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Polyphenylene Nanostructures

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I. Introduction

A considerable part of synthetic organic chemistry is derived from the functionalization of benzene, and the pharmaceutical industry has recognized the physiological effectiveness of tailor-made benzene derivatives since the introduction of aspirin, acetyl salicylic acid. Nevertheless, the chemistry of planar benzenoid compounds and the polyphenylenes thus derived is regarded today as unattractive and sterile. The compounds lack the appeal of stereogenic centers, a trait generally associated with chemical and biological activity.[1−3] In light of such disinterest, is benzene chemistry only suitable for the petrochemical generation of industrial intermediates?

Casting ones glance, for the moment, away from the constant efforts to increase synthetic efficiency, for example, by increasing selectivity and suppressing by-products, numerous researchers are seeking new information directed toward biological sciences or materials science. An important reason for this shift in interest is the perception of the active biological or physical function of synthetic compounds. If one considers the interdisciplinary connection between synthesis and material science, an impetus for research is only obtained when an additional condition is fulfilled: it is necessary to generate a defined, macroscopic architecture.[4] Accordingly, synthesis and processing must be regarded as a single unit to obtain the desired supramolecular ordering. Nanostructures are particularly attractive. Their production involves principally two different methods: designing from macroscopic precursors (e.g., lithographic techniques) or systematic synthesis and directed manipulation of individual macromolecules or molecular aggregates of defined shape and size.[5] The goal of the outlined development would be the management of individual molecules as elementary functional units.[6]

In this respect benzene has a new role. Its hexagonal symmetry, anisotropy, and functional versatility render it ideally suitable as a modular repeat unit. Therefore, the construction of macro- and supramolecular structures of various sizes and shapes using covalent and noncovalent bonds becomes possible. The repeated covalent coupling of benzene units leads, in fact, to homologous series of varying size and dimensionality. These include linear poly(*para*-phenylene)s (PPP, **1**)[7−9] and poly[*n*]acenes (**2**) (1-dimensional architectures),[10−15] compounds composed exclusively of benzene units such as the polycyclic aromatic hydrocarbons (PAH) like **3** (2-dimensional architectures)[10−17] and spherical polyphenylene dendrimers (e.g., **4**, 3-dimensional architectures) which are polymers with a high degree of regular branching but no cross-linking (from Greek: dendron = tree).[18−20] In many cases, the synthesis of alkyl-substituted derivatives of such compounds is an important additional step. Such alkyl substitution confers increased solubility in organic solvents and aids the formation of supramolecular ordering (see below).

In addition to the synthetic stimulation provided by such a type of modular benzene chemistry, one driving force for research is the wealth of varying physical properties of these compounds. Important industrial materials such as graphite are even today only understood at the macroscopic level. We are still waiting for experimental support of theoretical con-

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siderations at the molecular level. If we were to state a few typical questions here, they might be arranged in terms of the dimensionality of the molecular objects: (i) What is the effect of twisting in polyphenylene chains on the effective conjugation length?[13] (ii) Under what topological conditions and from what size do the electronic properties of extended PAHs converge with those of graphite? Could large-scale PAHs serve as molecularly defined models for graphite?[10,16,17,22−25] (iii) To what extent do polyphenylene dendrimers possess a persistent shape and easily functionalized surface, despite the free rotation of the individual phenylene units? In addition to the fundamental questions about the electronic properties or the molecular or supramolecular structure of these compounds, there are also questions about the potential applications. A few important considerations are as follows: (i) does the parallel ordering of polyphenylene chains into lamellar superstructures have consequences for their function as electronic materials, for example, in light-emitting diodes?[26] (ii) Does the organization of all-benzenoid PAHs in a discotic mesophase permit charge transport along the columnar axis?[27−31] (iii) Are linear or highly branched polyphenylenes suitable spacers for supramolecular or heterosupramolecular structures?

In this review we describe *synthetic approaches to polyphenylenes of varying dimensionality*. Naturally, we start with linear (1-dimensional) polyphenylenes (Chapter II) and then introduce various synthetic concepts for increasing the degree of branching within oligophenylbenzene repeat units (Chapter III). This design process, the essence of which is the *chemical control of size and shape of polyphenylenes*, ultimately leads to hyperbranched and dendritic 3-dimensional polyphenylenes (Chapter IV). While this approach increases the molecular complexity by proceeding from 1-dimensional to 2-dimensional to 3-dimensional polyphenylenes, the reverse process is also possible. It is a key feature of some polyphenylene dendrimers that they can be planarized and thus reduced in dimensionality by intramolecular cyclodehydrogenation (Chapter V).

Whereas the above protocol implies covalent bonding, mostly by phenyl−phenyl coupling and cycloaddition processes which form benzene rings, a complementary approach toward benzene-based nanostructures employs supramolecular ordering of poly-

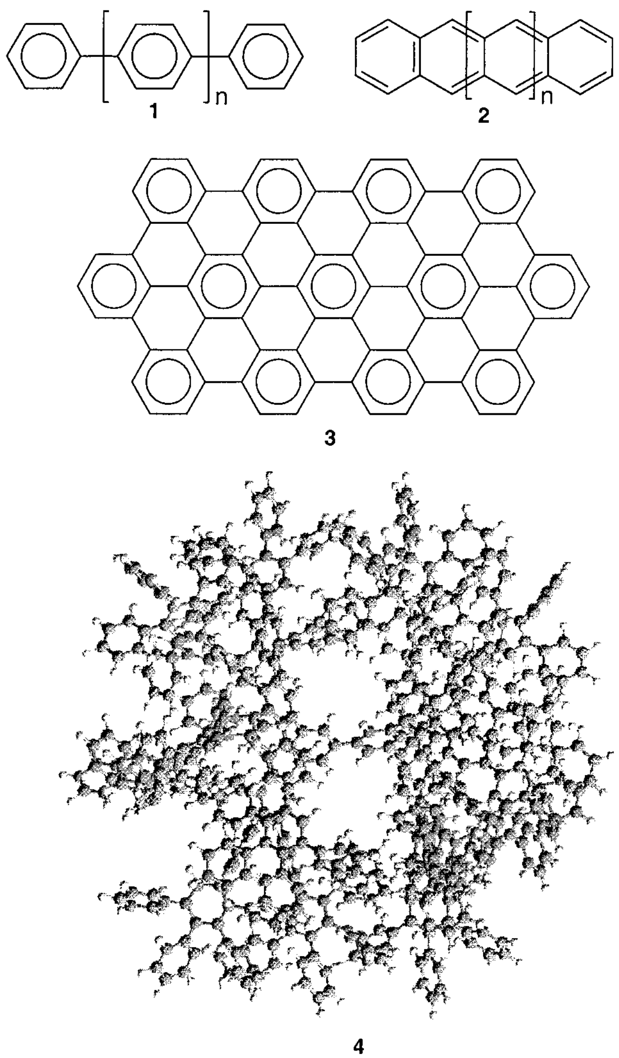


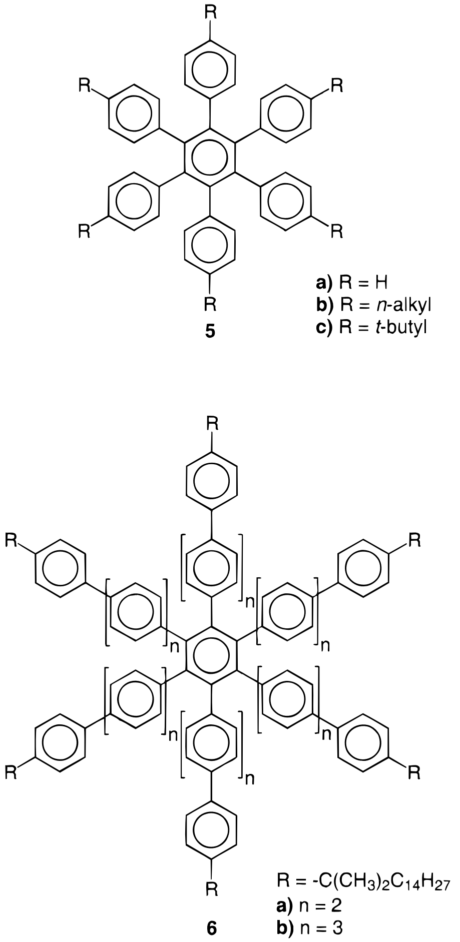
Figure 1. One-, two-, and three-dimensional polyphenylene structures, where **4** is shown as a computer-generated ball-and-stick model.

phenylene molecules (Chapter VI). This organization can occur in solution, in the bulk, and at interfaces. A great number of supramolecular patterns are feasible, such as (i) parallel arrays of 1-dimensional polyphenylenes, with the stiffness of the chains and the packing of alkyl substituents serving as structure-forming principles;[26,32] (ii) columnar arrangements or tightly packed monolayers formed from disc-type 2-dimensional polyphenylenes;[27] and (iii) lattices built up from 3-dimensional polyphenylenes.

A brief discussion of typical molecular sizes in oligo- and polyphenylenes is appropriate. Assuming a value of 0.28 nm for the diameter of a benzene ring and 0.15 nm for an inter-ring single bond, terphenyl and septiphenyl are 1.14 and 2.86 nm long, respectively. This also defines the diameter of the 2D structures hexaphenylbenzene (**5a**) as 1.14 nm and the aromatic part of hexa(terphenylyl)benzene (**6a**)[33] as 2.86 nm, Chart 1. Similarly, a spherical polyphenylene dendrimer such as **4**, which contains 102 benzene rings, has a diameter of about 4 nm.

Discussing ordered polyphenylenes requires a definition of the length scale of the particular supramolecular motif. It is a logical extension of such considerations to deal with the properties of polyphenylene molecules that are immobilized in a regular pattern. The solid-state structures of poly(*para*-phenylene)s usually show a parallel alignment of the PPP chains. The distances between the chains are dependent on the substituents attached to the PPP backbone and increase as the size of the substituents increases.

Chart 1



a) R = H
b) R = *n*-alkyl
c) R = *t*-butyl

R = -$C(CH_3)_2C_{14}H_{27}$
a) n = 2
b) n = 3

It seems highly appropriate when varying the size of 1-dimensional, 2-dimensional, or 3-dimensional molecules to consider polymers and their structurally related oligomers together. Oligomers possess only a few repeat units and can be regarded as smaller analogues of the corresponding polymers. Analogously to polymers, oligomers can also be polydisperse, that is, display a molecular weight distribution. Constructing a homologous series of monodisperse oligomers allows determination of more reliable structure−property relationships, such as wavelength of optical absorptions or cyclovoltammetric redox potentials as a function of the chain length. The structures of oligomers are often better defined than those of polymers, and purification is more straightforward. Studying the electronic behavior of oligomers and extrapolating toward the behavior of polymers has therefore been employed to characterize conjugated polymers in their true, defect-free state. A particularly important concept in this respect is the effective conjugation length.[34]

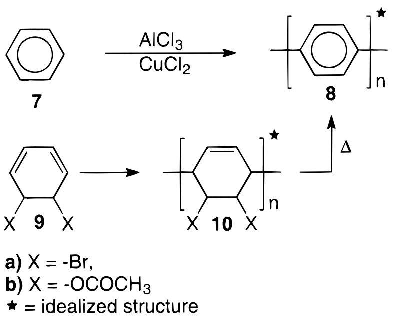
II. One-Dimensional Polyphenylenes as the Core for Multidimensional Systems

A. Poly(*para*-phenylene), Poly(*meta*-phenylene), and Poly(*ortho*-phenylene)

Linear oligo- and polyphenylenes can be regarded as the backbone from which multidimensional polyphenylene systems can be produced by functionalization and structural variation. In 1886 Goldschmiedt reported on the synthesis of a poly(*para*-phenylene).[35] He applied the Wurtz–Fittig reaction which coupled *para*-dibromobenzene using sodium. Relying on elemental analysis, he concluded that he had obtained fractions up to the tridecamer. In 1936, Busch et al. used the same monomer to obtain a PPP containing up to 16 benzene rings.[36] In this case, potassium hydroxide and iodine were used in the polymerization.

In the 1960s, Kovacic et al. reported on the oxidative polymerization of benzene (**7**) to prepare poly(*para*-phenylene) (**8**) using aluminum(III) chloride as a Lewis acid catalyst and copper(II) chloride as an oxidant (Scheme 1).[37–41] The polymer obtained was a black material, a large fraction of which was insoluble and contained numerous defects in the form of *ortho*- and *meta*-bridges as well as chlorination and intermolecular cross-links of individual polyphenylene chains.

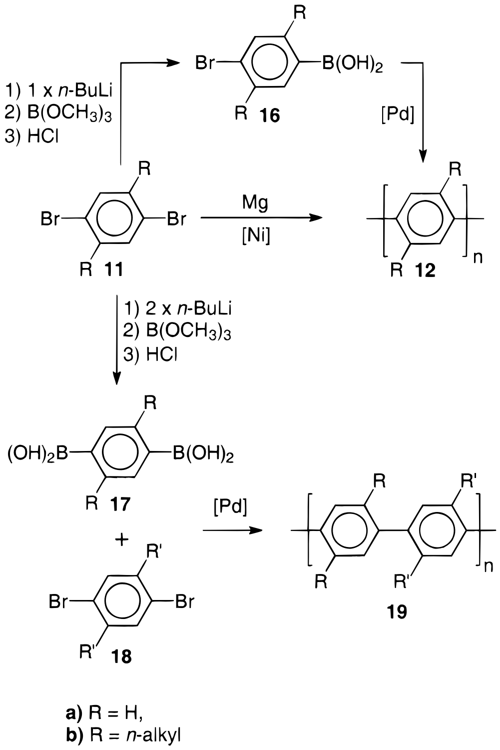
Scheme 1



As early as 1959, Marvel et al. introduced a synthetic sequence in which 5,6-dibromocyclohexa-1,3-diene (**9a**) was converted into poly(5,6-dibromo-1,4-cyclohex-2-ene) (**10a**) and subsequently into the desired PPP (**8**) in a thermally induced solid-state reaction with elimination of hydrogen bromide.[42,43] Nevertheless, the PPP (**8**) obtained by the precursor route also contained a substantial amount of defects, caused by incomplete elimination and cross-linking. However, this precursor concept experienced a renaissance in 1987 through Ballard et al., who replaced the bromo with an acetoxy function.[44–46] The thermal elimination of acetic acid from the poly(5,6-diacetoxy-1,4-cyclohex-2-ene) (**10b**) did not need to be carried out in the film, as the compound was sufficiently soluble. Still, a uniform PPP without defects could not be obtained in this manner. During the polymerization, about 10% yield of 1,2-coupled product occurs in addition to the preferred 1,4-coupling, leading after elimination to *ortho*-branches in the PPP. More recently, however, by using trimethylsiloxy protecting groups and a nickel catalyst, Grubbs et al. could significantly improve the polymerization to yield up to 96% of an exclusively 1,4-linked polymer.[47–51] For the subsequent aromatization it was necessary to convert the polymer into the corresponding acetoxy compound. Again, aspects of synthesis and processing must be combined in order to control the morphology of the final product. Thus, if a leaving group such as acetic acid is eliminated during the final aromatization, the precursor is transformed into an amorphous foam.

A milder route to PPP, in comparison with the thermolysis of appropriate precursors, consists of the polymer-analogous use of transition-metal-catalyzed aryl–aryl coupling. Difunctionalized benzene derivatives are used as starting materials. The reaction of 1,4-dibromobenzene (**11a**) with magnesium in the presence of various low-valent nickel catalysts was described as early as 1978 by Yamamoto et al. (Scheme 2).[52–55] The PPP thereby obtained (**12a**) was an exclusively *para*-coupled material, composed of chains 2.0–6.3 nm long with 5–15 repeat units. As a result of the mild coupling conditions, the product was light yellow, in comparison with the black PPP (**8**) obtained by Kovacic. The low molecular weight was a result of the low solubility of the PPP formed, which precipitated during the reaction, thereby preventing further conversion;[56] side reactions of the nickel-catalyzed Grignard coupling were also conceivable, leading to termination of the polycondensation. To circumvent the solubility problem, Yamamoto et al. used 1,4-dibromobenzene with solubilizing *n*-alkyl side chains[57–62] in the 2- and 5-positions (**11b**) as a monomeric building block in later work.[52–55,63] For the first time, the isolated *n*-alkyl-substituted PPP derivatives (**12b**) could be investigated in detail using various spectroscopic techniques, although

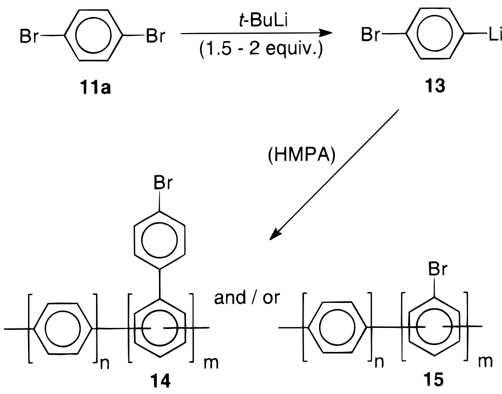
Scheme 2



again the polymer possessed only 15 repeat units. Yamamoto et al. considered difficulties with the stoichiometric ratios and terminal dehalogenation of the PPP chains to be the cause of the low molecular weight.

A very simple way to predominantly *para*-linked polyphenylenes was introduced by Tour and coworkers. They used 1,4-dibromobenzene (**11a**), which they were able to monolithiate followed by polymerization with hexamethylphosphoramide (HMPA) as depicted in Scheme 3.[64−67] Later, they also published a route in which the use of hexamethylphosphoramide could be avoided.[66−68] The polymers contained several bromo and/or bromophenyl substituents which could in turn be further functionalized.[66−68] X-ray diffraction studies of the brominated as well as the debrominated polymer did not show any diffraction pattern. This was supported by scanning electron microscopy displaying a globular morphology pattern.

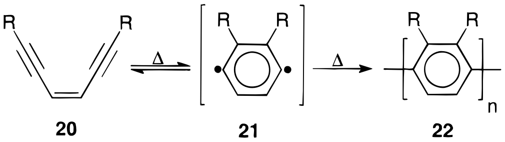
Scheme 3



In the search for transition-metal-catalyzed coupling reactions that could circumvent the problems mentioned, Schlüter, Wegner et al. used the palladium-catalyzed hetero-aryl−aryl coupling of various bromobenzene derivatives with phenylboronic acids (after Suzuki[69,70] and Miller[71]) and applied this technique to the polymer case (Scheme 2).[63] Starting from dialkyl-substituted dibromobenzenes **11b**, they prepared the corresponding AB-type building block (4-bromophenyl)boronic acid (**16b**), which, in the course of the polymer-analogous boronic acid coupling, led to soluble, *n*-alkyl-substituted PPP derivatives (**12b**) with up to 100 repeat units. Also, a system of AA- and BB-type building blocks such as **17** and **18** containing nucleophilic and electrophilic functionalities, respectively could be isolated and then introduced into the coupling reaction.[72−74] An important consequence of the use of phenylenediboronic acids is that one can achieve a heterocoupling of different building blocks.

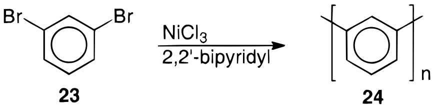
Tour et al. have recently presented a route to polyphenylenes using enediynes. When heated, enediynes form a benzene biradical, as shown in Scheme 4. This biradical undergoes a spontaneous polymerization forming a poly(*para*-phenylene).[75,76] A range of substituted monomers was employed to form a wide variety of polymers with the polymerization itself proceeding very quickly. Even in the presence of radical terminators, the yields of monomeric benzene derivatives were found to be very low.[75] Mechanistic studies showed that two biradicals react with each other to form the polymer, rather than one radical attacking an enediyne molecule and starting a chain reaction.[76]

Scheme 4



As a result of its angular structure, unsubstituted poly(*meta*-phenylene) (**24**, Scheme 5) is significantly more soluble in organic solvents than linear PPP (**12a**) of comparable molecular weight. Percec et al. described the synthesis of poly(*meta*-phenylene) (**24**) following the method of Yamamoto[52−54] starting from 1,3-dibromobenzene (**23**), catalyzed by nickel(II) chloride and 2,2′-bipyridyl.[77]

Scheme 5

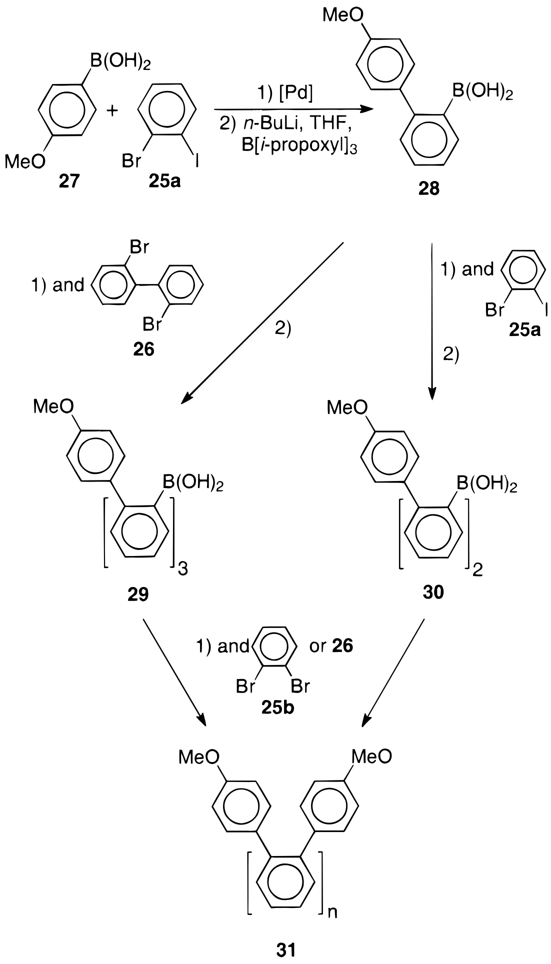


The third class of polyphenylenes, poly(*ortho*-phenylenes), have so far been explored very little.[78,79] However, Simpkins et al. recently published a novel set of oligo(*ortho*-phenylenes) (**31**) using repeated Suzuki coupling[69,70] of various *ortho*-substituted halobenzenes (**25**) and biphenylenes (**26**).[80] Even though the reaction yields were moderate, Simpkins et al. were able to prepare oligomers with up to nine repeat units (Scheme 6). As with poly(*meta*-phenylenes), the *ortho*-analogs are soluble even when unsubstituted.

On combining a stiff, insoluble, rodlike polymer such as PPP with a soft coil, for example, polystyrene, it is possible to form a new polymer with novel and interesting properties, as described in Chapter VI.A. The coupling of these rod and coil moieties can be achieved by either of two principles. A monofunctionalized block may be used as macroinitiator to start a “polymerization from”, as described by Zhong and François.[81−89] They used living polystyrene (**32**) as their macroinitiator, which was treated with cyclohexadiene (**33**) to form a polystyrene-*block*-poly(1,3-cyclohexadiene)(PS-*b*-PCHD) system (**34a**, Scheme 7). The PCHD block was then aromatized in the manner suggested by Marvel et al.[42] The degree of polymerization varied between 60 and 320 repeat units for the PS part and between 25 and 160 repeat units for the PCHD part. However, the aromatization was incomplete, so the PPP sequence contained several PPP blocks separated by nonaromatic cyclohexene rings. The average length of the PPP blocks varied depending on the aromatization conditions and PS-*b*-PCHD copolymer used.

The second method of preparing a block copolymer is by coupling two appropriately functionalized polymers. It is clear, however, that this approach requires a quantitative end-functionalization of the oligo- or polyphenylene component. Recently, the synthesis of a variety of luminescent rod−coil block copolymers

Scheme 6

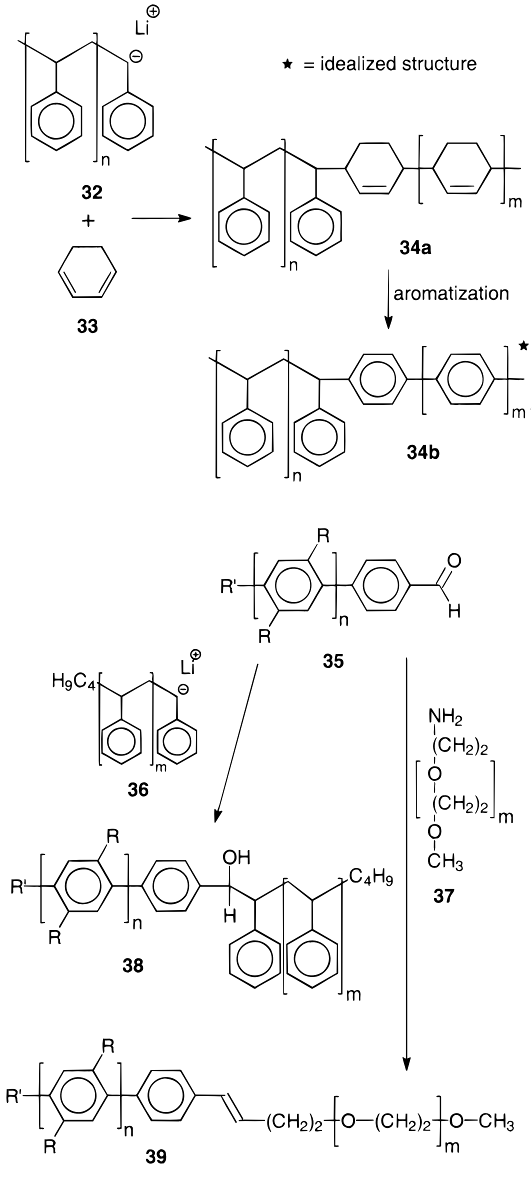


by condensation of perfectly end-functionalized poly(2,5-diheptyl-*para*-phenylenes) (**35**) (PPP) with polystyrene (PS) (**36**) or poly(ethylene oxide) (PEO) (**37**) was reported.[90] In this case, PPP chains with 7−10 repeat units were used. Employing the Suzuki coupling of aromatic monomers[69,70] in preparing the PPP block has the advantage of ensuring an aromatic block with far fewer defects.

B. Synthesis of Bridged Polyphenylenes: Step-Ladder and Ladder Polymers

Although alkyl substituents in the 2- and 5- positions lead to a considerable improvement in the solubility of poly(*para*-phenylene)s, they also have an important disadvantage with respect to the electronic properties of PPPs. As a result of the steric demands of the substituents, the dihedral angle between the individual polymer chains increases from 23° for an unsubstituted PPP[91] to 60−80° for dialkyl-substituted PPP derivatives,[92] which is coupled with a drastic reduction of the electronic conjugation along the main PPP chain. In Chapter VI the importance of alkyl groups in oligo- and polyphenylenes for the realization of supramolecular order will be shown. However, an important target in the synthesis of new PPP derivatives is the preparation of soluble, structurally defined phenylenes that are easy to process and that show, in comparison with the parent compound **12a**, intact or even increased π-electron conjugation.

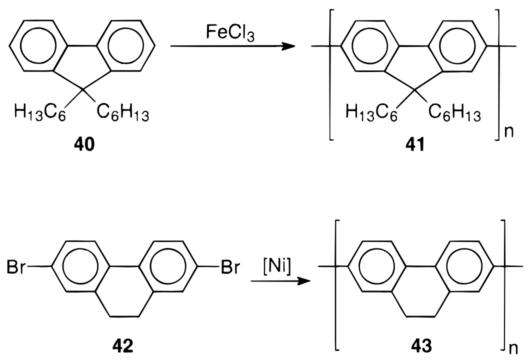
Scheme 7



a) $R = C_7H_{15}$, $R' = H$,
b) $R = C_7H_{15}$, $R' = C_6H_5$

A key synthetic step toward the realization of this target is the connection of solubilizing substituents with simultaneous conversion of neighboring *para*-phenylene units into planar or only slightly twisted conformations. This synthetic concept was realized by Yoshino et al.[93] through the iron(III) chloride catalyzed oxidative polymerization of 9,9-di-*n*-hexylfluorene (**40**, Scheme 8) under Kovacic conditions.[94,95] The di-*n*-hexylmethylene bridge provides adequate solubility in the poly(9,9-di-*n*-hexylfluorene-2,7-diyl) (**41**) and simultaneously forces the planar ordering of neighboring phenylene building blocks, which results in a 50 nm bathochromic shift of the long-wavelength absorption maxima in comparison with that of unsubstituted PPP (**12a**). However, the structural defects, which appear as the result of a 2,7-coupling during the aryl−aryl coupling, and the low degree of polymerization of maximum 20 aromatic rings remain a disadvantage.

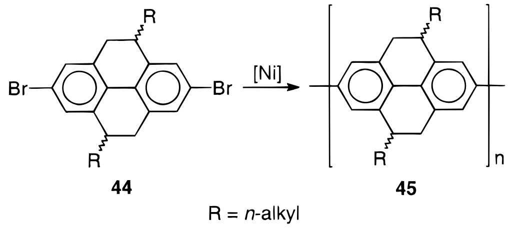
Scheme 8



In 1993, Yamamoto et al. described a simple approach to a further partially bridged PPP derivative with the synthesis of poly(9,10-dihydrophenanthrene-2,7-diyl) (**43**, Scheme 8). Starting from 2,7-dibromo-9,10-dihydrophenanthrene (**42**), they used the advantage of the efficient and highly selective nickel(0)-catalyzed homo-aryl−aryl coupling.[96] As a consequence of the low solubilizing effect of the ethanediyl bridges, only the oligomer fraction (M_n < 1000) of the resulting polymer **43** was soluble while the polymeric product precipitated from the reaction solution.

On the basis of these results, the nickel(0)-catalyzed aryl−aryl coupling of suitable alkyl-substituted dibromodihydrophenanthrenes or dibromotetrahydropyrenes for the preparation of soluble step-ladder polymers was an obvious choice. In 1995, Müllen et al. realized this synthetic concept,[21,97] by subjecting 2,7-dibromo-4,9-di-*n*-alkyl-4,5,9,10-tetrahydropyrene (**44**) as a monomeric building block to the conditions of the Yamamoto coupling (Scheme 9).

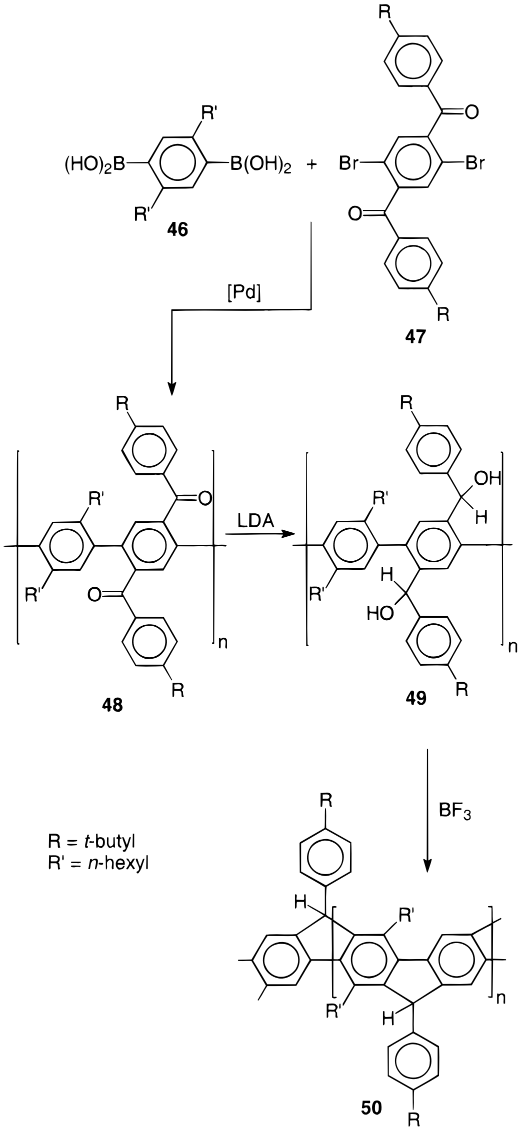
Scheme 9



The poly(4,9-di-*n*-alkyl-4,5,9,10-tetrahydropyrene-2,7-diyl)s (**45**) obtained were completely soluble and possessed relatively high molecular weights (M_n up to 20 000), corresponding to a chain length of approximately 46 repeat units. In subsequent work they also achieved separation of the diastereomers used as monomers by fractional crystallization and chromatography, whereby stereoregular poly(tetrahydropyrene)s **45** (*cis*- or *trans*-polymers) became accessible. The longest-wavelength absorption maximum λ_{max} of the poly(tetrahydropyrene)s **45** is 385 nm and is thus almost identical with the value determined by Yoshino et al. for the step-ladder polyfluorene **41**.[93] The poly(tetrahydropyrene)s **45** gave an intense blue photoluminescence in solution with a small Stokes shift (40 nm, λ_{max} emission: 425 nm) and also found was a slight bathochromic shift in the solid state as a result of aggregation. Thus, experiments were conceived to examine the suitability of the poly(tetrahydropyrendiyl)s **45** as emitters in the production of light-emitting diodes. In this respect, the principal use of suitably modified PPP derivatives was shown to be blue emitters.[21,97]

A further step in the concept of bridged PPP derivatives was the transition from step-ladder to ladder polymers. Twisting along the main polymer chain can be minimized by complete bridging of all phenylene rings with each of the respective neighboring monomer units. Thus, the maximum conjugation of π-electrons resulting from the planarization leads to an optimization of the chromophoric properties of poly(*para*-phenylene) compounds. An example of a ladder polymer synthesis of this type is the synthetic sequence published in 1991 by Scherf and Müllen,[98] which started from a dialkyl-substituted phenylenediboronic acid **46** and an aromatic dibromodiketone **47** and led, via the open-chain, single-stranded precursor PPP **48** in a multistep sequence, to the double-stranded ladder polymer **50**, Scheme 10. With the synthesis of the well-defined ladder polymer **50**, it was possible to show that the polymer-analogous ring closure by intramolecular Friedel−Crafts alky-

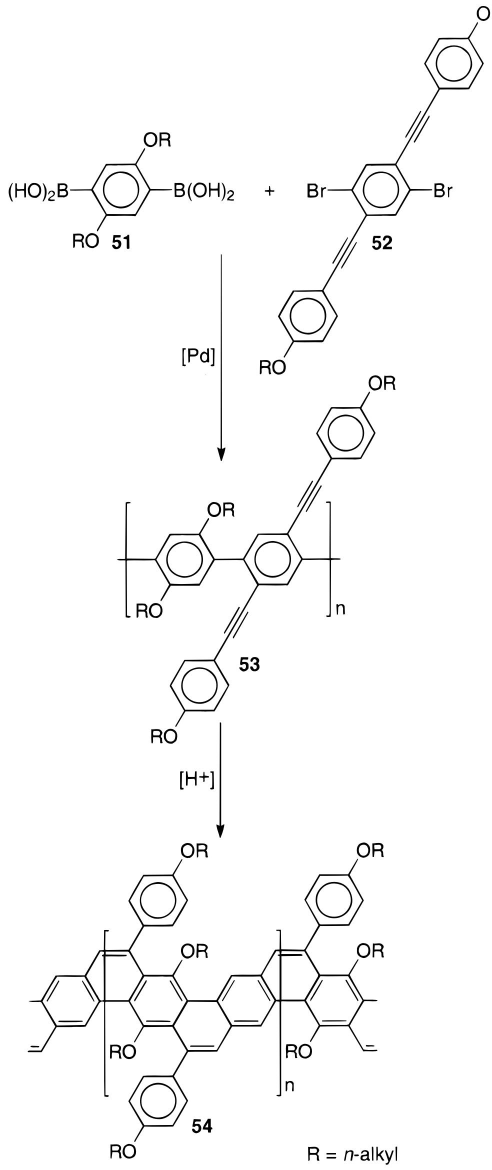
Scheme 10



lation, regarded as the critical reaction step, could be carried out quantitatively and regioselectively. The resulting soluble ladder polymer **50** shows an average molecular weight M_n of 25 000 (corresponding to approximately 65 phenylene units). The longest wavelength absorption maximum λ_{max} is 440−450 nm (a consequence of the bathochromic shift caused by the complete planarization), together with a high photoluminescence quantum yield. For these reasons, this ladder polymer is an attractive candidate for applications in light-emitting diodes.[99−112]

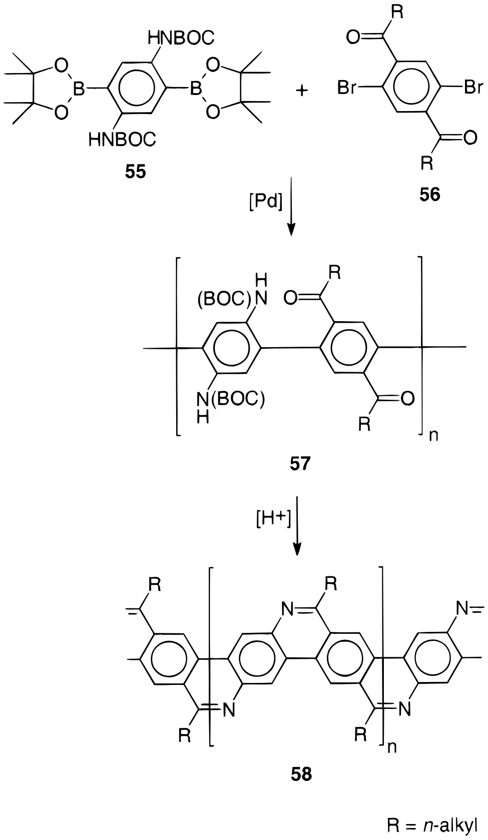
In 1994, Swager et al. used a variation on the ladder polymer concept of Scherf for the synthesis of the ladder polymer **54** (Scheme 11).[113] The boronic acid coupling of Suzuki[69,70] was also employed here to obtain, starting from the dialkoxy-substituted phenylene diboronic acid **51** and the diphenylethynyl-substituted phenylene dibromide **52**, the soluble precursor PPP **53**. Under acidic conditions, protonation of the ethynyl structure occurs. Formally, a vinyl cation is formed, which leads to an intramolecular electrophilic substitution on the neighboring phenylene unit. The resulting ladder polymer **54** can be regarded as an angular polyacene and thereby belongs to the class of ribbon polymers. Also, if one considers the ethenyl bridges as substituents and not as an integral component of the new polymer backbone, the PPP structure along the main polymer chain of **54** is retained. A theoretical comparison of the band gaps of the unsubstituted analogues of **54** and the (nonexistent) planar PPPs leads to almost identical values of approximately 2.8 eV, thereby supporting the description of the ladder polymer **54** as a PPP derivative.[114]

Scheme 11



In 1993, Tour et al. described the synthesis of the ladder polymer **58** containing an imine bridge as shown in Scheme 12.[115−120] The PPP backbone was once again produced using the Suzuki method.[69,70] The acidic deprotection of the amino group resulted in the immediate intramolecular reaction between the amine and the ketone to form the imine. The polymer thus formed is soluble in dichloromethane/trifluoroacetic acid mixtures. Optical measurements in solution showed wavelength absorption maxima λ_{max} at around 400 nm, i.e., in the range of other near-planar PPP derivatives.[98,115]

Scheme 12

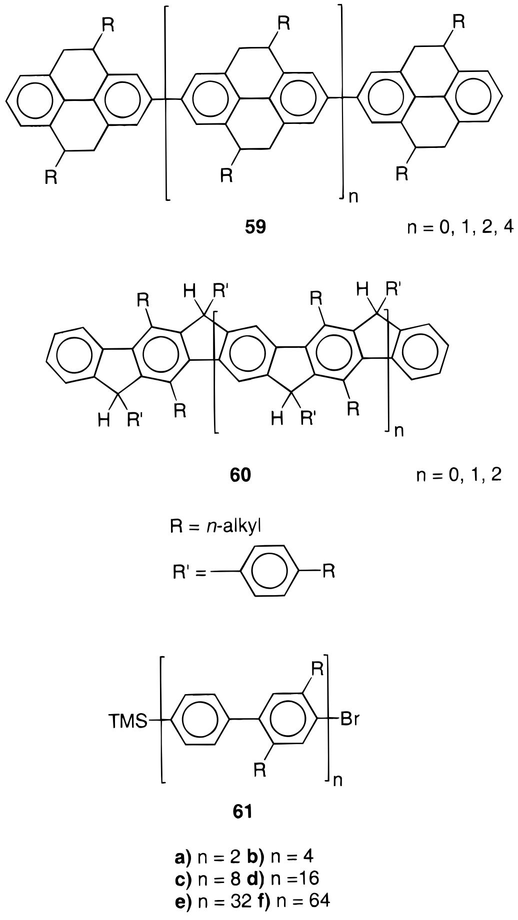


C. Oligophenylenes

Many of the above poly(*para*-phenylene) syntheses can be applied to afford related oligomers. One can thereby use a stepwise approach in order to obtain monodisperse species or a random approach, yielding, as in polymer synthesis, mixtures of different molecular weights. In the latter case, chromatographic separation is necessary to obtain monodisperse homologous oligomers.

Recently, several types of monodisperse oligophenylenes were presented with the aim of producing PPP models. Scherf et al. introduced two homologous series of oligomers[21] from which they were able to draw important conclusions as to the electronic structure of the corresponding polymers.[93,97] Both the poly(tetrahydropyrene)s, PTHP (**59**), and the ladder poly(*para*-phenylene) LPPP (**60**) were synthesized as polydisperse mixtures which could then be separated into the monodisperse oligomers using size-exclusion chromatography (Chart 2). For both series the energy of optical transitions (E_n) was measured and found to be proportional to the inverse chain length. Using the known values of E_n for the corresponding polymers, the effective conjugation length for both systems was estimated to comprise 20 (±1) benzene rings in the case of PTHP and 12 (±2) benzene rings in the case of the LPPP.[21] This result is remarkable as it would be anticipated that LPPP, as the flatter polyphenylene, should have a higher conjugation length.

Chart 2



59 n = 0, 1, 2, 4

60 n = 0, 1, 2

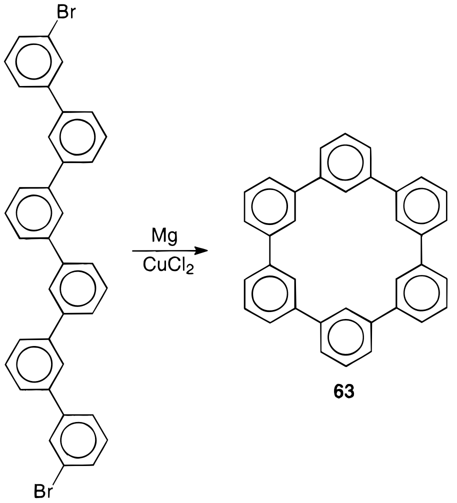
61

a) n = 2 **b)** n = 4
c) n = 8 **d)** n =16
e) n = 32 **f)** n = 64

Schlüter et al. introduced a homologous series of oligomers constructed from 2,5-dihexyl-4,4′-biphenyldiyl repeat units (**61**).[121] The aim in this case was to find GPC standards for other polyphenylenes, and it was shown that GPC analysis gave molecular weights 1.6 times lower than those of MS measurements. This confirmed the view that hydrodynamic volumes are higher for rigid rods than for flexible polymers.

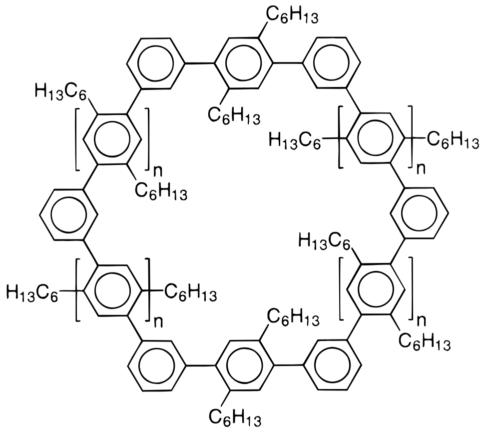
In 1967, Staab et al. obtained cyclic oligophenylene structures by the intramolecular aryl–aryl coupling of dihalogenated, *meta*-connected oligophenylenes.[122,123] For example, the synthesis of cyclic hexaphenylene **63** is shown in Scheme 13.

Scheme 13



62

63

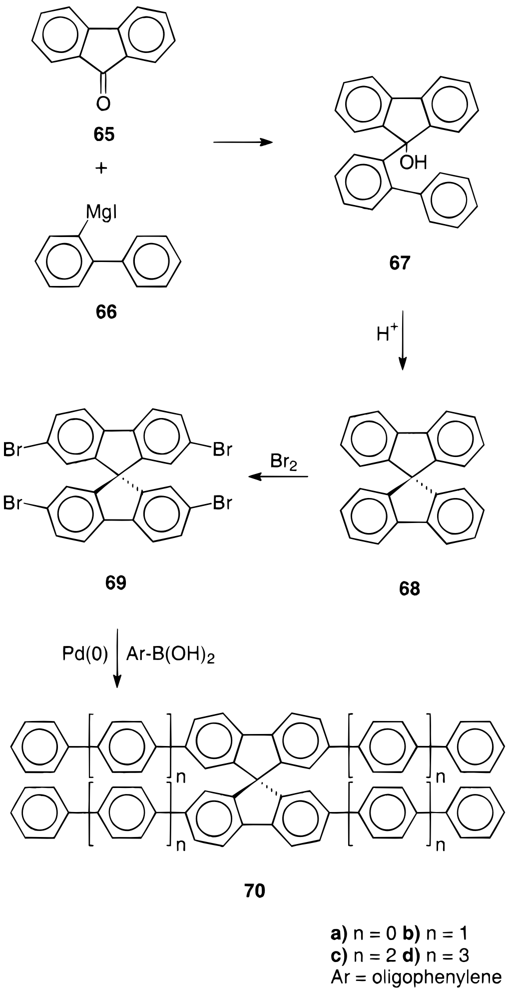


64 **a)** n = 1
b) n = 0

In 1984, a series of cyclic, unsubstituted oligophenylenes was presented containing both *meta*- and *para*-linkages. By coupling three dibromoterphenyls using the Grignard reaction, a compound with 12 phenylene rings containing *ortho*- and *meta*-linkages was obtained.[124] A further cycle containing 12 phenylene rings (**64a**) with a diameter of approximately 1.4 nm was synthesized by Schlüter et al. using Suzuki coupling.[69,70,125] In this case, the linkages were alternately *meta* and *para*. Furthermore, the *para*-linked rings were 2,5-dihexyl substituted to increase the solubility of the compounds. In the same paper Schlüter reported the synthesis of the eight-ring cycle **64b**. In contrast to **64a**, this compound was crystallized and the corresponding crystal structure determined.

An interesting class of oligophenylenes connected in pairs by a 9,9-spirofluorene (**68**) structure was presented by Tour et al.[126] and Salbeck et al.[127] On the basis of the 9,9-spirofluorene (**68**) synthesis by Clarkson et al.,[128] they were able to attach oligoaryl

Scheme 14



substituents in the 2, 2′, 7, and 7′ positions to obtain **70**, Scheme 14. The compounds obtained were more soluble than the corresponding single-chain oligophenylenes. Furthermore, these spiro compounds were shown to be organic glasses with extremely high glass-transition temperatures and high thermal stability (Chapter VI.A).[127,129]

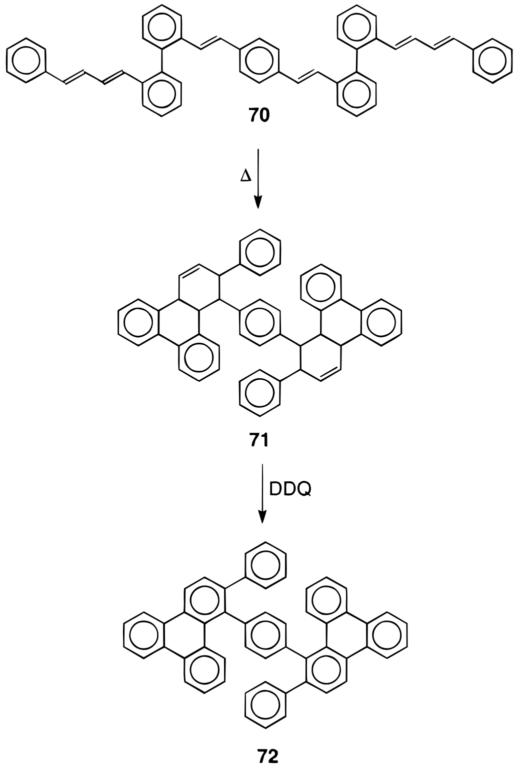
III. Routes To Branched Oligophenylenes

A. The Intramolecular [4+2]-Cycloaddition and Subsequent Aromatization of Appropriate Phenylenevinylene Derivatives

Even the step-ladder or ladder polymers **43**,[96] **45**,[97] **50**,[98] **58**,[115] and, in particular, the ribbon polymer **54**,[113] based on the 1-dimensional poly(*para*-phenylene) **12**, deviate from the topology of a single-stranded polymer through the bridging of neighboring *para*-phenylene units. In the following discussion, our attention will be on monodisperse, topologically defined oligophenylene derivatives in which the step from 1- to 2-dimensionality is complete.

An elegant entry to this type of branched oligophenylene structures was obtained, for example, by the intramolecular [4+2]-cycloaddition of suitable phenylenvinylene derivatives, followed by aromatization of the resulting cyclohexene structures.[130] This synthetic concept is shown in Scheme 15 for the thermal conversion of oligophenylenevinylene precursors, which display reactive diene and dienophilic components in close proximity.

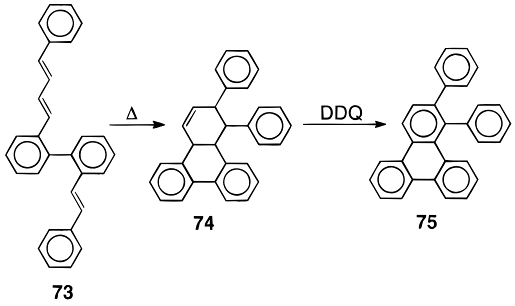
Scheme 15



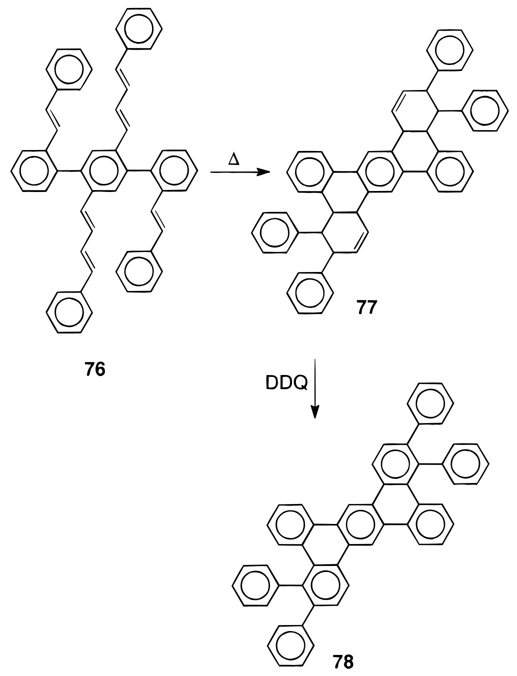
DDQ = 2,3-dichloro-5,6-dicyanobenzoquinone

The cyclohexene derivative **71**, isolated after quantitative, intramolecular Diels−Alder reactions, can be easily aromatized to the desired *para*-phenylene-bridged ditriphenylene **72** by subsequent treatment with 2,3-dichloro-5,6-dicyanoquinone. Simple variations in the phenylenevinylene-type starting material, following the synthetic concept introduced herein, permit entry to a series of other 2-dimensional oligophenylenes with defined topology.[131,132] Some examples are given in Schemes 15, 16, and 17. Even a polymer-analogous reaction is conceivable.[133] The presence of polycyclic aromatic subunits in compounds such as **72** and **78** will be important for their subsequent conversion into structure-defined graphite segments as they facilitate complete cyclodehydrogenation (Chapter V). However, access to the required Diels−Alders active phenylenevinylene precursors is, in some cases, preparatively demanding.

Scheme 16



Scheme 17

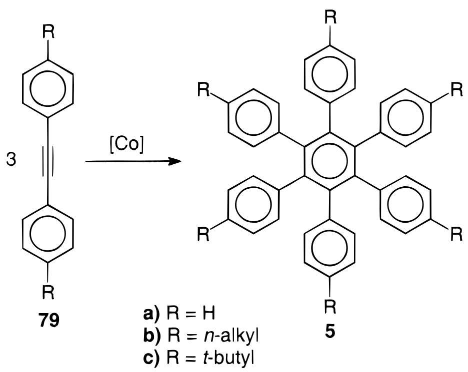


Thus, consideration of alternative approaches to the synthesis of complex oligophenylenes is recommended.

B. The Cyclotrimerization of Suitable Phenyleneethynylene Derivatives

From supramolecular aspects, which will be considered in Chapter VI, the synthesis of hexaphenylbenzene derivatives, which possess the hexagonal symmetry of benzene, is of particular interest. Examination of the literature shows that the synthesis of hexaphenylbenzene (**5**) is hardly possible by hexaaryl substitution of a hexahalobenzene. Instead, the well-established cyclotrimerization of 1,2-diphenylethyne (**79**, also known as tolane) to hexaphenylbenzene (**5**) by a catalytic reaction using dicobalt octacarbonyl following Vollhardt et al. (Scheme 18) is of more general use.[134−139]

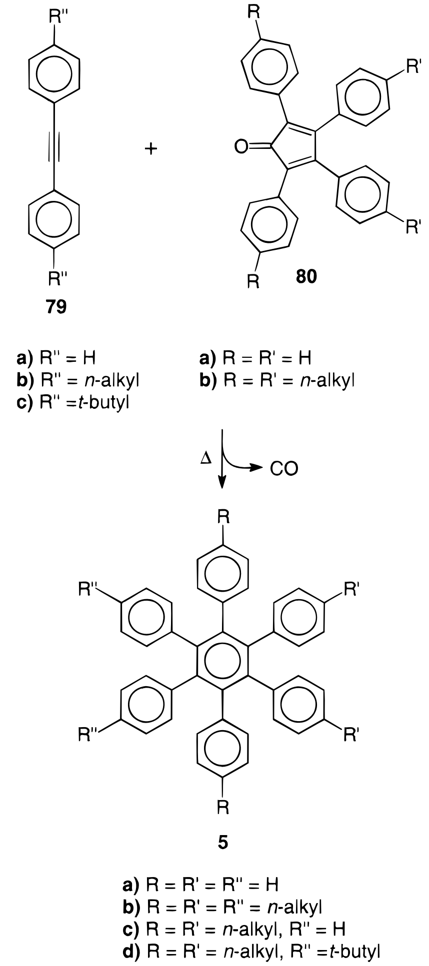
Scheme 18



The 1,2-diphenylethyne starting materials are, in contrast to the phenylenevinylene derivatives (Chapter III.A), easily accessible by palladium-catalyzed ethynyl−aryl coupling after Heck,[140] Cassar,[141] Hagihara, and Sonogashira.[142] As the reaction conditions required for the trimerization of 1,2-diphenylethynes tolerate a variety of functional groups such as alkyl or bromine, the cyclotrimerization is a preparatively useful route to oligophenylene derivatives that are either soluble or open to further derivatization.

In addition to the hexaphenylbenzene derivatives **5**, hexa(oligophenyl)benzenes are also available via synthesis involving cyclotrimerization described above (Scheme 19). For example, Müllen et al. published the synthesis of the starlike hexa(*para*-terphenyl-4-yl)benzene (**6a**) and the hexa(*para*-quaterphenyl-4-yl)benzene (**6b**), using oligophenylene-substituted acetylenes.[33] These compounds should be compared with *para*-septiphenyl and *para*-noniphenyl, respectively, whose starlike analogues they are. All possess a maximum extension of the aromatic part of about 2.9 and 3.7 nm. However, in the case of the starlike molecules, the extension is in two dimensions.

Scheme 19



One of the greatest problems hitherto in the area of solid-state luminescence investigations of poly(*para*-phenylene) derivatives lies in their tendency to form aggregates, thereby causing a red shift of the blue luminescence in solution.[21,99,101,102,107] The transition from linear, 1-dimensional to branched or dendritic, multidimensional PPP systems (see below) should hinder aggregation in the solid state and thereby the undesired red shift in the luminescence. The hexa(*para*-terphenyl-4-yl)benzene (**6a**) in the central benzene ring where three *para*-septiphenyl units cross can be regarded as a model compound for circumventing the aggregation problem of PPP derivatives.[33] The six peripheral *tert*-alkyl substituents contribute by hindering aggregate formation in the solid state and also by increasing the solubility of the rigid, star-shaped compounds **6** in organic media.

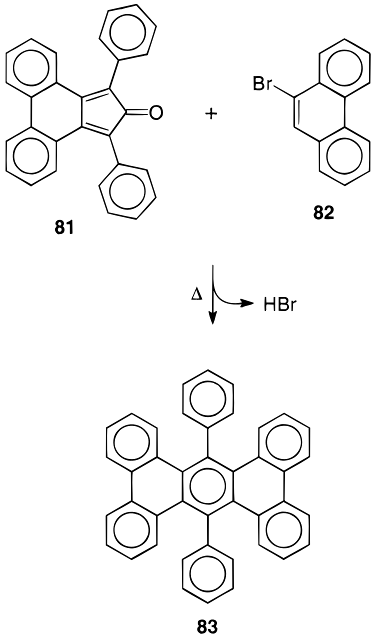
C. The Intermolecular [4+2]-Cycloaddition of Tetraphenylcyclopentadienone to Suitable Phenyleneethynylene Derivatives

The cyclotrimerization of 1,2-diphenylethynes allows only the uniform functionalization of all six phenyl substituents of hexa(oligophenylyl)benzene or the formation of product mixtures. However, if one subjects 1,2-diphenylethyne derivatives to an intermolecular [4+2]-cycloaddition with suitably substituted tetraphenylcyclopentadienones (**80**; also known as tetracyclones), intermediate Diels–Alder adducts are formed that spontaneously extrude carbon monoxide at a temperature of 230 °C, leading to the corresponding hexaphenylbenzenes **5**.[143–146]

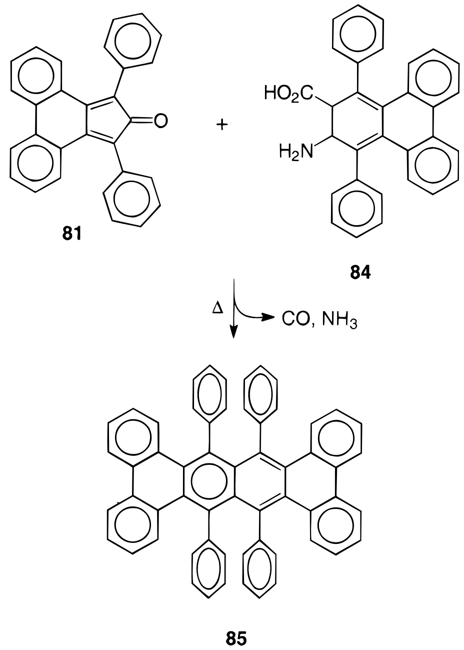
Through suitable choice of substituents the intermolecular Diels–Alder reaction opens the way to a broad spectrum of diversely functionalized hexaphenylbenzenes **5**, which are then available for cyclodehydrogenation to hexa-*peri*-hexabenzocoronenes, HBC (**140**), as described in Chapter V.[147,148]

As the intermolecular [4+2]-cycloaddition with tetraphenylcyclopentadienone (**80**) has been applied to phenyleneethynylene derivatives with various ethynyl groups, the possibility of easily preparing extended, structurally defined oligophenylene derivatives exists. These could then serve as precursors for large, all-benzenoid hydrocarbons with varying topology. Oligaruso[149–151] and Ried,[152–155] who prepared a multitude of unsubstituted oligophenylenes in the 1960s, must count among the pioneers in the synthesis of extended, 2-dimensional oligophenylenes by Diels–Alder reaction of tetraphenylcyclopentadienone (**80**) with suitable 1,2-diphenylethyne systems.

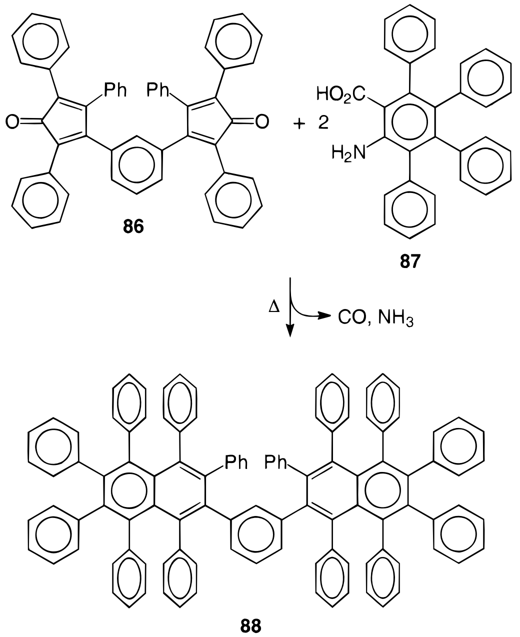
Scheme 20



Scheme 21



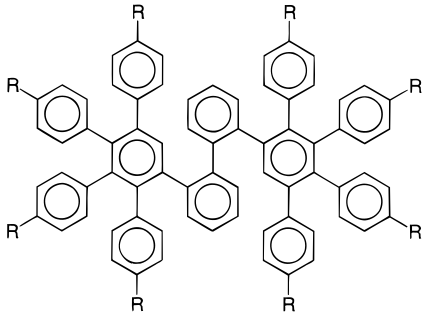
Scheme 22



Since 1986, Pascal et al. employed a series of cyclopentadienone derivatives together with various ethyne and aryne compounds in a [4+2]-cycloaddition reaction to produce twisted polycyclic aromatic hydrocarbons.[156–160] Compounds such as **83**, **85**, or the albatrossenes such as **88**, all containing oligophenylene as well as oligoacene motifs, became accessible (Schemes 20–22).

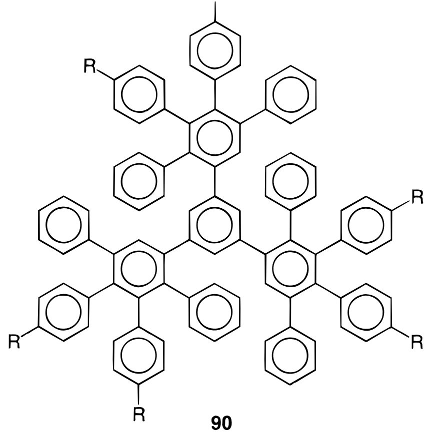
In 1997, the synthesis of branched, uncyclized oligophenylene systems experienced a renaissance.[139,161–164] Here, alkyl-substituted derivatives were synthesized preferentially due to their substantially higher solubility in comparison to the unsubstituted analogues, which guarantees easier processing. Two of these alkyl-substituted oligophenylenes, **89** and **90**, containing 12 and 16 phenylene units, respectively, prepared by double and triple cycload-

Chart 3



89

a) R = H
b) R = *n*-alkyl



90

dition of tetraphenylcyclopentadienone (**80**) to the corresponding 1,2-diphenylethynes, are shown in Chart 3.

A further interesting case is the synthesis of **94** shown in Scheme 23. This compound is based on the nonaromatic but-1,3-diyne and was prepared using a concept similar to the one employed in the dendrimer synthesis described in Chapter IV.C. During the first step, only one of the two triple bonds in 1,4-di(trimethylsilyl)buta-1,3-diyne reacted with **80**, since the second bond was sterically inaccessible. Thus, **92** was formed exclusively. However, after removal of the two silyl groups, the second triple bond was accessible for the second [4+2]-cycloaddition and the desired oligophenylene **94** was formed.[164]

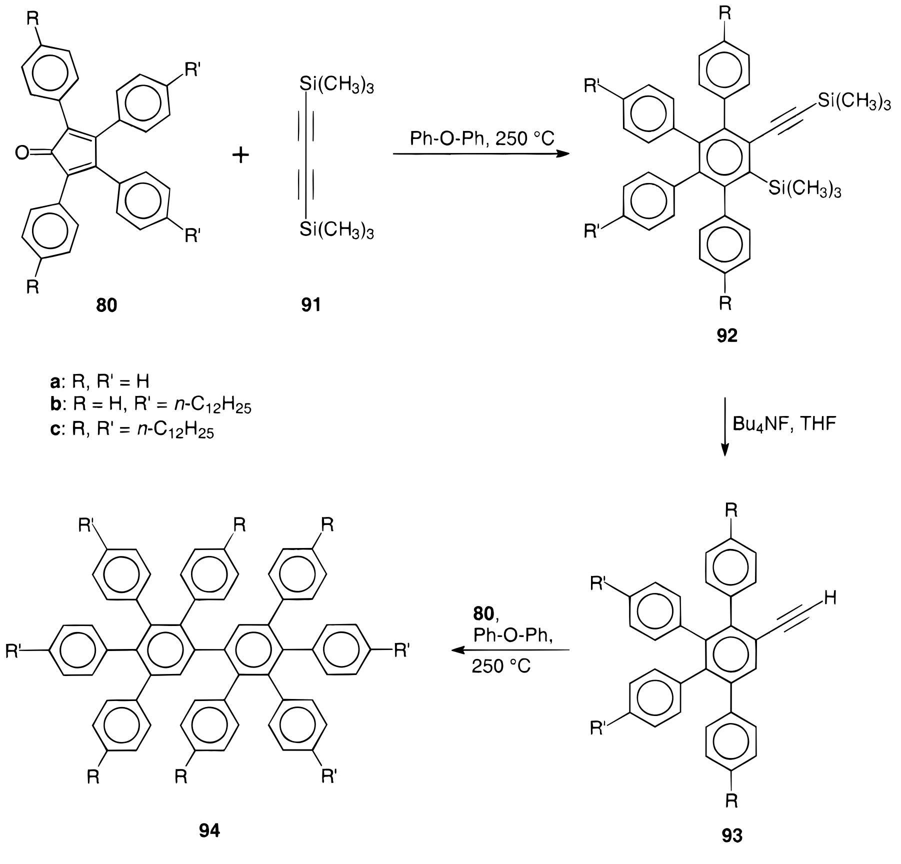
IV. Polyphenylenes by Intermolecular [4+2]-Cycloaddition: The Transition to 3D-Structures

A. Linear Polyphenylenes with Lateral Extension

After using the intermolecular Diels−Alder reaction of tetraphenylcyclopentadienone with mono-, di-, or triethynyl derivatives to establish an effective route to large monodisperse oligophenylenes, the synthesis of polymeric phenylene structures containing a multitude of phenyl substituents was obvious. The preparation of these types of linear polyphenylenes with a defined lateral extension was achieved by Stille et al.,[165−169] who allowed the diethynyl derivatives **96** and **97** to react with phenylene compounds **95**, which contained tetraphenylcyclopentadienone units.

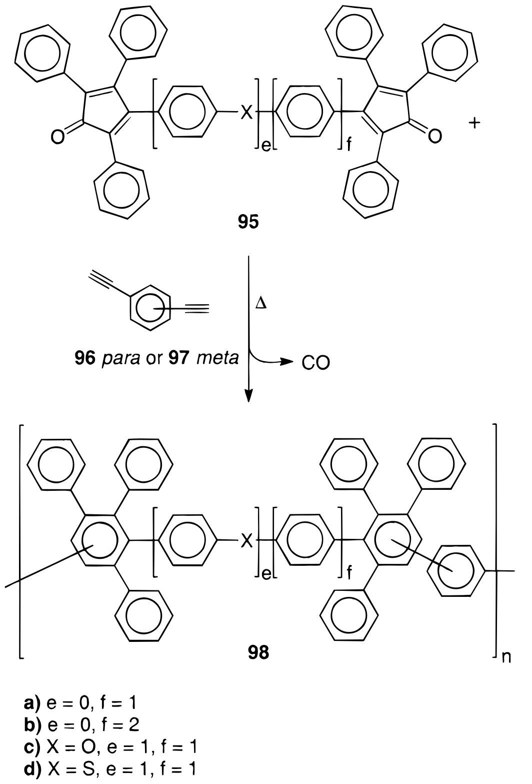
The polymerization, performed at a temperature of up to 250 °C led to a high yield of an almost colorless, amorphous polymerizate, which possessed

Scheme 23

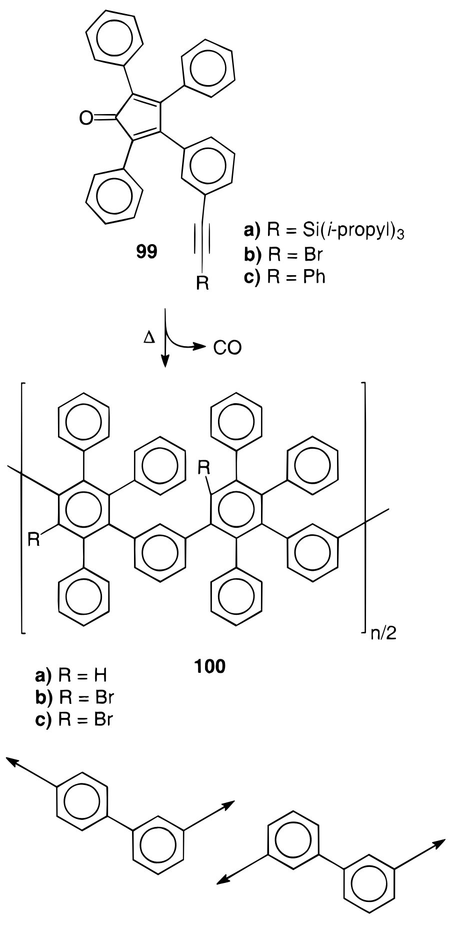


a: R, R' = H
b: R = H, R' = *n*-$C_{12}H_{25}$
c: R, R' = *n*-$C_{12}H_{25}$

Scheme 24



Scheme 25



The two possible ways the chain my be oriented.

a high molecular weight (M_n = 20 000−100 000). Nevertheless, an important consideration is that only 15% of the polymerizate was soluble in common organic solvents and could thus be investigated.[165]

In addition to the *para*- (**96**) and *meta*-diethynylbenzene (**97**) introduced in Scheme 24, phenylethynyl-substituted derivatives of benzene were also used. Although the latter possess a lower reactivity than the terminal ethynyl groups, nevertheless they led to a further increase in the degree of phenyl substitution on the main polyphenylene chain. The monomeric building block **95**, composed of two tetraphenylcyclopentadienone units, was also varied by Stille et al. (Scheme 24): the number of bridging phenylene units in the monomeric building block was modified; also, divalent heteroatoms, such as sulfur or oxygen, were inserted between two of the bridging phenylene units, whereby poly(aryl ether)s or poly(aryl thioether)s became simply accessible.[165−168]

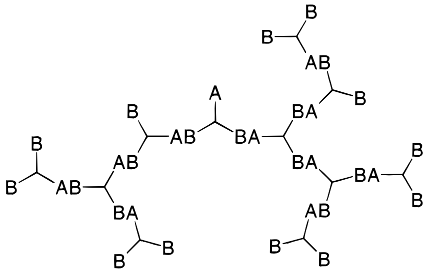
The polymer-analogous intermolecular Diels−Alder reaction of ethynyl compounds with tetraphenylcyclopentadienone derivatives (**95**) also possesses a disadvantage: even when using *para*-diethynylbenzene (**96**), a structurally unambiguous, phenyl-substituted poly(*para*-phenylene) cannot be formed. In principle, in each [4+2]-cycloaddition, two distinct regioisomers are possible. In the case of a polymer-analogous reaction, this leads to both *para*- and *meta*-couplings occurring within the main polymer chain.

In addition to the A_2 and B_2 monomers, the use of AB monomers is also conceivable in the case of the polymer-analogous [4+2]-cycloaddition of ethynyl compounds with tetraphenylcyclopentadienone components.[147,170] The ethynyl-substituted tetraphenylcyclopentadienone **99** is shown in Scheme 25 as a monomeric building block that fulfills the requirements for a self-condensation in the sense of the intermolecular Diels−Alder reaction just described. Nevertheless, regioisomers also appear when using AB monomers in the case of a polymer-analogous [4+2]-cycloaddition, so that in every repeat unit, as depicted in Scheme 25, either *para*- or *meta*-bridging of the main polymer chain must occur, in addition to a *meta*-link within each repeat unit.

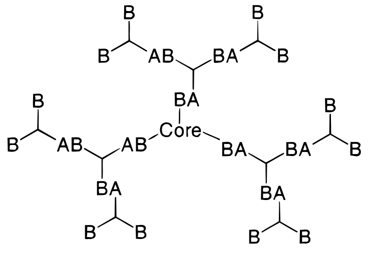
B. Highly Branched Polyphenylenes

The term highly branched or hyperbranched polymers (e.g., **101**) describes polymers that display a high degree of branching but are nevertheless not cross-linked (Chart 4). Such polymers are formed when a monomer which possesses two corresponding functionalities in the ratio 1:*n* (AB_n) is subjected to polymerization conditions. If a reaction then takes place between the two B groups of one monomer and the A functions of two further monomers, a molecule results that contains only one A group but four B functions. When this procedure is repeated several times, a system is formed that contains a multitude of branches and B functions but only a solitary A function. However, on both steric and statistical grounds, not all available B groups are converted in reactions with an A function of a further building block, which will lead to defects and thus to a certain polydispersity.[171]

Chart 4



101

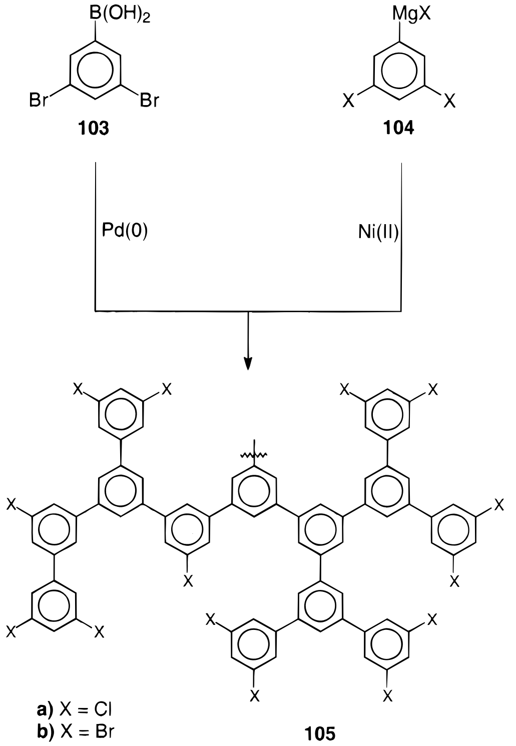


102

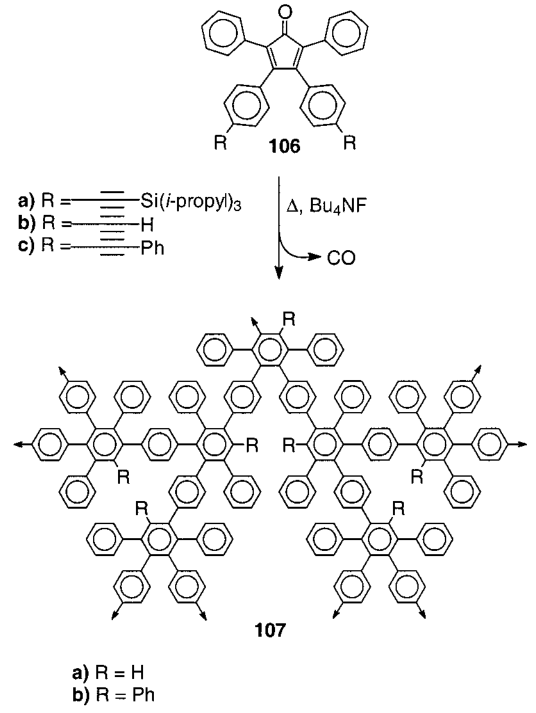
In contrast to a hyperbranched polymer, a dendrimer (e.g., **102**) is monodisperse and possesses a well-defined chemical structure with a regular branching pattern.[172] The two general possibilities of dendrimer formation, the divergent and convergent synthesis, are described in Chapter IV.C.

Kim and Webster were the first to describe hyperbranched polyphenylenes.[171,173,174] Their structures were derived from 1,3,5-trisubstituted benzene compounds **105**, as portrayed in Scheme 19. The synthesis used a modified Suzuki coupling of the boronic acid **103**[69,70] or the Yamamoto coupling of one of the Grignard compounds **104**, Scheme 26.[52] The corresponding products can be differentiated in terms of the degree of branching and in the polydispersity. The product obtained by the Suzuki coupling shows a higher level of branching and narrower dispersion. Typical reaction conditions gave M_w/M_n values of 5750/3820, compared with 7077/3910 for the Yamamoto coupling.[53] In contrast, Yamamoto coupling permitted the conversion of larger quantities of the starting material.[55] However, the polymer growth was limited, not by reaching the critical packing state or by insufficient solubility of the product, but mainly by the poor yield of the aryl−aryl coupling. In contrast, the advantage of these polymers lies in their high thermal stability as well as in the possibility of functionalizing them and thereby influencing their properties.

Scheme 26



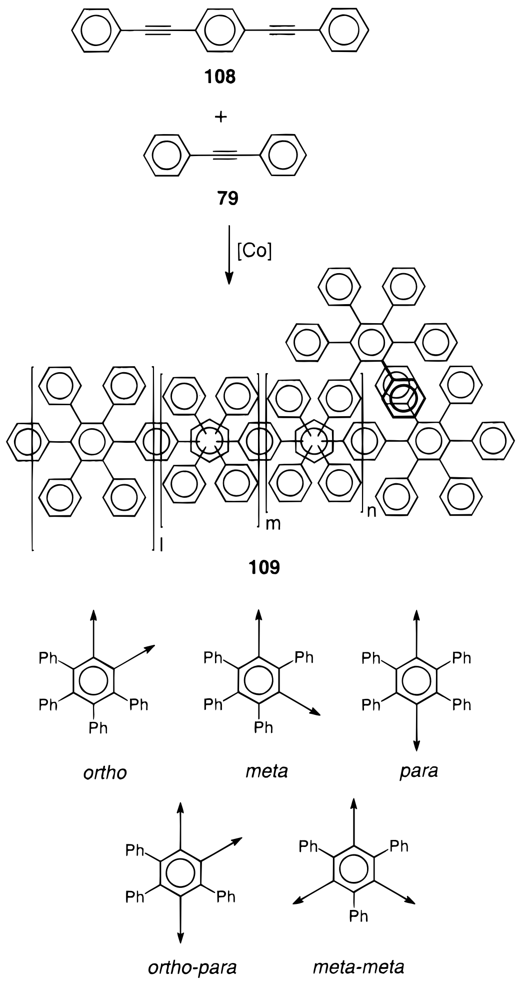
Scheme 27



A further method for the synthesis of highly branched polyphenylenes (Scheme 27) follows from the successful application of the AB monomer **99** to the construction of linear, partially angled polyphenylene structures by way of the [4+2]-cycloaddition (Chapter IV.C). Most recently, the preparation of 3-dimensional networks, composed exclusively of pentaphenylbenzene units, and accessible by self-condensation of the AB_2 monomer 3,4-di(ethyn-4-yl)-phenyl-2,5-diphenylcyclopentadienone (**106**), has been reported by Müllen et al.[175−177] Similar to **99**, this molecule possesses both diene and dienophile functions, however, in this case in the ratio 2:1. The ethynyl groups are, furthermore, situated at the *para*-position of the phenylene rings. The high degree of branching in the resulting polyphenylene **107** is depicted in Scheme 27.

The highly branched polyphenylene **107a** is a poorly soluble, light-brown, amorphous solid. As a consequence of the synthetic concept, it still contains a multitude of reactive terminal ethynyl groups next to the phenylene structure. This is due to steric and

Scheme 28



statistical aspects.[177] The advantage, in comparison with the hyperbranched polymer of Kim and Webster, lies in the denser packing of benzene rings and in the higher molecular weight. On using the AB_2 monomer **106c**, a more soluble polymer containing hexaphenylbenzene units was obtained. This polymer was characterized by dynamic light scattering,[178] showing that on average the structure, which was assumed to be spherical, has a diameter of about 15 nm, i.e., polymers **107a** and **107b** can be considered as polydisperse polyphenylene nanoparticles.[177,179]

As an alternative to the preparation of the polyphenylene **107** by the intermolecular Diels–Alder reaction described above, the possibility of using the cobalt-catalyzed cyclotrimerization introduced in Chapter III.B exists. This allows the simple construction of 3-dimensional polymers composed exclusively of phenylene units, although with a lower degree of structural precision.[170] A fraction of the 1,2-diphenylethyne (**79**) used in the cyclotrimerization to obtain hexaphenylbenzene (**5**, Scheme 19) must be replaced by the bifunctional 1,4-di(phenylethynyl)benzene (**108**). Depending on the ratio of 1,2-diphenylethyne (**79**) to the diethynyl component **108**, the resulting 3-dimensional structure **109**, composed of hexaphenylbenzene units, displays differing degrees of branching (Scheme 28). Thus, the material properties of the highly branched polymer can be influenced by means of the ratio of the two starting materials employed. As in **107**, the branching pattern obtained obeys exclusively steric and statistical rules (typical values for M_w and M_n are 100 000 and 20 000, respectively). In addition to the conceivable *ortho*-, *meta*-, and *para*-linkages in the main polymer chain, the two branching patterns possible from the cyclotrimerization are shown in Scheme 24. The 3-dimensional structure of the resulting polyphenylene **109** is quite clear in the schematic planar representation of the polymer by the overlap of individual phenyl substituents.

By cyclodehydrogenation of these polyphenylene structures with iron(III) chloride under Kovacic conditions (see also Chapter V), the formation of hexa-*peri*-hexabenzocoronene segments within the molecule was possible.[180] Analysis of the X-ray diffractogram gave distances of 0.34 and 1.6 nm, which can be traced back to the distances between the layers and to the size of the hexa-*peri*-hexabenzocoronene repeat units, respectively. This material also permitted the intercalation of Li atoms, rendering it a potential candidate for electrochemical energy storage in battery elements, in particular since, in contrast to graphite, the individual layers are assumed to be ordered in three dimensions and should thus permit conductivity in all three directions.[180]

When dealing with 3-dimensional polyphenylene structures, it is appropriate to refer to cubic carbon phases containing the structural motif of PPP but also containing PPP chains linearly extended in three dimensions.[181–185] Cubic graphite (**110**, Figure 2) has obtained its name from the cubic symmetry of such a phase rather than the relationship between its solid-state structure and that of normal graphite.[184] The material is still elusive but has attracted great interest since it has been predicted to have useful properties, such as high mechanical and thermal stability, probably above those obtainable for conventional conjugated polymers. In particular, the absence of required phase nucleation and growth during charging processes and the presence of sufficiently large diffusion channels for lithium cations have led to the prediction that cubic graphite may be suitable for rechargeable batteries. In cubic graphite the benzene ring is part of three equivalent PPP chains, and four neighboring benzene rings form a tetraphenylene ring with a strong mutual twist between the benzene rings (Figure 2b). As a result, all carbon atoms of such a phase become equivalent.

A selected 3-dimensional polyphenylene structure (**114**), which contains tetraphenylene subunits, has recently been synthesized thermally without using further reagents.[186] It starts with the preparation of the tris(biphenylenyl)benzene compound **113** and concludes with the thermal ring opening of biphenylene units which subsequently undergo dimerization to tetraphenylene (Scheme 29). A series of other oligobiphenylenyl precursors can conceivably lead to other 3-dimensional polyphenylenes.

C. Dendrimers Based on Polyphenylene

As the preparation of 3-dimensional polyphenylene structures was made possible by the intramolecular Diels–Alder reaction of suitable ethynyl-substituted tetraphenylcyclopentadienone derivatives,[175–176] the

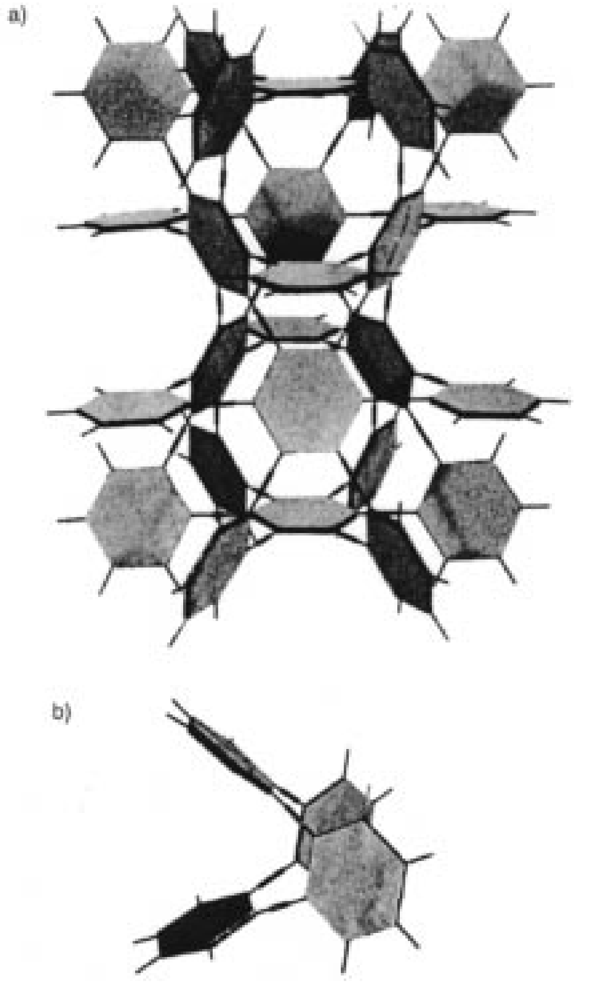


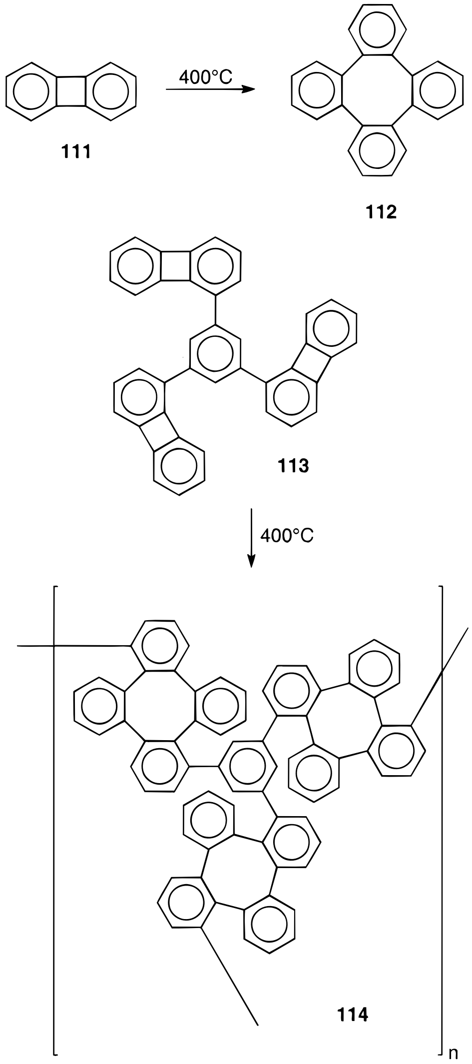
Figure 2. (a) Three-dimensional picture of cubic graphite (**110**).[181] (b) Subunit of cubic graphite containing the central eight-membered ring.[181]

synthesis of highly branched, monodisperse polyphenylene systems based on the established [4+2]-cycloaddition route offered a new preparative and intellectual challenge. Starting from polyfunctional central building blocks, a generation-by-generation build up of structurally defined, highly branched polyphenylene dendrimers should be possible by the repetitive use of the intermolecular Diels–Alder reaction with suitable tetracyclopentadienone components (e.g., Scheme 31).

The first dendrimers based on polyphenylene were introduced in 1992 by Miller, Neenan, and coworkers.[187−189] The formation of these structurally defined, 3-dimensional molecules resulted from the concept of convergent synthesis, as shown in Scheme 30. Similar to the hyperbranched polyphenylenes by Kim and Webster, described in Chapter IV.B, [171,173] these dendrimers were also based on 1,3,5-trisubstituted benzene repeat units with their synthesis based on the boronic acid coupling of two aryl systems.

In contrast to the divergent synthesis, the convergent build up begins at the periphery of the final dendrimer and concludes with the attachment of the preformed branches to the core. Thus, in principle, the convergent synthesis, as used by Miller, Neenan, and co-workers,[187,188] requires for each coupling step only the formation of a relatively small number of new bonds. However, steric aspects lead, in particular in the synthesis of higher generations of dendrimers, to only partial substitution of the functional groups at the central building block. Nevertheless, the number of new bonds formed during one reaction cycle is constant and equal to the number of B functions on the AB_n monomer. This is important when the yields of the coupling reaction employed are not high.

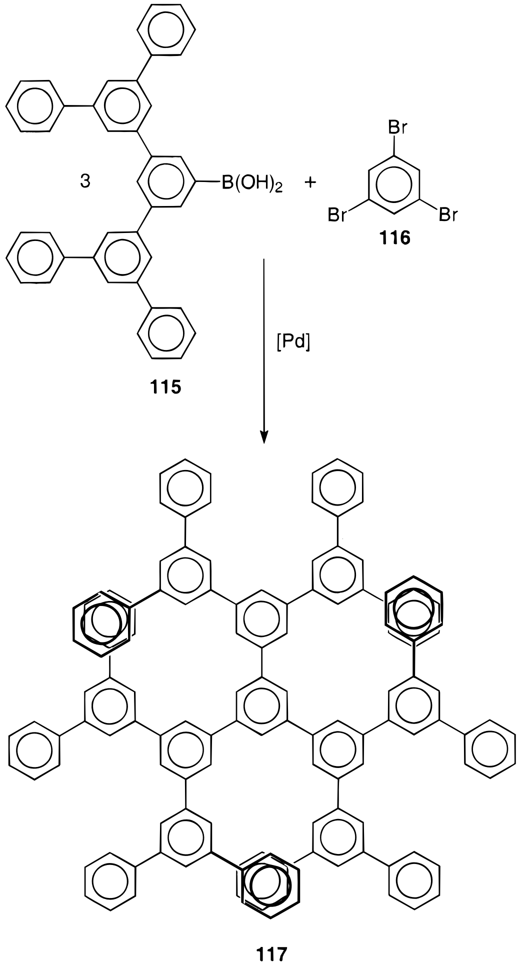
Scheme 29



Unlike the convergent synthesis, the concept of the divergent dendrimer synthesis begins at the core and leads to exponential growth of the functional groups, required for further construction, from generation to generation. Therefore, the number of bonds that have to be formed during one reaction cycle grows exponentially. A major advantage of this method is the fact that all functional groups are usually located on the surface of the molecule and are thus sterically accessible to the rather small AB_n building blocks.

The first divergent synthesis of a polyphenylene dendrimer was described in 1997.[20] In contrast to the convergent synthesis by Miller, Neenan, et al.[187,188] no transition-metal-catalyzed aryl–aryl couplings were employed in this divergent synthesis.[175,176,190−192] Instead, the intermolecular, metal-free [4+2]-cycloaddition of tetraphenylcyclopentadienone deriva-

Scheme 30

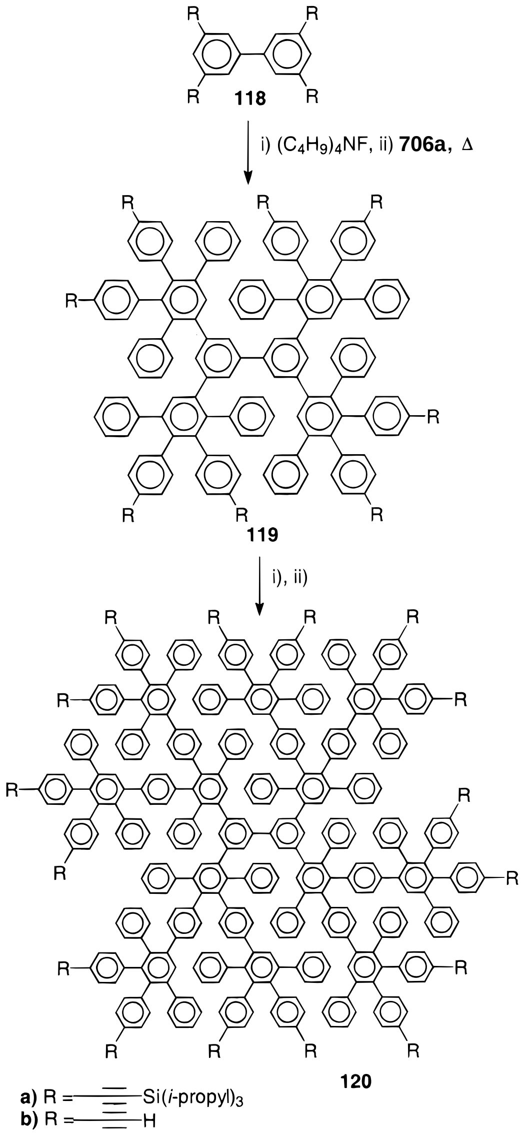


tives with suitable ethynyl compounds was again used. The enormous thermal and chemical stability of the polyphenylene structure allowed the use of a reaction temperature that guaranteed, even by the exponential increase in functional groups per molecule resulting from the generation-by-generation build up, complete reaction of all ethynyl groups with an overall yield of >85%.

Müllen et al. were recently also able to synthesize their dendrimers using the convergent method starting with the deprotection of 4,4′-di(triisopropyl)-ethynylbenzil (**123a**), a tetraphenylcyclopentadienone precursor.[180] The product was successfully treated with unsubstituted tetraphenylcyclopentadienone (**80a**) followed by 1,3-diphenylacetone (**125**) to form the cyclopentadienone **126** (Scheme 32) which can be regarded as one branch of a convergent dendrimer. This method is useful in the rapid synthesis of several dendrimers and in the formation of further hyperbranched polyphenylenes of greater size and with fewer growth imperfections.[180]

A selective generation-by-generation build up in the scope of the divergent dendrimer synthesis described above was obtained using the difference in Diels−Alder activity of the free ethynyl groups and those protected by triisopropylsilyl groups. Thus, the activation of the dienophile units takes place in an initial reaction step by the cleavage of the silyl protecting groups. The construction procedure based on the [4+2]-cycloaddition of tetraphenylcyclopentadienone derivatives, which are once again equipped with ethynyl functions protected with triisopropylsilyl groups, then follows.[20,175,176,190,191]

Scheme 31



It is a key feature of the polyphenylene dendrimer synthesis that the [4+2]-cycloaddition is not influenced by further substituents on the tetraphenylcyclopentadienones, as long as the latter survive the reaction conditions.[175,176] Therefore, it is possible to introduce a variety of functional groups in the final generation using disubstituted tetraphenylcyclopentadienones such as **127** (Chart 5). These functional groups are exclusively located on the surface of the dendrimer.[175,176] This approach provided dendrimers carrying, for example, methylthiofunctions, and it was possible to deposit the dendrimers by physisorption from solution onto gold surfaces.[176] Visualization by atomic force microscopy (AFM) indeed revealed the existence of single species corresponding to the expected dendrimer size; however, particle aggregates were also observed.[177] This seems to be due to the relatively weak interaction of the dendrimers with the surface. The synthesis of thiol-functionalized

Scheme 32

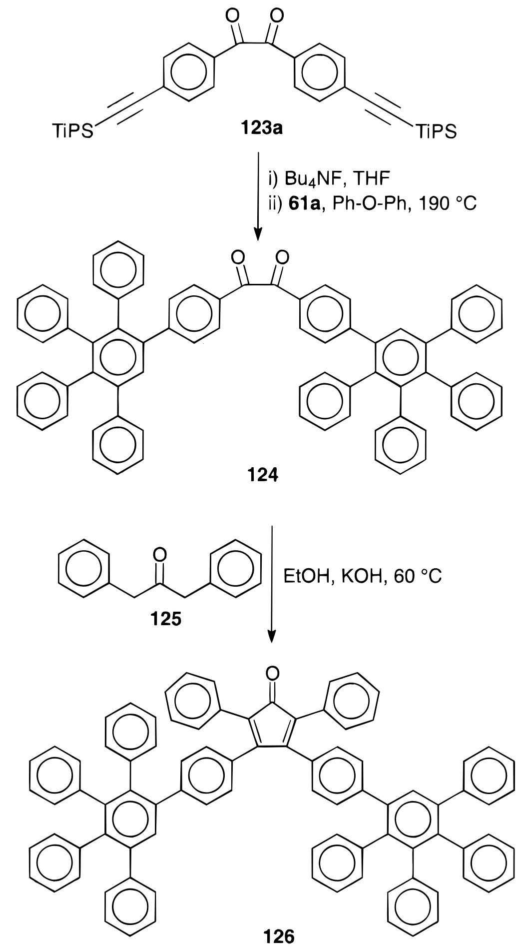
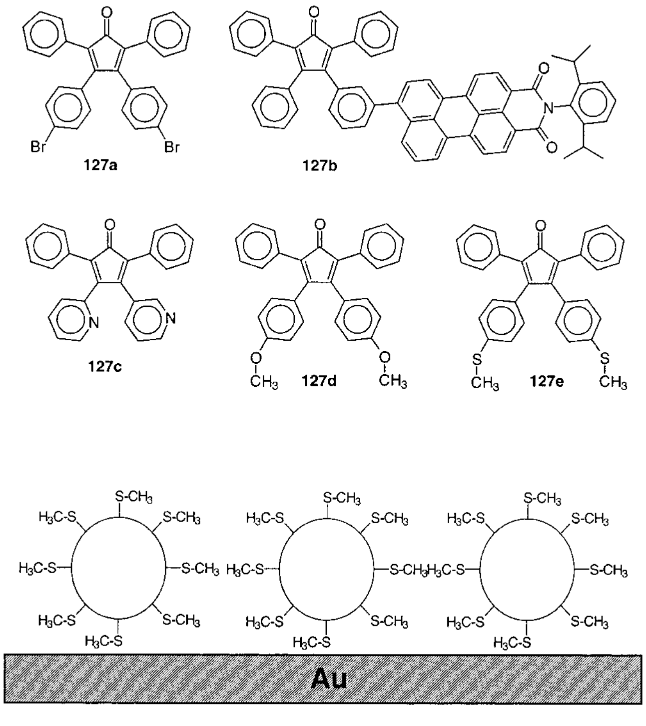


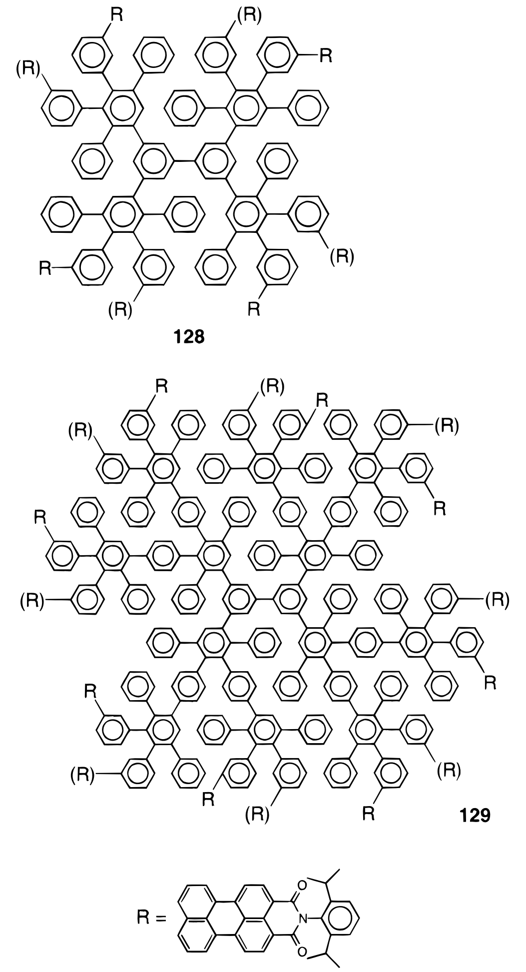
Chart 5



dendrimers capable of giving stable chemisorbed surface layers is underway.

An intriguing consequence of the chemical functionalization of these nanoparticles, which were shown to be shape-persistent (see below), is the formation of strongly emitting nanoparticles when fluorophores are attached to the surface. Typical structures that have been prepared are **128** and **129** (Chart 6).[193,194] Their optical properties have been studied in solution and in the matrix, including spatially resolved methods, and it is a particularly exciting result that single nanoemitters can be visualized by near-field-optical microscopy.[193,195−198]

Chart 6



The 3-dimensional ball-and-stick models[190,199,200] of the first four generations of the Müllen dendrimers depict the exponential growth caused by the synthetic concept employed with an increase in the maximum extension of the unsubstituted form from 2 to 6 nm. Also, the dumb-bell-shaped surface of all dendrimer generations, which are determined not only by the branching element but essentially by the choice of the tetraethynyl-substituted biphenyl core **118**, can be observed. Molecular dynamics simulations,[201] where one allows some rotation of the benzene rings about the inter-ring bonds, show that such mobilities do not significantly affect the overall shape of the dendrimers, that is, they are dumb-bell like shape-persistent nanoparticles.[190] This is in contrast to conventional dendrimers, which are built-up from σ-bonds and can, thus, adopt many different conformations. However, certain mobility of the benzene rings including torsional effects is expected to play a key role in the exceptionally good solubility of even

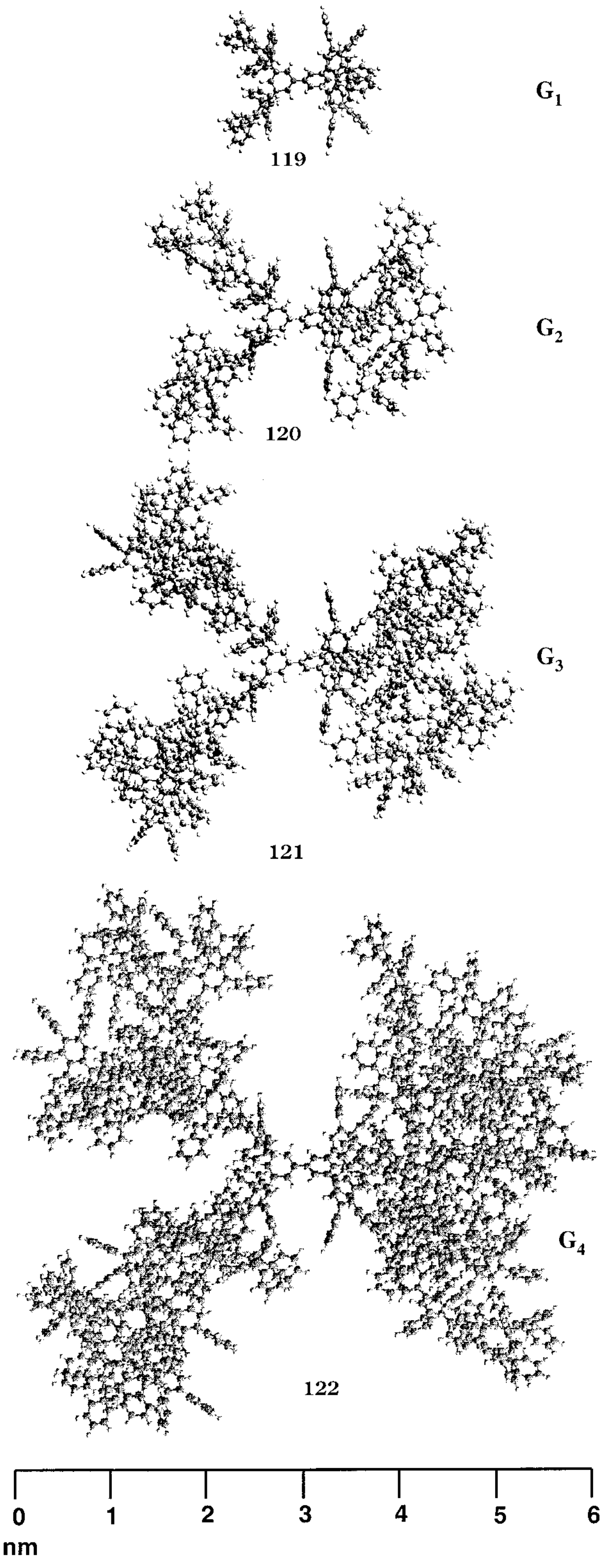


Figure 3. Three-dimensional ball-and-stick models of the first four generations of a polyphenylene dendrimer built from the biphenylene core **118** and the AB_2 building block **106**.

the fourth-generation dendrimer **122** in common organic solvents.[200] Solid-state proton NMR measurements are underway to obtain information on the dynamic behavior of these molecules.[202,203]

The above-mentioned solubility permits that the particle size may be determined using light scattering,[178] and it is quite remarkable that hydrodynamic radii thus obtained fall into the range of those predicted using the computer-generated, ball-and-stick molecular models.[176,190]

The 3-dimensional structure of the dendrimers can be determined by the choice of the core.[176,192,200] If the tetrahedral tetraethynyltetraphenylmethane **130** is used in place of the biphenyl derivative **118**, even the second generation **132** of the resulting dendrimer shows a more pronounced spherical shape than that of the comparable dendritic polyphenylene **120**, although both are calculated to possess a maximum extension of approximately 3.7 or 3.8 nm. As the hydrodynamic radii determined for the dendrimer based on **118** correspond very well to those calculated, these values are assumed to be reliable.[177] The formation of **132** takes place in an analogous fashion to the dendrimer synthesis shown in Scheme 31; a comparative portrayal of each of the second generations **120** and **132**, respectively, is shown in Figure 4.

Although the tetrahedral or the dumb-bell shape of the core is still reflected in the geometry- and energy-optimized surface of the dendrimer, according to force-field calculations using the program Cerius2, considerable differences appear in the spatial distribution of the individual repeat units. These differences are found even when using the same branching units. Therefore, they can only be explained by the geometry of the central building block. Further variations in the ethynyl-substituted starting molecule,[176] as can be seen in Figure 4, provide an impression of the various shapes of the dendrimers that are easily accessible through the application of different cores in a sort of “building block kit”. In both of these further cases, a change in the overall space filling can be observed through the markedly different geometry of the core. The calculated diameter of **135** and **137** amounts to approximately 3.5 and 5.0 nm, respectively.[200] Moreover, in the case of **137**, the number of phenylene rings is approximately twice as high as that in **135**. As the available space is different by a factor of approximately two, both should have a similar density of phenylene rings.

Of all the above cores, 1,3,5-triethynylbenzene (**133**)[176] permits the best comparison of the Miller and Neenan dendrimers with the Müllen dendrimers. While the third generation **117** of the dendrimer synthesized by Miller and Neenan using aryl−aryl coupling is composed of only 22 phenylene units,[187,188] the second generation **135** (shown in Scheme 33) of the Müllen dendrimer prepared by divergent Diels−Alder synthesis possesses 46 phenylene rings, more than twice as many. The astonishingly rapid growth of dendrimer **135** is advantageous in comparison with the fact that only one additional phenylene unit is obtained through a transition-metal-catalyzed coupling of an aryl−aryl bond, whereas an additional five phenylene groups are obtained by a Diels−Alder reaction with tetraphenylcyclopentadienone. Considering the length of one repeat unit to be approximately 0.4 nm, this would mean that the third generation of the Miller and Neenan dendrimer possesses a maximum diameter of about 2.2−2.3 nm

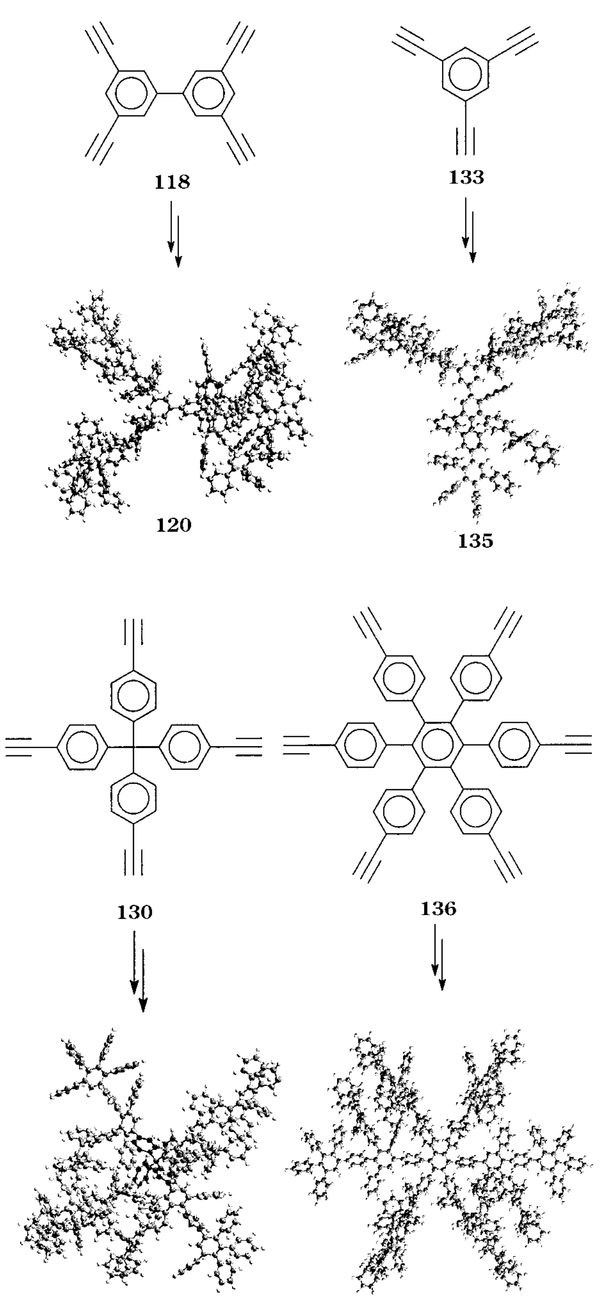


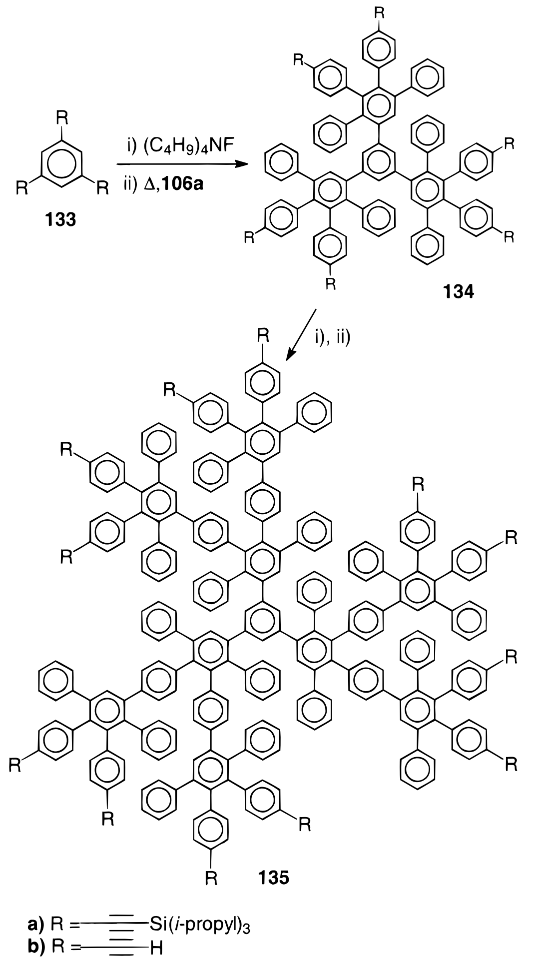
Figure 4. Cores **118**, **130**, **133**, and **136** and ball-and-stick models of the corresponding second-generation dendrimers **120**, **132**, **135**, and **137**.

while the corresponding Müllen dendrimer would have a maximum diameter of around about 4.0 nm. This suggests that the density of phenylene rings inside **135** is about one-third larger than that of **117**.

In addition to the large influence of the central building block on the geometry of the dendrimer surface is the effect on the filling of space exerted by the branching unit which is used much more frequently. The Diels–Alder reaction of ethynyl groups with appropriately substituted tetraphenylcyclopentadienones for construction of the dendrimer system (Scheme 31) permits a degree of branching significantly higher than those obtained before.[176,192]

The dendrimer **120**, formed from AB_2-branching units **106a**, still displays a dumb-bell-like surface in the second generation. In contrast, the second generation **4** of the dendrimer, prepared using the same core, **118**, but the AB_4-type building block **138**, possesses a significantly more closed, spherical shape with subsequently better space filling, as the number of benzene rings has increased from 62 to 102. According to ball-and-stick models (Scheme 34), both polyphenylene nanoparticles have a similar maximum extension of approximately 4 nm. It should also be mentioned that the second generation **4** could only be prepared in the unsubstituted form. Reaction of the corresponding first generation **139** with **138** gave a mixture of products mainly consisting of the 14-fold adduct with only traces of the desired 16-fold addition product.[192] However, reaction of **139** with tetraphenylcyclopentadienone (**80a**) produced only the 16-fold adduct. This finding was explained by the dense packing of arylene rings in the resultant product and the large difference in size of the two tetraphenylcyclopentadienones used. According to Tomalia, the formation of the 14-fold product can be seen as the sterically induced stoichiometry.[204] Furthermore, this is good proof of the concept of densest packing according to the theory of de Gennes and Hervet.[205]

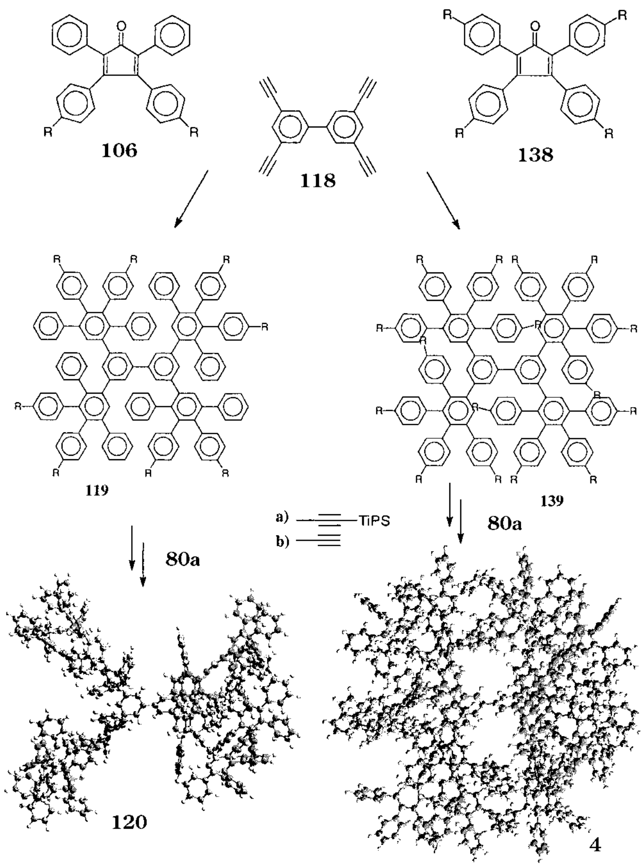
Scheme 33



V. All-Benzenoid 2D-Hydrocarbons by Planarization of 3D-Polyphenylene Structures

Polyphenylene nanoparticles possess a persistent 3-dimensional surface. However, in some cases a

Scheme 34



conformation is conceivable in which only steric hindrance of the hydrogen atoms forbids the molecules to adopt a planar configuration. Thus, for example, the first or second generation of the dendrimer (**119** or **120**, respectively), based on the biphenyl nucleus, is depicted in Scheme 31 in a seemingly planar conformation.[20,177,191]

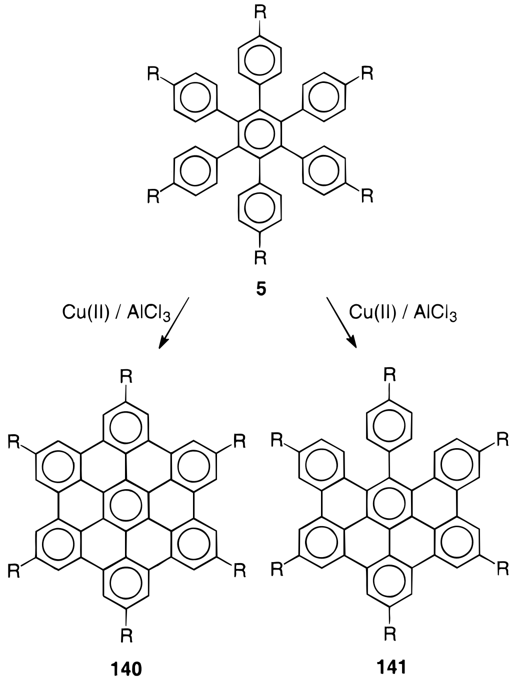
The possibility of a 2-dimensional representation of some of the 3-dimensional polyphenylene nanoparticles is manifest for organic chemists, to reflect on a complete intramolecular cross-linking of all phenylene rings with abstraction of all nonperipheral hydrogen atoms. Such an intramolecular cyclodehydrogenation of 3-dimensional oligo- or polyphenylenes, which can exist in a 2-dimensional conformation, leads exclusively to polycyclic aromatic hydrocarbons (PAHs), which possess an all-benzenoid electron configuration as described by Clar's π-sextet model.[10,16,17,206] This model divides the carbon $2p_z$ electrons into groups of π-electrons so that the electron density can be assigned to specific, defined C_6 rings within the molecule concerned. This is done in such a way that the maximum number of rings containing π-electron sextets is obtained. However, to avoid biradical structures, the electrons may only be arranged in neighboring pairs. Clar's theory is based on the work of Robinson, who assumed, in analogy to the octet rule known from inorganic chemistry, that in benzene with its six electrons a stable electron configuration is reached.[207] Following from this, Clar predicted that all-benzenoid hydrocarbons, which only contain C_6 rings with either six π-electrons or no π-electrons, are, due to their completely aromatic character, the most stable class of PAHs. This assumption was verified experimentally as they are stable against sulfuric acid, have a low tendency to undergo Diels–Alder reactions, and are thermally stable.[10,16,17]

In principle, the intramolecular cyclodehydrogenation of oligophenylene derivatives discussed here can occur under thermal or photochemical initiation or under reductive or oxidative reaction conditions. In the literature, one finds mostly oxidative cyclodehydrogenation, for example, with vanadium(V) salts,[208–212] thallium(III) salts,[213–216] or iron(III) chloride,[217] as well as photochemical cyclodehydrogenation[218–221] in the presence of elemental iodine. Reductive cyclodehydrogenation with elemental lithium[222] or potassium[223] is encountered less often. In exceptional cases, thermally induced platinum(0)- or palladium(0)-catalyzed cyclodehydrogenation at a temperature of 400 °C or higher has been reported, although these processes rarely lead to uniform products in high yield.[224]

The reaction conditions used by Kovacic et al. for the polymerization of benzene to poly(*para*-phenylene)s (**8**, Chapter II.A, Scheme 1) have proven to be extremely valuable in the intramolecular cyclodehydrogenation of oligo- and polyphenylene derivatives.[37–39,94,95,225–227] During the polymerization of benzene to poly(*para*-phenylene) (**8**) using copper(II) chloride and aluminum(III) chloride, the formation of the undesired *meta*- or *ortho*-linkages may occur. In addition, chlorination of the product and/or the synthesis of cross-linked networks is possible. In contrast, the intramolecular cyclodehydrogenation of polyphenylenes using the same conditions is highly selective.[130,161,164,175,177,191]

The synthesis of hexa-*peri*-hexabenzocoronene (**140**, HBC) is one of the most investigated examples of the

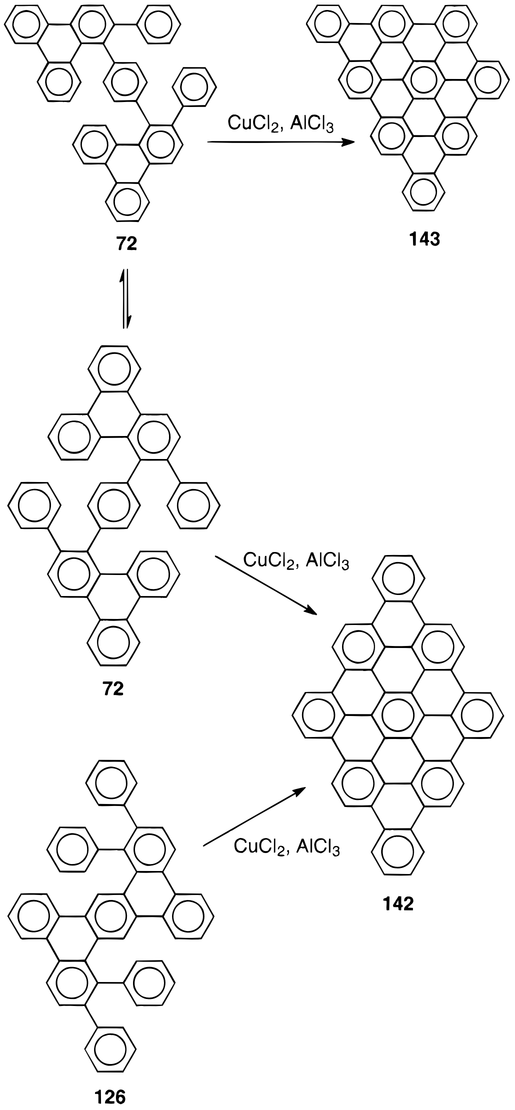
Scheme 35



a) R = H
b) R = *n*-alkyl
c) R = *t*-butyl

oxidative intramolecular cyclodehydrogenation under the conditions employed by Kovacic et al.[37−39,94,95] This compound was first prepared in 1958 by Halleux et al. by treatment with an aluminum(III) chloride melt.[228] Starting from hexaphenylbenzene (**5**), introduced in Chapter III.B, under the influence of copper(II) salts under Lewis acid conditions in an inert solvent a multiple, intramolecular cyclodehydrogenation was achieved for the first time at room temperature, leading to complete aromatization of the desired product **140** in almost quantitative yield.[161] In the scope of this cyclization, neither partially cyclodehydrogenated products, nor intermolecular bond formation, nor chlorinated products were observed. Nevertheless, for alkyl substituents on hexaphenylbenzene (**5b**,**c**), a slight modification of the reaction conditions was made necessary as the aluminum(III) chloride used as a Lewis acid could cause cleavage or migration of the alkyl substituents. Iron(III) chloride, which is a weaker acid, was used here as an alternative Lewis acid, thus avoiding migration problems. In addition, iron(III) chloride could render the copper(II) salts superfluous as it can also act as an oxidant.[162,164]

Scheme 36

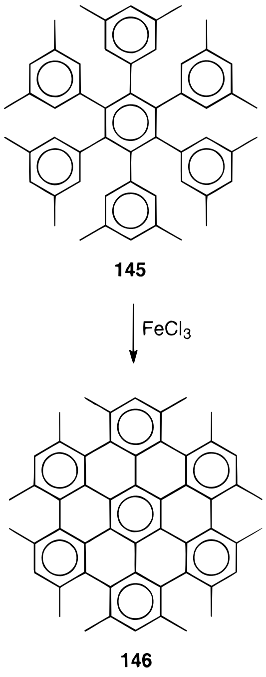


As further experiments showed, the cyclodehydrogenation process established for HBC is also valid for other unsubstituted discs such as **72**,[130] **75**,[130] **78**,[131] **89a**[164] and **90a**[164] as well as substituted discs such as **89b**[164] and **90b**.[164] Here, the best planarization results for substituted compounds were also obtained with iron(III) chloride.[164] As shown in Scheme 36, compound **72** is expected to form different PAHs, **142** and **143**, upon cyclodehydrogenation, and indeed treatment with copper(II) chloride and aluminum(III) chloride gave an inseparable mixture of both products.[130] Nonetheless, **142** was obtained as the single product when the precursor oligophenylene **144** was used.[131]

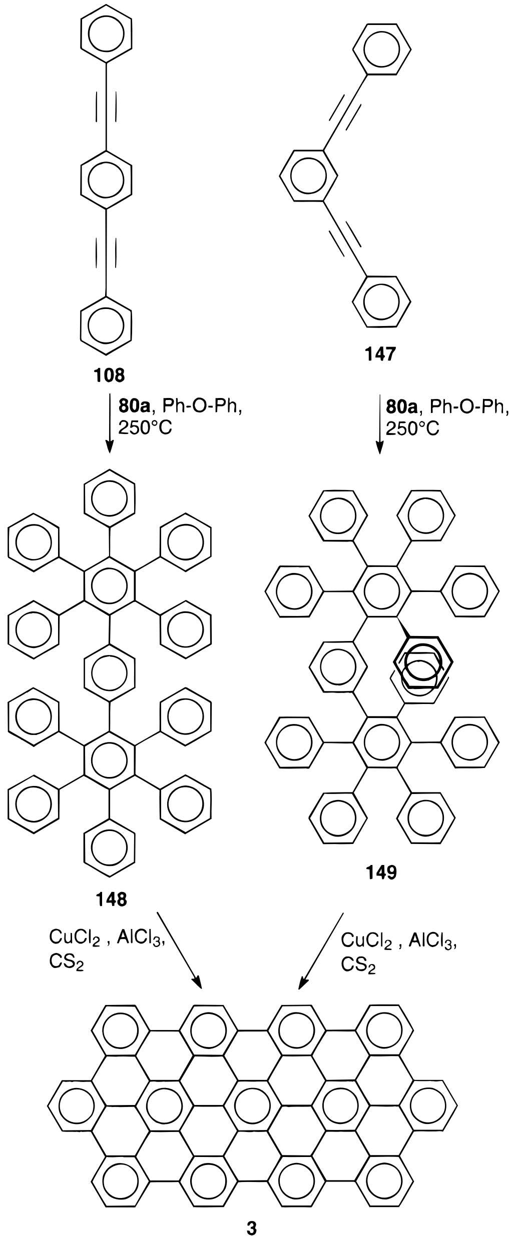
The transformation of **5** into **140** proceeds in a stepwise fashion, a conclusion that is supported by the isolation of **141**.[229] The latter is more soluble in organic solvents than hexa-*peri*-hexabenzocoronene; this can be ascribed to the nonplanar geometry in which one single phenylene ring is oriented approximately orthogonal to the other sheetlike molecule. Interestingly, compounds **140** and **141** have very similar absorption spectra despite their quite different π-topology.

Two further features are important for the intramolecular cyclodehydrogenation. First, the mild planarization reaction tolerates a large degree of steric strain, thus the dodecamethyl derivative **145** can be transformed into the hexa-*peri*-hexabenzocoronene **146** (Scheme 37) in high yield.[230] Second, the formation of polycyclic aromatic hydrocarbons is also successful for oligophenylene precursors with “sterically overlapping phenylene rings”:[163] the two isomers 1,4-diphenylethynylbenzene (**108**) and 1,3-diphenylethynylbenzene (**147**) can be transformed into the oligophenylenes **148** and **149** by Diels−Alder reaction with tetraphenylcyclopentadienone **80a**. While the formation of the planarized C_{78}-hydrocar-

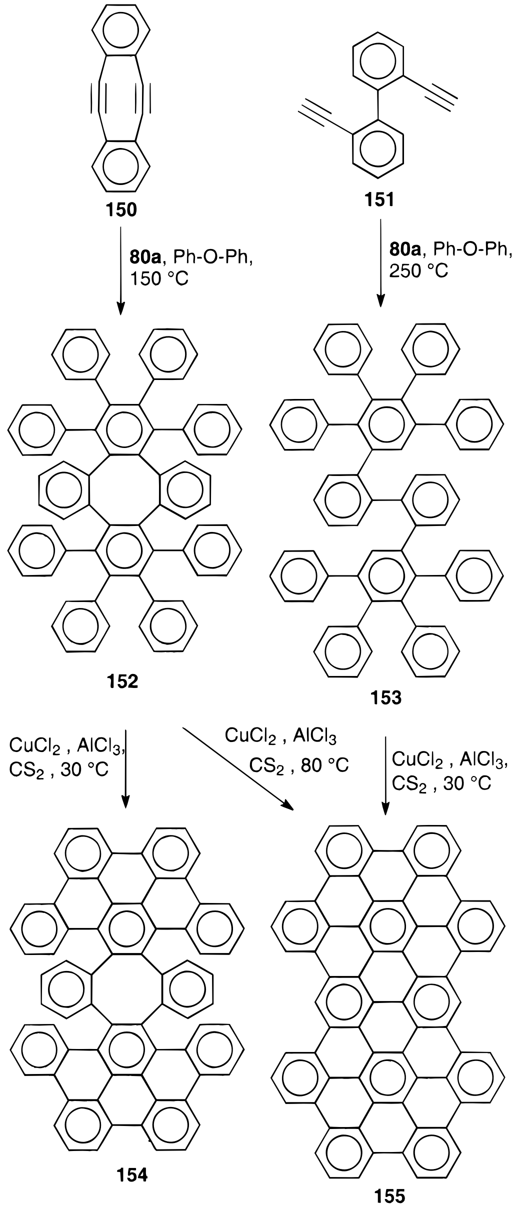
Scheme 37



Scheme 38



Scheme 39



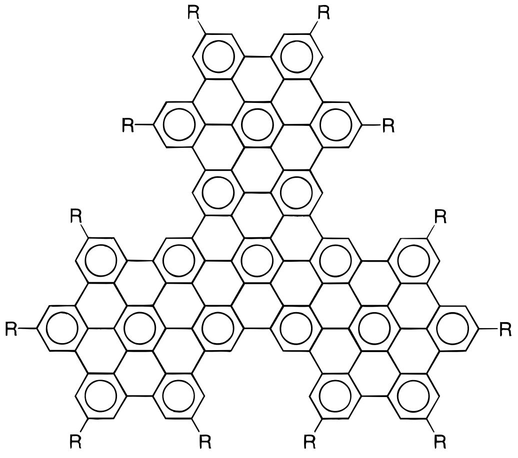
bon **3** from **148** is expected, as discussed above, the formation of the same product from **149** is surprising (Scheme 38). This can be explained by a quantitative 1,2-phenyl migration at the central *meta*-substituted benzene ring.[163] Even more remarkable is the fact that cyclodehydrogenation of the tetraphenylene **152** occurs by a different route depending on the reaction temperature. Reaction with copper(II) chloride and aluminum(III) chloride in carbon disulfide at 30 °C leads to the quantitative removal of 12 hydrogens providing **154**, while the same reaction at 80 °C in 1,1,2,2-tetrachloroethane provides **155** (Scheme 39). This can only be explained by assuming a rearrangement of the central eight-membered ring into a dibenzopyrene unit and subsequent dehydrogenation.[163] Not surprisingly, **155** can also be obtained from the oligophenyl precursor **153**, which can readily be made from the Diels–Alder reaction of 2,2′-diethynylbiphenyl (**151**) and **80a**.[163]

The above examples provide clear evidence that the cyclodehydrogenation is applicable to polycyclic aromatic hydrocarbons much larger than **5**. In view of its hexagonal symmetry, **140** is considered as a superbenzene,[228] **155** can be regarded as supernaphthalene[162] and higher superacenes, such as the supertriphenylene[163] topology **156**, can also be prepared (Chart 7).

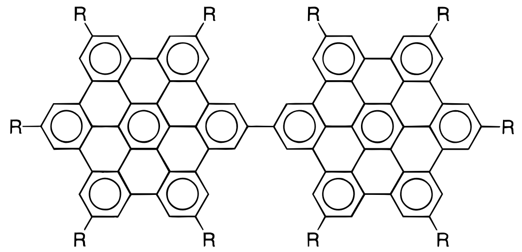
A related structure is the superbiphenyl **157**,[230] which could be synthesized from a bromo-substituted hexa-*peri*-hexabenzocoronene derivative and which in one dimension contains a sexiphenyl axis corresponding to a length of approximately 2.4 nm.

The systematic variation of size and shape of PAHs, i.e., of 2-dimensional nanostructures, can also be used to build up a homologous series, such as the one comprising C_{24} (**158**),[231,232] C_{42} (**140**),[228] C_{60} (**159a**),[163] C_{78} (**3**),[163] and C_{96} (**160**)[230] ($C_x = C_6 + nC_{18}$, $n \geq 1$) leading to an all-ribbon polymer with C_4 (Chart 8). It should be noted that there is a systematic increase in area of the disc-type molecular

Chart 7



156



157

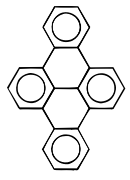
R = *t*-butyl

graphite subunits down the series. The preparation of C_{60} (**159a**)[163] from the oligophenylene precursor **94** is similar to the preparation of **140** and **3**.

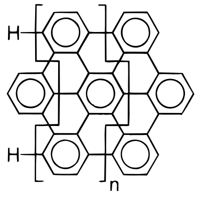
A key concern in the above syntheses is the limited solubility of the planar structures in organic solvents, which hampers purification and processing. The presence of alkyl groups renders discs such as **140** and **159** soluble so that they can be subjected to full spectroscopic characterization[161,233] but is also important for the formation of 2- and 3-dimensional supramolecular architectures (Chapter VI.B). However, as mentioned for compound **140**, the presence of alkyl chains can create problems during the oxidative cyclodehydrogenation. Nevertheless, the octa-*n*-alkyl derivative of C_{60} **159c** has been prepared,[163] (Scheme 40) although the first oxidative cyclodehydrogenation provides only partially dehydrogenated products, which can then be transformed into the disc structure only by a second reductive cyclodehydrogenation.

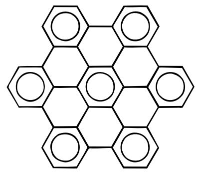
An important aspect in view of the direct visualization of single disc-type molecules by scanning tunneling microscopy and the recording of current–potential curves of single molecules (Chapter VI.B) is the fact that modification of the above synthetic procedures also provides functionalized derivatives of hexa-*peri*-hexabenzocoronene, such as **161**, **162**, and **163** (Chart 9).[230] This not only allows subsequent chemical transformation but also a significant change in the energy of the frontier orbitals, which is thought to be relevant to the magnitude of the tunneling current seen in an STM experiment.[230]

Chart 8

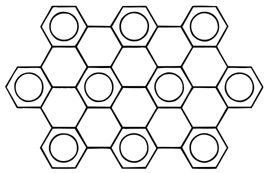


158

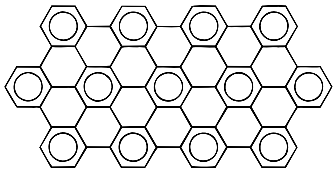




140a



159a



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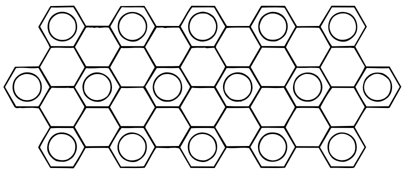


160

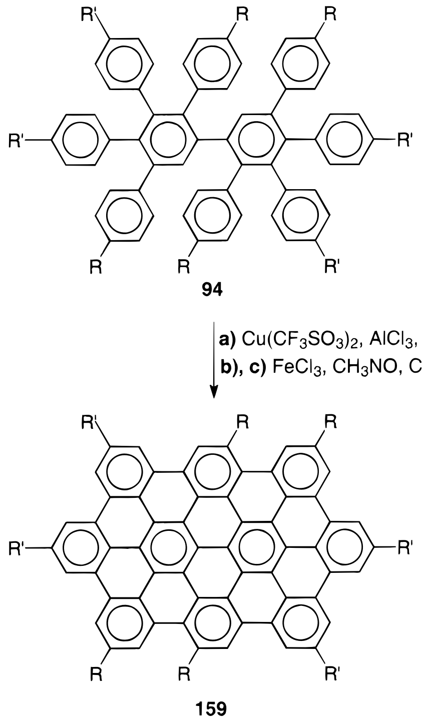
VI. Supramolecular Ordering

A. Linear Polyphenylenes

The key structural factor in describing the supramolecular ordering of PPPs is their anisotropic shape, which follows from a rodlike architecture that differentiates them from flexible polymers. Rigid-rod polymers are characterized by a stiff backbone, allowing only one single rotation about the chain axis. This class of polymers includes, other than PPPs, polymers such as poly(*para*-phenylene)-2,6-benzodiimide (**164**) and poly(*para*-phenylene)ethynylene (**165**) (Chart 10).[234,235] However, it should be noted that the design of rigid-rod polymers is not restricted to chain structures consisting of aromatic building blocks but also includes multilayered systems such as the phthalocyanatopolysiloxanes (**166**).[32]

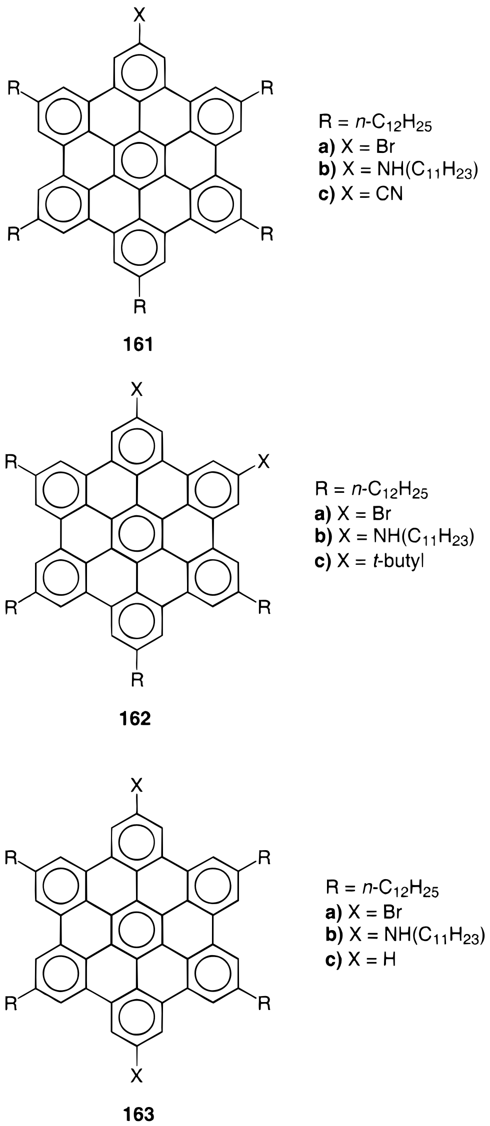
Unfortunately, PPPs are insoluble in many organic solvents, which limits their processability. Therefore, attachment of conformationally mobile alkyl side chains to the backbone has been important because it has allowed the controlled synthesis of soluble and

Scheme 40



a) R, R' = H
b) R = H, R' = n-$C_{12}H_{25}$
c) R, R' = n-$C_{12}H_{25}$

Chart 9

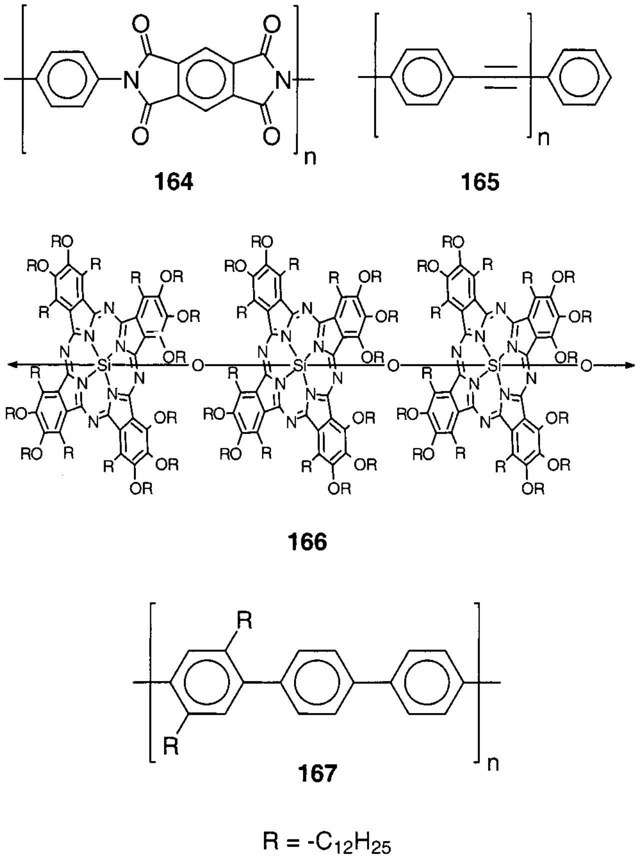


processable PPPs with high molecular weight.[52−54,63] In view of the expected large persistence length (for definition see below) of the main chain and of the flexibility of the side chains, such molecules have been termed hairy-rod polymers.[32] Unlike other rigid-rod polymers, PPPs show significant optical polarizability and anisotropy, which is particularly important when trying to obtain information on the orientational dynamics in solution.[236−238] Useful methods for studying the dynamic behavior of rigid-rod chains are static and dynamic light scattering as they are very sensitive probes for collective orientation fluctuations. Measurements obtained from dilute solutions lead to the conclusion that poly(2,5-di-*n*-dodecyl-*para*-terphenyl-4,4″-diyl) (**167**) forms small aggregates typically consisting of trimers with a parallel arrangement of the molecules.[239] In semidilute solution, additional relaxation processes (slow and ultra-slow) can be detected in addition to the faster cooperative diffusion and reorientation of the trimers. X-ray scattering experiments suggest that these can be ascribed to the formation of large anisotropic clusters of about 570 nm size with inherent crystallization.[239] The formation of these large clusters at room temperature requires approximately 1 week after preparation from the solution, and the clusters disappear upon heating to 65 °C. After standing, the clusters precipitate under gravity and form an opaque sediment.[239]

In the 1920s, Vorländer reported that quinquephenyl (**168**) and sexiphenyl (**169**) formed liquid crystalline melts (Chart 11).[240,241] The liquid crystalline character of methyl-substituted oligophenylenes was also established.[242] It is generally assumed for the melts of monodisperse polymers that an axial ratio of 6.2 is required for the occurrence of liquid crystallinity.[243−245] Unfortunately, since the melt contains molecular weight distributions, induced fractionation could occur.[246] Lower molecular weight poly(2,5-di-*n*-dodecyl-1,4-phenylene)s (**171a**) give only isotropic phases upon melting while the higher molecular analogues exhibit anisotropic phases as well as isotropic ones.[247] Later investigations of the high molecular weight fraction of polymers **171a** with M_w approximately 137 000 g mol^{-1} showed that only one anisotropic phase is obtained.[243] It is important, in this context, that rigid-rod polymers with a stiff backbone and shape anisotropy are predicted to have outstanding mechanical properties. While the presence of alkyl chains is important for solution and melt-processing often under the formation of order, the presence of side chains could compromise the mechanical properties of PPPs due to the chemical instability of the side groups and to their liquidlike character at relatively low temperatures.[243]

Conduction processes in linear conjugated polymers such as PPP cannot be discussed without referring to information on 3-dimensional structures. The difficulty of obtaining crystal structures from conju-

Chart 10

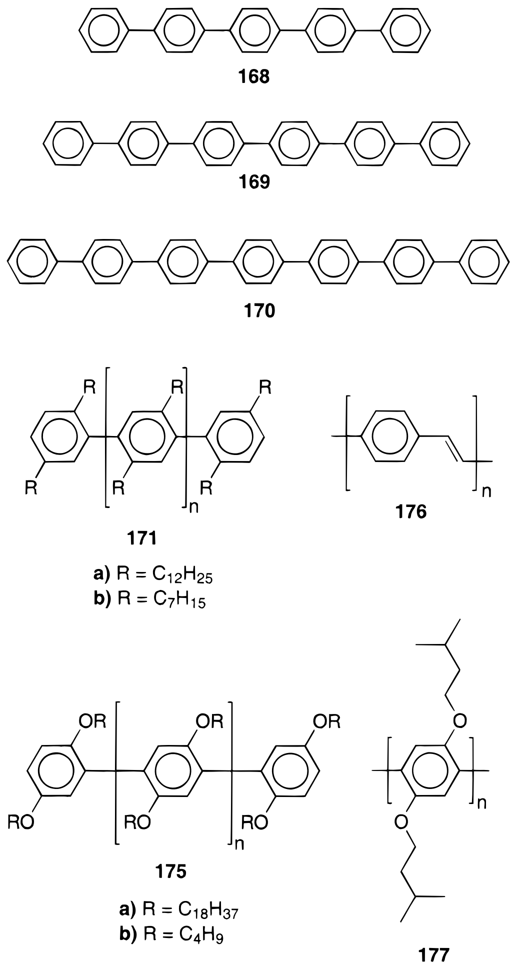


gated polymers is that there is often little usable diffraction data. However, oligophenylenes, where the bulk solid structures of the homologous series up to septiphenyl (**170**) have been studied,[248−251] can be regarded as ideal models for undoped PPPs.[252] It was shown that all oligophenylenes pack in a type of herringbone structure. In this structure the chains are aligned parallel to each other, with a small tilt of the molecular axis with respect to the longest crystallographic axis. This was proposed to be due to the interaction of the terminal hydrogen atoms.[251,252] Furthermore, this tilt showed an odd−even effect with a larger angle for oligophenylenes possessing an even number of phenylene rings. Finally, the base of the unit cells determined from X-ray diffraction data remained constant at approximately 0.55−0.56 nm by 0.80−0.81 nm, while the height increases only by approximately 0.41 nm rather than 0.43 nm, as expected from the size of one phenylene repeat unit.[250] This may be due to compression or bending of the chain or the tilting with respect to the molecular axis.[250]

The case of *meta*-bridged oligophenylenes is less well studied. Here, only the crystal structure of *meta*-deciphenyl (**172**) was determined.[253] As expected, the oligomer forms a helix with a pitch of 1.1 nm and five benzene rings to each turn of the helix. These helices were shown to be aligned parallel and interweaving as shown in Figure 5.

Similarly, poly(*ortho*-phenylene) was shown to adopt a helical structure in the solid state, as well.[80] The X-ray analysis of an *ortho*-sexiphenyl derivative (**173**) showed a helix with a pitch as little as 0.37−0.39 nm and only three phenylene-rings per turn. That is, the fourth ring in the chain is overlaying the first one at a very short distance. Even though this is caused by the tight twist imposed upon the molecule, it also suggests that some sort of $\pi-\pi$ interaction might be active between these two very close aromatic rings.

Chart 11



The crystallographic results obtained for oligophenylenes can be compared to those of poly(*para*-phenylene)s. Thus, the PPP chains also arrange alongside each other, and the dimensions of their unit cells correspond very well with the values expected from the oligophenylenes. The height of the cells in this case is approximately 0.4−0.5 nm, which corresponds to the diameter of about one phenylene ring plus a single bond, the basic repeat unit of the polymer chain.[254−256]

Of the conducting, doped oligophenylenes, the radical−cation quaterphenyl salt $QP_3(QP)(SbF_6)_3$ (**174**) has been studied in detail.[252,257−260] It was found that the quaterphenyl molecules were packed in layers which were separated by rows of the counterions. Each layer contained the radical cations and one neutral quaterphenyl molecule. Here again, the terminal hydrogen atom caused a tilt in the quaterphenyl layers. A subsection of the crystallographic unit cell, having the composition $(C_6H_4)_8(SbF_6)_3$, was used to construct a model of the corresponding PPP salt. The orthorhombic unit cell thus obtained ($a =$

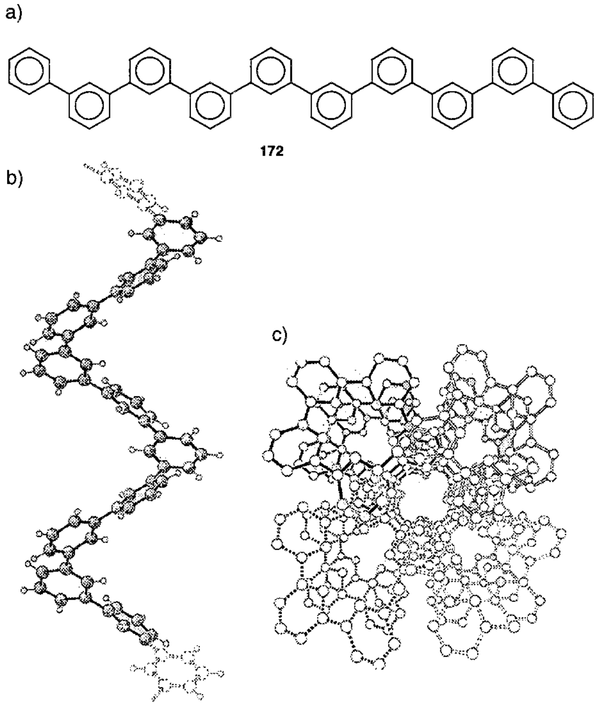


Figure 5. (a) *meta*-Deciphenyl (**172**). (b) Helical chain conformation of *meta*-deciphenyl. (c) Structure of the interleaving helices as found in the crystal.[253]

1.0 nm, $b = 0.7$ nm, $c = 1.7$ nm) was in good agreement with the experimental diffraction data of an AsF_6-doped polymer with a 40% conversion per phenylene ring achieved almost quantitatively.[252,257,259,261]

The morphology of PPPs prepared by oxidative coupling of benzene has been studied by different techniques. For example, electron microscopy showed formation of fibril structures, which result from simultaneous polymerization and crystallization.[41] It has been proposed that the reaction of the originally formed linear PPP (with preferential *para*-coupling) with benzene to form polyphenylene side chains or even polycyclic subunits prevented the formation of the fibril structure with a higher crystallinity.[256] In an independent approach, the internal and external porous structures of PPP films prepared by electrochemical oxidation of benzene in concentrated sulfuric acid were demonstrated by porosimetry techniques to be highly regular with two characteristic ranges of porosity up to 2.5 and 80−200 nm.[262]

Recently, an electrochemical preparation of a PPP film was reported in which the single polymer molecules were claimed to adopt a crystalline, fibril structure. However, the crystallinity was dependent on the thickness of the film, with thick films being completely amorphous.[263]

The bulk solid-state structure of 2,5-dialkyl- (**171**) and 2,5-dialkoxy-substituted PPPs (**175**) has also been investigated by X-ray methods.[264] For PPPs with long alkoxy chains (e.g., octadodecyloxy, **175a**) an intensive small angle reflection is detected in the X-ray powder diffractogram which can be ascribed to the periodicity, d, of a layer structure. The value of d varies linearly with the length of the side chains, with a slope of 1.25 Å per methylene group, which corresponds to an all-trans conformation of the carbon atoms in the side chain.[264] In contrast, the diffractograms of PPPs with short side chains (e.g., *n*-butoxy, **175b**) do not fit the assumption of a layerlike structure. This result is also supported by differential scanning calorimetry. Looking at the projection along the backbone axis, the PPP molecules with shorter alkyl chains are described as forming a more cylindrical cross-section.[264]

Recently, Wegner et al. have also reported the synthesis of various PPPs with linear and branched PEO side chains.[265,266] Like the substituted PPPs described above, the polymers with linear side chains adopt, in the bulk, a structure with the phenylene backbones aligned parallel to each other, separated by the PEO side chains.[265] Using DSC it was shown that a liquid crystalline phase exists up to about 80−120 °C, depending on the length of the side chain. Due to the large polydispersity of these PPPs, the melting occurred over a range of up to 100 °C, which was verified by X-ray scattering experiments. These showed a sharp peak corresponding to the distance between two PPP backbones separated by the PEO chains. This peak began to diminish at temperatures above 100 °C, in agreement with the DSC results, i.e., when the structure melted. In contrast to this, the PPP with branched PEO side chains were found to be completely amorphous with no liquid crystalline phase.

PPPs constitute rigid-rod structures with extended π-conjugation. This feature qualifies PPPs as electronic materials and, thus, as active components in devices such as field-effect transistors or light-emitting diodes. Poly(*para*-phenylenevinylene)s (**176**), which have been most intensively studied as emitters for LEDs, give a yellow or yellow-green emission.[267−269] In the search for blue light emitters, PPPs have attracted particular attention due to their large band gap.[270,271] Thin emitting layers are mostly obtained by spin coating or casting, which has the disadvantage that control of molecular order or alignment is difficult to achieve.[26,272] However, Fitzsimmons et al. have recently published a route to a self-assembled bilayer film consisting of a positively charged poly(diallyl dimethylammonium chloride) (PDDA) layer and a negatively charged sulfonated and carboxylated PPP layer having a λ_{max} of 411 nm.[273]

When investigating optical, electrical, and electroluminescent applications, thin films with an alignment of the polymer chains appear as an important requirement.[267,274−276] Here again, oligophenylenes may be used as model compounds for PPPs. Sexiphenylene (**169**) films deposited on various surfaces using high-vacuum deposition has been particularly well studied.[277−280] Depending on the conditions used, such as substrate temperature, deposition rates, or substrate materials, the film structure could be varied and preparation of unoriented and oriented films was possible. Thus, a series of fibril structures with the direction of the fiber axis perpendicular to the surface of the substrate was prepared.[280] Within these structures, the sexiphenyl molecules are distributed randomly around the axis of the fiber. The oligophenylenes are tilted at an angle of about 17°

to this axis or lie parallel to the surface of the substrate.

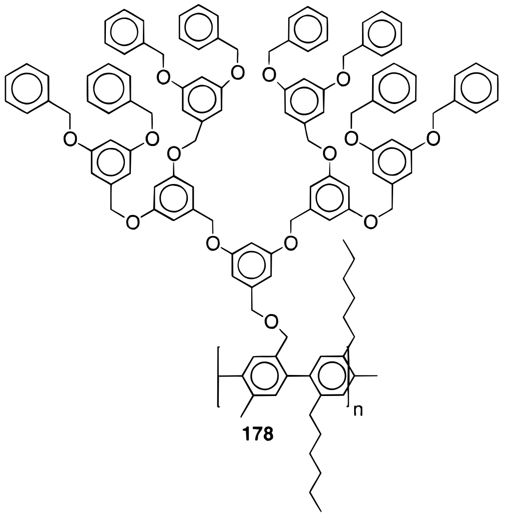
The specific orthogonal structure of the two oligomer chains within spiro oligophenyls (**70**, Chapter II.C, Scheme 14) leads to various characteristic physical properties.[127,281] The spiro oligophenyls show a surprisingly high solubility in organic solvents, several orders of magnitude higher when compared with the corresponding linear oligophenylene analogues.[281] They are characterized by the ability to form high-quality, transparent thin films. Such films of the spiro oligomers (**70**) show only a very low tendency to undergo solid-state recrystallization processes with the crosslike geometry of the molecules stabilizing the glassy state. Recrystallization processes are often unwanted, for example, in the active layers of organic materials in light-emitting diodes, since the recrystallization of the emitter material is accompanied by a dramatic decrease of the photo- and electroluminescence quantum yields.[281] The spiro oligophenyls (**70**) display high glass, transition temperatures (T_g > 200 °C), thereby fulfilling another prerequisite for an application in light-emitting diodes: morphological stability in the temperature range of device operation.[127]

When using substituted PPPs it is possible to apply stretch alignment of films,[282] while an alternative approach is the formation of ordered ultrathin films upon ordered substrates such as poly(tetrafluoroethylene) (PTFE) on silicon wafers.[283,284] The necessary films are easily prepared by drawing rods of PTFE over freshly etched silicon wafers followed by solution casting of the conjugated polymer. During this process thin films of poly(2,5-diheptyl-1,4-phenylene) (**171b**) are prepared in an oriented structure.[26] The spatial characteristics of the ordered layers were determined by atomic force microscopy and the electronic structure by angle-resolved ultraviolet photoelectron spectroscopy. It appears that approximation of the PPP polymer as a 1D system is valid and, somewhat unexpectedly, that the polymer films appear to be ordered with the polymer backbone approximately orthogonal to the PTFE fibers.[283] A similar experiment was performed by Witteler using PTFE on a glass surface to investigate the disclination density of his poly(2,5-dihexyl-*para*-phenylene) in oriented states.[285] Using polarization microscopy he also found ordered films (low disclination density) lying on the PTFE surface and reported on the relation between the film thickness and the disclination density. As expected, the latter increased with the thickness of the film. However, the method used here was not able to detect the direction of the orientation of the polymer film on the PTFE, but the difference between an orientated film on the PTFE surface and a nonorientated one on the untreated glass was clearly distinguished.[285]

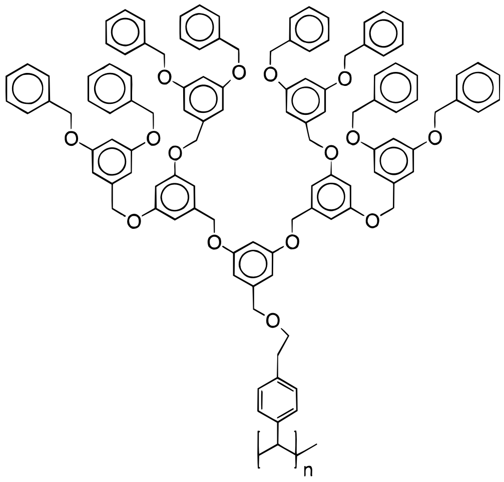
A particularly exciting aspect of thin-film formation is the occurrence of *monolayers* originating spontaneously upon adsorption from solution.[286−292] Studies of self-assembled monolayers on surfaces have mostly concerned low molecular weight compounds, and self-assembled polymer layers are rarely mentioned.[293−295] One notable exception is the self-assembled polymer layer formed from poly(2,5-dodecyl-*para*-terphenyl-4,4″-diyl) (**167**).[295] This particular material contains an average of 90 phenylene rings and an average length of approximately 39 nm, whereby the regioregular substitution with the alkyl chains is important. The polymer was adsorbed from solution onto gold films on Si(111) wafers, whereby ellipsometry showed a layer thickness of about 2 nm. AFM images of the polymer coatings revealed the formation of structured islands in unstructured surroundings, with the size of the structure domains corresponding roughly to the length of the PPP molecules. In the ordered domains, bent striae separated by about 1−1.5 nm were detected. It is charasteristic that the lateral dimensions of these stripes agree with the molecular size of the PPP chains, and it is thus appropriate to describe the self-assembled monolayer as a 2-dimensional liquid crystal. The reason for the surprisingly high resolution of the AFM pictures can be seen in the restricted mobility of chain segments of the rigid polymer whose motion is slow with respect to the AFM time scale.[295]

A good case can be made when comparing the structures of the adsorbed rigid-rod polymers with their equilibrium conformations occurring in solution or the melt. The stiffness of a rigid-rod polymer can be described in terms of the so-called persistence length derived from the Kratky−Porod model of a “wormlike” polymer chain.[296−298] The persistence length is the characteristic distance at which the directional correlation of two vectors, tangential to the contour of the polymer, is reduced by a factor of 1/e. Light scattering and neutron scattering experiments using rigid-rod polymers have generally shown that the values determined are usually smaller than expected.[237,299−303] In the case of PPP, a persistence length of about 13 nm was determined by light scattering using a sulfonated PPP,[304] and a value of 16 nm has been reported for alkyl-substituted PPPs.[305] Using Rayleigh scattering on a series of unsubstituted and alkyl-substituted polyphenylenes and oligophenylenes, a value of up to 28 nm has also been found.[238] However, this value was considered to be too high due to the limited range of molecular weights available. In general, the persistence lengths measured by these methods should be treated with care, as the experimental error may be considerable. Nevertheless, they show that the difference between flexible polymers and PPPs is about 1 order of magnitude.[304] The above AFM pictures disclose a persistence length in the order of 10 nm, providing an interesting comparison with information obtained from solution. Computer simulations have suggested, as well, that the polymer chains retain a certain flexibility so that persistence lengths at around 22 nm were calculated.[306] Thus, an unambiguous interpretation of the persistence lengths requires further, more detailed experimental and theoretical work.[303] A remarkable case is polymer **50** (Chapter II.B, Scheme 10). It was expected that this compound would have a very large persistence length due to its ladder-type structure; however, a value of only 6.5 nm was determined experimentally.[303]

Chart 12



178



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To overcome the problem caused by bending, the approach of Schlüter et al. is promising.[307−312] They showed that the stiffness of a PPP chain can be increased by attaching spacious side chains such as dendrons to the polymer backbone. Scanning force microscopy pictures of polymer **178**, whose length was determined to be 90 nm (over 100 repeat units), showed domains of parallel linear rows with a periodicity of 4.8 ± 0.5 nm (Chart 12). As these distances are comparable to the molecular diameters, Schlüter et al. concluded that these rows represent the single molecules.[311] Molecular dynamics simulations on single polymer molecules suggest an almost stretched conformation in which the dendritic layer around the PPP backbone is nearly compact. Due to the not fully compact structure, the diameter calculated for **178** varies between 2 and 4 nm.[311] These data led to the conclusion that **178** is an ellipsoidally flattened cylinder, indicating the presence of some residual conformational flexibility. Considering the distance of 0.83 nm between adjacent dendrons and the fact that a similar experiment with the same dendron attached to polystyrene (**179**) placing the dendrons only 0.25 nm apart was successful in providing a rigid, cylindrical polymer, using somewhat more spacious dendrons in the PPP case is suggested.[311]

For the deposition of thin films of PPPs on substrate surfaces, the Langmuir−Blodgett (LB) method has become an important method.[32] Originally, ordered films were obtained by applying LB methods to amphiphilic molecules, which were spread as monolayers at the air−water interphase of a LB trough and after compression transferred to a solid planar substrate.[313,314] Interestingly, it could be shown that the same approach was successful for hairy rods as well.[26,315−323] Thereby, hairy-rod PPPs were transferred in single layers by each dipping and undipping. Orientation of the rods occurs in the dipping direction, thus giving rise to anisotropic multilayers. This is an exciting supramolecular architecture since the alkyl side chains form a continuous matrix in which the rigid backbones are embedded as reinforcing components.[32,265,317] In an extension of such investigations, chemically different rods could be applied, giving rise to types of nanocomposites which are made from layers possessing different chemical structures and different rod directions.[32]

An important consequence of depositing PPP chains using the Langmuir−Blodgett technique is the fabrication of LEDs with polarized light emission.[26] The first LED with polarized emission was obtained from stretch-oriented films of polythiophene.[324] The experiment described below is based on the defined stacking of rigid-rod polymers using the Langmuir−Blodgett technique. An LB film was formed from a PPP with 2,5-diisopentoxy substituents (**177**), whereby the choice of the substituents was made to improve solubility in organic solvents and also to prevent crystallization of the side chains. Here again, the resulting films contain polymer chains oriented parallel to the plane of the substrates and, as a result of the homogeneous flow of the molecules on the water surface during the transfer process, show a preferential orientation of the polymer chain along the dipping direction. Photoluminescence and electroluminescence spectra were obtained. The important result is that the ratio of light emission intensity polarized parallel and perpendicular to the dipping direction was in both cases larger than three.[26]

One of the most ambitious research fields is the topic of molecular electronics due to the drastically growing demand for smaller and better electronic devices.[325] Readily available 1,4-dithiolbenzene was self-assembled in the gap formed by the two gold electrodes of a mechanically controllable break junction. Subsequent current−voltage measurements constituted an important approach toward the conductance of an adjunction containing a single molecule.[326,327] The emphasis of this project lies not so much on the synthesis but on the construction of the gold−sulfur−aryl-sulfur−gold heterosupramolecular system. In the search for other molecular-wire candidates, in particular for reducing the significance of the tunneling current, it would be straightforward to (i) proceed to higher oligophenylenes and (ii) include other conjugated rigid-rod molecules.[328,329]

Rod−coil block copolymers (Chapter II.A) constitute a unique class of polymeric materials as the covalently connected dissimilar polymer chains undergo microscopic or nanoscopic phase separation.[81−90,330]

This is a result of the unfavorable mixing enthalpy and the very small mixing entropy, while at the same time the covalent bond between the rod and coil units prevents the system from undergoing macroscopic phase separation. Important parameters which control the microscopic phase separation are the total degree of polymerization, the polydispersity, the Flory−Huggins interaction parameter, the temperature and the volume fraction of the two blocks.[332] If one of the blocks is a liquid crystalline polymer, the morphology of the resulting block copolymer may be influenced by two different structural effects: phase separation through the two immiscible blocks and the spontaneous orientation of the mesogens according to the nematic director. It is generally assumed that the interaction parameter, χ, in liquid crystalline block copolymers is quite large due to the mesophase separation and, thus, induces a much higher order/disorder transition temperature. Poly(*para*-phenylene)-*block*-polystyrene (**34b**, Scheme 7) materials exhibit special nonequilibrium honeycomb morphologies in which monodispersed pores arrange in hexagonal arrays.[89] This novel morphology is proposed to be due to micelle formation. Interestingly, the presence of defects in the PPP sequence does not have a significant effect on the honeycomb morphology. For the study of the optoelectronic properties of block copolymers, a defect-free structure of the π-conjugated system is also crucial. François et al. showed that rod−coil block copolymers containing such π-conjugated rigid rods represent attractive materials as they provide novel ways for probing the influence of the supramolecular order on the optoelectronic properties of the luminescent rods.[271] In other words, the synthesis of luminescent rod−coil block copolymers is a novel intrinsic approach to improve device performance and their stability for potential applications.

3-Dimensional polyphenylenes, such as the hyperbranched polymers and dendrimers, should allow more complex modes of supramolecular ordering in the solid state than their linear analogues. The linear structure of PPP favors an orientation of the chains alongside each other.[251,255] However, for the more complex, branched polymers such as the dumb-bell-like dendrimer **120**, which can undergo small conformational changes due to internal rotation, a parallel alignment would be unfavorable and thus a supramolecular ordering, if any, is almost impossible to predict.[331−338] However, as shown by Percec et al., it is principally possible to cause dendrons to self-assemble into 3-dimensional, cyclindrical, or spherical nanostructures.[334,339,340] Having a polymerizable monomer attached to such a dendron, located at the center of a cylinder or sphere, allows the formation of a nanoparticle with a defined shape. The formation of these particles is very dependent on the exact nature of the dendron used.[340] In contrast, the cylindrical dendrimers by Schlüter et al. are not formed due to self-assembly of the dendrons but due to the very tight packing of the dendritic groups as described earlier in this chapter.[311] Another aspect relevant to the formation of ordered solid-state structures of 3D nanoparticles is the possibility of synthesizing core−shell systems with the polyphenylene as a rigid core and flexible polymer chains as the soft shell. The latter has been shown for other dendrimers to be important during the formation of ordered solid-state lattices.[341−344]

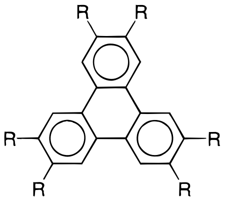
B. Disc-Type Polycyclic Aromatic Hydrocarbons

In the crystalline state, most unsubstituted PAHs adopt one of four structures: herringbone, sandwich−herringbone, γ, or β, as classified by Desiraju and Gavezzotti.[345−347] The parameter which distinguishes these four structures is the shortest crystallographic axis in the screw axis direction. This is largest for the herringbone structure and decreases considerably to the β structure. The other cell parameters can vary freely and depend on the molecular geometry.[345,348] This behavior is explained by the competition between the carbon−carbon and the carbon−hydrogen interactions. While the carbon−carbon interactions of the aromatics in the crystal ideally promote molecular stacks, the carbon−hydrogen interaction leads to a staggered arrangement of the molecules with respect to each other at optimal molecular packing. The more extended these discs become, the more important are the carbon−carbon interactions. Therefore, upon increasing the size of the disc, the adopted structure transforms from herringbone structure to the β structure and eventually to the planar graphitic structure.[345]

In contrast to the unsubstituted PAHs, many substituted ones, such as triphenylene (**180**),[27,349−351] dibenzopyrene (**181**)[352−354] or hexa-*peri*-hexabenzocoronene (**140**),[233,355] are known to form columnar mesophases (Chart 13). The most extensively studied compounds of this class are the hexaalkoxy and the hexaalkanoate derivatives of triphenylene.[27] All hexaethers larger than hexabutoxytriphenylene (**180a**) form a hexagonally ordered columnar discotic mesophase (D_{ho}).[356−360] The temperature at which these compounds form a mesophase may be lowered considerably by increasing the chain length of the substituents. However, at the same time the temperature range in which the mesophase exists decreases. For example, the liquid crystalline phase of 2,3,6,7,10,11-hexabutoxytriphenylene (**180a**) is found between 89 and 146 °C;[357,358] the analogous hexaundecoxy compound (**180b**) shows a mesophase between 54 and 66 °C.[356,358] Some of the hexaalkanoate derivatives of triphenylene (**180c**) display a third transition between two different columnar mesophases, as determined by high-resolution X-ray studies.[356,358,361,362] Upon melting, a rectangular discotic mesophase (D_r) is formed in which the aromatic core forms a herringbone arrangement with the side chains parallel to the columnar axis. Upon further heating, the phase changes to the hexagonal discotic mesophase D_h. Here the triphenylene discs are tilted too but the azimuthal angle is not uniform,[357,363] i.e., this transition increases the disorder within the molecular superstructure.[364−366]

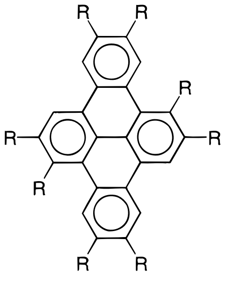
In contrast to the triphenylenes, the liquid crystalline behavior of the substituted dibenzopyrene and hexa-*peri*-hexabenzocoronene derivatives has been less well studied. In the case of the former, the main

Chart 13



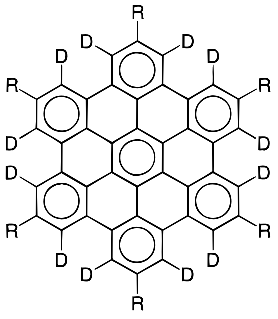
a) R = $-O-n-C_4H_9$
b) R = $-O-n-C_{11}H_{23}$
c) R = -OCO-alkyl
d) R = $-S-n-C_6H_{13}$

180



a) R = $-OCO-CH(CH_3)-O-n-C_6H_{13}$
b) R = $-OCO-CH(CH_3)-O-n-C_7H_{15}$
c) R = $-O-n-C_5H_{11}$

181



R = $-n-C_{14}H_{29}$

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interest is in the preparation of ferroelectrically switchable *columnar* liquid crystal.[352] When experiments with several substituted triphenylenes proved fruitless, experiments using octasubstituted dibenzopyrene derivatives ($-OCOCH(CH_3)OC_6H_{13}$, **181a**, and $-OCOCH(CH_3)OC_7H_{15}$, **181b**) were performed. It was shown that dibenzopyrene derivatives allow the formation of a columnar mesophase even if the chains are branched at the α position. This, together with the fact that due to the limited space the rotation of the chains in position 1 and 8 is very limited, ensure a sufficiently large tilt-induced dipole,[352] and **181a** and **181b** were shown to be ferroelectrically switchable as desired.[352,367]

The largest known PAHs that display liquid cristalline behavior are the hexasubstituted hexa-*peri*-hexabenzocoronenes such as **140**.[233,355] The X-ray diffractograms showed that these compounds form an ordered hexagonal columnar superstructure (D_{ho}), as shown in Figure 7. An alkyl chain halo in the diffractogram displays the disordered liquid character of these substituents in the mesophase.[233] According to differential scanning calorimetry measurements, the liquid crystals were stable over a range of about 300 °. The isotropization points were dependent on the degree of branching of the substituents. Thus, for example, the inclusion of two *tert*-butyl groups as in **162c** could lower both points considerably as expected.[230] On further variation of the substitution pattern, it was determined that the D_{ho} phase is formed with numerous substituents and that the attachment of four side chains at the PAH core is sufficient for the formation of the mesophase.[230] It should also be mentioned that compounds **140b** and **140c** contain no heteroatoms but are pure hydrocarbons.

The dynamic behavior of these mesophases was studied by solid-state deuterium NMR, where the most prominent motion is the rotation about the columnar axis.[27,233,368,369] In the case of hexaalkylhexa-*peri*-hexabenzocoronene **182**, ^2H NMR measurements showed a Pake pattern in the fast motion limit, which was only one-half as wide as that for a rigid solid.[233,368−372] Comparing the order parameters of typical hexaalkoxytriphenylenes with those of hexaalkylhexa-*peri*-hexabenzocoronene, a decreased order along the column of the latter is observed. While the triphenylene derivatives display values greater than 0.90, and therefore very close to the maximum of 1, the order parameter of compound **182** is only 0.84.[233,368,370] This can be explained by the fact that larger discs can form columns with substantial aromatic overlap more easily than smaller discs. Thus, the order decreases when going to larger discs without the column collapsing.

On stacking disc-type molecules as in columnar mesophases, a channel for charge transport is formed through the π-overlap of coplanar molecules and a type of 1-dimensional photoconductor can be created.[28−31] Large PAHs may be regarded as a nanoscale oligomeric section of an infinite 2-dimensional graphite sheet. The organized domains within the columnar discotic mesophase can be considered as consisting, effectively, of bunches of coaxially insulated wires of 1-dimensional graphite. It is therefore remarkable that such phases formed from large PAHs have been shown to possess high 1-dimensional charge-carrier mobility along the columnar axis.[27,355,373−377] This charge-carrier mobility increases going from triphenylene to hexa-*peri*-hexabenzocoronene to highly oriented pyrolytic graphite (HOPG). This can be readily explained by the increase in effective $\pi-\pi$ overlap between the sheets.[355] A notable exception is the hexagonal phase formed by 2,3,6,7,10,11-hexahexylthiotriphenylene (**180d**).[378] The phase, formed by cooling the isotropic liquid melt, displayed a charge-carrier mobility of about 0.1 $cm^2\ V^{-1}\ s^{-1}$, which is approximately 3 orders of magnitude greater than the value determined for HOPG. This finding would strongly suggest the application of these materials as transport layers in electrocopying or electrophotography or as nanowires in monocular electronic devices. Such approaches, while intriguing, require the solution of further supramolecular problems such as control of the orientation of the columns with respect to the electrodes or the stabilization of ordered mesophases at room temperature.

When considering large PAHs as molecular models of graphite, a particularly important supramolecular motif is that of monolayers of PAHs on substrate surfaces. A classical way of making monolayers is via

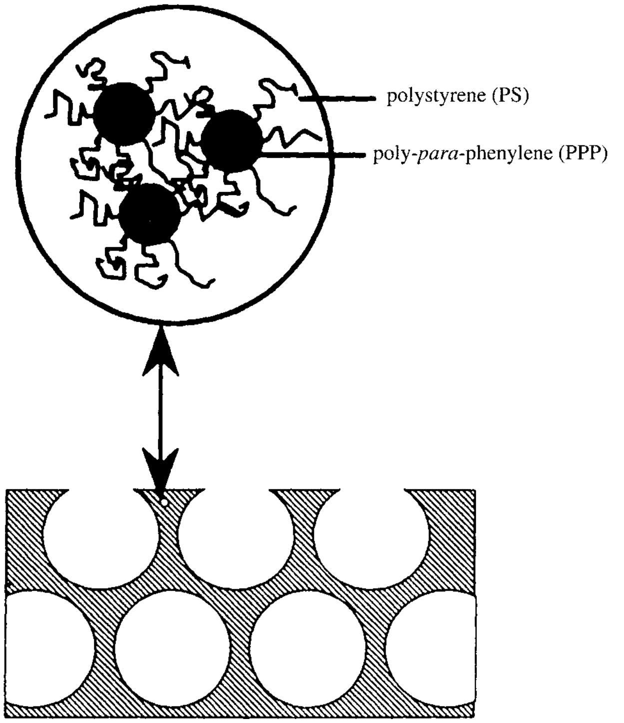
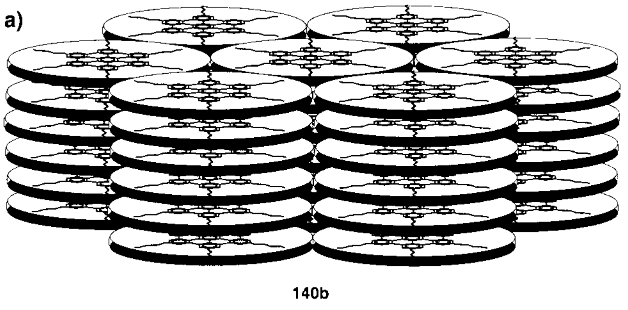


Figure 6. Schematic cross-section of a microporous film of a rod–coil polystyrene–poly-*para*-phenylene blockcopolymer (**34**) as described by Francois et al. [87] (Reprinted with permission from ref 87. Copyright 1994 Macmillan Magazines Limited.)

deposition from ultrahigh vacuum, whereby careful control of the process using an ultramicrobalance is crucial to allow epitaxial growth. An important requirement for the formation of tightly packed layers is the coincidence of substrate and adsorbate symmetries. It is therefore important that PAHs of different size and shape have been included in these studies, such as **140** (HBC) and **142** (C_{54}).[131,379,380] In the case of the latter, the binding energy of the molecule on the surface was determined by desorption spectroscopy to be up to 2 eV, mol^{-1}.[131] The resulting patterns could be determined by low-energy electron diffraction (LEED) or by scanning tunneling microscopy (STM). The LEED pattern of a monolayer of **142** (C_{54}) on a MoS_2 substrate showed a unit mesh of 1.42 nm by 1.42 nm with an angle of $\gamma = 84.9°$ between the two sides. The size of the mesh lead to the conclusion that only one C_{54} molecule is contained therein. The structure given in Figure 8c was in good agreement with the LEED pattern and was furthermore found to be the only structure possible with no free space between the single molecules.[131,380] The STM pictures of **142** on MoS_2 and graphite gave direct pictures of the monolayers and information about the extensions of the domains. The mesh determined agreed with the LEED data, and the largest domain found on graphite extended for up to 70 nm.[380–382] Furthermore, the STM picture of **142** on graphite showed nine tunneling current maxima per molecule which corresponded to Clar's theory about the electron sextet, i.e., the nine maxima correspond to the nine rings which are attributed an electron sextet according to Clar's nomenclature (Figure 8b).[16,17,383]



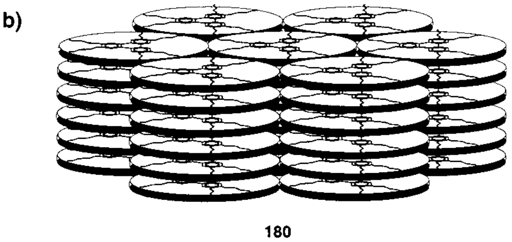


Figure 7. Representation of the hexagonal discotic mesophase formed by (a) hexabenzocoronene (**140**) and (b) triphenylene (**180**).

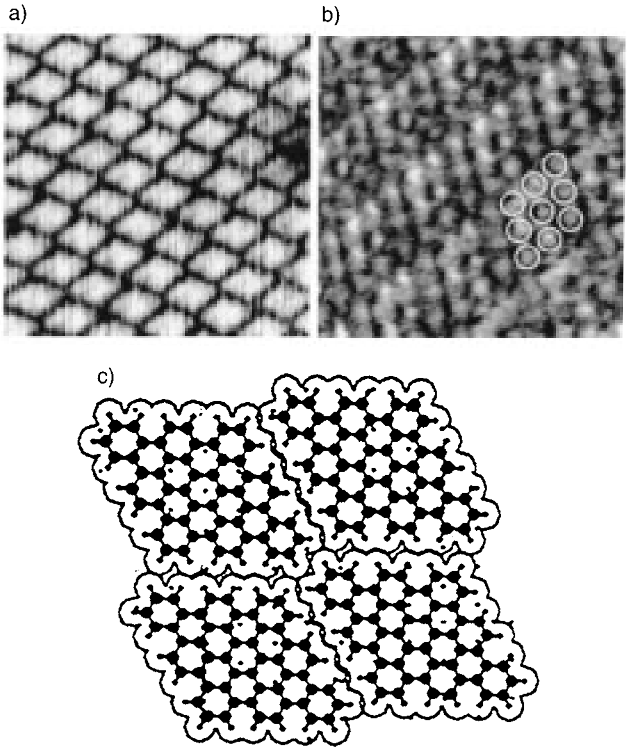


Figure 8. STM pictures of **142** (a) on a (0001)-MoS_2 substrate and (b) on highly oriented pyrolytic graphite (HOPG). (c) Proposed 2-dimensional packing in the film of this rhombus-like molecule.

Monolayer formation by UHV techniques is limited by the vapor pressure of the molecules and, thus, the size of the discs. Therefore, it is important that PAHs, when solubilized by suitable alkyl chains, can also be deposited by physisorption from solution. Regularly ordered monolayers are formed where the alkyl chains fill the space between the aromatic discs and are able to undergo a series of conformational changes in order to improve packing. Here again, the resulting

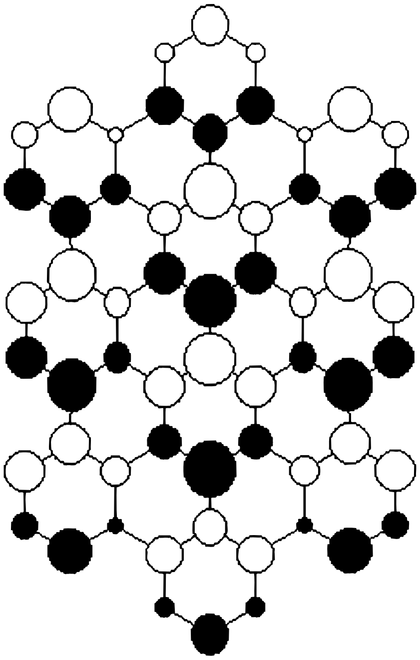


Figure 9. Highest occupied molecular orbital of **159** as calculated by semiempirical AM1.

patterns can be visualized by scanning tunneling microscopy. Submolecular resolution was obtained by STM for hexaalkylhexa-*peri*-hexabenzocoronene (**140b**), which is a molecule with a terphenyl-type diameter. This enables one to perform scanning tunneling spectroscopy on the sample.[161] Current–potential curves were recorded for single molecules and revealed characteristic differences between the aromatic and aliphatic domains. The curve of the aromatic region, unlike that of the aliphatic region, exhibits a strong asymmetry and diode-like behavior. The exact physical origin of these current–voltage phenomena is still a matter of debate. However, two factors seem to be important. First, the energy of the highest occupied molecular orbital (HOMO) of the aromatic section is within the range of the Fermi level of the elctrodes, in contrast to that of the aliphatic HOMOs. Second, a break in the geometric symmetry in the experiment, as a result of HBC being closer to the substrate than the tip, results in an asymmetric current response of the system. However, it should be emphasized that the synthesis of well-defined benzene-based nanostructures paves the way for the measurement of electronic functions of single molecules.[161]

Hexa-*peri*-hexabenzocoronene can be synthesized with different electron-withdrawing and -donating substituents (e.g., **161**, **162**, and **163**), as already mentioned at the end of Chapter V. These substituted derivatives can be physisorbed into regular monolayers. However, the resulting patterns strongly depend on the nature of the particular substituent. While the origin of these differences is not clear, it seems that an understanding of 2-dimensional crystallization will require extensive experimental and theoretical studies (Chapter V).[230] Furthermore, changing the substituents on hexa-*peri*-hexabenzocoronene from electron-withdrawing to electron-donating functions allows fine-tuning of orbital energies of the molecules, which can then be correlated with the tunnel currents detected for single molecules.[230]

It has been shown that studies directed toward the understanding of the electronic properties of polyphenylenes have greatly benefited from the inclusion of the corresponding oligomers. Also, linear oligophenylenes allow systematic increase of the chain length of nano-objects. The construction of different homologous series of PAHs enables a similar approach for 2-dimensional structures, and the length of a homologous series such as C_{24} (**158**), C_{42} (**140a**), C_{60} (**159a**), C_{78} (**3**), and C_{96} (**160**) is obvious from that of the longest oligophenylene chain. That the identification of separate oligophenylene moieties in PAHs may well have some electronic background was observed from the STM pictures obtained for monolayers of C_{60} (**159**).[164] The molecules organize into double-row patterns; however, the picture recorded for the single molecule shows three bright parallel stripes roughly corresponding to three parallel oligophenylene subunits. While the theoretical significance of this outcome is not yet understood, it should be noted that the HOMO of C_{60} (**159**) possesses nodes, as indicated in Figure 9, partitioning the molecule into three oligophenylene moieties.

VII. Conclusions

There is no doubt that visualization and manipulation of single molecules or of small aggregates of molecules have become major themes of scientific research and that such a nanoscience is highly relevant for future nanotechnology.[6] Closely related to this is the concept of molecular electronics which focuses on charge-carrier transport through single molecules.[325] The reliable fabrication of solid-state electronic circuitry operating reproducibly on the nanometer scale remains difficult. Although single junctions have been obtained,[326] it is still a concern of how to fabricate circuits and this, necessarily, raises the question of selecting suitable molecules. π-Conjugation is certainly a prerequisite for efficient charge or energy transport. However, it is known that materials prepared from conjugated polymers often exhibit low charge-carrier mobility. This may not be the case for single molecules without chemical defects and relatively high shape persistence since it is expected that coherent transport through single quantum states will occur. Oligo- and polyphenylenes can adopt a pivotal role in synthesis-driven approaches toward molecular electronics since they combine the advantage of extended π-conjugation with their ability to self-assemble into various supramolecular patterns. The latter feature could also be relevant when interfacing molecules with electronic circuitry. This can be achieved via the tip of a STM or, technologically more important, via suitable nanoelectrodes placed on an insulating substrate. For interfacing via an STM tip, the molecules should be immobilized in a supramolecular pattern on a substrate surface and, when bridging the gap between nanoelectrodes on a substrate, a molecular wire could consist of single PPP molecules or of well-defined aggregates of PPP molecules. Chemical modifications of the molecular wires such as alkyl substition, attachment of heteroatoms at the chain ends, or transition from poly(*para*-phenylene)s to poly(*para*-phenyleneethynylene)s are important steps in the molecular and supramolecular design.[328,384,385]

The role of polyphenylenes as electronic materials is generally bound to extended π-conjugation as occurring, for example, in chain structures. In contrast, the dendritic 3-dimensional polyphenylenes do not possess these electronic properties as they are composed of tightly packed but strongly twisted phenylene units. The resulting macromolecules can be regarded as shape-persistent nanoparticles, carrying a variety of chemical functions. While their role as nanoemitters has been mentioned, functionalization can also be used to create supported catalysts or on-bead assays amenable to full structural elucidation. Thus, with the input from nanoscience, benzene-based oligophenylene and polyphenylene structures are attracting renewed interest and are about to create exciting challenges for future research.

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