

New carbon-rich materials for electronics, lithium battery, and hydrogen storage applications

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Methods for the preparation of novel carbon-rich materials for use in electronic devices, lithium batteries or possible hydrogen storage applications are presented.

Introduction

In all the attention given to new functional organic materials, *e.g.* conjugated polymers, it is sometimes overlooked that carbon itself has some very interesting materials properties. Thus diamond which consists of sp^3 -hybridised carbon atoms is one of the hardest substances known, while graphite, which contains sheets of sp^2 -carbon atoms, is conductive. As a result carbonaceous materials based on graphite-like structures, for example carbon nanotubes¹ and fullerenes,² have potential applications in electronic devices, and so have been the subject of considerable research interest in recent times, not just into their fundamental properties but also for practical applications.³ There are three main areas of application for such carbon-rich materials. First, their intrinsic conducting or semiconducting properties makes them suitable for use in electronic devices such as field-effect transistors (FETs),⁴ or solar cells.⁵ Second, it has been shown that materials based on graphene sheets can store lithium for use in secondary batteries.⁶ Third, it has been demonstrated that graphene sheets can adsorb hydrogen, which means they may be able to store hydrogen for use as an alternative fuel in new energy producing technology, *e.g.* fuel cells.⁷ In this article we present an overview of recent progress made at Mainz into the synthesis and characterisation of novel carbon-rich materials for use in the above applications.

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Andrew Grimsdale received his PhD from the University of Auckland, New Zealand (1990) under the supervision of Prof. R. C. Cambie. After performing postdoctoral research with Prof. A. Pelter at University of Wales, Swansea, and Prof. A. B. Holmes at the University of Cambridge, he joined the group of Klaus Müllen in 1999, where he is project leader in charge of research into conjugated polymers. His current research interest is into the synthesis of phenylene-based materials for optoelectronic applications.

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New hexa-*peri*-hexabenzocoronenes with high charge carrier mobilities

Hexa-*peri*-hexabenzocoronene (HBC, **1a**) derivatives form a class of discotic polycyclic aromatic hydrocarbons (PAHs). The discs π -stack to form columnar thermotropic liquid crystalline phases which show very high charge carrier mobilities along the axis of the columns.⁸ As a result solution processable HBCs with alkyl (**1b**) or alkaryl (**2**) substituents have found application as active materials in efficient organic FETs⁹ and solar cells.¹⁰ A major focus of our research into HBCs has been on investigating ways to control their phase-forming properties.¹¹ Of particular importance is the optimisation of the order both within and between the columns as this leads to the highest charge carrier mobilities. Recently we have developed a new method using the hexaiodo derivatives **3** and **4** to make star-shaped HBCs with particularly well-ordered columnar mesophases.^{12,13}

The key step in this new synthesis (Scheme 1) is a six-fold Sonagashira–Hagihara coupling of an alkyne with the hexaiodo HBCs to produce the hexa-alkynes **5** and **6**. What is most remarkable about this synthesis is that the starting hexaiodides are almost totally insoluble in the reaction medium, and yet the reactions typically proceed in quantitative yield, even when the products are also virtually insoluble, *e.g.* **6d**.

The thermotropic phase behaviour of the HBCs **6** is of great interest as it indicates the degree of order in the columns which in turn determines the charge carrier mobility. The hexa-alkylethynyl derivative **6a** shows similar phase behaviour to the alkaryl HBCs **2**, as it exists in a hexagonal columnar phase

Johannes-Gutenberg University, Mainz (2004) for work under Professor Müllen on the synthesis and supramolecular chemistry of discotic graphitic materials. He is currently project leader for the synthesis and materials applications of polycyclic aromatic hydrocarbons within the group of Professor Müllen.

Klaus Müllen received his Diplom-Chemiker degree from Cologne University (1969) and his PhD from the University of Basel, (1972) under the supervision of Prof. F. Gerson. After habilitating from the group of Prof. J. F. M. Oth at ETH, Zürich, (1977) he accepted chairs at Cologne and then Mainz, before joining the Max-Planck Society as a director of the Max-Planck-Institute for Polymer Research, Mainz, in 1989. His current research interests are centred around synthetic macromolecular chemistry and materials science.

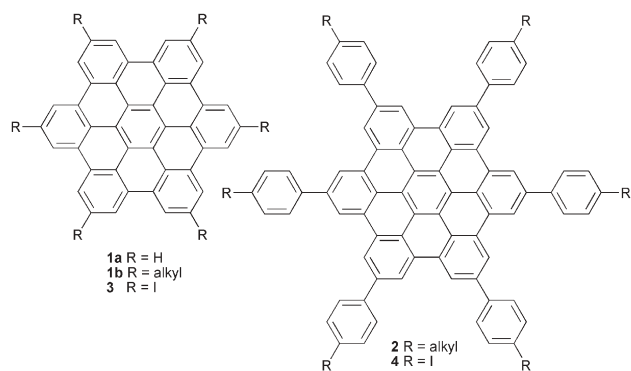


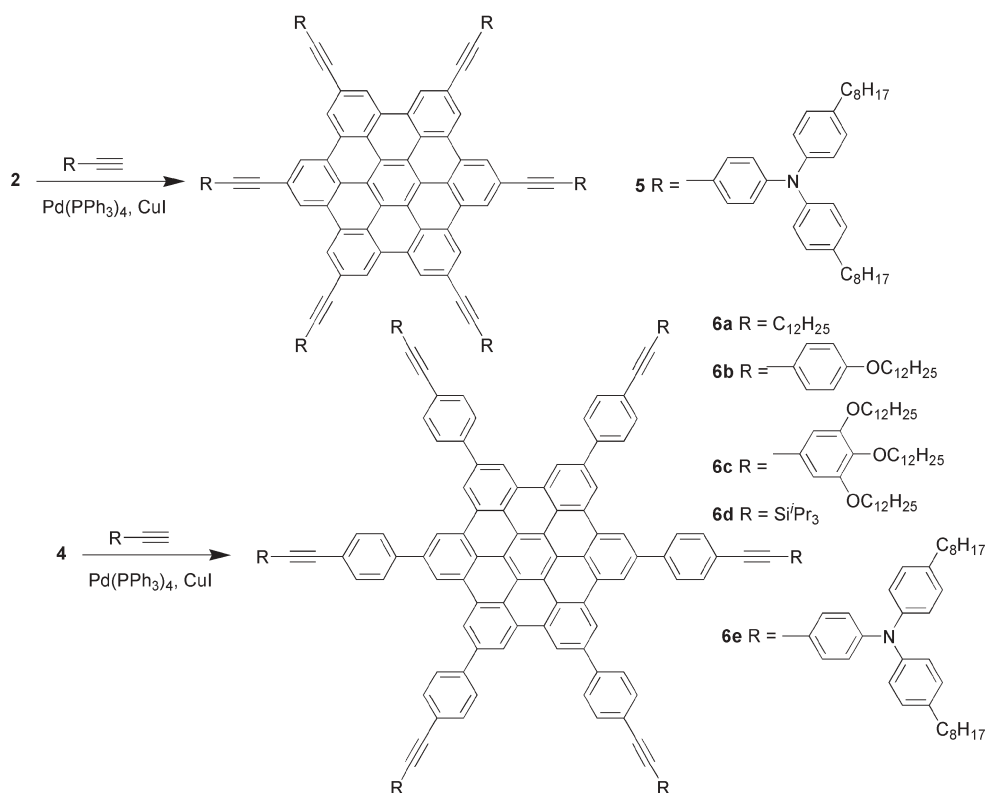
Fig. 1 Alkyl- and iodo-substituted HBC derivatives.

(**D_h**) at room temperature, with two phase transitions between columnar mesophases detected at lower temperature by differential scanning calorimetry (DSC). By contrast **6b** with an alkaryl group on the other side of the ethynyl bonds forms a **D_h** phase only after heating to ~ 86 °C, and is in a hexagonal helical phase (**D_{hh}**) at room temperature. A derivative **6c** with three alkoxy substituents on the outermost aryl rings also displays an ordered helical **D_{hh}** phase at room temperature, but a disordered columnar phase above 75 °C.^{12b} These differences in phase behaviour are attributable to the increasing steric bulk of the terminal substituents as one goes from **6a** to **6c**, which affects the packing.

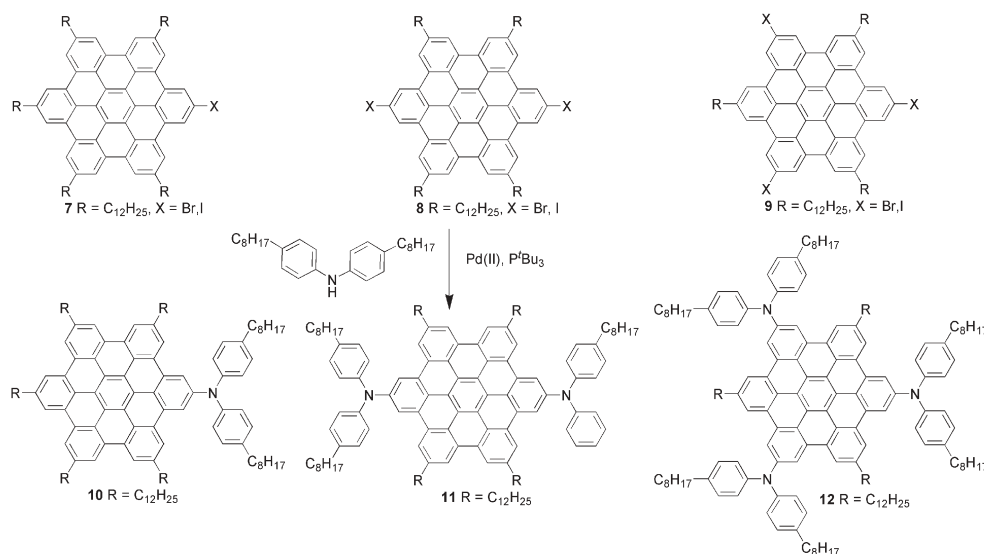
It was anticipated that attachment of electroactive triarylamine substituents around the periphery of HBCs might enhance their hole mobilities, as a coaxial columnar stacking

would produce two paths for charge transport – along the stacks of the amines on the outside and along the HBC columns in the core – a so-called “double-cable” approach. Accordingly the derivatives **5** and **6d** were prepared. These materials do not show any phase transitions on DSC, but two-dimensional wide-angle X-ray diffraction (2D WAXD) measurements on extruded fibres revealed hexagonal columnar stacking arrangements over a wide temperature range.^{13a} The room temperature charge carrier mobilities for **5** and **6d** were determined to be 0.03 and 0.04 cm² V⁻¹ s⁻¹ by pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) measurements.^{13a} These values are lower than the value of 0.22 cm² V⁻¹ s⁻¹ observed for the room temperature liquid crystalline phase of an alkaryl HBC (**2** R = C₁₂H₂₅)⁸ which is consistent with the lower degrees of order seen in these materials. Accordingly the HBCs **7–9** with 1–3 iodine (or bromine) substituents were subjected to Buchwald coupling with a diarylamine to give the triarylamine-substituted derivatives **10–12** (Scheme 2).^{13a}

These materials, unlike **5** and **6d**, do show phase transitions in DSC, with both **10** and **11** possessing both columnar microcrystalline and liquid crystalline phases, while **12** showed only a crystalline phase below its melting point. The room temperature charge carrier mobilities obtained by PR-TRMC for **10–12** were 0.11, 0.21, and 0.01 cm² V⁻¹ s⁻¹ respectively. The orders of mobilities are in qualitative agreement with the degree of sharpness of the images obtained from WAXD experiments, which again illustrates the correlation between packing order and charge carrier mobility. One unanswered question is whether the high charge carrier mobility reflects



Scheme 1 Hagihara route to new star-like HBC derivatives.



Scheme 2 Buchwald route to triarylamine-substituted HBC derivatives.

efficient hole transport between the amine units, which would imply that these discotic materials have much higher hole carrier mobilities than are seen in disordered triarylamine solids, or that the electrons which remain localised on the HBC cores after formation of holes on the amine units, have an intracolumnar mobility comparable with that for holes. As PR-TRMC is insensitive to charge sign it cannot distinguish between these possibilities.

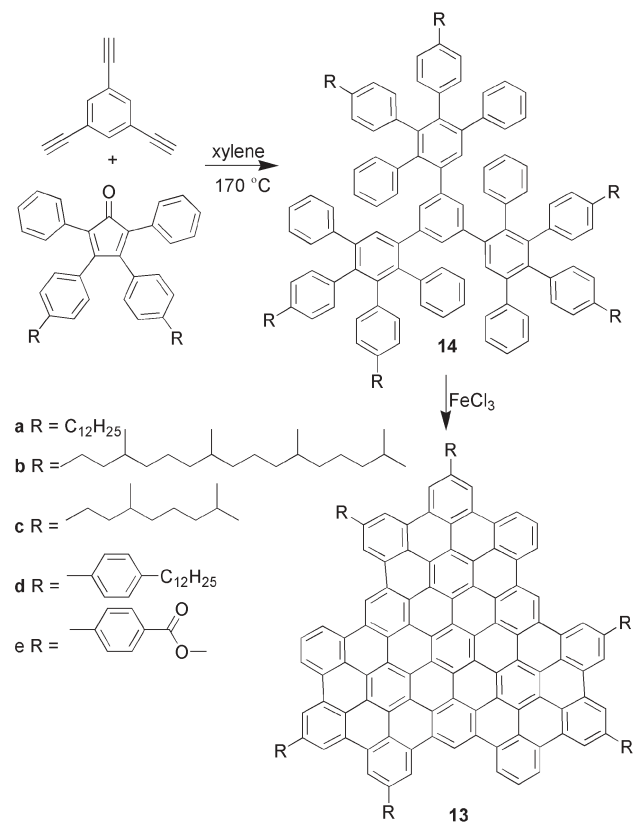
New large discotic polyphenylenes

Increasing the size of the core of discotic materials is predicted to improve the columnar stability and order and thus enhance the charge carrier mobility.¹⁴ It is also expected that at some point an increase in size will produce new types of mesophases as the tendency for smaller discs to tilt against the columnar axis will be replaced by a simple lateral offset, as graphite-like stacking is adopted to optimise orbital interactions. We have accordingly investigated ways to synthesise soluble discotic PAHs with cores significantly larger than in HBC.

As shown in Scheme 3 we have now developed a short, efficient route to superphenalenenes **13** containing 96 carbon atoms in their cores.¹⁵ The first step is a threefold Diels–Alder cycloaddition of a substituted cyclopentadienone to 1,3,5-trisubstituted benzene, which proceeds essentially quantitatively to give the oligophenylenes **14**. Oxidative cyclodehydrogenation of **14** to produce **13** requires longer reaction times and greater amounts of oxidant than are needed for the corresponding synthesis of HBCs, but with 90 equiv. of oxidant quantitative yields of **13** are obtained. The derivatives **13a–c** with *n*-dodecyl, phityl, and 4-methoxycarbonylphenylene substituents were freely soluble in common organic solvents and do not precipitate upon concentration to lyotropic phases. This was somewhat surprising, since as the size of the core increased the solubility was expected to become more problematic—already for alkyl HBCs (**1b**) gel formation due to self-assembly is a significant problem. Conversely **13d–e** with 4-dodecylphenylene and 3,7-dimethyloctyl chains, which

impart good solubility to HBCs, showed poor solubility. This remarkable difference in the effects of side-chains on the solubility of HBCs and superphenalenenes must reflect differences in the space-filling and packing of the substituents, but no clear correlation is as yet derivable.

Of these derivatives only **13a** displayed a thermal transition between $-100\text{ }^{\circ}\text{C}$ and $250\text{ }^{\circ}\text{C}$ on DSC. It showed a single reversible endotherm at $38\text{ }^{\circ}\text{C}$, and remained birefringent up to



Scheme 3 Synthesis of superphenalenenes.

550 °C. As yet the liquid crystalline phase(s) of **13a** have not been assigned, but 2D-WAXD on extruded fibres of **13a** and **13b** revealed hexagonally packed columnar mesophases with disc planes perpendicular to the columnar axes.

A major difference between the superphenalenes **13** and HBCs is that the former possess D_{3h} and the latter D_{6h} symmetry. We have now extended the synthesis of materials with threefold symmetry to the C_{150} disc **15** and the C_{90} disc **16**.¹⁶ The former is the largest disc with threefold symmetry yet made, while the latter is non-planar due to the five-membered rings, and so offers a possible route through to bowl-shaped molecules. Both of these are insoluble due to the lack of substituents so that they had to be characterised by matrix-assisted laser desorption ionisation time-of-flight (MALDI-TOF) mass spectrometry, which confirmed that complete dehydrogenation had occurred in both materials. (Elemental microanalysis is not reliable for such materials due to incomplete combustion.) Further work to produce soluble derivatives and to elucidate their self-assembly and charge transport properties is underway.

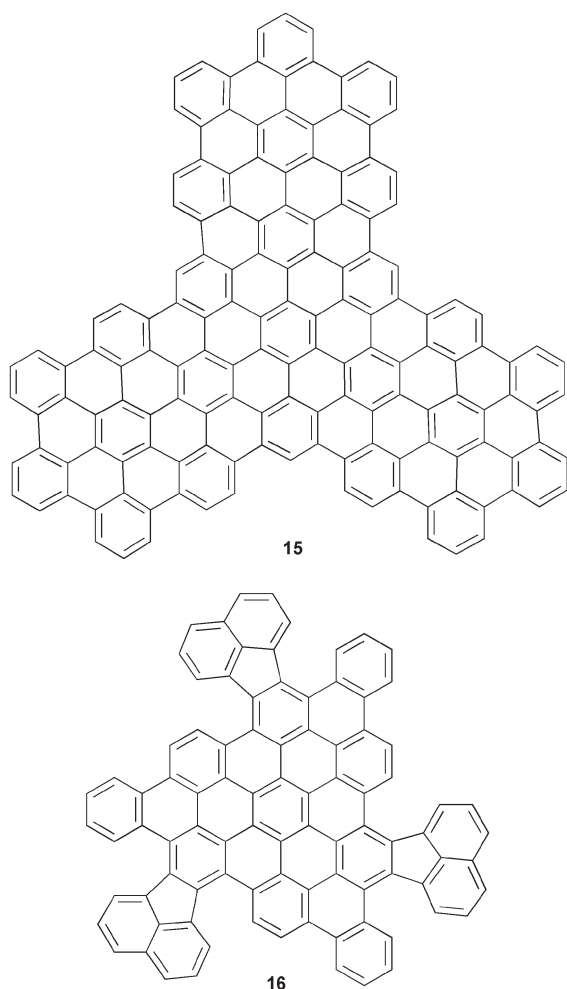


Fig. 2 New discs with threefold symmetry.

Molecular propellers by partial dehydrogenation of polyphenylene dendrimers

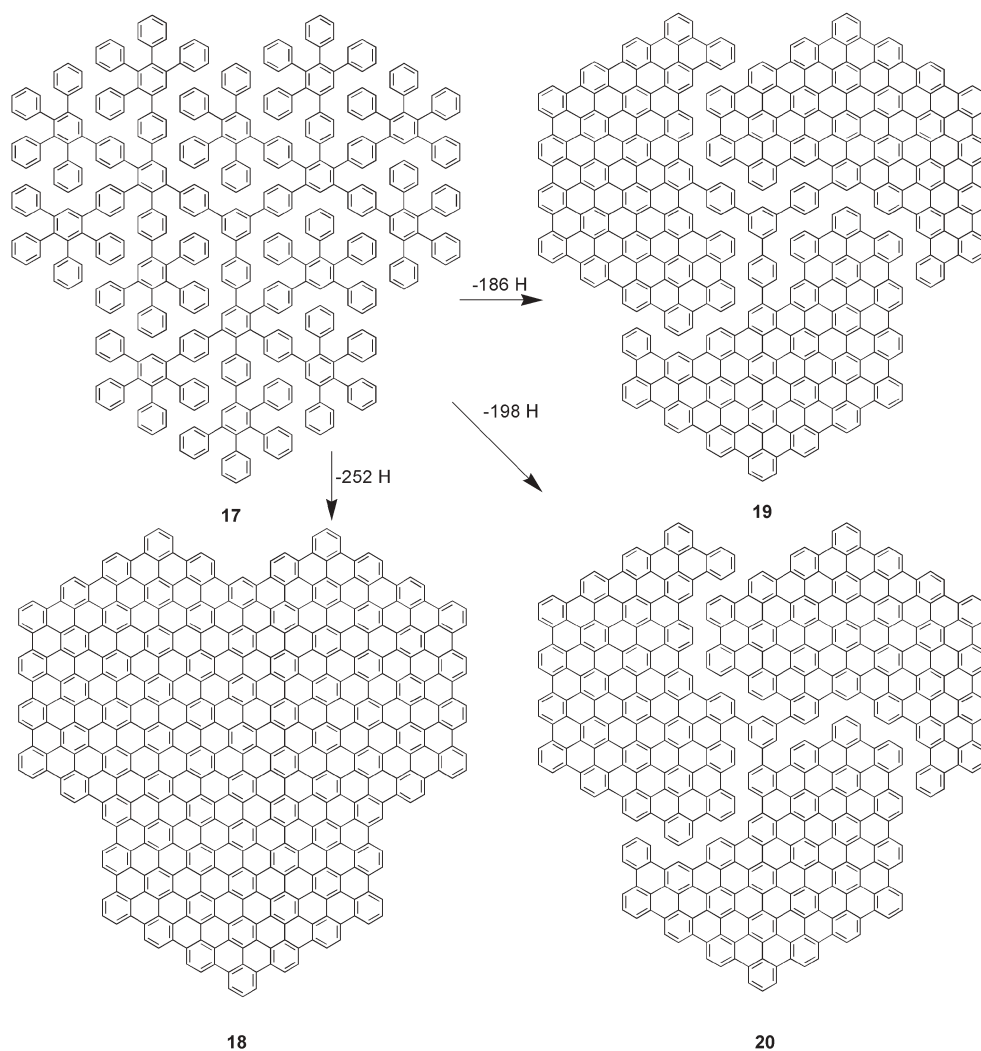
An obvious modification of the synthesis of large PAHs as discussed above is to fuse only some of the rings together, *i.e.* to perform a partial cyclodehydrogenation. The result of such a process would be that the three-dimensional dendrimer would be only partially planarised and so one would produce a three-dimensional molecule containing a number of planar graphene units. By controlling the degree of dehydrogenation one could aim to determine both the size of the graphene units and their spatial relationships. As graphene units have been shown to intercalate lithium atoms⁶ and to bind hydrogen molecules,⁷ such materials would have potential applications in lithium batteries or in hydrogen storage.

Accordingly we have investigated the oxidative cyclodehydrogenation of the dendrimer **17** with various amounts of oxidant to see if we could control the oxidation so as to produce such materials (Scheme 4).¹⁷ Use of 189 equiv. of iron(III) chloride, *i.e.* 0.75 equiv. per hydrogen (complete dehydrogenation involves loss of 252 hydrogens), resulted in the formation of a partially cyclised product with a peak maximum in the MALDI-TOF at 5890 Da, corresponding to loss of about 120 hydrogens. The optimal oxidation conditions involved use of 1.5 equiv. of the oxidant per hydrogen (*i.e.* 378 equiv. per mole of **17**), when a product with a sharp main peak at 5830 Da, corresponding to loss of almost 200 hydrogens, could be obtained reproducibly, together with a small peak at 5760 corresponding to the fully dehydrogenated product **18**.

Due to the insolubility of the products, characterisation could be performed only by mass spectrometry and solid-state UV-Vis absorbance spectroscopy. The product was treated with aluminium chloride/sodium chloride in the melt, under which conditions PAHs are stable but single aryl-aryl bonds can break, produced new fragments with peaks at 1842 and 1914 Da corresponding to PAHs with 150 and 156 carbons. This suggested the product contained the propeller-like structures **19** and **20** which contain three such fragments as blades around a central benzene. A C156 model compound was synthesised and its UV-Vis spectrum was found to closely match that of the product with a maximum at about 560 nm. This supports the proposed structures, as computer modelling confirms that as would be expected, the graphene fragments in **19** and **20** are not coplanar and thus not conjugated to each other, so their UV-Vis spectra should resemble those of a single blade. This was further confirmed by the synthesis of a model compound **21** containing three HBC units around a central benzene whose UV-Vis spectrum conspicuously resembled that of an isolated HBC. The proposed structures are consistent with the dehydrogenation and accompanying planarisation commencing at the periphery of the dendrimer and the planarisation at the core being the final stage of the process.

New carbonaceous materials by pyrolysis of PAHs in the mesophase

The standard methods for preparing carbon nanotubes and fullerenes typically involve very high temperatures or



Scheme 4 Molecular propellers by partial dehydrogenation of a dendrimer.

pressures, *e.g.* electric arc discharge of graphite electrodes¹ or laser ablation of graphite.¹⁸ Pyrolytic techniques such as vacuum pyrolysis, catalytic chemical vapour deposition and catalytic chemical pyrolysis have also been used to make carbon nanoparticles,¹⁹ but again either catalysis or drastic conditions are required. We have now developed a new milder method for prepared carbon nanoparticles by a two-stage pyrolysis of an alkyl HBC (**1b** R = C₁₂H₂₅).²⁰

The concept as shown in Fig. 4 is that the first stage of the pyrolysis occurs at 400 °C at which temperature the HBCs are in an ordered liquid crystalline mesophase. This results in the formation of large PAH intermediates which still preserve some mesomorphic order. In the second step, pyrolysis at 800 °C results in graphitisation to produce carbon nano- and microparticles with graphitic nanostructures. This temperature is well below the temperature range of 2000–3000 °C normally used to induce graphitisation.²¹

Monitoring of the first stage by MALDI-TOF showed that some of the starting material was still intact even after 72 h at 400 °C, but that significant amounts of materials with structures based on oligomers of HBC had been formed. As

the pyrolysis continued there was a general trend towards the formation of products of increasing molecular weight and increasing carbon content. The MALDI-TOF results further revealed that the oligomerisation proceeded by preferential cleavage of the C_α–C_β alkyl bonds to form free radicals followed by their intermolecular cross-linking.

Optical microscopic study between crossed polarisers of the product from pyrolysis at 400 °C for 72 h, showed that the material retained well-defined birefringent domains which displayed the textures characteristic for a columnar mesophase, which suggest that the liquid crystalline order persisted even during alkyl chain cleavage and intermolecular cross-linking. These textures were not destroyed upon further heating to 600 °C (the limit for the hot stage of the microscope) suggesting that the material may retain some organisation at the beginning of the second stage of the pyrolysis.

This organisation was found to be important for obtaining defined nanoparticles, as when the HBC was heated directly at 800 °C, with no first step, only an irregular film without any detectable micro- or nano- objects was obtained. The pyrolysis temperature and the substrate were found to

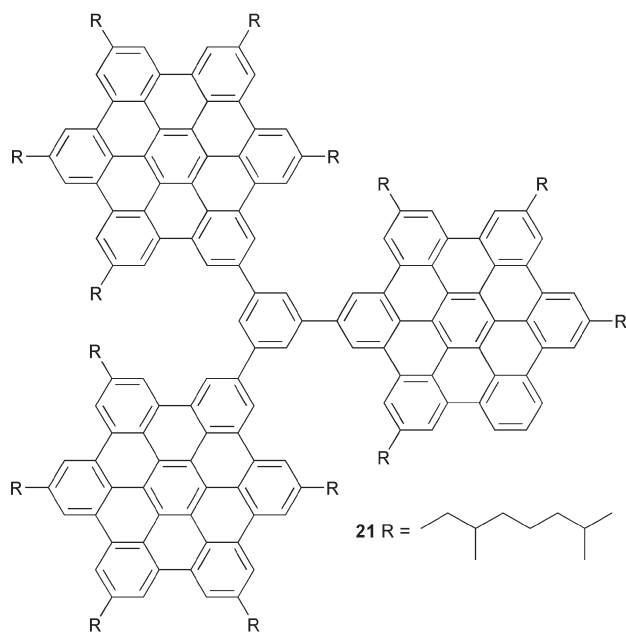


Fig. 3 Soluble model propeller compound.

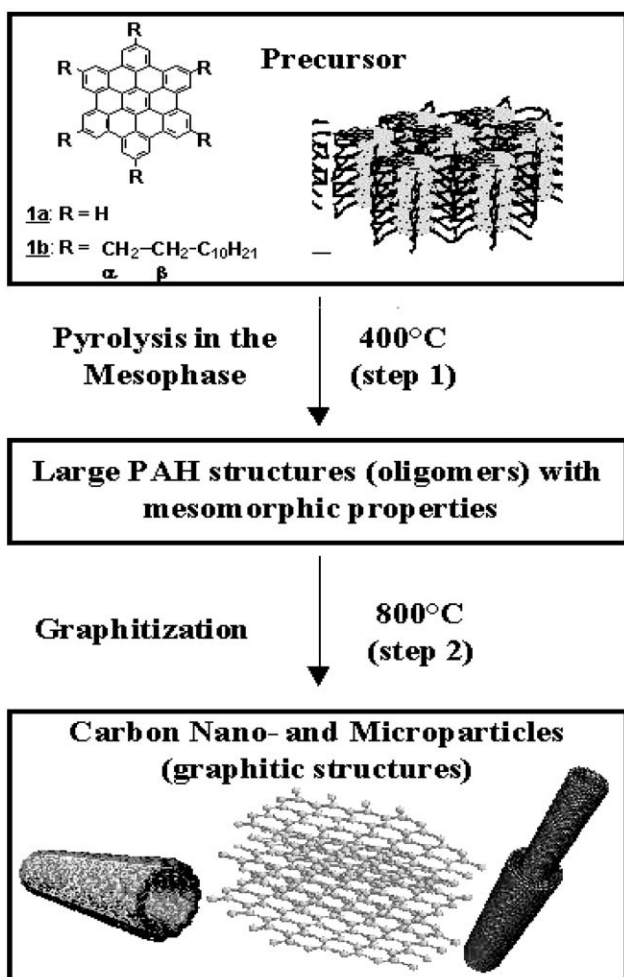


Fig. 4 Pyrolytic approach to carbon nanoparticles.

profoundly influence the nature of the nano-objects produced. Thus pyrolysis on quartz at 400 °C, followed by 800 °C produced a mixture of spherical (Fig. 5 left), and linear objects. The latter included both fibers of diameter up to 10 μm, with lengths of 10–20 μm, and nanowires with diameters of 20 nm, and lengths of a few hundred nm to a few μm. If an additional pretreatment at 220 °C for 10 min to form the anisotropic melt without bond cleavage was performed before heating to 400 °C, then cylindrical nanorods, some with 90° kinks (Fig. 5 right), with diameters of 100 nm and lengths up to a few μm were formed. If the final pyrolysis step was performed at 650 °C instead of 800 °C, then doughnut-like nanoparticles with dimensions below 200 nm were produced.

Pyrolysis on mica produced a mixture of films coated on the surface and discrete nanoparticles, whose shapes were totally different from those formed on quartz. The preferred shape appeared to be a hexagonally symmetric zigzag. Large micro-objects were detected possessing this geometry with cross-sections of 1–10 nm, and lengths in the μm range (Fig. 6, left). Also seen were root-like micro-objects with cross sections of 400 nm–1 μm and lengths of >30 μm. Their branches (Fig. 6 right) also show a hexagonal zigzag geometry. It is proposed that the metal oxides in the mica interact with the organic materials to produce nuclei for growth both of nanoparticles and branched structures.

The presence of the alkyl chains was found to be important as pyrolysis of unsubstituted HBC (**1a** R = H) which cannot form an ordered mesophase, produced disordered, spongy products with an absence of micro- or nanoparticles.

These new carbonaceous materials from pyrolysis are being tested for possible applications in electronics (*cf.* nanotubes) or in hydrogen or lithium storage.

More recently we have discovered that pyrolysis of an HBC cobalt complex **22** in the solid state produces carbon nanotubes (Scheme 5).²² Nearly quantitative yields of uniform either “bamboo-shaped” or straight nanotubes were obtained.

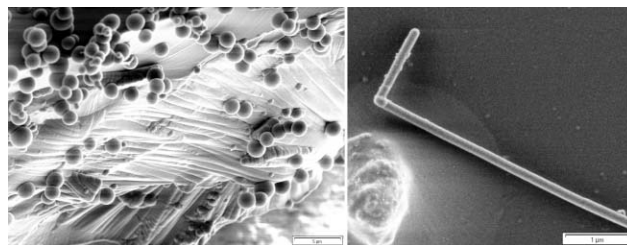


Fig. 5 Spherical (left) and rod-like (right) particles obtained by pyrolysis on quartz.

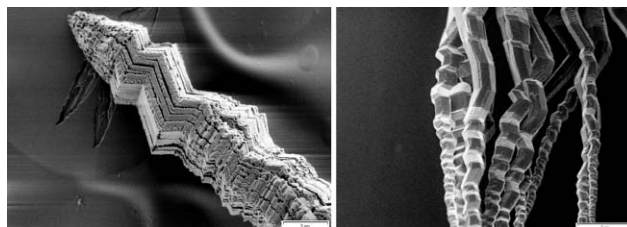
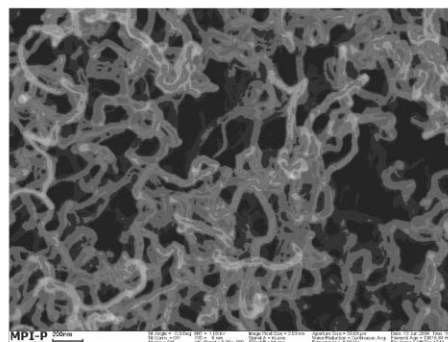
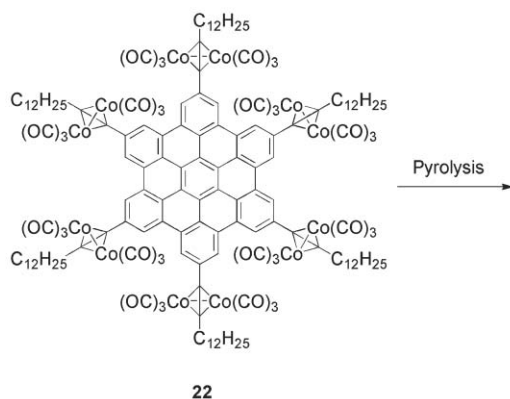


Fig. 6 Micro-objects formed by pyrolysis on mica.



Scheme 5 High-yielding synthesis of carbon nanotubes by pyrolysis of an HBC–cobalt complex in the solid-state.

The shape and yield of the carbon nanostructures can be finely controlled by regulation of the heating process. This provides an alternative high-yielding synthesis of carbon nanotubes to supplement the existing methods such as carbon vapour deposition, electron discharge and laser ablation. The precursor **22** contains both an as-ready graphite carbon source (HBC) and a catalyst precursor ($\text{Co}_2(\text{CO})_6$), and at high temperatures the graphite islands form tube-like graphene structures on the cobalt catalyst units.

We have investigated ways to use the ordering of graphite molecules such as HBC to induce order in the nanotube pyrolysis products. Thus a well-controlled pyrolysis of HBC molecules has been performed in a porous alumina membrane which acts as a template.²³ The HBC molecules were introduced to the nanochannels within the alumina template by a simple wetting process, and then subjected to pyrolysis by various temperature procedures. After dissolution of the template, uniform carbon nanotubes with graphene layers perpendicular to the nanotube axis were obtained. It was found that the ordered pre-organization of the liquid crystalline HBC molecules on the surface of the membrane played a key role in obtaining carbon nanotubes with controlled graphene layer orientation.

Conclusion

HBCs with electroactive substituents and soluble large PAHs can be made which show high charge carrier mobilities making them suitable for a variety of electronic applications. Partial dehydrogenation of polyphenylene dendrimers can be performed to produce propeller-like molecules with 3-dimensional arrays of graphene sheets. Finally controlled pyrolysis of HBCs in their ordered mesophases can be used as means to obtain carbonaceous materials with controlled geometries. These last two types of materials may have applications in lithium batteries or hydrogen storage.

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