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The benzene ring as modulus: synthesis and supramolecular ordering of novel conjugated polymers

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Conjugated polymers possess attractive electronic and optical properties which also qualify them as active components of devices. Many conjugated polymers are made up of benzenoid building blocks. The functionalization of benzene rings is therefore a key step in polymer synthesis. Particularly important are functionalizations leading to direct aryl–aryl coupling and to the incorporation of vinylene and ethynylene units.

On the other hand the benzene ring serves as a modular building block for controlling the supramolecular structures of macromolecules. The formation of aggregates or of liquid crystalline phases are typical examples (Dietrich *et al.* 1993).

Herein, we present modular approaches towards the synthesis and supramolecular ordering of:

- (1) ladder-type poly(para-phenylene) (LPP);
- (2) donor–acceptor-substituted poly(para-phenylene-vinylene) (D/A-PPV);
- (3) poly(para-phenylenesulphide-para-phenyleneamine) (PPSA);
- (4) graphite sheets.

1. Ladder-type poly(para-phenylene) (LPP)

Typical structures are the polymers **1** and **2**, which show the fundamental repeat units for ‘step-ladder’ polymers fused by an ethanediyl bridge (Kreyenschmidt *et al.* 1994*a, b*).

As an alternative approach, ladder-type polymers can be synthesized via introduction of a single carbon or heteroatom to form perfectly flat five-membered rings. Here we present ladder-type poly(para-phenylene) (LPPP) (**3**) as an example of such a soluble easily processable and fully conjugated ladder-type polymer (Grüner *et al.* 1994). LPPP **3** possesses number average molecular weights M_n of $25.000 \text{ g mol}^{-1}$, corresponding to *ca.* 60 1,4-linked phenylene subunits. LPPP-type materials have been successfully applied as active components in organic materials based light emitting diodes (LEDs) (Scherf & Müllen 1991).

The photoluminescence (in solution) of LPPP **3** is very intense and blue (λ_{max} emission: 450–460 nm). The Stokes shift between absorption and emission is extremely small (*ca.* 150 cm^{-1}), a consequence of the geometric fixation of the chromophore in the ladder structure. The photoluminescence (PL) quantum yields are

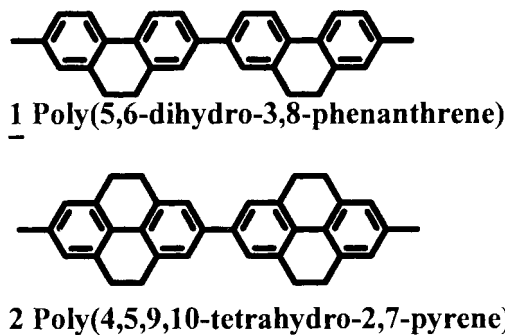


Figure 1.

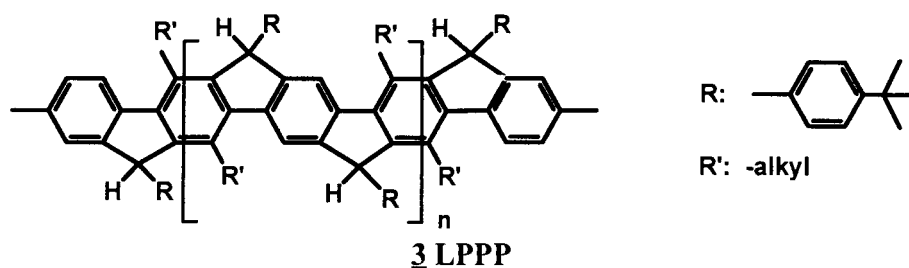


Figure 2.

huge in comparison with those of many other conjugated polymers: in solution values between 60 and 86% have been measured, in the solid state up to 30% (Stampfl *et al.* 1995). In addition to primary emission of the LPPP **3** chromophore in the blue region, the PL and electroluminescence (EL) spectra show an unstructured broad emission band in the yellow region (*ca.* 600 nm) (Huber *et al.* 1994; Mahrt *et al.* 1995).

The yellow emission band could then be characterized unequivocally in photophysical experiments as aggregate emission (Mahrt *et al.* 1995; Grüner *et al.* 1994).

EL experiments showed that the yellow-emitting LEDs prepared from LPPP **3** exhibit quite remarkable characteristics (single layer construction ITO–LPPP **3**–Ca; quantum efficiency: *ca.* 0.8%, applied voltage: 4–6 V, drop in intensity less than 5% in 24 h operation at constant current (Grüner *et al.* 1994)). These figures are in the range of the best values described hitherto for polymeric emitters, for example, poly(para-phenylenevinylene) PPV and PPV derivatives.

From the perspective of the strategies aimed at fabrication of efficient blue LEDs, the results outlined above regarding yellow LPPP light emitting diodes are, nevertheless, unsatisfactory. In order to prepare blue LEDs from LPPP materials, it is necessary to efficiently suppress the dominant yellow aggregate emission. Precisely, the preparation of blue LEDs would use the inherent advantage of LPPP **3** (band gap energy *ca.* 2.75 eV). Using other conjugated polymers with smaller band gap energy, such as PPV, blue LEDs cannot normally be prepared.

One possibility to mask out the yellow aggregate emission is the transition from completely planar LPPPs **3** to statistical ‘step-ladder’ copolymers **4**, composed of planar LPPP emitter segments that are connected by spacer units.

The intermediate groups (‘spacers’) effect a twisting of the subunits, which decisively hinder aggregation. The principle could be realized by adding a di-

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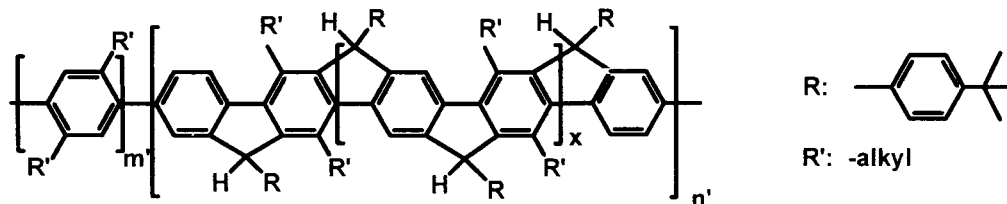
**4 CoLPPP**

Figure 3.

bromo comonomer (2,5-dihexyl-1,4-dibromobenzene), which does not form methylene bridges during the cyclization, to the monomer mixture for the Suzuki aryl–aryl coupling.

LPPP copolymers of the type, CoLPPP **4** (Grem *et al.* 1995), show, above a ‘spacer’ fraction of about 50%, the disappearance of the aggregate emission band in the solid state and also after thermal annealing of the samples.

Thus, CoLPPPs **4** are highly efficient luminophores in the blue region of the spectrum (λ_{\max} emission: *ca.* 450 nm) both in photo- and electroluminescence. The PL quantum yields are, at 85%, remarkably high (Stampfl *et al.* 1995). In a single layer construction ITO–CoLPPP **4**–Ca unusually efficient pure blue LEDs can be constructed (external quantum yields of up to 1%). Regarding the applied voltage (*ca.* 15–20 V), the light intensity (*ca.* 1000 C m⁻²) and the stability of the light emission (half-life times of about 10 h) the results are also particularly promising.

The synthetic construction principles which we adopt allow a systematic variation of size and shape. Star shaped structures (e.g. **5**) promise easy processibility in films and show dramatically increased solubility due to their steric needs (Keegstra *et al.* 1996).

2. Donor–acceptor-substituted poly(para-phenylene-vinylene) (D/A-PPV)

The incorporation of donor–acceptor moieties into PPV, which allows the combination of extended (π -conjugation with strong dipole moments, has been accomplished by a new synthetic approach (Klärner *et al.* 1996). Here, the central benzene rings carry a cation and an anion function (**6**, **7**). The new connective C–C-coupling reaction, based on the simple cation–anion addition, enables the formation of the donor–acceptor-substituted vinylene unit **8a**, **b** under very mild conditions with high conversion of functional groups.

The donor–acceptor-stilbene **8b** constitutes an attractive material in its own right, as this compound represents the basic building block of the corresponding PPV **9** and enables the investigation of optical, dielectrical and redox properties of this structure type.

We applied this synthetic strategy for the successive build-up of oligomers as well as AB-type and AABB-type polycondensations. The oligomeric and polymeric materials **9**, **10** allow the investigation of strong dipole moments along the mainchain by dielectric spectroscopy.

The benzene rings serve as spacers for the systematic separation of dipole units along the mainchain in order to study cooperative dipole–dipole interactions. To un-

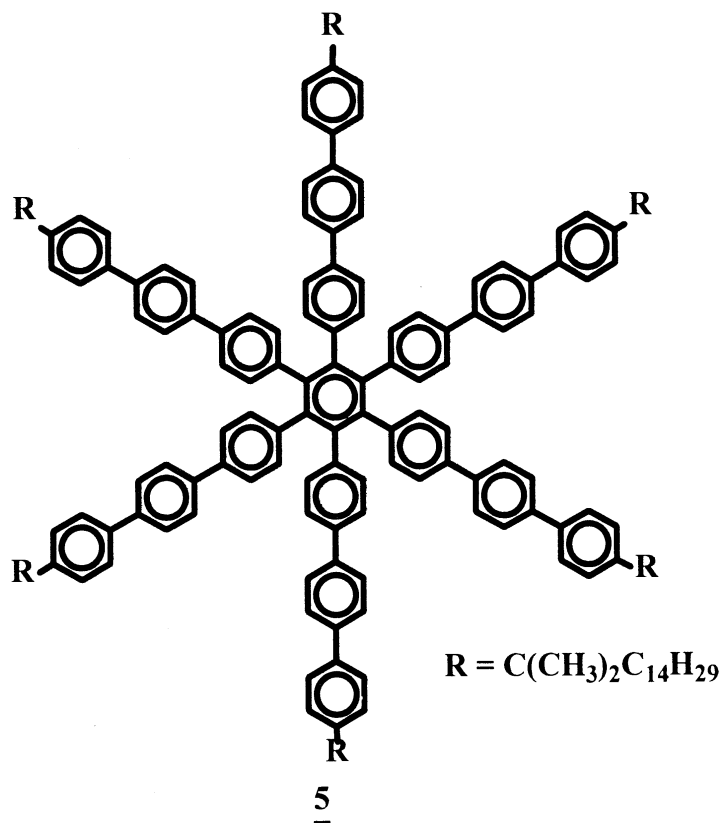
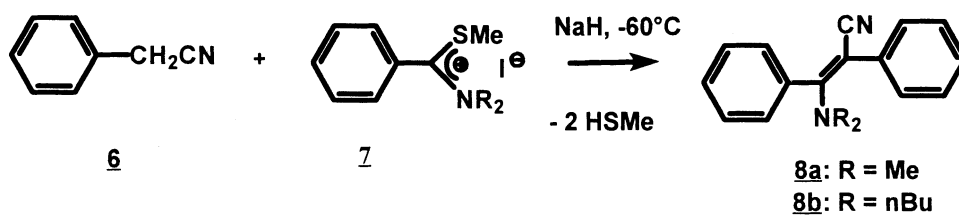


Figure 4.



Scheme 1.

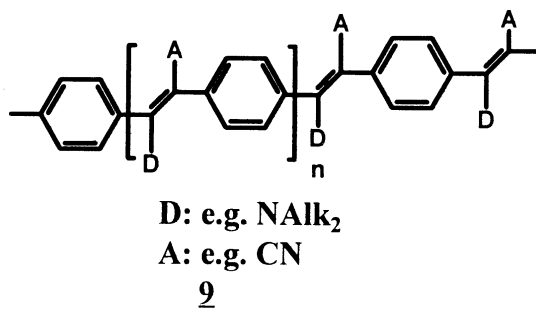


Figure 5.

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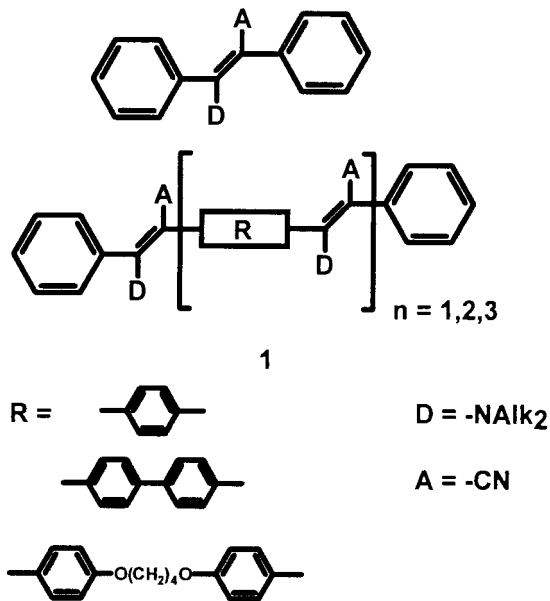


Figure 6.

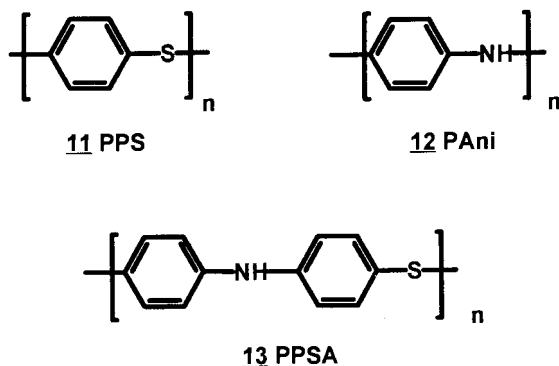


Figure 7.

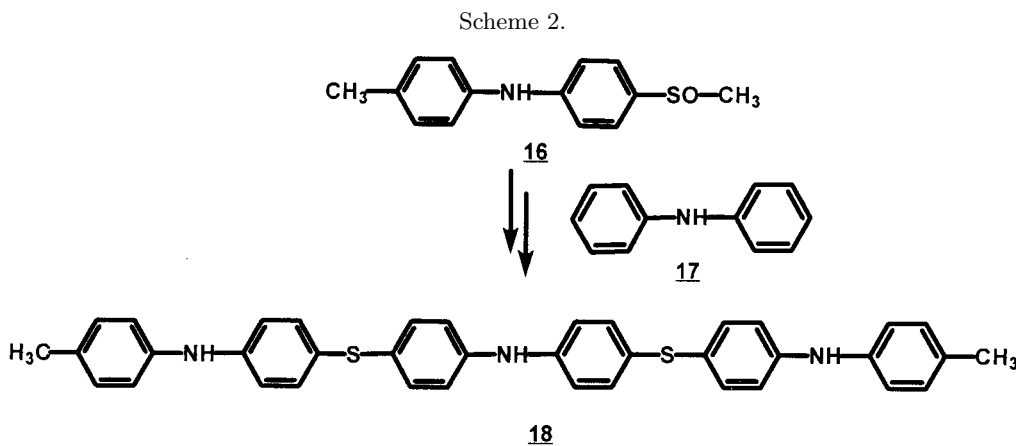
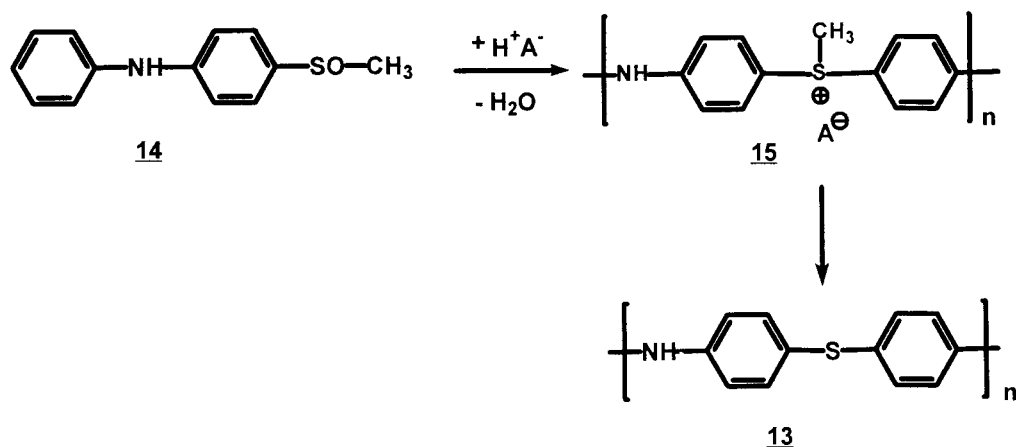
derstand the dipole additivity of the donor–acceptor units along the mainchain of the oligomers **10** in solution, it is necessary to take conformational and configurational changes as well as Coulomb interactions into consideration.

This approach is intended to, for example, improve the poling stability of polymers in nonlinear optical devices and increase second-order optical susceptibilities.

3. Poly(para-phenylenesulphide-para-phenyleneamine) (PPSA)

In poly(para-phenylenesulphide-para-phenyleneamine) (PPSA) **13** the benzene ring represents a modulus for the combination of two well-known polymers, poly(para-phenylenesulphide) (PPS) **11** and polyaniline (PAni) **12** (Wang *et al.* 1996).

The acid induced AB-type polycondensation of the aromatic sulphoxide **14** provides the precursor polysulphonium cation **15**. The key step in this reaction is the



electrophilic attack of the benzene unit. The demethylation of **15** leads to the defect-free high molecular weight material **13** ($M_n = 120\,000$).

The absence of crosslinking and the amorphous structure of PPSA provide high solubility in solvents like THF, DMF and NMP. The polymer **13** forms free-standing films, which exhibit good conductivities upon doping. A further attractive aspect concerns the dehydrogenation of PPSA producing, eventually, an organic analogue of poly(sulphurnitride).

We were able to apply this synthetic strategy for the build-up of oligomers with well-defined structures.

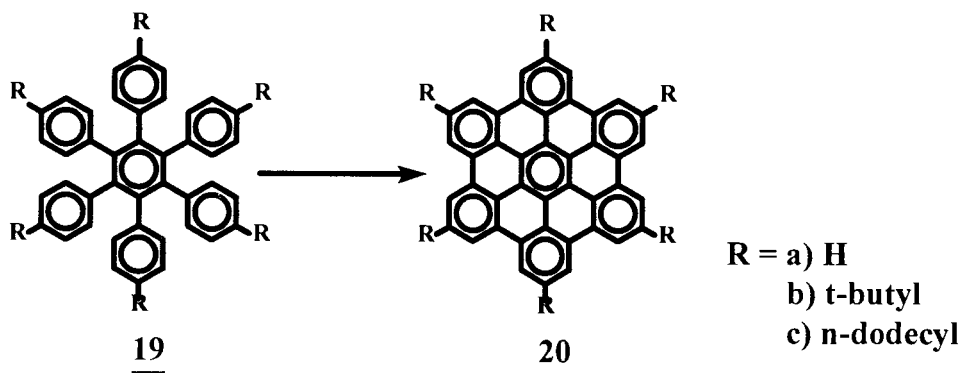
The oligomer **18** represents a valuable model compound for the generation of aminyl radicals and their investigation by ESR-spectroscopy.

4. Graphite sheets

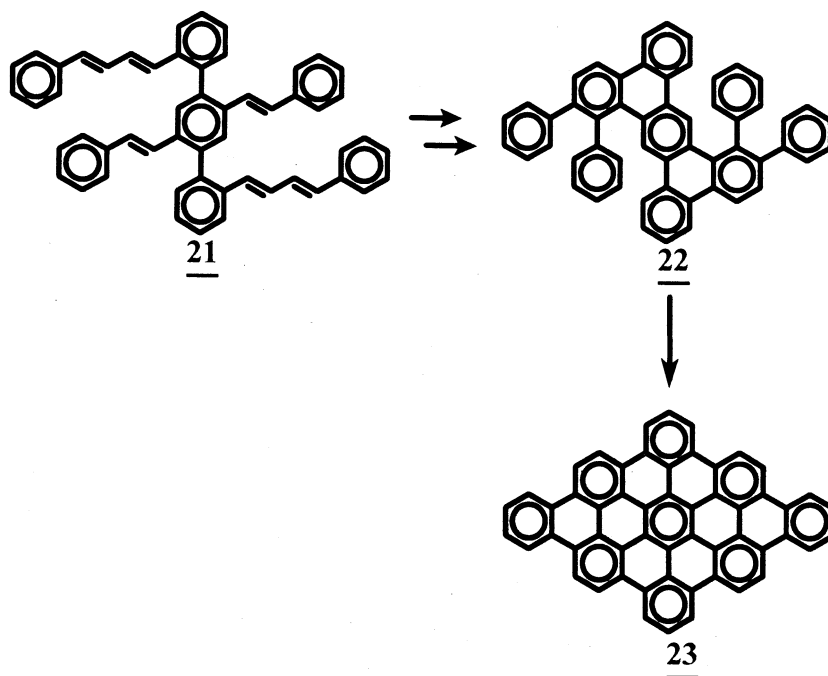
Ribbon-type polymers, such as $[n]$ acenes, are electronically attractive due to their low band gap. We have recently used pentacene as an active component of field effect transistors with a high charge carrier mobility, whereby the mode of processing appears to be crucial (Brown *et al.* 1996). Unfortunately, stability problems arise in low band gap materials even in the case of the lower homologues (Horn *et al.*

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Scheme 4.



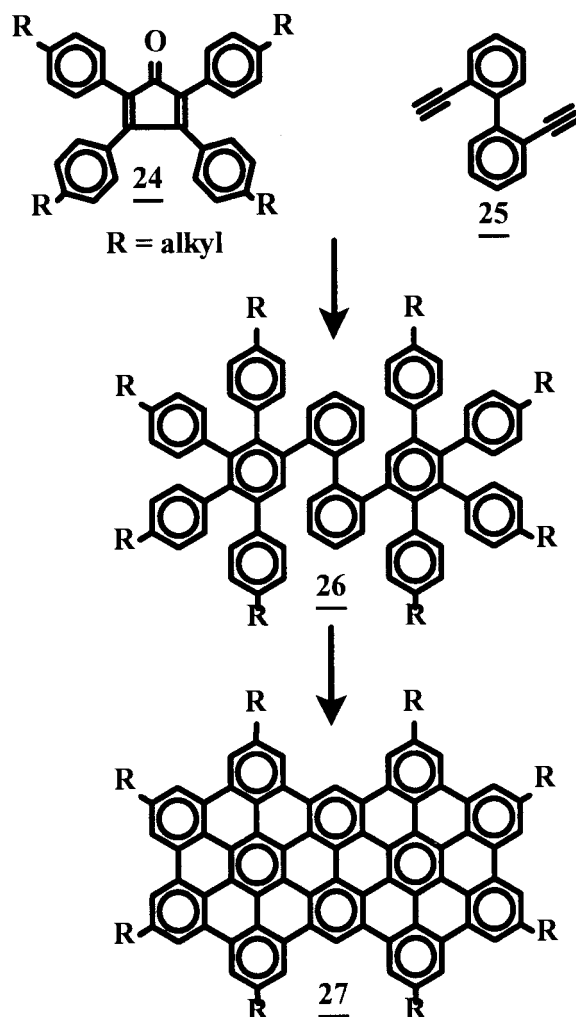
Scheme 5.

1995; Scherf & Müllen 1995). One of our approaches is therefore restricted to those polybenzenoid hydrocarbons which are stable according to Clar's predictions (Clar 1972).

The synthetic routes adopted for the fusion of benzene rings involve:

(1) cyclodehydrogenation of oligophenyl precursors: thus hexaphenylbenzenes **19** produce hexa-peri-hexabenzocoronenes **20** (R = H, t-butyl, n-dodecyl) with hexagonal symmetry. Thereby, solubility and processability are achieved via alkyl substitution (scheme 4) (Stabel *et al.* 1995*a, b*);

(2) intramolecular Diels–Alder cycloaddition of oligophenylene vinylene precursors: in this case **21** is transformed into **23** via a sequence involving cycloaddition, dehydrogenation and electron-transfer induced cyclodehydrogenation (scheme 5) (Müller *et al.* 1995*a, b*, 1996).

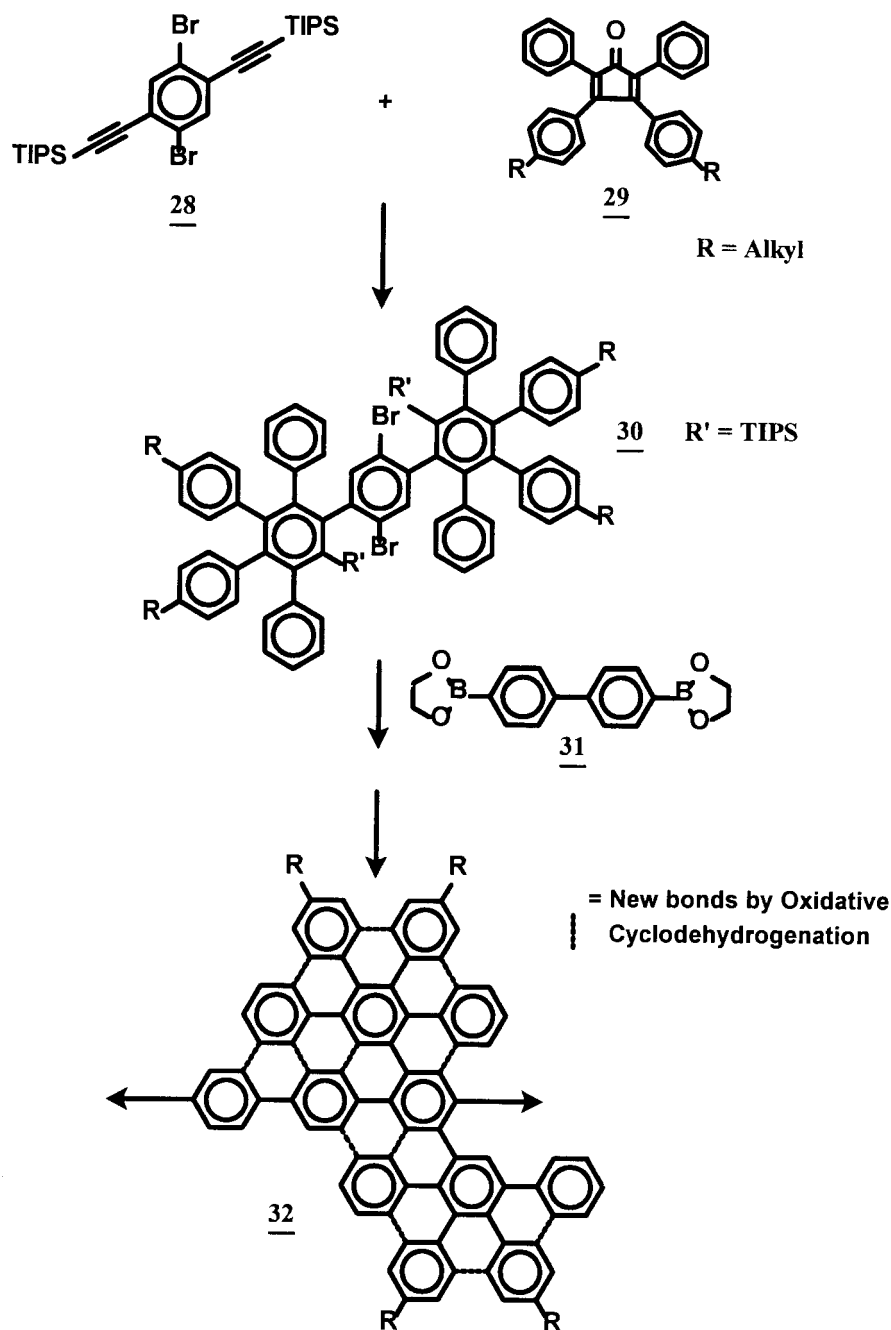


Scheme 6.

As another approach towards large polybenzenoid hydrocarbons it is possible to react phenyl substituted cyclopentadienones, such as compound **24**, with acetylene derivatives, e.g. **25**, in a [2 + 4] cycloaddition with extrusion of carbon monoxide (Morgenroth *et al.* 1997; Iger *et al.* 1997). One of the various shapes of the obtainable polybenzenoid structures that can be established by this simple synthetic sequence, starting from readily available compounds, is shown in scheme 6. In this case again the final reaction step towards the hydrocarbon **27** includes an oxidative cyclodehydrogenation.

It is obvious that the synthesis of polybenzenoid discs via a Diels–Alder reaction of cyclopentadienones and acetylene derivatives can be easily transferred into a construction concept for polymer synthesis to form higher homologues of **27**. Here we present the synthesis of the soluble and easily processible hydrocarbon **30**, formed by Diels–Alder reaction of acetylene **28** and cyclopentadienone **29**. Polymerisation of **30** via Suzuki coupling with **31** and final cyclodehydrogenation lead to the carbon strip polymer **32** with well-defined width and edges.

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Scheme 7.

The key design principles can thus be summarized as follows: benzene is used as a rigid modulus whereby one crucial fusion process is cyclodehydrogenation of the processible precursors built by [2 + 4] cycloaddition or trimerization reactions.

Accordingly, in the construction of the oligophenyl and oligophenylenevinylene precursors, branching will be avoided; instead, the building blocks should always be

able to converge to closed loops. Alkyl substitution will, in many cases, be unavoidable to achieve soluble and processable discs.

Having available extended polyaromatic hydrocarbons, two supramolecular motifs can be considered: the formation of columnar arrangements as a model of three-dimensional graphite, and the formation of monomolecular adsorbate layers as a model of two-dimensional graphite. With respect to the latter topic, it should be mentioned that graphitic structures have recently been manipulated by using the tip of an atomic force microscope and 'graphene' sheets have been achieved (Hiura & Ebbesen 1995). The graphite strip polymers can be considered as the missing link between structurally undefined macroscopic graphite and large well-defined polyaromatic hydrocarbons.

A typical structural motif of polycyclic benzenoid hydrocarbons is the formation of columns via π -stacking. Crystallization, cocrystallization, electrocrystallization and charge-transfer complex formation of large discs are considered to be possible approaches towards multilayered solid-state structures. Gavezzoti (1988) and Desiraju & Gavezzoti (1989) have analysed the packing modes occurring in single crystals of polybenzenoid aromatic hydrocarbons. It is clear that an inclusion of much larger discs is an important ingredient of such an approach. We have grown single crystals of, e.g., hexa-*t*-butylhexabenzocoronene **20b**, which shows a sandwich herringbone motif (Herwig *et al.*, unpublished results) in contrast to the simple herringbone motif of the unsubstituted hexabenzocoronene **20a** (Goddard *et al.* 1995).

More interesting from a practical point of view—e.g. processability or fibre formation—is the occurrence of mesophases eventually with columnar structures. According to differential scanning calorimetry and X-ray diffractometry, hexadodecylhexabenzocoronene **6c** forms a very stable columnar mesophase with a hexagonal superstructure (Herwig *et al.* 1996). The very high isotropization temperatures of hexaalkyl substituted hexabenzocoronene (often in excess of 400 °C) suggest the comparison with the so-called carbomesophases formed above 400 °C during the production of technical graphite from an isotropic coke (Marsh 1989). Also, it is shown by solid-state deuterium NMR-spectroscopy that large discs can maintain a stable columnar super structure, while at the same time having a lower degree of ordering than smaller discs (Swalen *et al.* 1987).

Using graphite itself as a reference system for the analysis of large polybenzenoid hydrocarbons, another challenge is obvious: the formation of highly ordered monomolecular layers on substrate surfaces. Such layers are relevant for many fields of research, e.g. as active components in sensors or, somewhat more remotely, as elements of molecular electronics (Swalen *et al.* 1987). One anticipates such layers result from a subtle balance of substrate–adsorbate and adsorbate–adsorbate interactions and sensitively depend upon size and symmetry of the molecules.

An immobilization of a single molecule, e.g. as part of monomolecular adsorbate layer on highly ordered pyrolytic graphite, is also a precondition for its description by scanning tunnelling microscopy. This method has recently found a wider application (Pomerantz *et al.* 1992). However, there are only few successful studies of scanning tunnelling spectroscopy in which, due to a submolecular resolution, one would achieve a chemical sensitivity of the STM technique. Prototype molecules would be alkyl-substituted aromatic hydrocarbons, which possess spatially separated domains of significantly different electronic properties. Thereby the electronic states of the alkyl units are energetically far away from the Fermi level of the electrode. Here again, the size of the graphite subunits appears to be crucial.

Based on benzene units as modular building blocks the present contribution has been focusing on new synthetic approaches toward extended polyaromatic hydrocarbons, their homologous polymers and the resulting opportunities for supramolecular ordering (i) in two-dimensional adsorbate layers on substrates and (ii) in three-dimensional columnar arrangements. Photoconductivity occurring in columnar mesophases, an eventual increase of charge carrier mobility and electrical conductivity seen in monomolecular adsorbate layers define our current investigations.

5. Conclusions

The examples discussed in the course of this article underline the key role of the benzene ring for synthesis and supramolecular ordering of conjugated oligomers and polymers.

The functionalized benzene ring enables a wide range of coupling methods such as Suzuki and Yamamoto reactions. The introduction of cation and anion functions leads to new connective C–C-coupling reactions to incorporate donor–acceptor-moieties into a conjugated polymer mainchain. For the PPSA, the benzene ring allows the structural combination of two classical polymers, PPS and PANi.

As a motif for geometry control the benzene ring serves as an element for (i) the planarization of PPP-type structures, (ii) the systematic separation of dipoles and (iii) the design of molecular objects differing in size and shape in order to achieve the phenomenon of supramolecular ordering.

The new quality of these approaches is in particular the availability of well-defined and readily processable materials with tailor-made electronic properties.

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