Expanding benzene to giant graphenes: towards molecular devices

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Phenylene-based conjugated materials provide versatile platforms for the development of molecular devices. Architectures of one- and two-dimensional polyphenylenes, which self-assemble into three-dimensional objects with advantageous electronic properties, have been investigated. Systematic relations between the size, substitution and shape with function were found, which enabled the further optimization of the materials. Hand in hand with the development of suitable methods for visualization and processing, promising results were obtained for performance of nanoscale electronic devices.

Keywords: conjugated polymers; polycyclic aromatic hydrocarbons; self-assembly; optoelectronic devices; pyrolysis

1. Introduction

A widespread application of electronic devices based on organic nanomaterials is one of the major objectives of modern science (Shirota 2000; Grimsdale & Müllen 2005). Ambitious goals as such require smart syntheses of suitable nanomaterials as well as a complete understanding of their properties as single molecules and in supramolecular arrays, the latter of which is essential for the performance in a device (Simpson et al. 2004). Different polyphenylene architectures pass for promising materials in this field: rigid-rod phenylene-based conjugated polymers and oligomers (one-dimensional polyphenylenes), planar polycyclic aromatic hydrocarbons (PAHs, two-dimensional polyphenylenes), polyphenylene dendrimers (three-dimensional polyphenylenes), as well as various combinations thereof to maximize beneficial and minimize undesirable interactions (Wu et al. 2005b).

This paper describes recent work on polyphenylene materials towards molecular devices. After challenging synthesis and complete characterization, the optical, mechanical and electronic properties of the materials were studied by methods which probe the materials at the nanolevel, such as scanning tunnelling microscopy (STM) or atomic force microscopy (AFM). As the solid-state organization of a material is crucial for its performance in a device, different alignment techniques were applied to preorganize the materials into columnar suprastructures. These assemblies were characterized by differential scanning...
calorimetry (DSC), polarization optical microscopy (POM) and two-dimensional wide-angle X-ray scattering (WAXS). The device performance was investigated for some of the materials. Pyrolysis of the carbon-rich materials led to carbon nanoparticles with defined morphologies, which are of great academic and industrial interest owing to their unique electronic properties and many potential applications (Gherghel et al. 2002).

2. Conjugated polymers

Phenylene-based polymers and oligomers are one of the most important classes of conjugated materials for electronic applications such as light-emitting diodes (LEDs), solar cells or field-effect transistors (FETs; Yu & Heeger 1997; Bunz 2000). Oligomers can thereby serve either as active compounds or as models for their polymeric analogues (El-ghayoury et al. 2001).

Polyfluorenes (PFs) 1, polyindenofluorenes (PIFs) 2 and ladder-type poly-p-phenylenes (LPPPs) 3 have been of particular interest (scheme 1). These materials all show blue or blue-green emission in solution with maxima at 420 nm for 1, 430 nm for 2 and 450 nm for 3. The bathochromic shift of the emission maximum within this series of compounds is attributed to the increasing planarity and rigidity of the conjugated chains. However, the blue emission in the solid state is unstable, showing an additional long-wavelength emission band due to oxidative electro- and photodegradation, thus leading to ketone formation at the methane bridges. This ketone formation has been suppressed by alkyl or aryl substitution of the bridgehead (Jacob et al. 2004).

Scheme 1. Polyphenylene-based conjugated polymers.
Unfortunately, substitution also changes the optical properties, as in the case of LPPP, where a methyl substituent led to a bathochromically shifted emission of 470 nm. The human eye is not particularly sensitive in the region between 425 and 435 nm. The combination of a PIF (2) and a methylated LPPP (3a) as realized in the poly-pentaphenylene 4 gave materials with an emission maximum around 445 nm. Single-layer organic light-emitting diodes (OLEDs) with 4 (R1=R2=C8H17) showed a stable pure blue emission with brightness of over 200 cd m\(^{-2}\) at 7 V (Jacob et al. 2004).

Poly(2,7-carbazole) derivatives (PCzs) 5 represent another class of bridged phenylene-based polymers (Morin et al. 2005; scheme 2). Owing to the substituted nitrogen in the polycyclic system, formation of oxidation defects is excluded, which led to stable materials with good solubility, high processability and optical properties covering the blue, green and red ranges (Morin & Leclerc 2002). As carbazole is a well-known electron-donating material, its polymers are attractive candidates as \(p\)-type materials for solar cells. Owing to the decreased energy of their highest occupied molecular orbital (HOMO), compared to poly(thiophene), which has been used in combination with fullerenes as acceptors in solar cells (Wienk et al. 2003; Cremer et al. 2006), these polymers are less easily oxidized. The bandgap in polycarbazole is larger, however, so that a material which shows a stronger absorption than fullerenes in this range is required as the acceptor for a high-power conversion from solar light. A bulk heterojunction device with poly(carbazole) as donor material and a perylene tetracarboxydiimide as acceptor exhibited an external quantum efficiency (EQE) of 16% at 490 nm and a power efficiency of 0.6% under illumination with solar light (Li et al. 2006). The UV–vis spectrum of this mixture shows a good spectral overlap with the strongest part of the natural solar spectrum. These results thus extend the choice of applicable materials for organic solar cells.

Scheme 2. Poly(2,7-carbazole)s.
Recently, the template-assisted synthesis of a monodisperse fully conjugated 2,7-carbazole-based macrocyclic dodecamer 6 was reported (Jung et al. 2006), which raises fascinating opportunities towards energy and charge transporting superstructures also known from other macrocyclic systems (Mena-Osteritz & Bäuerle 2001).

3. Graphite molecules

Planar PAHs can be regarded as molecular subunits of graphite. Depending on their size and shape, these materials possess the ability to form ordered columnar mesophases with high charge carrier mobilities along the columnar axis, which makes them suitable as semiconducting materials. Furthermore, they furnish monomolecular absorbate layers on highly oriented pyrolytic graphite (HOPG), making them important objects in the visualization of single molecules by STM (Watson et al. 2001).

Hexa-peri-hexabenzocoronenes (HBSs) 10 exhibit one of the highest intrinsic charge carrier mobilities for a discotic material (Van de Craats & Warman 2001). Their syntheses are based on the planarization of suitable hexaphenylbenzenes 9 by oxidative cyclodehydrogenation, which is formed either by cyclotrimerization of diphenylacetlenes 7 (i) or by Diels–Alder cycloaddition (ii) of a tetraphenylcyclopentadienone 8 to a diphenylacetylene 7 (Berresheim et al. 1999; scheme 3).

A radical cationic mechanism is assumed for the intramolecular fusion reactions in the last step, such that the geometry, charge and spin distribution are decisive for the bond formation (Rempala et al. 2004). Recent work supported this hypothesis, demonstrating that the success of the cyclodehydrogenation strongly depended upon the oligophenylene precursor (Feng et al. 2006; scheme 4).

The variation of the periphery, topology, size and shape of a hexa-peri-hexabenzocoronene (HBC) has a distinct impact upon the electronic properties and the self-assembling behaviour into columnar superstructures.

(a) Size

Increasing size leads to greater delocalization of the $\pi$ electrons and to a decreased difference between the HOMO and the lowest unoccupied molecular orbital (LUMO), which is readily visible in the colour of the material (Grimsdale & Müllen 2005). A linear relationship was observed between the absorption maximum of the $\alpha$-band and the number of ‘full’ aromatic rings (Watson et al. 2001; figure 1).

Furthermore, a strong dependence of the intercolumnar packing dimensions as well as the charge transfer mobility values of the PAHs on the aromatic core size was shown (Debije et al. 2004; Pisula et al. 2005c). The synthesis of higher homologues of HBC, such as 17 and 18, is also based on the preparation of polyphenylene precursors, which are subsequently planarized by cyclodehydration (Simpson et al. 2002; Wasserfallen et al. 2006).

(b) Substitution

Not surprisingly, the PAHs with R=H show extremely low solubility and are therefore difficult to characterize and process. Branched or $n$-alkyl substitution led to soluble materials and enabled complete spectroscopic characterization of

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Scheme 4. Cyclodehydrogenation of different oligophenylene precursors.

14a $X = H$
14b $X = m-l$
14c $X = p-l$
these compounds (Kastler et al. 2005). The alkyl substitution also influences the surface organization and self-assembly of the resulting HBCs (scheme 5). With increasing number of the alkyl chains, the phase transition temperature from the crystalline phase to the mesophase decreased. Branching and the density of substitution, which also influences the steric hindrance, show an additional effect (Kastler et al. 2006). The majority of HBCs prefer an edge-on arrangement with respect to a surface; however, by the choice of the substituents it was possible to induce a homeotropic alignment. Incorporation of heteroatoms in the side chains enhances this tendency as they interact favourably with glass and aluminium surfaces (Pisula et al. 2005b).

(c) Periphery

HBCs contain an ‘arm-chained’ periphery. The formal introduction of C2 units into the ‘arm-chained’ sites of an HBC led to not-fully benzenoid PAHs with partial ‘zigzag’ peripheries, whose introduction was predicted to lower the
HOMO–LUMO gap (Stein & Brown 1987). A series of compounds with different sizes and symmetries (19–23) were synthesized based on precursor molecules containing phenanthrenyl units. Indeed, the change of periphery and symmetry had a pronounced influence upon the electronic spectra, showing that the typical $\alpha$- and $\beta$-bands of a PAH depended linearly upon the overall size, while the $p$-band was mainly influenced by symmetry (Kastler et al. 2006; figure 2).

The periphery also influences the self-assembly properties of the PAHs. Perimeter effects on the two-dimensional self-assembly on a surface and the molecular electronic properties have been investigated by STM (Wu et al. in preparation). The two-dimensional WAXS experiments suggest that an aromatic core with higher symmetry enhances the supramolecular order (Kastler et al. 2006).

(d) Shape

Oligomers up to a trimer with different geometries were successfully synthesized by coupling reactions of single HBC moieties or by cyclohydrogenation of corresponding branched oligo(phenylenes) (scheme 6). Remarkably, the HBC dimer 24a, trimer 25 and the ‘superfluorene’ 26 reveal an ordered columnar stacking, which might allow charge carrier transport along HBC multicolumns (Wu et al. 2004b).

All parameters intriguingly influence the material’s properties such that the careful molecular and supramolecular design is required to obtain optimum performance in a device.

4. Single-molecule devices

The STM visualization of thin layers of molecules on a surface provides valuable information about the self-assembly behaviour of the material investigated. Interesting observations were monitored in monolayers of organic molecules on
HOPG such as codeposition with solvents (Vanoppen et al. 1996), influence of chiral centres upon the ordering (De Feyter et al. 2000) and chemical reactions like cis–trans isomerization (Vanoppen et al. 1996) or polymerization in the monolayer film only possible due to the order (Miura et al. 2003) to name just a few. Such layers have been achieved either by ultrahigh vacuum (UHV) deposition or by physisorption from solution. In the case of PAHs, unsubstituted discs up to a certain size may be deposited from the gas phase, whereas larger ones require temperatures above their decomposition temperature. Alkyl substitution usually increases the solubility of the molecules, allowing processing from solution (Kastler et al. 2005). Addition of an acceptor molecule, e.g. a coronene tetracarboxydiimide (CDI) 28, is also assumed to increase the solubility of PAHs due to the temporary formation of donor–acceptor aggregates, so that the donors in a cluster are separated from one another (Samori et al. 2002). π interactions between the absorbate and the HOPG as well as the van der Waals interactions of the alkyl chains are driving forces for the deposition (figure 3).

Using STM in a spectroscopic fashion (scanning tunnelling spectroscopy, STS), it has become possible to record current–potential curves for single PAH molecules, which offers new possibilities for the research towards monomolecular electronics (Ito et al. 2000b). Various PAHs show asymmetric I/V characteristics (diode-like), when the tip was passed over the aromatic cores, which was attributed either to a lateral displacement of the molecules with regard to the underlying layer or to the asymmetry of the frontier orbitals relative to the electrodes. A symmetric curve was found in the region of the aliphatic chains (Jäckel et al. 2006).

Transistor-like behaviour has been demonstrated at the solid–liquid interface for an HBC 30, which was decorated with six anthraquinone moieties in its periphery (figure 4). Both the HBC donor and the anthraquinone acceptors lay flat on the surface. Addition of 9,10-dimethoxyanthracene (29) led to the formation of a charge transfer complex with anthraquinone, thereby changing the work

Scheme 6. Combined one- and two-dimensional HBC structures.
function of the substrate such that a detectable change in the I/V characteristics of the HBC core was recognized with an STM tip (Jäckel 2004a,b). Even though the currents involved are too small to be of practical value in a real FET, this is a fascinating experiment towards devices based on single molecules.

5. Supramolecular arrays: formation, processing and optimization towards application in devices

The processability of materials into highly ordered supramolecular structures on surfaces is a key factor towards obtaining good device performance. There are many diverse alignment techniques, whose applicabilities strongly depend on the different materials (Bushby & Lozman 2002). The formation of defect-free single crystals is highly desirable; however, in most cases these are not easily achieved. As mentioned above, thermally stable molecules can be oriented by UHV deposition. The formation of ordered films by the Langmuir–Blodgett technique is also known, but an amphiphilic character of the molecules is essential. Soluble HBCs decorated with alkyl chains form thermotropic liquid crystalline phases and align into nanoscale columnar structures. This process is driven by the π interaction between the aromatic cores as well as by the concomitant nanophase separation of the aromatics and the alkyl chains (Kopitzke & Wendorff 2000). The efficient overlapping of the molecular orbitals of the core enables charge transport along the columnar axis, giving rise to nanowire characteristics (Lemaur et al. 2004). In a device, the semiconducting columns must be aligned perpendicular to the electrodes, which requires an edge-on orientation for FETs or a face-on orientation for a photovoltaic device (Simpson et al. 2004; figure 5).

Two methods have been used to produce aligned films of HBCs on a surface: (i) spin casting of a solution of HBCs on a preoriented polytetrafluoroethylene (PTFE) layer using the surface roughness (Van de Craats et al. 2003) or (ii) zone casting from the solution or melt (Tracz et al. 2003; Pisula et al. 2005a; figure 6).

Hexa-alkyl HBC derivatives have displayed charge carrier mobilities of over 1 cm² V⁻¹ s⁻¹ (pulse radiolysis time-resolved microwave conductivity measurements; Van de Craats et al. 1998, 1999). These high values were obtained only in crystalline phases while a decrease in mobility was observed in the mesophase. The charge carrier mobility in a mesophase has been improved by increasing the intra- and intermolecular order of the columns. One strategy is the insertion of arylacetylenes between the alkyl substituents in 10b and the HBC core (10c). Compared to the normal alkyl HBCs, the HBC 10c exhibited more highly ordered columnar phases, including three-dimensional helical superstructures (Wu et al. 2004c). Attachment of hole transporting triarylamines units also increased the charge carrier mobility, as the HBC core and the triarylamines both provide pathways for the charges to move along (Wu et al. 2004a). An improved order within the columns was also achieved in the case of the carboxylic acid functionalized HBC 10e. Hydrogen bonding led to a stronger intermolecular order and thus to a higher transition temperature to the mesophase representing a higher order in the bulk (Wasserfallen et al. 2005). A bioinspired arrangement was attained when the carboxy-HBC 10e was
complexed with poly(ethylene oxide)-block-poly(l-lysine) (Thünemann et al. 2003; figure 7). The poly(l-lysine) blocks formed a \( \alpha \)-helical secondary structure and each helix was then symmetrically surrounded by six discotic HBC columns, giving a material that combines the structural properties of liquid crystals with a well-ordered structural element derived from a protein.

Figure 3. STM images of multilayers of (a) HBC 10a (in the presence of the CDI 28) and (b) ‘superbiphenyl’ 24b at the solid–liquid interface between HOPG and trichlorobenzene. Reproduced with permission from Ito et al. (2000a) and Jäckel et al. (2006).

Figure 4. Single-molecule chemical FET.

\( R_1 = R_2 = \text{C}_{10}H_{20} \)

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The combination of one- and two-dimensional structural motifs supports the enhanced intercolumnar order of the materials. Blending HBCs with an HBC dimer 31 linked together different columns and thereby generated ‘bypasses’ for the movement of charge in large networks (Oldrige 2006; figure 8).

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Soft-landing mass spectrometry was recently presented as a new route to obtain ultrapure crystalline architectures of giant graphene molecules (Räder et al. 2006). This method relies on the soft landing of ions, generated by solvent-free matrix-assisted laser desorption/ionization (MALDI). The nanographenes are transferred to the gas phase, purified and absorbed on a surface (figure 9). The STM measurements clearly demonstrated highly ordered nanoscale suprastructures of the molecules.

Some of the materials mentioned above have been tested in optoelectronic devices. A FET, fabricated by zone casting of HBC-C12 10b on top of an SiO2 insulating layer on a silicon substrate (figure 10), showed a very good on–off ratio of $10^4$, a high field-effect mobility of $5 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and a turn-on voltage of approximately $-15 \text{ V}$ (Pisula et al. 2005a).

On the way to solar cells based on organic materials, thin films of the electron-donating, room temperature liquid crystalline HBC 32 and an electron-accepting perylene tetracarboxydiimide 33 were achieved by spin coating of a solution of an...
HBC–perylene mixture. Vertically segregated perylene and hexabenzocoronene areas were obtained, which is favourable for the rapid transport of electrons and holes created by photoinduced charge separation within the device (figure 11). The EQE of these films in the device reached high values up to 34% near 490 nm (Schmidt-Mende et al. 2001).

A homeotropic alignment of the two compounds in separated columns next to each other would clearly enhance the performance of the device and is therefore a target of current research.

Figure 9. Principle of soft landing in solvent-free matrix-assisted laser desorption/ionization (MALDI) mass spectrometry.

Figure 10. (a) Large-area image from high-resolution transmission electron microscopy (HRTEM) of a zone-cast HBC 10b. (b) Schematic side view of the constructed FET device. Reproduced with permission from Pisula et al. (2005a).
Carbon allotropes are of great interest owing to their ability to intercalate lithium ions (Herold 1955). Presently, commercially available lithium ion batteries use a graphite anode whose specific capacity is limited to 372 mAh g\(^{-1}\), corresponding to one lithium per six carbon atoms (Bonino et al. 2005). A carbon material with a higher lithium capacity due to a different morphology is highly desirable in order to improve the batteries for ongoing market innovations.

The organization of discotic graphite molecules into columnar structures is applicable to the generation of carbon micro- and nanoparticles. Pyrolysis of HBCs under relatively mild conditions and in the absence of metal centres, which are known to catalyse the formation of aryl–aryl bonds, produced carbon nano- and microstructures, ranging from discrete microspheres, through branched nanosticks, to nanowires (Gherghel et al. 2002). The different organizations were visualized by scanning and transmission electron microscopy. The range of structures obtained was mainly determined by the pyrolysis temperature, but other attempts have been undertaken to control the morphology of the products. HBC molecules were introduced into the nanochannels within a porous alumina template membrane. After pyrolysis and dissolution of the template, carbon nanotubes were identified with graphite layers perpendicular to the nanotube axis (Zhi et al. 2005; figure 12).

Figure 11. (a) Schematic design of a solar cell. (b) Tapping-mode AFM image of a film spin coated from a 40 : 60 blend solution of HBC 32 and perylene tetracarboxydiimide 33. Reproduced with permission from Schmidt-Mende et al. (2001).

6. Carbonaceous nanostructures

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Figure 12. (a) Template-assisted formation of carbon nanotubes. (b) SEM image of carbon nanotubes in the template channels. (c) HRTEM of the nanotubes. Reproduced with permission from Zhi et al. (2005).

Figure 13. SEM image of the pyrolyzed HBC-co-complex 34. Reproduced with permission from Grimsdale & Müllen (2005).

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Another approach to induce nanotube formation, instead of other geometries, is the combination of a phase forming graphite carbon source and a metal catalyst precursor within the same molecule as realized in HBC 34. Pyrolysis of 34 yielded nearly quantitative amounts of either ‘bamboo-shaped’ or straight carbon nanotubes (Wu et al. 2005a; figure 13).

Future work will also be performed on pyrolysis of dendritic polyphenylene structures, as there is hope that these materials pyrolyze under the formation of porous carbon materials with improved lithium storage capacities. The pyrolysis of the HBC precursor hexa(phenyl)benzene 9 (R=H) or its hexabromo derivative (R=Br), which can both be regarded as small dendritic molecules, led to materials with lithium storage capacities up to 600 mAh g⁻¹ in preliminary electrochemical measurements (Renouard et al. 2005).

All of these results demonstrate the construction of well-defined carbon nanoparticles based on polyphenylene subunits as well as porous carbon materials, which have potential application in lithium storage. Clearly, the conversion of HBCs into well-defined carbon nanotubes is also attractive for other applications, such as those in nanoscale electronics.

7. Conclusions

The performance of electronic devices based on inorganic semiconductors still exceeds those constituted from organic components and will in the near future. However, the optimization of inorganic devices has reached a certain limit, particularly with respect to cost and processability of the materials. Cheaper and better processable materials for device applications may become possible as soon as organic materials are suitable alternatives to the inorganic materials. Miniaturization down to the single-molecule level is also highly desired. Different approaches have been initiated to realize this goal, reaching from one-dimensional organic semiconducting polymers to supramolecular structures of various nanomaterials.

In this paper, we have presented a selection of our investigations towards organic nanomaterials based on polyphenylene architectures. The optical, electronic and self-assembly properties of poly-\(p\)-phenylene and two-dimensional extended PAHs have been tuned by synthetic efforts, leading to tailored compounds for device application in the bulk and as single objects. For example, promising results were obtained for both polycarbazole and HBCs in combination with perylene dyes for efficient solar cells. A transistor activity of a single molecule, consisting of six anthraquinones decorated around an HBC, was demonstrated, and an assembly of HBCs showed good performance in a FET. Pyrolysis of self-assembled graphite subunits led to carbon nanoparticles with different morphologies with potential application in energy storage and electronic devices.

Considerable work must be carried out before such devices are used in everyday life, but the results above strongly suggest that true nanotechnology based on organic materials is a realistic goal.

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