access to functional

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carbonaceous materials, that is, carbon nanostructures with controlled morphology, surface topology, surface chemistry, and carbon microstructure, as well as novel types of carbon–inorganic hybrid materials. Moreover, such functional derivatives would extend the scope of possible applications, as they may allow for a broader range of processing methods, a better control of the supramolecular organization of the carbon nanostructures, and the preparation of stimulus-responsive materials.

It may be envisioned that, similar to the “bottom-up” approaches which were developed for the preparation of functional inorganic nanostructured materials from molecular precursors (such as molten-salt syntheses, solvothermal procedures, or templated syntheses),^[32] research on the preparation of nanostructured carbon materials would greatly benefit from the development of comparably simple methods. In fact, the underlying approach of using molecular precursors for the preparation of “unusual” forms of carbon was conjectured almost 20 years ago.^[33,34] In the present Review we, therefore, intend to critically review the progress in this field from different perspectives. We start with a cursory overview of the “classical” preparative methods for the currently most widely investigated carbon nanostructures (fullerenes, CNTs, carbon nanofibers, graphene, as well as nanodiamond), and assess the potential of these methods for the production of functional carbon as a point of reference. We will then discuss recent advances in the stepwise organic synthesis of molecular carbon and carbon-rich nanostructures, such as fullerenes and fullerene fragments, acetylenic scaffolds, poly(phenylene) dendrimers, and polycyclic aro-

matic hydrocarbons (PAHs). Finally, we give a detailed overview of recent research concerning the preparation of functional nanostructured carbon materials starting from appropriate molecular precursors, such as carbohydrates, PAHs, and oligo(ethynylene)s, and critically discuss their scope and limitations compared to the other approaches.

2. “Classical” Approaches towards Nanostructured Carbon Materials

2.1. Fullerenes and Carbon Nanotubes

The discovery and preparation of fullerenes^[35–38] and, later, multiwall as well as single-wall CNTs^[39–44] may be regarded as the starting point for the rapid development in the field of molecular carbon nanostructures and nanostructured carbon materials. This has opened up a new era in materials science and nanotechnology over the past two decades. While fullerenes belong to the realm of molecular structures, CNTs hold a unique intermediate position between molecular nanostructures and nanostructured materials. The unusual combination of size, form anisotropy, and material properties (such as high mechanical strength, elasticity, and 1D electric (semi-)conductivity) makes CNTs interesting candidates for applications in various fields.^[41,45–47] However, the production cost of large quantities of pure material has precluded their broad application to date. Typical preparative methods have recently been reviewed,^[3] and encompass arc-discharge methods,^[39,40,44,48–53] laser-abla-



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tion techniques,^[42,54–62] oxidative combustion of molecular precursors,^[63] and chemical vapor deposition (CVD).^[64–68] These “physical” methods of preparation typically yield major concentrations of impurities, that is, catalyst contamination, amorphous carbonaceous materials, defect structures, as well as mixtures of different CNT modifications and fullerenes of different sizes and topologies. Furthermore, they are associated with harsh reaction conditions and, therefore, preclude the presence of chemical functionalities. Whereas a comprehensive set of synthetic organic methods has since been developed for the postsynthetic functionalization of fullerenes,^[69–71] the outstanding chemical stability of CNTs comes at the price of a challenging postsynthetic functionalization and difficult processability because of their low solubility.^[72,73] A number of purification and functionalization procedures for CNTs have been published,^[74–77] but they are often accompanied by structural changes, and there is little control over the aggregation and self-assembly of the obtained carbon species.^[73]

2.2. Graphene

The field of carbon nanostructures experienced a renewed impetus with the recent preparation of pristine graphene,^[78] that is, the single, constituent layers of graphite. This achievement not only represented an extension from zero-dimensional (fullerenes) and one-dimensional (CNTs) to two-dimensional sp^2 -hybridized carbon nanostructures (Figure 1), it also allowed the intriguing properties of single

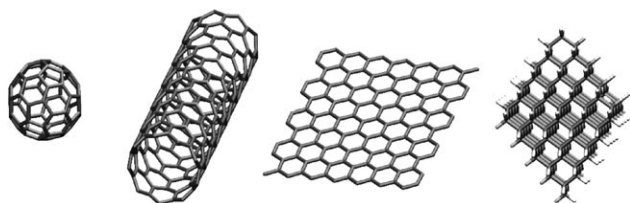


Figure 1. Fullerenes, single-wall carbon nanotubes, graphene, and nanodiamonds are examples of zero-, one-, and two-dimensional sp^2 -hybridized as well as three-dimensional sp^3 -hybridized carbon nanostructures.

graphene layers to be studied. Such properties include their extraordinarily high charge carrier mobility ($2 \times 10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),^[79] their ambipolarity which allows the Fermi level to be altered by applying a gate bias,^[80] as well as a high performance in sensing applications.^[81] A plethora of studies on graphene and related topics have, in the meantime, been published and recently extensively reviewed.^[80,82–85]

Graphene of the highest structural integrity has been obtained following the mechanical exfoliation method developed by Geim and co-workers.^[78,86] Graphenes with only a few layers were then discriminated from thicker slabs by their interference color under an optical microscope. Single-layer graphenes were ultimately identified by atomic force microscopy (AFM). While this method produces “perfect” graphene

layers which are ideal for studying the physical properties, it can not be scaled up for industrial purposes. Chemical vapor deposition of low-molecular-weight hydrocarbon precursors on heated transition-metal surfaces has been identified as an alternative method, which would also allow for the incorporation of B or N to obtain p- or n-doped graphene.^[87] Although sheets on a centimeter scale have been prepared with this method,^[88] the thickness of the film is sometimes difficult to control (Figure 2).^[89] A solution-based approach

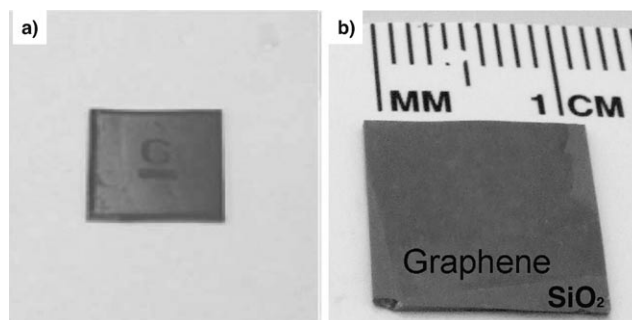


Figure 2. Photographs of single graphene layers grown by chemical vapor deposition. a) Example of a patterned graphene layer with dimensions on the centimeter scale which has been transferred onto a SiO_2 substrate by using a poly(dimethylsiloxane) stamp.^[89] b) “Perfect” single graphene sheet on a SiO_2 substrate grown by CVD on a thin copper foil.^[88] Reprinted from a) *Nature*; copyright 2009 Nature Publishing Group; b) *Science*; copyright 2009 American Association for the Advancement of Science, with permission.

developed by Hummers and Offeman relies on the oxidation of graphite.^[90] Subsequent chemical reduction of the resulting graphite oxide in the presence of a stabilizing polymer^[91] or at elevated pH values^[92,93] yields stable and processable colloidal suspensions of graphene that are well-suited for the preparation of devices.^[85] This process, however, produces structurally less-perfect graphene, the properties of which are not as good as pristine graphene, as can be seen, for example, in the reduced charge carrier mobility of less than $1 \times 10^3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^[83]

2.3. Carbon Fibers and Nanodiamond

Carbon fibers are examples of nanostructured carbonaceous materials that have been used in industrial applications. They are typically produced by spinning polyacrylonitrile (PAN) or, less commonly, petroleum pitch into fibers, followed by thermal treatment (stabilization at 200–300 °C, carbonization at 1000–1700 °C, and, possibly, graphitization at 2000–3000 °C).^[94–96] The resulting fibers usually have an ordered core, with a microstructure similar to multi-wall CNTs, and an outer shell, which consists of disordered graphitic planes parallel to the fiber axis. Their mechanical strength is limited as they contain a variety of structural defects.^[97] Alternatively, carbon fibers can be obtained by the dehydrogenation of gaseous hydrocarbons at high temper-

atures (1100 °C) in the presence of a metal catalyst.^[98,99] The core of the thus prepared fibers consists of stacked graphitic nanocones surrounded by a disordered outer layer of graphitic planes parallel to the fiber axis (Figure 3).

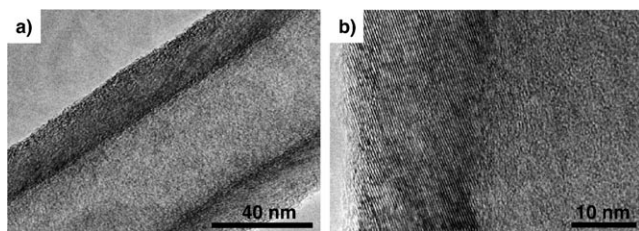


Figure 3. TEM images of “vapor-grown carbon fibers”.^[98] Reprinted from *Compos. Sci. Technol.*; copyright 2007 Elsevier, with permission.

Carbon fibers have become an important component for the preparation of fiber-reinforced composites with applications in, for example, the automotive and the aerospace industry because of their high tensile strength (3–7 GPa), high modulus of elasticity (200–500 Pa), and low density (1.75–2.00 g cm⁻³).^[96,97] Their functionalization, however, is restricted to postsynthetic processes, which, similar to the case of carbon nanotubes, limits their applicability.

All the previously discussed forms of carbon nanostructures contain sp²-hybridized carbon atoms. Research on sp³-hybridized nanodiamonds has increased only in the last five years,^[100,101] despite their independent discovery by several researchers in the former Soviet Union and the USA in the 1960s.^[102] Nanodiamond is produced on a technical scale by a process called “detonation synthesis”, in which an oxygen-deficient explosive (such as TNT/hexogen 3:2) is ignited in an oxygen-deficient atmosphere.^[103] Incomplete combustion under optimal conditions furnishes up to 80 % diamond nanoparticles in the detonation soot, which amounts to 4–10 % overall yield. After a manifold of purification steps, such as sieving to separate the diamond nanoparticles from larger particles, oxidative treatment with mineral acids to remove metal impurities and non-diamondoid carbon, and bead milling to break up aggregates into primary particles, stable colloidal dispersions of nanodiamonds with average diameters of about 5 nm and narrow size distributions are obtained.^[101,102] Heating or electron irradiation converts the diamond nanoparticles into onionlike graphitic material, thus highlighting the intricate equilibrium between sp²- and sp³-hybridized carbon nanostructures, which only for a certain minimum size appears to allow the observation of stable diamondoid structures under ambient conditions.

As a result of the preparative and purification methods, the nanodiamond surfaces are functionalized (with carboxylic acid, lactone, ketone, and alcohol functions), which allows for a straightforward (although unselective) postsynthetic functionalization.^[104] More recently, biological applications of doped, functionalized nanodiamonds, for example, as fluorescent labels, have emerged as a highly attractive field of investigations that focuses on their pathways of cellular uptake, biolocalization, and metabolism.^[105]

2.4. Scope and Limitations of the “Classical” Methods

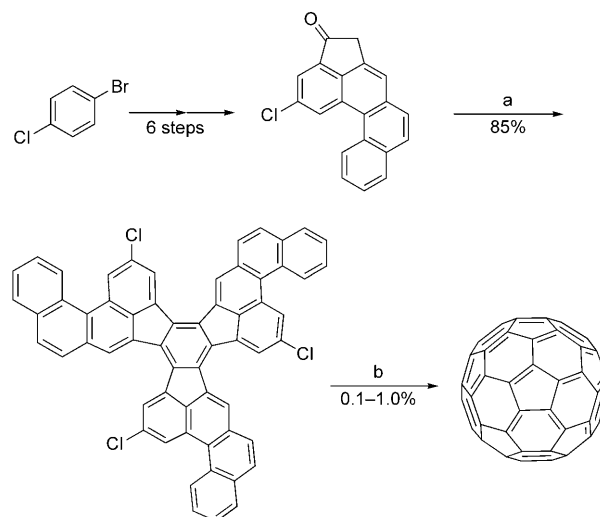
In summary, the classical physical methods have provided access to a broad range of nanostructured carbon materials. However, the major disadvantages of these simple preparative methods are the purification and processing of the different carbon allotropes formed in these processes, the lack of control over the surface morphology and carbon microstructure, as well as, most importantly, the limitations in regard to the chemical functionalization of the obtained carbon materials. These issues leave sufficient room to explore alternative “bottom-up” approaches starting from well-defined molecular precursors.

3. Stepwise Organic Synthesis of Molecular Carbon-Rich Nanostructures

The difficulties outlined above combined with indications that the preparative methods described for fullerenes and CNTs may, in fact, proceed via molecularly defined intermediates^[106] have motivated organic chemists to develop stepwise synthetic approaches toward molecular carbon nanostructures.

3.1. Total Synthesis and Modification of Fullerenes

In a seminal example of the stepwise synthesis of molecular carbon nanostructures, Scott and co-workers reported the total synthesis of C₆₀ by the preparation of complex polycyclic aromatic hydrocarbons (PAHs) followed by flash-vacuum pyrolysis (FVP; Scheme 1).^[107–109] In an alternative approach, Tobe et al. prepared strained three-dimensional oligo(ethynylene) precursors which gave rise to fullerenes in a mass spectrometer.^[110,111] Despite these impressive achievements, the purely synthetic organic



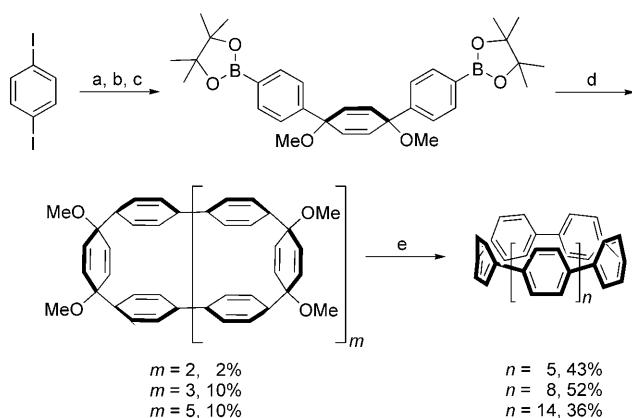
Scheme 1. Synthesis of Buckminsterfullerene C₆₀ by flash vacuum pyrolysis of a polyarene precursor.^[109] Reagents and conditions: a) TiCl₄, *o*-dichlorobenzene; b) FVP, 1100 °C, 0.1 mm Hg.

approaches are limited by the tedious multistep synthetic strategies which do not allow for the necessary scale-up to prepare sizeable amounts of material. Furthermore, as already described in Section 2, a broad range of methods for the postsynthetic chemical functionalization of fullerenes obtained by the “classical” methods has been developed^[69–71] which appear to render the stepwise organic synthesis of functional fullerene derivatives obsolete.

3.2. Synthesis of Fullerene Fragments, Aromatic Belts, and “Unusual” Carbon-Rich Molecules

The same arguments do not, of course, apply to molecular carbon and carbon-rich nanostructures that are inaccessible by other methods. For example, defined conjugated carbon-only structures, such as sp^2 -hybridized aromatic macrocycles and belts, bowl-shaped molecules, as well as unusual molecular scaffolds incorporating acetylenic building blocks constitute fascinating and challenging targets for both synthetic chemists and theoreticians.^[112,113]

The synthesis of conjugated carbon-only macrocycles and belts, which represent the shortest form of either zig-zag or armchair CNTs, was addressed as early as 1954,^[114] and research efforts are still on-going.^[112,115] A recent breakthrough toward molecular belts formally derived from armchair CNTs was the straightforward synthesis of the first representatives of $[n]$ paraphenylene macrocycles by Bertozzi and co-workers (Scheme 2).^[116] Furthermore, Bodwell and co-

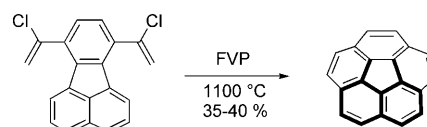


Scheme 2. Synthesis of $[n]$ paraphenylene macrocycles by Bertozzi and co-workers.^[116] Reagents and conditions: a) 1. $n\text{BuLi}$, THF, -78°C , 2. benzoquinone; b) 1. NaH, THF, 0°C , 2. MeI, 0°C to RT; c) 1. $n\text{BuLi}$, THF, -78°C , 2. isopropylpinacolborate, -78°C ; d) $[\text{Pd}(\text{PPh}_3)_4]$, Cs_2CO_3 , toluene/methanol (10:1), 80°C ; e) lithium naphthalide, THF, -78°C .

workers were able to bend a teropyrene to the previously unobserved angle of 167° , thereby constructing a large segment of an (8,8) armchair single-wall CNT.^[117] In stark contrast to these advances, the synthesis of the $[n]$ cyclacenes, that is, molecular fragments of zig-zag single-wall CNTs, has not yet been met with similar success. A common problem observed in the different attempted syntheses reported by the

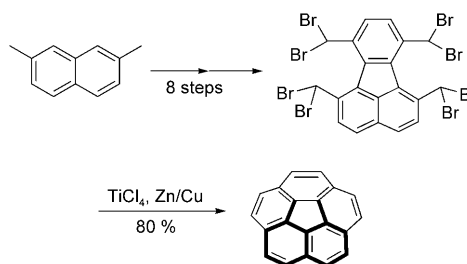
research groups of Schlüter,^[118] Stoddart,^[119,120] and Cory^[121,122] is that the final aromatization of promising, partially saturated precursors failed.^[112] Theoretical analyses of the $[n]$ cyclacenes indicate that the aromatic stabilization energy may just be insufficient to compensate for the high molecular strain.^[112,123] The calculated difference in energy between the singlet and the triplet state is inherently low for both even and odd $[n]$ cyclacenes, and thus they have been predicted to possess a (bi)radical character. In mass spectrometric investigations of related precursors for the belt of C_{84} fullerene, Schlüter and co-workers observed different, often unusual rearrangements of the molecules instead of the generation of the fully aromatic product.^[124]

Barth and Lawton were the pioneers in the field of bowl-shaped hydrocarbons and reported a 16-step protocol starting from acenaphthene for the synthesis of the parent representative corannulene.^[125,126] The discovery of fullerenes in 1985^[35] provided a new impetus for research into this class of compounds. This resulted in two main approaches that have recently been reviewed.^[127,128] Thus, Scott et al. were the first to report the utilization of suitably substituted fluoranthene skeletons in a FVP that resulted in the formation of corannulene.^[129–131] Siegel and co-workers, independently, reported the successful FVP of similar precursors shortly thereafter.^[132] Of the various precursors tested, the FVP of bis(1-chlorovinyl)fluoranthene afforded the highest yields of 35–40% (Scheme 3).^[131] The lack of selective functionaliza-



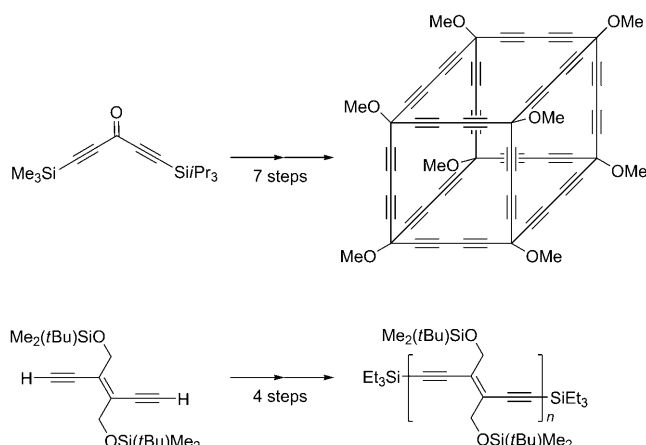
Scheme 3. FVP of bis(1-chlorovinyl)fluoranthene.^[131]

tion with the FVP process motivated the development of appropriate solution-based methods. The initial efforts by Siegel and co-workers yielded 2,5-dimethylcorannulene.^[133] A modified approach afforded corannulene from commercially available 2,7-dimethylnaphthalene in 9 steps and 19% overall yield (Scheme 4).^[134] Concurrently, Sygula and Rabideau published a similar approach,^[135] and further refinement of the synthetic protocol toward greater functional-group tolerance paved the way for the preparation of various substituted corannulenes.^[127]



Scheme 4. Solution-based synthesis of corannulene by Siegel and co-workers starting from 2,7-dimethylnaphthalene.^[134]

In an attempt to modularize the otherwise complex stepwise synthesis of carbon-rich molecular nanostructures, Diederich and co-workers pioneered^[33,34] and recently reviewed^[136] the field of “acetylenic scaffolding”, in which a small and simple set of (*E*)-1,2-diethynylethene, 1,1,2,2-tetraethynylethene, and related derivatives are used as building blocks for the construction of large carbon-rich molecules (Scheme 5). This approach resulted in impressive



Scheme 5. Series of oligo(triacetylene)s up to the 24 mer,^[137] and an expanded octa(methoxy)cubane^[138] synthesized by Diederich and co-workers.

molecular structures such as a 17.8 nm long fully conjugated oligo(triacetylene),^[137] an expanded octa(methoxy)-cubane,^[138] as well as a [6]radialene in which the perethynylated core adopted a nearly perfect chairlike conformation.^[137,139] These results highlight the power of combining modern synthetic organic methods with a modular approach in which simple building blocks are utilized. However, the originally conjectured idea to extend this approach toward novel carbon materials, potentially even including “unusual” novel carbon allotropes,^[33,34] has not been explored to date.^[113]

3.3. Synthesis of Poly(phenylene) Dendrimers and Polycyclic Aromatic Hydrocarbons

Müllen and co-workers reported the versatile stepwise preparation of poly(phenylene) dendrimers by the Diels–Alder addition of acetylenes to tetraphenylcyclopentadienone derivatives substituted with acetylene moieties protected with triisopropylsilyl (TIPS) groups (Scheme 6).^[140,141] This strategy allowed for the synthesis of huge dendrimers which were found to be monodisperse, shape-persistent, carbon-rich molecular nanostructures with sizes of up to 5 nm, as determined by AFM.^[142] In one case, a size of up to 22 nm was determined by dynamic light scattering (DLS) and transmission electron microscopy (TEM).^[143]

The subsequent planarization of the poly(phenylene) dendrimer precursors by oxidative cyclodehydrogenation yielded PAHs of different sizes, geometries, and peripheral

topologies.^[144–146] In particular, graphite nanoribbons^[147] as well as a large, well-defined nanographene sheet with 222 carbon atoms^[147,148] were generated in this way (Scheme 6). Furthermore, a highly fluorescent, triangularly shaped PAH incorporating five-membered rings in the periphery was synthesized, which failed, however, to form bowl-shaped polyarenes by intramolecular cyclization.^[149] In other cases where the geometry of the poly(phenylene) precursor did not allow for a complete planarization during the oxidative cyclodehydrogenation, the authors claimed the formation of three-dimensional nanostructures, such as propeller-shaped molecules.^[150]

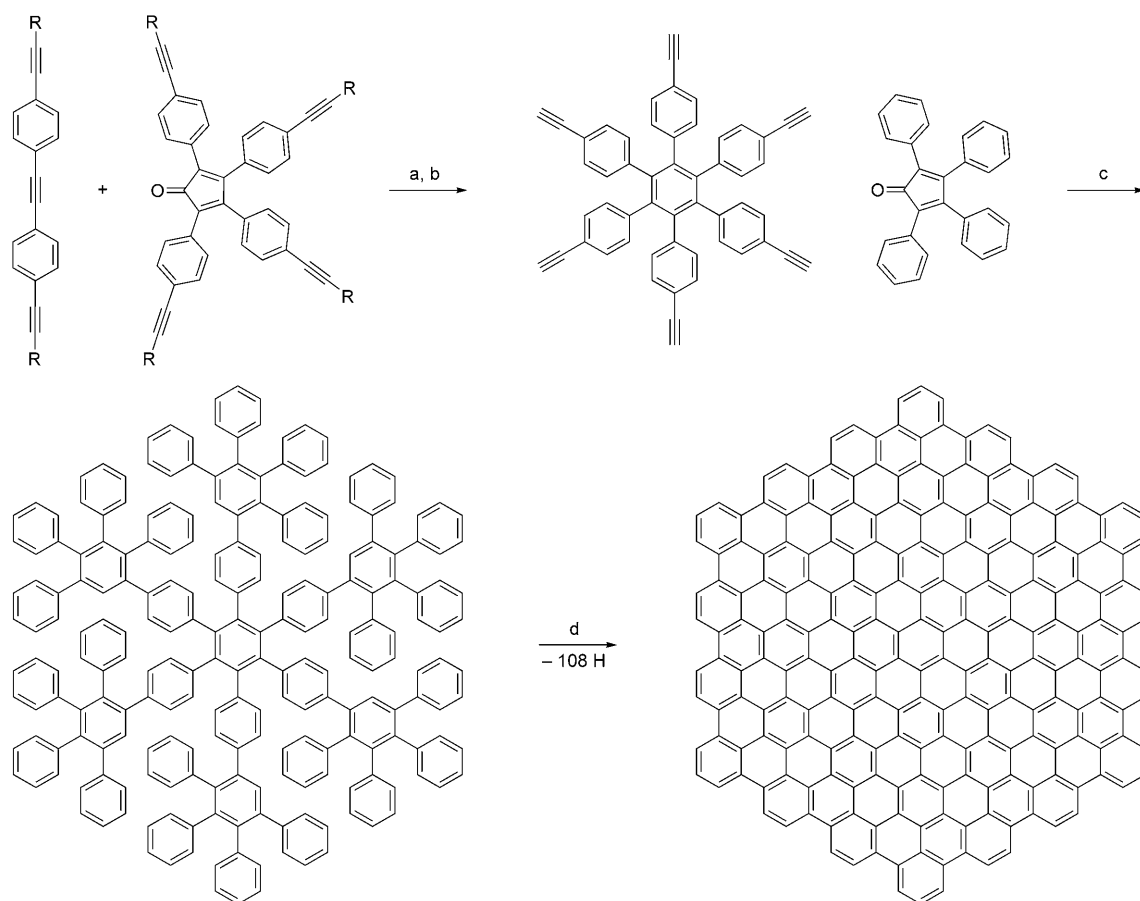
Finally, some of the simpler representatives of functionalized PAHs were investigated as molecular precursors for the preparation of carbon nanostructures or bulk carbon materials by self-assembly and subsequent pyrolysis, as will be discussed in detail in Section 5.

3.4. Scope and Limitations of Synthetic Organic Methods

The stepwise synthetic organic methods have provided access to a large number of synthetically challenging and theoretically highly interesting novel (and sometimes “unusual”) carbon-rich molecular structures not accessible by other methods. The degree of control that has been accomplished at each stage over the often highly complex structures in the synthetic pathway demonstrates the power of modern organic-synthetic methods beyond natural product synthesis. However, the previous approaches have mainly targeted molecular carbon or carbon-rich nanostructures rather than functional, nanostructured carbon materials. The “physical” methods briefly highlighted in Section 2 and the stepwise organic total syntheses summarized in Section 3 represent the two extremes of the “top-down” and “bottom-up” approaches for the preparation of carbon nanostructures. The two strategic approaches come with their own set of advantages and disadvantages. The “classical” methods are simple, scalable processes, but they do not provide good structural control, as can be achieved by multistep syntheses. In contrast, organic total synthesis typically involves highly complex and tedious synthetic procedures that are not appropriate for the preparation of materials on a large scale. The perfect approach would, of course, both convey a high degree of structural control throughout a short and simple preparation process and yield functionalizable or already functionalized products at the same time. For this reason, approaches involving simple, designed molecular precursors prepared in short stepwise synthetic pathways from readily available starting materials may be a viable alternative for the preparation of bulk quantities of functional carbon materials.

4. Hydrothermal Syntheses of Carbon and Carbon–Inorganic Hybrid Nanostructures

Since, for the reasons outlined in the previous sections, the purely “physical” methods and the total syntheses both have



Scheme 6. Synthetic pathway involving repetitive Diels–Alder additions for the preparation and subsequent planarization of poly(*p*-phenylene) dendrimers. Reagents and conditions: a) Ph_2O , 200 °C, 11 days, 72%; b) Bu_4NF , THF, RT, 89%; c) Ph_2O , 190 °C, 11 h, 89%; d) $\text{Cu}(\text{OTf})_2$, AlCl_3 , CS_2 , 30 °C. R = triisopropylsilyl, OTf = triflate.^[148]

limited prospects for the preparation of carbonaceous materials, lessons may be learned from other research fields. For example, a variety of methods are known for the preparation of nanostructured functional *inorganic* materials.^[32] Thus, molten-salt syntheses, solvothermal procedures, or templated syntheses yield (anisotropic) nanostructures both in the absence and presence of surfactants. This poses the question of whether similar “wet chemical” methods could be applied successfully to the preparation of nanostructured carbon materials.

4.1. Carbon Nanospheres from Carbohydrate Precursors

The mild hydrothermal carbonization of molecular precursors such as carbohydrates, which has recently been reviewed,^[151] is one example of such an approach. Originally, interest in an accelerated, noncatalytic degradation of cellulose led to the report of an acid-free hydrothermal process by Adschiri et al.^[152] One of the side products of this process was later identified by Sakaki and co-workers as dehydrated and aromatized species.^[153] This discovery has, more recently, prompted investigations of hydrothermal processes as a means for the preparation of carbon nanostructures. Thus,

Huang and co-workers obtained microporous carbon microspheres with a narrow size distribution from sucrose in a hydrothermal process at 190 °C followed by annealing at 1000 °C or 2500 °C in an argon atmosphere.^[154,155]

The carbohydrates used as the molecular precursors in this process may formally be regarded as a “hydrated form of carbon”, and their complete dehydration under hydrothermal conditions is, in one sense, an accelerated version of the natural conversion of biomass into coal, oil, or diamond. Despite this illustrative analogy, relatively little is known about the mechanistic pathway of this conversion. The formation of micrometer-sized carbon spheres was proposed to proceed by some sort of emulsion polymerization during which adjacent sugar molecules are dehydrated and polymerized in a polycondensation reaction upon heating.^[155,156] The emerging amphiphilic species then, supposedly, undergo phase segregation and aggregate into spherical particles as soon as their critical micelle concentration is reached. After nucleation, these micelles continue to grow by carbonization of further precursor molecules at the surface, until the supply of them in the solution is depleted.

Sun and Li exploited the time-dependence of this growth process to prepare carbon nano- and microspheres with tailored sizes.^[156] Depending on the reaction time, particles

with diameters ranging from 200 to 1500 nm were obtained (Figure 4). Furthermore, carbon–inorganic composites were prepared by depositing silver and palladium nanoparticles on the surfaces of the carbon nanospheres by a postmodification

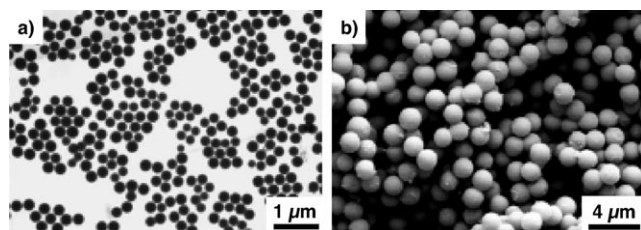


Figure 4. The hydrothermal carbonization of glucose to give carbon nanospheres, the sizes of which were tuned by altering the reaction time.^[156]

process. Alternatively, the spheres were internally loaded with noble-metal nanoparticles by carrying out the process in the presence of silver colloids or by an in situ reduction of gold tetrachloric acid during the hydrothermal process. Further decoration with platinum nanoparticles yielded interesting three-layer (silver–carbon–platinum) nanostructures.

4.2. Anisometric Carbon–Inorganic Composites from Carbohydrates and Transition-Metal Salts

Antonietti and co-workers found that, while the hydrothermal processing of pure aqueous solutions of carbohydrates produced carbon microspheres, the hydrothermal treatment of carbohydrate precursors in the presence of transition-metal salts led to the formation of one-dimensional carbon–inorganic hybrid nanostructures.^[157] Thus, the hydrothermal processing of glucose or starch in aqueous AgNO_3 solutions yielded coaxial carbon-coated silver nanowires with a diameter of 200–250 nm and a length of several micrometers (Figure 5). Both closed and open-ended tubes were observed. The diameter of the wires and the relative diameters of the metal core and the carbon shell could be tuned by altering the reaction conditions, such as the temperature, the starch/silver ratio, or the relative starch concentration. Yu et al. developed a microwave-accelerated variant of this hydrothermal process and obtained straight, open-ended carbon/silver nanowires

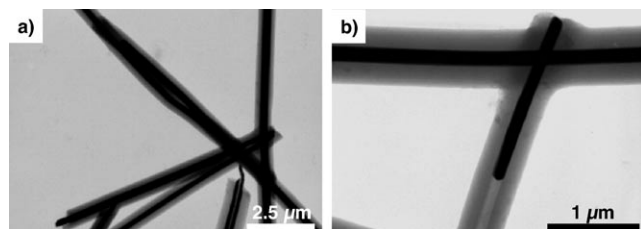


Figure 5. The hydrothermal carbonization of starch (and other glucose derivatives) in the presence of AgNO_3 yielded carbon-coated silver nanowires.^[157]

with lengths in the range of 50 nm to 2 μm starting from sucrose in aqueous AgNO_3 solutions.^[158]

The mechanism for the formation of the obtained one-dimensional nanostructures may involve the anisotropic growth of inorganic crystals, which was postulated to proceed by an “oriented attachment” mechanism under hydrothermal conditions.^[159] The crystallites preferably coalesce at high-energy interfaces to minimize the surface energy. The presence of organic molecules is known to modify this process. In biomineralization, for example, surfactants and polymers adsorbed onto inorganic nanoparticles determine the shape and morphology of the obtained crystals. In this case, the preferential adsorption of organic molecules to different faces of inorganic crystallites prohibits crystal growth or nanoparticle aggregation, and fusion in these crystallographic directions results in anisotropic growth.^[160] It was speculated for the observed hydrothermal carbonization that, by analogy, a starch-gel matrix formed in situ may have served as a structure-directing agent for the growing silver nanowire, thereby aligning the silver nanoparticles in the preceding examples.^[157]

4.3. Related Carbonization Reactions with Additional Structure-Directing Agents

Yu and co-workers used poly(vinyl alcohol) (PVA) both as the carbon source and the structure-directing agent in their investigations. The authors subjected PVA to a hydrothermal treatment in the presence of AgNO_3 and obtained silver nanocables many micrometers long and coated with cross-linked PVA.^[161] The cables gave rise to bundles, and their tendency to entangle indicated a certain degree of flexibility. The addition of glucose derivatives to the reaction mixture led to less entangled “cables” with a higher aspect ratio (Figure 6).^[162] Interestingly, the utilization of fructose instead of glucose as the molecular precursor yielded carbon nanospheres, whereas sucrose led to a mixture of both “cables” and spheres. This significant and intricate effect of the molecular structure of the precursors on the outcome of the carbonization is in no way explained by either of the mechanistic models outlined above and, thus, highlights that a better understanding of the underlying processes is still required.

Furthermore, Yu and co-workers demonstrated that the concerted process of metal-ion reduction and carbonization

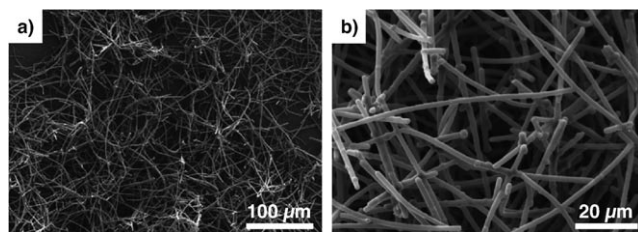


Figure 6. The addition of poly(vinyl alcohol) as a directing agent in the hydrothermal processing of starch yielded carbon-coated silver nanowires with a very uniform diameter of 1 μm .^[162] Reprinted from *Chem. Commun.*; copyright 2006 The Royal Chemical Society, with permission.

could be decoupled.^[163] Thus, poly(vinylpyrrolidone) (PVP) was used as a stabilizing and structure-directing agent^[164] as the first step in the synthesis of tellurium nanowires. In a second step, the nanowires were coated with a partially graphitic carbon shell derived from the hydrothermal carbonization of glucose. The thickness of the shell was adjusted by the reaction time and, similar to the development of the molecular weight in polycondensations, a particularly rapid increase was found toward the end of the reaction. Moreover, irregularly shaped, carbon-coated Se nanocapsules were obtained by subjecting selenous acid and starch to the microwave-assisted hydrothermal carbonization.^[165] Simple heating to 250 °C in a vacuum sufficed to quantitatively remove the selenium cores to afford micrometer-sized hollow carbon capsules.

Low-molecular-weight surfactants instead of polymers have also been used as structure-directing agents in the hydrothermal carbonization. For example, Xu and co-workers prepared carbon/copper nanowires from hexamethylenetetramine as the carbon source in the presence of cetyltrimethylammonium bromide (CTAB).^[166] The obtained nanowires were up to 40 μm long, had diameters in the range of 80 to 400 nm, and appeared to be rigid, with occasional 90° kinks. Fang et al. reported that the observed morphology of Ag/C hybrid nanoparticles from silver nitrate and ascorbic acid depended on the concentration of CTAB.^[167] Spheres were obtained at low concentrations of the surfactant, while cables were produced at higher concentrations. Similarly, Ma et al. prepared Ag/C nanocables up to 180 μm long from salicylic acid, sulfamic acid, and AgNO_3 in aqueous solution.^[168]

4.4. Scope and Limitations of Hydrothermal Syntheses

As illustrated by the above examples, hydrothermal treatment of carbohydrates represents a viable and simple route to prepare intriguing novel types of carbon as well as carbon–inorganic hybrid nanostructures. However, virtually nothing is known about the mechanism of the carbonization on the molecular level and, hence, the potential origin of structural control. The explicit role of the structure-directing agents is yet to be elucidated, and there is no control over the microstructure of the obtained carbon materials. An improved understanding of the mechanism of the carbonization and formation of the nanostructure is required to pave the way for the synthesis of materials with tailored morphology and carbon microstructure. Some sort of carbon-rich intermediates must eventually be formed during the process, and the amphiphilicity of these intermediates must play a role in controlling the mesoscopic morphology of the assembling aggregates. For this reason, the synthesis and self-organization of well-defined carbon-rich molecular precursors and their subsequent conversion into carbon materials may provide both an insight into the mechanism of the hydrothermal carbonization and an alternative pathway toward novel carbon nanostructures. The status of research in this area will be discussed in the following section.

5. Self-Assembly and Pyrolysis of Carbon-Rich Molecular Precursors

In view of the ambiguities in the hydrothermal processes outlined above, that is the lack of knowledge concerning the mechanism of formation of carbon nanostructures and, in particular, the role of the directing agent in this process, the direct utilization of well-defined carbon-rich molecular precursors and their self-assembly into nanostructured phases prior to carbonization by pyrolysis appears to be a viable alternative.^[169] In addition to a certain degree of predictability of the obtained mesoscopic structures, this strategy may allow for “error-correction” before the system is covalently captured in the course of carbonization.

5.1. Self-Assembly of Polycyclic Aromatic Hydrocarbons

Müllen and co-workers pursued a promising approach in which alkyl-decorated polycyclic aromatic hydrocarbons (PAHs) were used. These molecules formed liquid-crystalline phases in the bulk phase or self-assembled nanostructures in solution, and were subsequently pyrolyzed in a stepwise manner in these ordered phases. In addition to their solubilizing effect, the attached alkyl chains provide a strong driving force for supramolecular self-assembly.^[170–172] The disk-shaped PAHs are efficient mesogens which, upon decoration with alkyl groups, exhibit phase segregation between the aromatic cores and the aliphatic peripheries, and thus reliably give rise to hexagonal columnar phases (HCPs). While changes in the number, position, or nature of the attached alkyl chains did not lead to the formation of different mesophases, the thermal stability of the aggregates was influenced by the symmetry of the aromatic core.^[172,173] Thus, the formed HCPs were stable over a broad range of temperatures for many hexa-*peri*-hexabenzocoronene (HBC) derivatives,^[170] and the HCP of one large PAH derivative was even stable up to 550 °C.^[174]

The phase segregation between the alkyl substituents in the periphery and the aromatic cores in combination with the extensive π – π stacking of the large aromatic systems and the high degree of order inside the columns of the HCPs gives rise to a high charge carrier mobility along the column axis. This property makes these systems interesting candidates for application in photovoltaic devices or organic field-effect transistors (OFETs).^[175,176] For the last application, an edge-on alignment of the PAH molecules on the gate and insulator surface is required. Several manufacturing techniques have been developed to meet this requirement,^[176] among which the films obtained by soft-landing mass spectrometry excelled because of their high crystallinity (Figure 7);^[177] however, the scalability of this approach is probably limited.

In a complementary solution-based approach, Aida and co-workers prepared graphitic nanotubes with a uniform diameter of 20 nm and lengths of hundreds of nanometers by self-assembly of an amphiphilic hexa-*peri*-hexabenzocoronene in THF (Figure 8). The addition of water to the solution resulted in the observation of both helices and tubes. The authors thus speculated that the amphiphiles aggregated into

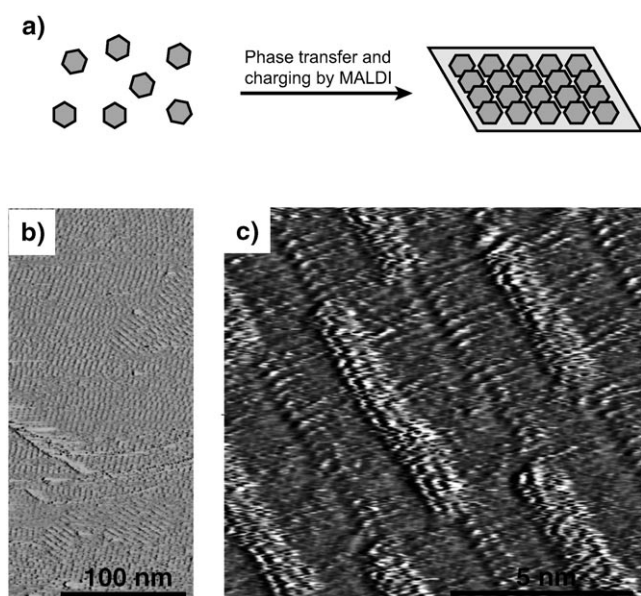


Figure 7. Top: Schematic representation of the preparation of highly crystalline monomolecular films made from hexa-*peri*-hexabenzocoronene (HBC) by soft-landing mass spectrometry. Bottom: STM overview and high magnification image of a highly crystalline film of the HBC film.^[177] Reprinted from *Nature Materials*; copyright 2006 Nature Publishing Group, with permission.

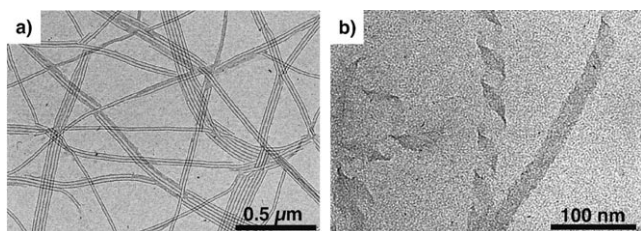


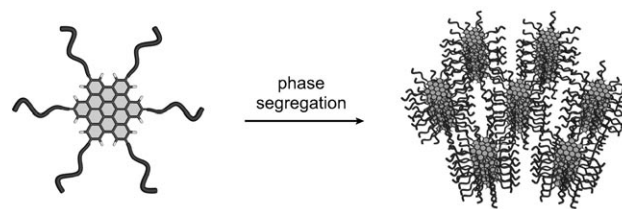
Figure 8. TEM images of self-assembled aggregates of an amphiphilic HBC derivative. a) Tubes with a uniform diameter were observed in a THF solution. b) The addition of water to the THF solution resulted in the observation of both tubes and helices.^[178] Reprinted from *Science*; copyright 2004 American Association for the Advancement of Science, with permission.

tapelike mesostructures which were then rolled up to form the observed tubules.^[178] A systematic investigation of this system allowed Jin, Fukushima, Aida, and co-workers to establish that the amphiphilic character is essential for the nanotubular assembly and to deduce important structural parameters. Most importantly, a desymmetrization of the molecule by incorporation of two phenyl rings on one side of the HBC allowed the molecules to π - π stack into a stable helical superstructure.^[179]

5.2. Pyrolysis in Ordered Phases of Simple Polycyclic Aromatic Hydrocarbons

The alkyl-decorated HBC derivatives, in particular, are ideal precursors for the preparation of nanostructured carbonaceous materials by mild pyrolysis because of their

convenient synthetic accessibility from small poly(phenylene) dendrimers and the reliable formation of a HCP as a defined supramolecular architecture (Scheme 7).^[180] Thus, Müllen and



Scheme 7. Discotic hexakis(dodecyl)-HBC forms a hexagonal columnar mesophase which is stable to temperatures of up to 400°C.

co-workers prepared carbon nanostructures from hexakis-(dodecyl)hexa-*peri*-hexabenzocoronene by utilizing a two-step heating protocol. In the first stage, the sample was heated to 400°C, which is below the isotropization temperature of the HCP but, at the same time, provides enough energy to promote partial cleavage of the alkyl groups, thereby producing a network of larger PAH structures and establishing a new discotic mesophase stable up to 600°C. After this pretreatment, the actual pyrolysis was initiated by heating the sample to 800°C for 24 h. Among the observed carbon nanostructures were spheres, bamboo-shaped microfibers, and multi-wall nanotubes (Figure 9a–d). Both the support (for example, quartz or mica) and the pyrolysis temperature had a significant influence on the morphology of the obtained nanostructures. Thus, microspheres as well as nanocolumns with a square cross-section were obtained on quartz at 800°C, while donut-shaped nanoparticles were obtained at 650°C.^[181]

The propensity of alkylated HBC derivatives to form columns aligned edge-on on glass or aluminum oxide surfaces was exploited by Müllen and co-workers in a templated version of this pyrolysis to prepare nanostructured carbon materials with tailored mesoscopic morphology and novel types of carbon microstructures.^[182] Thus, a solution of hexakis(4-dodecylphenyl)-HBC was dispersed in a macroporous anodic alumina membrane with straight channels. Upon evaporation of the solvent, the channels of the alumina template were coated with a thin film of the HBC derivative, which formed densely packed columns that were aligned parallel to the axes of the channels. This self-assembled molecular precursor phase was then pyrolyzed in a two-step temperature protocol. Annealing at temperatures of 400–650°C served to stabilize the obtained supramolecular structure. In a second step, carbonization at 900°C followed by removal of the template using aqueous sodium hydroxide then yielded unusual, “brick-walled” carbon nanotubes with 20 nm thick graphitic layers oriented perpendicularly to the tube axis (Figure 9e–g). In contrast, samples heated directly to 900°C had less-ordered graphene layers in their walls, thus highlighting the role of supramolecular preorganization and the associated importance of the chosen processing methods.^[183] Similarly, the utilization of diethynyl-substituted tetraarylcyclopentadienone derivatives as the precursors in the presence of an alumina template yielded hyperbranched

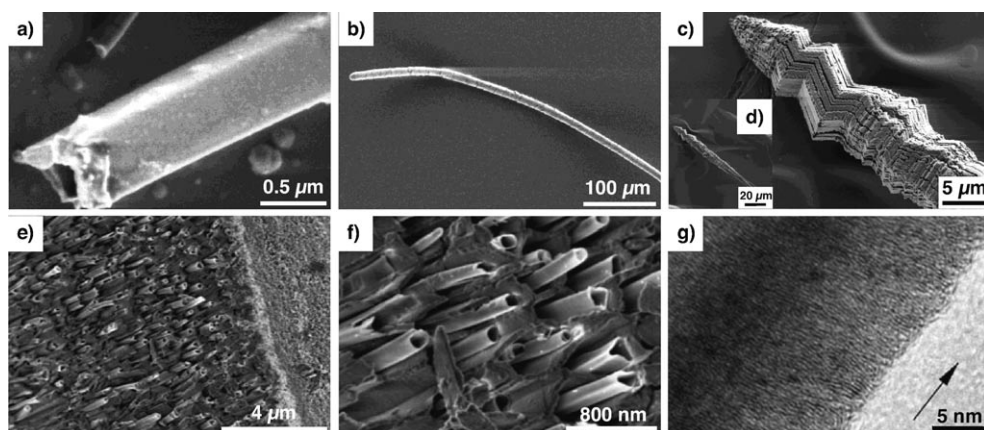


Figure 9. Carbonaceous nanostructures obtained from the pyrolysis of HBC derivatives. a) Hollow nanotubes with a rectangular base, b) bamboo-shaped carbon microfibers, and c,d) zigzag-shaped carbon nanostructures with a length of several millimeters were obtained by pyrolysis of hexakis(dodecyl)-HBC in its mesophase.^[187] e,f) The pyrolysis of hexakis(4-dodecylphenyl)-HBC in an anodic alumina template yielded uniform predominantly open-ended carbon nanotubes. The walls consist of graphene layers which are oriented perpendicularly to the stacking direction.^[183] Reprinted (a–d) from *J. Am. Chem. Soc.*; copyright 2002 American Chemical Society, with permission.

poly(phenylene)s, which were subsequently converted into porous carbon nanotubes. After dispersing a solution of the substrate in the template followed by evaporation of the solvent, the sample was heated to 200 °C to ensure homogeneous coverage of the channel walls. At 250 °C, cross-linking occurred through a Diels–Alder reaction. Pyrolysis at 600 °C yielded carbonaceous nanotubes with highly porous tube walls after etching away the template with aqueous sodium hydroxide.^[184]

The template employed had a significant influence on the morphology of the obtained carbon-rich nanostructure. Thus, when hexakis(4-dodecylphenyl)-HBC was pyrolyzed in an inverse silica opal by a three-step temperature protocol, solid carbon nanoparticles were obtained after removal of the template with dilute hydrofluoric acid. The particles exhibited a layered structure that was probably derived from the precursor molecules. The use of an alkylated diethynyl-substituted tetraarylcyclopentadienone as the molecular precursor in the same template led to the formation of solid spheres when the sample was heated to 350 °C. Further heating to 600 °C yielded highly porous carbon nanoparticles as a result of the loss of pendant alkyl chains.^[185]

5.3. Pyrolysis of Transition-Metal-Containing Precursors

In a seminal paper, Kroto and co-workers investigated the use of various transition-metal catalysts in the pyrolytic preparation of carbon nanotubes from acetylene gas.^[186] According to their investigation, $[\text{Mn}_2(\text{CO})_{10}]$ and $[\text{Co}_4(\text{CO})_{10}]$ proved to be the best catalyst precursors for the formation of nanotubes. Vollhardt and co-workers later modified this strategy and synthesized tetraphenyldehydro[20]annulene to which $[\text{Co}_2(\text{CO})_8]$ was complexed, thus incorporating the catalyst precursor in the carbon-rich molecular precursor itself. Large quantities of carbon onions

as well as multi-wall carbon nanotubes were formed upon heating this compound to 800 °C.^[187]

Bunz and co-workers similarly obtained carbon onions in the explosive decomposition of a ferrocene-containing dehydro[18]annulene. Supramolecular preorganization was crucial in these transformations, since only single-crystalline material exhibiting van der Waals contacts between acetylene carbon atoms yielded the desired carbonaceous material.^[188] Intriguingly, significantly simpler precursor molecules could be employed in the metal-assisted pyrolytic preparation of comparable

carbon nanostructures, as demonstrated by Vollhardt and co-workers. Thus, large quantities of carbon nanotubes were obtained when $[\text{Co}_2(\text{CO})_8]$ was complexed to tolane and the resulting material annealed at 650 °C (Figure 10). Interest-

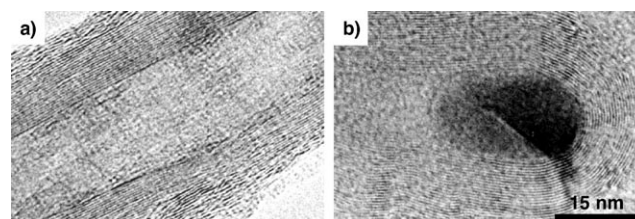


Figure 10. Annealing of $[\text{Co}_2(\text{CO})_8](\text{PhC}_2\text{Ph})$ at 650 °C yielded large amounts of multi-wall CNTs. The tips occasionally contained small cobalt crystals.^[189]

ingly, the use of an excess of tolane or adding hexaphenylbenzene as a substrate yielded essentially the same carbon nanostructures, which was interpreted as circumstantial evidence for an initial cyclotrimerization of the transition-metal complex during the process.^[189]

The incorporation of cobalt catalyst precursors into a PAH was accomplished by complexing $[\text{Co}_2(\text{CO})_8]$ to the acetylene moieties of hexakis(1-dodecylethynyl)-HBC. Pyrolysis was carried out at 600 °C, 800 °C, or 1000 °C after an initial heating to 250 °C to prepare the catalyst. While reactions at 800 °C or 1000 °C yielded bamboo-shaped carbon nanoparticles, prolonged annealing at 600 °C favored the formation of straight carbon nanotubes.^[190] In a large survey, various transition-metal complexes of carbon-rich molecular precursors, including three HBC derivatives, a hexaphenylbenzene derivative, a thiophene derivative, larger PAHs, as well as linear and star-shaped oligo(phenyleneethynylene)s were heated to different temperatures.^[191] Cobalt-containing PAH

precursors all resulted in multi-wall CNTs, with the yield increasing with the amount of cobalt. Interestingly, the related ruthenium-containing precursor produced carbon nanorods, thus indicating the influence of the metal on the obtained nanostructures. The branched 1,3,5-tris(phenylethynyl)benzene yielded carbon nanospheres when the pyrolysis was carried out at 700°C, or rods when the temperature was 850°C.^[191]

5.4. Pyrolysis of Heteroaromatic Compounds

The pyrolysis of heteroaromatic compounds enables the preparation of carbon-rich nanostructures with a heteroatom dopant. Thus, Müllen and co-workers pyrolyzed cobalt-containing phthalocyanines at 600°C, 800°C, and 1000°C. At 800°C and 1000°C, kinked carbon nanotubes were obtained, but the amount of nitrogen dopant incorporated into the tubes decreased as the pyrolysis temperature increased.^[192]

In a templated approach, *tert*-butylnaphthalocyaninato-nickel, which tends to form columns similar to the HBC derivatives, was carbonized inside a macroporous aluminum oxide template. Annealing at 400°C sufficed to cleave the *tert*-butyl groups, and pyrolysis at 600°C then yielded carbon nanotubes after removal of the template with aqueous NaOH. Similar to the related templated carbonization of PAHs inside alumina templates, the stacking direction of the graphite layers was perpendicular to the tube axis, and small nickel crystallites were found to be enclosed in the walls.^[193]

By analogy to the preparation of carbon fibers from polyacrylonitrile, polymer precursors have also been used for the preparation of carbon nanostructures with retention of their mesoscopic morphology by utilizing a pyrolytic process in the presence of a transition metal. For example, Jang and Yoon prepared polypyrrole (PPy) nanoparticles with a diameter of 62 nm by an emulsion polymerization of pyrrole using FeCl₃ in the presence of decyl alcohol as an emulsifier.^[194] Subsequent pyrolysis at 800°C then yielded graphitized carbon nanoparticles which were magnetic as a result of incorporated γ -Fe₂O₃ (Figure 11a,b). In another investigation, pyrrole was polymerized using CuCl₂ in a microemulsion polymerization, which yielded alcohol-soluble PPy nanoparticles.^[195] The addition of more monomer followed by FeCl₃ resulted in the formation of a shell of insoluble and, presumably, cross-linked PPy around the initial polymer. The resulting core-shell nanoparticles had a diameter of 33 nm. Methanolysis of the core yielded hollow PPy nanospheres which were then converted into hollow carbon nanocapsules by pyrolysis at 1000°C. Similar to the previous example, a layered graphitic structure was observed in high-resolution TEM (HRTEM) images (Figure 11c).

Moreover, Jang and Oh demonstrated that the same approach could be used to produce nanostructures constructed from a single layer of graphite. Thus, pyrolysis of PPy precursors with diameters as small as 2 nm at 950°C afforded a mixture of fullerenes (predominantly C₆₀, less C₇₀, and small amounts of higher fullerene species) in a yield of 18% from the crude product after extraction with toluene. The yield

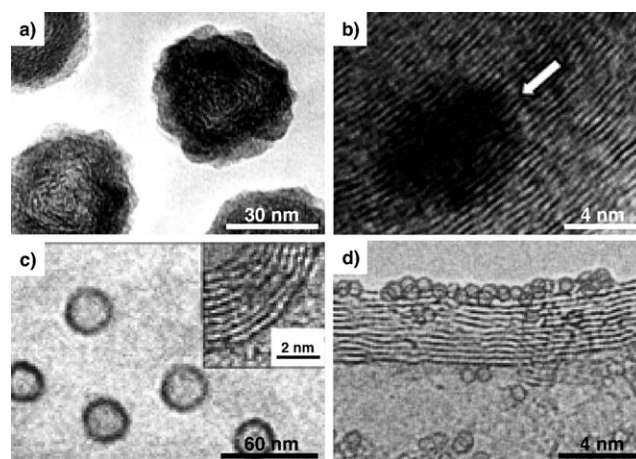


Figure 11. a,b) TEM images of magnetic carbon nanoparticles prepared by pyrolysis of 62 nm large PPy nanoparticles. γ -Fe₂O₃ is embedded into the layered carbon structure of the porous nanoparticles (as indicated by the white arrow; b).^[194] c) TEM image of hollow carbon nanospheres obtained after pyrolysis of 33 nm large hollow PPy nanoparticles. The inset shows the layered structure of the shell.^[195] d) Fullerenes on multi-wall CNTs prepared by pyrolysis of PPy precursor molecules with a diameter of 2 nm. The multi-wall CNTs were added to visualize the fullerenes which were otherwise invisible because of their very small contrast against the thin carbon film of the TEM grid.^[196] Reprinted (c) from *Chem. Commun.*; copyright 2006 The Royal Chemical Society, with permission.

could be increased to 24% at a pyrolysis temperature of 1100°C (Figure 11d).^[196]

PPy nanotubes were prepared by vapor deposition polymerization in an anodic alumina template which had been pretreated with FeCl₃. Etching the template with NaOH yielded pyrolysis precursors with a tubular morphology that gave rise to carbon nanotubes with imperfect graphite layers oriented parallel to the tube axis after pyrolysis at 1000°C or 2000°C.^[197] In a related solution-based approach, Shang et al. used the fibrillar aggregates of the anionic form of methyl orange (sodium 4-[4-(dimethylamino)-phenyldiazo]phenyl-sulfonate) and FeCl₃ as a reactive self-degradable seed template.^[198] The resulting PPy nanotubes were pyrolyzed at 900°C to yield nitrogen-doped amorphous carbon nanotubes.

5.5. Scope and Limitations of the Pyrolysis of Carbon-Rich Molecular Precursors

In summary, the self-assembly and subsequent pyrolytic conversion of molecularly defined, carbon-rich precursors into carbon nanostructures constitutes a simple and efficient approach toward novel types of carbon nanostructures. It is important to note that supramolecular preorganization plays a crucial role in exerting control over the mesoscopic morphology of the final carbon materials. At the same time, however, it must be acknowledged that the number of realizable supramolecular structures from HBC derivatives is somewhat limited to columnar aggregates because the strong π - π stacking tendency of these molecules will dominate over any other intermolecular interactions. As the

aromatic cores do not only provide the driving force for the formation of supramolecular structures, but also represent the carbon source, the scope of this approach is strongly biased toward one-dimensional (tubular or rod-shaped) carbon nanostructures. Although the elegant synthesis of HBC precursors appears to be sufficiently concise and efficient to be conveniently applied on a larger reaction scale, the synthesis of the precursor molecules may still be too complex in other cases. Most importantly, however, the temperatures required for the carbonization reaction remain prohibitively high for the incorporation of functional groups, even in the case of transition-metal-catalyzed carbonizations, and will, hence, limit the use of these pyrolytic approaches in the fabrication of functional carbon nanostructures.

6. Electrochemical Carbonization of Perfluorocarbons

In contrast to the “classical” methods highlighted in Section 2, the pyrolysis of carbon-rich molecular precursors discussed in Section 5 made good use of the supramolecular preorganization of the precursor molecules, but the employed reaction conditions were still drastic. A complementary approach is the electrochemical carbonization of molecular precursors by using amalgamates. This method is similar to the “classical” methods in the sense that no element of supramolecular control is present, but it can be performed at room temperature.^[199] For example, poly(tetrafluoroethylene) (PTFE) was successfully carbonized using amalgamates or electrochemically in electrolyte solutions. The resulting materials contained a high content of sp-hybridized carbon.^[199,200] Carbonization of highly oriented PTFE films with liquid lithium and sodium amalgams yielded grained carbon films in which the “ribbed” structure of the PTFE precursor was conserved to some extent, as evidenced by AFM. Similarly, vapors of low-molecular-weight perfluorinated alkanes were carbonized with alkali amalgams to produce films. The morphology and microstructure of these films were, however, not further characterized.^[201] A 1 μm thick carbon film supposedly containing acetylenic structures was formed by using a sacrificial Mg anode. TEM measurements revealed that the crystallinity of the PTFE precursor was completely destroyed.^[202] Postsynthetic annealing of the obtained films at 600 °C or 800 °C in combination with electron irradiation in a transmission electron microscope was reported to yield carbon nanotubes.^[203,204] Despite these efforts, the scope of the electrochemical approach seems limited by the exclusive use of perfluorocarbon precursors, the lack of supramolecular control, and because the utilization of amalgamate reactants, while allowing for notably milder conditions in terms of temperature, is still incompatible with most functional groups.

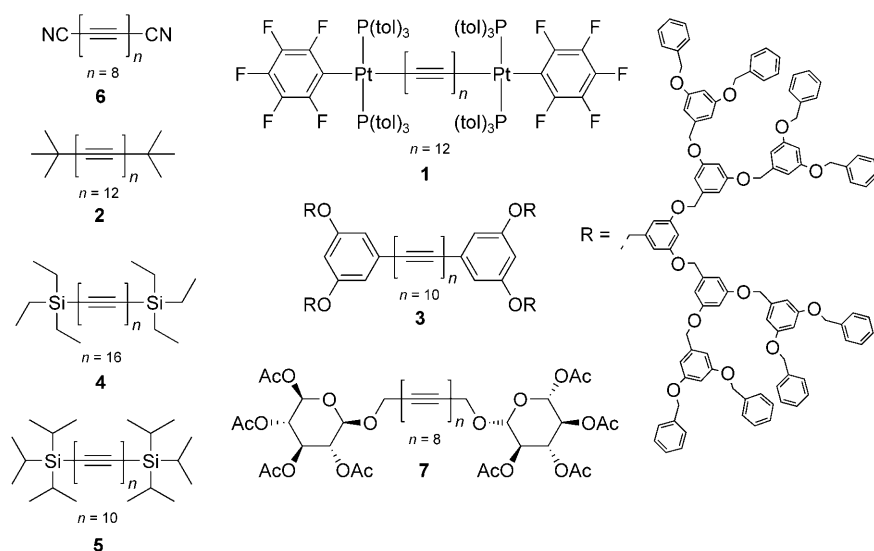
7. Carbonization of Energy-Rich Precursors

Since surface functionalization of the carbon-rich materials and control over their mesoscopic morphology are both

important aspects for many applications, the combination of mild carbonization conditions and supramolecular preorganization of the functionalized precursors are desirable. This goal may be achieved with energy-rich carbon-rich molecular precursors, that is, molecules that are thermodynamically metastable in the sense that they have an inherent reactivity toward rearrangement into other carbon allotropes. Examples of such molecules are linear oligo(ethynylene)s, cyclo-[*n*]carbons, perethynylated olefins and arenes, dehydroannulenes, or radialenes, as had already been conjectured by Diederich et al.^[33,34] Among the possible candidates, oligo(ethynylene)s appear to be the ideal choice because they are reactive, yet stable enough to be prepared and handled in macroscopic quantities.

7.1. Reactivity of Oligo(ethynylene)s

Sufficiently long oligo(ethynylene)s are thermodynamically unstable and exhibit an inherent reactivity toward rearrangement into other, more-stable carbon allotropes. A possible involvement of oligo(ethynylene)s in the formation mechanism of fullerenes has been discussed,^[205] and the generation of dicyanide-end-capped oligo(ethynylene)s by means of evaporation of graphite in the presence of (CN)₂ may be interpreted as circumstantial evidence for this hypothesis.^[206] However, the deliberate utilization of oligo(ethynylene)s as precursors for carbon-rich materials has rarely been addressed to date, mainly because most investigations concerning oligo(ethynylene)s have explicitly aimed at the preparation of stable derivatives as model compounds for the hypothetical, one-dimensional sp-hybridized carbon allotrope “carbyne” (C \equiv C)_∞. The achievements in this field have recently been reviewed,^[207] as has an impressive collection of crystallographically characterized oligo(ethynylene)s.^[208] While the thermodynamic stability of the reported oligo(ethynylene) derivatives R-(C \equiv C)_{*n*}-R drastically decreases as the number *n* of repeating units increases, they may be kinetically stabilized by an increasing steric demand of the substituents R (see Scheme 8). For example, butadiyne can be distilled, but rapidly polymerizes above 0 °C, while neat hexatriyne is reported to be explosive.^[209] End-capped oligo(ethynylene)s with up to 14 conjugated triple bonds have been isolated, such as Me-(C \equiv C)₆-Me,^[210] Pfp-(C \equiv C)₈-Pfp,^[211] (Pfp = pentafluorophenyl), (CH₃)₃C-(C \equiv C)₁₀-C(CH₃)₃,^[212,213] and TIPS-(C \equiv C)₁₀-TIPS.^[214] In the latter case, the differential scanning calorimetry traces of the series of bis(triisopropyl)-substituted derivatives TIPS-(C \equiv C)_{*n*}-TIPS showed reversible melting for the di- to the hexa(ethynylene). However, the tetra(ethynylene) and all higher homologues exhibited irreversible exothermic transitions at higher temperatures, thus indicating an insufficient kinetic stabilization by the TIPS end groups. Hirsch and co-workers attempted to maximize the steric shielding by attaching third generation (G3) Fréchet-type dendrons as end groups and, in this way, obtained the stable (G3)-(C \equiv C)₁₀-(G3).^[215] Furthermore, Zheng and Gladysz successfully prepared L_{*n*}Pt-(C \equiv C)₁₄-PtL_{*n*}.^[216]



Scheme 8. Various oligo(ethynylene) compounds synthesized so far on the way to carbyne. Dodecayne **1** was synthesized by Gladysz and co-workers.^[217] Walton and co-workers synthesized *tert*-butyl-functionalized dodecayne **2**^[218] and the record-breaking oligo(ethynylene) **4**, which was identified by UV spectroscopy.^[219] The massively shielded series of oligo(ethynylene)s **3** up to the decayne^[220] and the nitrile-capped series of oligo(ethynylene)s **6**^[221] were reported by Hirsch and co-workers. The triisopropylsilyl-protected decayne **5** was synthesized and characterized by Tykwinski and co-workers.^[214] Glycosylated octayne **7** was prepared by Hoheisel and Frauenrath.^[222]

7.2. Nontemplated Carbonization of Oligo(ethynylene)s

In an investigation originally aimed at the preparation of “carbyne” ($\text{C}\equiv\text{C}$)_∞, Lagow et al. were the first to report the accidental use of oligo(ethynylene)s as molecular precursors for carbonaceous materials. When testing the stability of $(\text{CH}_3)_3\text{C}-(\text{C}\equiv\text{C})_4-\text{C}(\text{CH}_3)_3$ under pressure, 2 % of the material underwent graphitization at 60 kbar.^[106] Kavan and Hlavaty, on the other hand, had postulated the presence of a reactive, disordered form of poly(ethynylene)s as the intermediates in their investigations on the preparation of fullerenes and CNTs by electrochemical defluorination of PTFE (Section 6),^[223] and, therefore, explored the “polymerization” of 1-iodohexatriyne, hexatriyne, as well as its dialkylaluminum salts in organic solution at or below room temperature.^[224, 225] The unsubstituted hexatriyne and 1-iodohexatriyne started to react readily at 0 °C and room temperature, respectively, to afford mixtures of different carbonaceous materials containing a few instances of multi-wall carbon nanotubes among the different types of amorphous carbon material.^[224] The carbon nanotubes had diameters of 10–20 nm and lengths of 100–200 nm, and were end-capped with “onionlike” nanoparticles. The corresponding dilithium and dipotassium α,ω -hexatriynides could not be isolated because “carbonization” already occurred during their synthesis.^[225] A few cases of multi-wall carbon nanotubes were observed upon hydrolysis of the poly(dilithiumhexatriynide), whereas the dipotassium oligo(ethynylene) did not yield defined material. Ill-defined carbonaceous materials with a graphitic microstructure were obtained from the in situ deprotection and “polymerization” of bis(triisopropyl)-capped oligo(ethynylene)s.^[226] Finally, the

laser-promoted polymerization of gaseous diacetylene in a nitrogen atmosphere yielded amorphous carbonaceous films.^[227]

Although all of the preceding examples may be regarded as indicative of the potential of oligo(ethynylene)s to be used as molecular precursors for the preparation of carbon materials under mild conditions, it should be noted that, in all cases, the conversion lacks any element of supramolecular control, nothing is known about the pathway of carbonization, product mixtures and only low amounts of defined carbon nanostructures have typically been obtained, and the products have been poorly characterized in most cases.

7.3. Topochemical Polymerization of Oligo(ethynylene)s

The limited control over the morphology of the obtained carbonaceous materials in the preceding examples may be overcome by conducting the carbonization of higher oligo(ethynylene)s in single crystals, in analogy to the well-understood topochemical polymerization of diacetylenes.^[228, 229] Baughman and Yee were the first to report an attempt to topochemically polymerize an octatetrayne dicarbamate.^[230] The polymerization was reported to proceed by a 1,4-polyaddition with unclear regioselectivity. The results were later interpreted by Nakanishi and co-workers as an unselective reaction of the remaining acetylene units after formation of a poly(diacetylene).^[231] These authors also prepared different tetraynes, pentaynes, as well as hexaynes, and investigated their topochemical polymerizability in the solid state.^[231] The polymerization of dithiophene- and diquinoline-substituted tetraynes was achieved by thermal annealing. The recorded UV spectra showed a broad absorption consistent with a controlled 1,4-polymerization.^[232] In both cases, the crystallographic data suggested that a polymerization would more likely proceed by a 1,2-polyaddition, but no residual acetylene bands were detected in the IR spectra or solid-state ¹³C NMR spectra. Likewise, single crystals of a bis(tetradecyl)-substituted hexayne started to polymerize at ambient temperature in the dark, and their color changed from green to black.^[233] The acetylene peaks in the IR spectra disappeared, and the UV/Vis/NIR spectra showed several bands, with the maximum absorption at 776 nm. The UV absorption became very broad over a couple of days, and the resonances in the corresponding solid-state ¹³C NMR spectra were interpreted in terms of the slow formation of a butadiyne-bridged poly(diacetylene) ladder polymer from the initially formed tetrayne-substituted poly(diacetylene). The authors later tentatively interpreted the results in both cases in terms of a subsequent cyclization

reaction toward graphitic ribbon polymers, but the actual experimental evidence to support this claim remains scant.^[231]

Such topochemical reactions offer the ultimate means of control over the preorganization of the molecular precursors. However, their scope in the preparation of carbonaceous materials is probably limited because they impose strict geometric requirements which drastically limit the choice of side groups. In some cases they may even completely prohibit the carbonization. The most important impediment appears to be the fact that the carbon atom density of a “one-dimensional stack of oligo(ethynylene)s” is significantly lower than that of the corresponding graphene ribbon with the same number of carbon atoms per side group. Hence, the carbonization must inevitably be accompanied by an increase in the number of carbon atoms per length unit in the ribbon direction. This must in turn lead to a considerable lateral contraction which is unlikely to be tolerable without destruction of the crystal structure. Moreover, such single-crystal carbonizations would only yield insoluble material with a limited variation of accessible morphologies.

7.4. Carbonization of Oligo(ethynylene)s in Ordered Phases

Self-assembly in solution or in the mesophase may offer more flexibility in this regard and, at the same time, allow for error correction before the structure is “covalently captured” by carbonization. By exploiting this strategy, Ding and Olesik obtained carbon nanospheres with hydrophilic surfaces when they dispersed deca-2,4,6,8-tetrayne-1,10-diol in a THF/water mixture, heated the mixture to 70 °C, and filtered off the product. The addition of surfactants helped to control the size of the obtained nanospheres efficiently.^[234]

The authors suggested that, initially, ultrathin films had been formed from the amphiphilic molecules, which melted upon heating, were transformed into droplets, and then polymerized into the observed carbon nanospheres (Figure 12). XPS data revealed the presence of a large

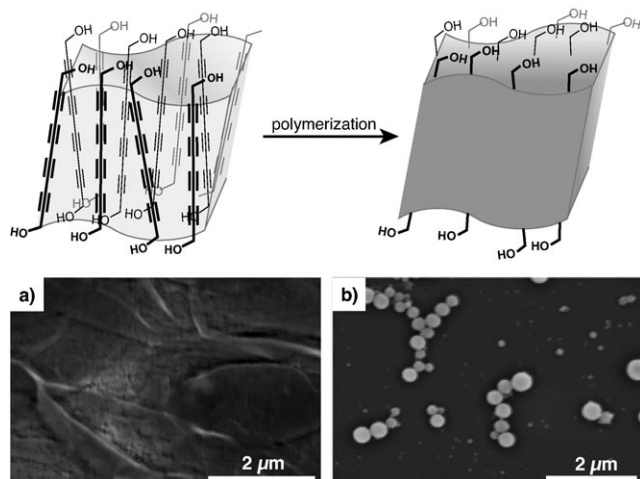


Figure 12. Deca-2,4,6,8-tetrayne-1,10-diol self-assembled into films a) which melted into droplets and b) subsequently polymerized.^[234] Reprinted from *Nano Letters*; copyright 2004 American Chemical Society, with permission.

number of hydroxy groups on the water-soluble nanospheres. Annealing the nanospheres at 150 °C for 12 h and later at 800 °C for 24 h resulted in a weight loss of 39%, which corresponds to the cleavage of the surface hydroxymethyl groups to yield carbon nanospheres. Furthermore, the analogous dibutyloxy derivative was polymerized in the neat liquid state and in an aqueous emulsion with PVA as the emulsifier.^[235] In this case, carbon beads with typical diameters of up to hundreds of micrometers were obtained by pyrolysis at 800 °C. These microbeads could easily be dispersed in organic solvents and did not fuse at elevated temperatures, even at high pressure. In a similar experiment, carbon nanospheres were prepared by Zhao and co-workers from fullerene-substituted tetraynes (Figure 13).^[236] An amor-

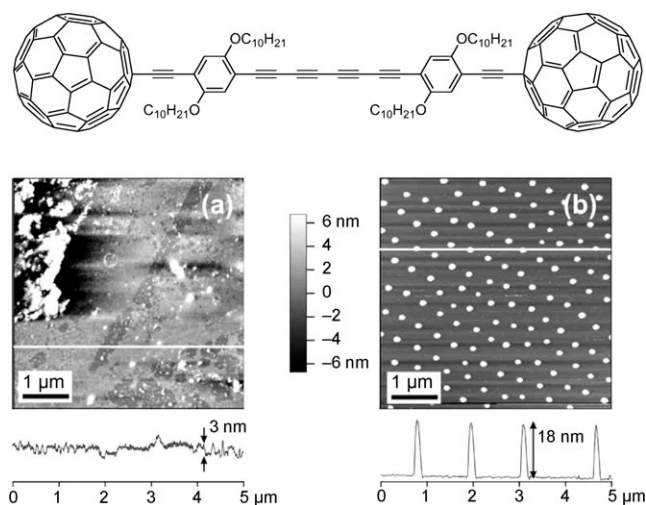


Figure 13. AFM image of a thin film of the fullerene-tetrayne before (left) and after (right) thermal annealing at 160 °C for 1 h.^[236] Reprinted from *J. Am. Chem. Soc.*; copyright 2005 American Chemical Society, with permission.

phous monomer film was observed by AFM after drop-casting a solution of the monomer in toluene on mica. Above temperatures of 160 °, this film was converted into carbon nanospheres with a uniform diameter below 20 nm. The tetra(ethynylene) absorptions in the UV/Vis spectra disappeared during the course of this conversion.^[236]

8. Conclusions

The field of molecular carbon nanostructures and nanostructured carbon materials has seen tremendous progress over the past decade. Very different approaches have been taken, including the now “classical” top-down methods, stepwise organic syntheses, bottom-up approaches such as hydrothermal carbonization, and the self-assembly and carbonization of carbon-rich precursors. It is impossible to say which one of the different strategies is “better” or will deliver materials relevant to technological applications in the near future, because each of them has distinct advantages and

limitations. In each field, landmark results have been achieved in recent years that have provided access to novel types of carbon nanostructures which are currently under active investigation in materials science applications. Among the highlights are the preparation of single graphene sheets, the total synthesis of fullerenes, the preparation of well-defined large or “unusual” polycyclic aromatic hydrocarbons, the hydrothermal synthesis of coaxial carbon–metal nanowires, and the first attempts to utilize oligo(ethynylene)s as energy-rich molecular precursors.

Nonetheless, the desirable preparation of functional nanostructured carbon materials with tailored surfaces, controlled mesoscopic morphology, and defined carbon microstructure remains a distant goal and leaves ample room for exploring novel approaches. Perhaps combining the already employed strategies to make use of their respective advantages may emerge as a viable alternative. A good starting point may be the preparation of well-defined, but sufficiently simple molecular precursors which are conveniently accessible by short and efficient stepwise organic syntheses and then processed by using methods from materials science. Such an approach combines both “bottom-up” and “top-down” elements in that the self-assembly of molecular precursors on the mesoscopic level can be paralleled with a manipulation of the processing parameters on the macroscopic level. As the studies on carbon-rich precursors have demonstrated, control of supramolecular self-organization prior to carbonization is a crucial prerequisite for tailoring the mesoscopic morphology of the obtained materials. Carbonization of the self-assembled precursors under retention or, at least, controlled conversion of the previously attained morphology may then be achieved by employing energy-rich precursors since these would allow sufficiently mild reaction conditions to be employed and, at the same time, be compatible with the incorporation of functional groups. The relevance of novel types of carbon materials for applications in various emerging technologies, such as novel energy sources, efficient energy storage, sustainable chemical technology, and organic electronic materials, renders the search for methods to prepare tailor-made functional nanostructured carbon materials in the coming years an intriguing research field.

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