J. Am. Chem. Soc. **2000,** *122,* 7707−7717

Synthesis of Large Polycyclic Aromatic Hydrocarbons: Variation of Size and Periphery

Florian Dötz, Johann Diedrich Brand, Shunji Ito, Lileta Gherghel, and Klaus Müllen*

*Contribution from the *Max-Planck-Institute for Polymer Research, Ackermannweg 10,*
55128 Mainz, Germany

Received March 7, 2000

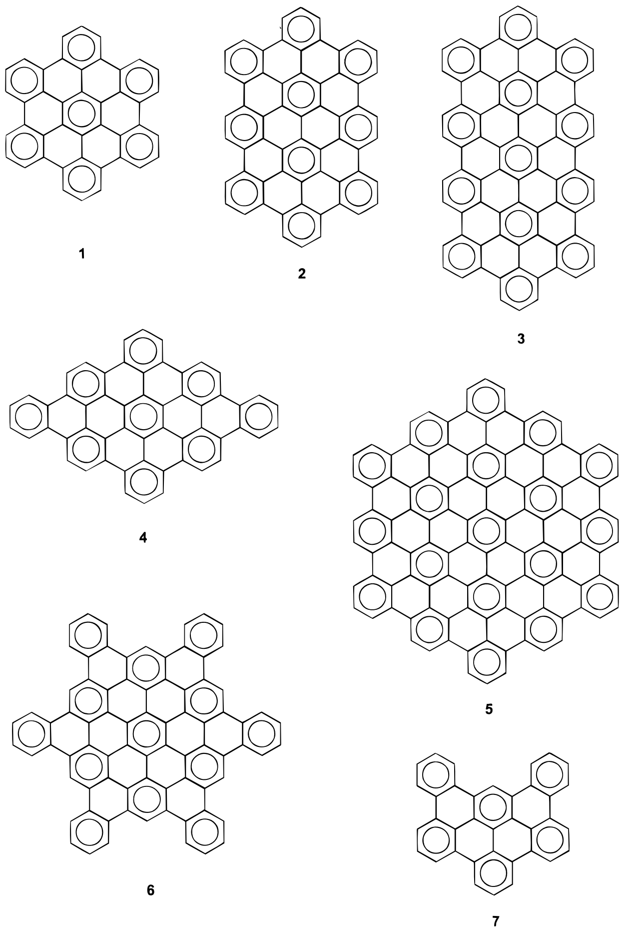
Abstract: A new series of polycyclic aromatic hydrocarbons (PAHs) with different peripheries was synthesized via oxidative cyclodehydrogenation of suitable oligophenylene precursors under mild conditions. Such large PAHs are considered to be two-dimensional graphite sections whose electronic properties are expected to converge to those of macroscopic graphite. The synthetic buildup of the oligophenylene frameworks was mainly based either on Diels−Alder reactions or on cyclotrimerizations. They were subsequently converted into planar aromatic hydrocarbons containing up to 78 carbon atoms. Due to the insufficient solubility of extended PAHs, characterization was achieved by laser desorption/ionization time-of-flight mass spectrometry and UV/visible spectroscopy of thin films.

Introduction

Due to its hexagonal symmetry, hexa-*peri*-hexabenzocoronene (HBC, **1**, Chart 1) serves as an intriguing homologue of benzene with unique electronic properties.[1] Polycyclic aromatic hydrocarbons (PAHs) larger than HBC have also become accessible that constitute molecularly defined models of graphite.[2] Compounds **2** (C_{60}) and **3** (C_{78}) are the first members of a homologous series in which the HBC moiety is "extended" along one symmetry axis.[3] While in a formal sense **2** and **3** can be described as consisting of three oligophenylene chains with n, $n + 1$, and n benzene rings, the rhombus **4** (C_{54}) establishes still another topology, namely, that of three parallel terphenyl chains, i.e., [3,3,3].[4]

The idea of using HBC as starting point of a benzene-like chemistry of molecular graphite subunits suggests a series of further structural modifications.[5] The first step would be to maintain the hexagonal symmetry, but to proceed to the next higher homologue of **1**, i.e., the C_{114} compound **5**. On the other hand, the electronic structure of large PAHs has been shown to

Chart 1. A Variety of Extended, All-Benzenoid Hydrocarbons



---

* Corresponding author: (fax) (+49) 6131-379350; (e-mail) muellen@mpip-mainz.mpg.de.

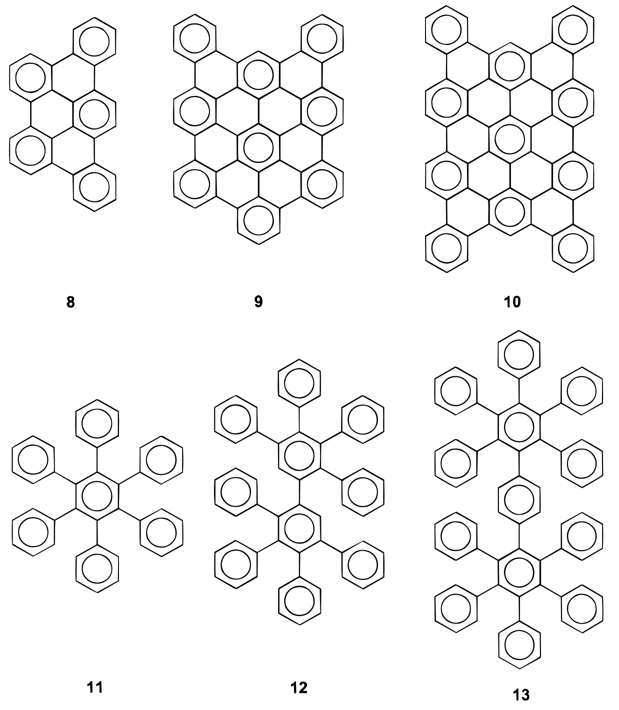
[1] (a) Herwig, P.; Kayser, C. W.; Müllen, K.; Spiess, H. W. *Adv. Mater.* **1996**, *8*, 510. (b) Stabel, A.; Herwig, P.; Müllen, K.; Rabe, J. P. *Angew. Chem.* **1995**, *107*, 1768; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1609. (c) van de Craats, A. M.; Warman, J. M.; Müllen, K.; Geerts, Y.; Brand, J. D. *Adv. Mater.* **1998**, *10*, 36.

[2] (a) Clar, E. *Aromatische Kohlenwasserstoffe-Polycyclische Systeme*; Springer, Berlin, 1952. (b) Clar, E. *The Aromatic Sextet*; Wiley: London, 1972. (c) Dias, J. R. *Handbook of Polycyclic Hydrocarbons. Part a: Benzenoid Hydrocarbons*; Elsevier: Amsterdam, 1987. (d) Fetzer, J. C. *Polycycl. Aromat. Comput.* **1996**, *11* (1−4), 317. (e) Diederich, F.; Rubin, Y. *Angew. Chem.* **1992**, *104*, 1123; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1101. (f) Hudgins, D. M.; Allamandola, L. J. *J. Phys. Chem.* **1995**, *99*, 3033. (g) Scott, L. T.; Cheng, P.-C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1997**, *119*, 10963. (h) Faust, R. *Angew. Chem.* **1995**, *107*, 1559; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1429. (i) Müller, M.; Petersen, J.; Strohmaier, R.; Günther, C.; Karl, N.; Müllen, K. *Angew. Chem.* **1996**, *108,* 947; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 886. (j) Iyer, V. S.; Wehmeier, M.; Brand, J. D.; Keegstra, M. A.; Müllen, K. *Angew. Chem.* **1997**, *109*, 1675; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1604. (k) Müller, M.; Kübel, C.; Müllen, K. *Chem. Eur. J.* **1998**, *4*, 2099. (l) Ito, S.; Wehmeier, M.; Brand, J. D.; Kübel, C.; Epsch, R.; Rabe, J. P.; Müllen, K. *Chem. Eur. J.*, in press.

[3] (a) Iyer, V. S.; Yoshimura, K.; Enkelmann, V.; Epsch, R.; Rabe, J. P.; Müllen, K. *Angew. Chem.* **1998**, *110*, 2843; *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2696. (b) Iyer, V. S.;Wehmeier, M.; Brand, J. D.; Keegstra, M. A.; Müllen, K. *Angew. Chem.* **1997**, *109*, 1679; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1607. (c) Broene, R. D.; Diederich, F. *Tetrahedron Lett.* **1991**, *32*, 5227.

10.1021/ja000832x CCC: $19.00

Chart 2. A Variety of Extended, All-Benzenoid Hydrocarbons and Exemplary Precursor Molecules



depend not only upon the size of the molecules but also upon the nature of their periphery:[6] While four different perimeter types of hexagonal analogues of **1** have been envisaged, we introduce here the hexagon **6** containing a "cove"-type rather than an "armchair" periphery as occurring in **1**−**5**.

When investigating the series of hexagons **1**, **5**, and **6**, one would also suggest combining different periphery types in one and the same molecule.[7] From a design aspect, this can readily be achieved by removing one benzene ring from **1**, thus arriving at **7** (C_{36}) with one core.[8] Removal of a second benzene ring would then furnish **8** (C_{30}, Chart 2), again a subunit of **1** with only "armchairs" in the periphery.[9] Along the same line, one can design models for hexagon **5** by adding benzene to the HBC core, thus arriving at the new compounds **9** (C_{54}), which is an isomer of the rhombus **4**, and **10** (C_{60}).[10]

Increasing the size and varying the periphery of disk-type PAH molecules should influence not only their electronic properties but also their two- and three-dimensional superstructures. Typical examples are the formation of densely packed monolayers of PAHs on surfaces that depend sensitively on the coincidence of adsorbate and substrate symmetries and of stable discotic mesophases with a stacking of the π-layers.[3a,4,11] Alkyl-substituted derivatives of aromatic molecules such as triphenylene or HBC form discotic liquid crystals and, therefore, provide opportunities for materials with one-dimensional transport processes such as energy migration, electric conductivity and photoconductivity.[12] Characterization and visualization of monolayers of such compounds with molecular resolution can be obtained by scanning tunneling microscopy (STM). PAHs are therefore becoming increasingly important as functional materials in optoelectronics and molecular electronics.[1]

We have recently reported that extended PAHs are readily available by a two-step protocol.[2k] This includes the synthesis of nonplanar oligophenylene precursors which are then subjected to an intramolecular cyclodehydrogenation reaction forcing planarization and formation of the polycyclic target structures. The prototype of the cyclodehydrogenation is the successful transformation of hexaphenylbenzene (**11**) into HBC (**1**).[1b] The formation of **2** and **3** from **12** and **13**, respectively, is impressive but nevertheless a straightforward extension of this concept. The design process leading to the appropriate oligophenylene precursors of PAHs and the scope and limitation of the subsequent cyclodehydrogenation process are key synthetic issues of this paper.

The above-mentioned oligophenylene compounds are soluble in organic solvents. In contrast, the corresponding PAHs are nearly insoluble, which limits the role of conventional techniques in structure elucidation. Two experimental aspects are therefore important: laser desorption time-of-flight (LD-TOF) or matrix-assisted laser desorption/ionization) time-of-flight (MALDI-TOF) mass spectrometry can prove the success of the cyclodehydrogenation process and UV/visible spectroscopy, recorded for thin solid films of PAHs, can provide information as to the electronic structure.[13,14] The synthetic approach mentioned above can be modified to afford alkyl-substituted PAHs. Alkyl substituents are important since they can render the PAHs soluble and assist in their supramolecular ordering. Having available soluble, alkyl-substituted derivatives of **1**, **7**, **8**, and **9**, we can also compare UV/visible spectra in solution with those of thin solid films.

Results and Discussion

The synthetic concept of the PAH family presented herein is based on symmetry and size arguments. Different topologies can be achieved either by extending the aromatic system along one symmetry axis or by inducing a starburstlike growth in all directions. In addition, different perimeter types can be introduced. These design principles—classifying PAHs according to their symmetry and periphery—were established by Stein and Brown, who suggested two series of all-benzenoid PAHs starting from benzene as the smallest subunit.[6] The next member in both series is HBC, which is followed in the first series by the PAH **5** containing 114 carbons and in the second one by the PAH **6,** which shows a "cove"-type periphery. The calculations of Stein and Brown proved that resonance energies are strongly influenced by the edge structure of the molecules, i.e., the periphery, and the size of the PAHs. Interior carbon atoms several bond

---

(4) Müller, M.; Petersen, J.; Strohmaier, R.; Günther, C.; Karl, N.; Müllen, K. *Angew. Chem.* **1996**, *108*, 947, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 886.

(5) Ito, S.; Herwig, P. T.; Böhme, T.; Rabe, J. P.; Rettig, W.; Müllen, K. *J. Am. Chem. Soc.* **2000**, *122*, 7698−7706.

(6) Stein, S. E.; Brown, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 3721.

(7) (a) Tong, L.; Lau, H.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1998**, *120*, 6000. (b) Debad, J. D.; Bard, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 2476.

(8) Clar et al. already synthesized the unsubstituted analogues, **7** and **8**, respectively, in a multistep procedure. See: (a) Clar, E.; Zander, M. *J. Chem. Soc.* **1959**, 142. (b) Clar, E.; Zander, M. *J. Chem. Soc.* **1958**, 1861.

(9) Another approach to **8** via an intramolecular Diels−Alder cycloaddition is given in: Müller, M.; Mauermann-Düll, H.; Wagner, M.; Enkelmann, V.; Müllen, K. *Angew. Chem.* **1995**, *107*, 1751; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1583.

(10) Shifrina, Z. B.; Averina, M. S.; Rusanov, A. L.; Wagner, M.; Müllen, K. *Macromolecules* **2000**, *33*, 3525.

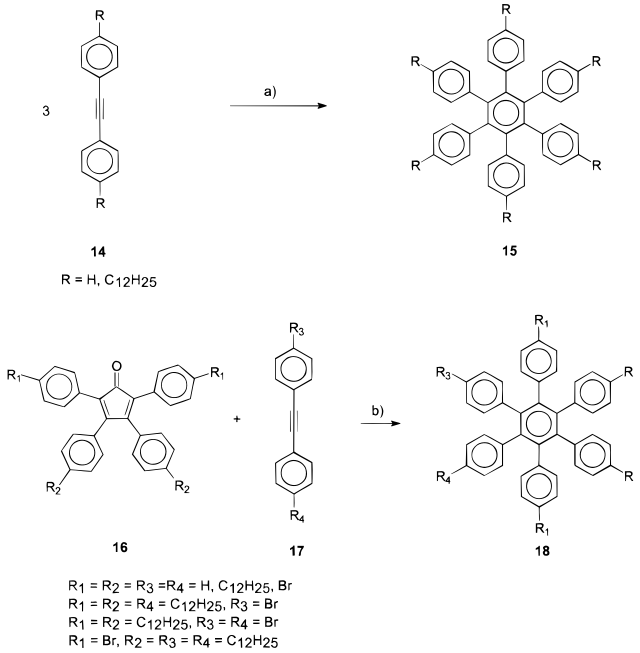
(11) Weiss, K.; Beernink, G.; Dötz, F.; Birkner, A.; Müllen, K.; Wöll, Ch. *Angew. Chem.* **1999**, *111*, 3974; *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3748.

(12) (a) van de Craats, A. M.; Warman, J. M.; Müllen, K.; Geerts, Y.; Brand, J. D. *Adv. Mater.* **1998**, *10*, 36. (b) Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141.

(13) (a) Yoshimura, K.; Brand, J. D.; Wehmeier, M.; Ito, S.; Räder, H.-J.; Müllen, K. *Macromol. Chem. Phys.*, submitted. (b) Przybilla, L.; Brand, J. D.; Räder, H.-J.; Müllen, K. *Anal. Chem.*, submitted.

(14) Gherghel, L.; Müllen, K., in preparation.

Scheme 1. Two Alternative Routes to Large Oligophenylenes: Cyclotrimerization and Diels−Alder Reaction[a]



[a] Conditions: (a) $Co_2(CO)_8$, 1,4-dioxane, 100 °C, 6 h, 99% ($R{=}C_{12}H_{25}$); (b) diphenyl ether, reflux, 24 h, 69−95%.

lengths from an edge were found to have properties similar to those in an infinite graphite sheet. These theoretical investigations show a progression from benzene via extended PAHs to macroscopic graphite and, therefore, provide a guideline for our research in this field.

Our synthetic approach to large PAH molecules consists mainly of two steps: the synthesis of a nonplanar and soluble oligophenylene precursor and its oxidative cyclodehydrogenation to an all-benzenoid hydrocarbon. Two entries to the oligophenylene precursors have turned out to be the most convenient and successful. A quite elegant and facile access to large oligophenylenes is the dicobaltoctacarbonyl-catalyzed trimerization of suitably substituted diphenylacetylenes which leads to PAHs with hexagonal symmetry (Scheme 1).[15] Hexaphenylbenzene is easily synthesized in this way, and this method can also be extended to the preparation of higher hexaarylbenzenes as potential precursors for HBC homologues such as **5**. A more general approach toward hexaphenylbenzenes is the Diels−Alder cycloaddition between tetraarylcyclopentadienones and diphenylacetylenes.[16] This method requires more synthetic effort but opens new possibilities of functionalization. Whereas the cyclotrimerization route permits only uniform substitution of all phenyl rings, the cycloaddition method leads to a broad spectrum of various functionalized oligophenylenes. This has recently allowed us to synthesize unsymmetrical HBCs with different functional groups according to Scheme 1. Both routes afford oligophenylene precursors that are easily characterized and processable.

The final step in the synthesis of extended PAHs is the oxidative cyclodehydrogenation of suitably substituted oligophenylenes which is performed under Lewis acidic conditions.[17] Commonly used are copper(II) chloride/aluminum(III) chloride, copper(II)−trifluoromethanesulfonate/aluminum(III) chloride and iron(III) chloride. Unfortunately, the use of the former causes unfavorable side reactions such as chlorination;[2k] therefore, all of the cyclodehydrogenation reactions leading to unsubstituted PAHs more extended than HBC, e.g., **2**, **5**, and **6**, were carried out with the use of copper(II)−trifluoromethanesulfonate/aluminum(III) chloride. Contrary to that, optimization of the appropriate cyclization conditions of alkyl-substituted oligophenylenes proved iron(III) chloride to be superior to all other reagents since it did not suffer from severe disadvantages such as dealkylation, chlorination, or even migration of the alkyl substituents.[2j] Retention of the desired substitution pattern was achieved, and the cyclization reaction proceeded smoothly at room temperature, in all cases being completed in less than 24 h.

Since nearly all of the investigated hydrocarbons in this study show extremely low solubility, the applied analytical methods are restricted to LD-TOF mass spectrometry and UV/visible spectroscopy, i.e., solid-state characterization. These two techniques represent the basic tools of structure elucidation for the PAHs reported herein and, therefore, need to be proved with respect to reliability and accuracy. Two compounds of the presented PAH family, **7a** and **8a** (Scheme 2), respectively, permit processing and characterization easily, due to their solubilizing side chains and relatively small aromatic core. Considering the small PAHs **7a** and **8a** as model compounds, the reliability of the analytical methods could be shown by simply comparing mass and UV/visible spectra of **7a** and **8a** recorded for different conditions: measurements from solution (field desorption, FD) or solid state (LD-TOF) concerning mass spectrometry and from solution or in film concerning UV/visible spectroscopy. No difference in the spectra was observed, which proved both techniques to be suitable for the characterization of still more extended PAHs.

In view of the well-established synthesis of HBCs from **16** and **17,** the route to **7a** and **8a** is straightforward (Scheme 2).[8,9] The oligophenylene precursor **20** was prepared by Diels−Alder cycloaddition between tetraphenylcyclopentadienone **16** and 4-octyne (**19)**, with concomitant extrusion of carbon monoxide (44%, a relatively low yield due to difficulties in removing diphenyl ether). The cyclodehydrogenation of **20** with iron(III) chloride finally led to **8a**. Cycloaddition between **16** and 4-dodecyl(phenyl)acetylene (**21**) under similar conditions afforded the precursor **22** (99%) and finally **7a**.

Having available the pure and reliably identified PAHs **7a** and **8a**, one can now, for the first time, analyze their UV/visible and NMR spectra in detail. The latter are well resolved and support the expected structure; the former clearly show the three bands typically observed for PAHs (α, *β*, p) and are in agreement with Clar*'s* results.[8] A more detailed discussion is given below.

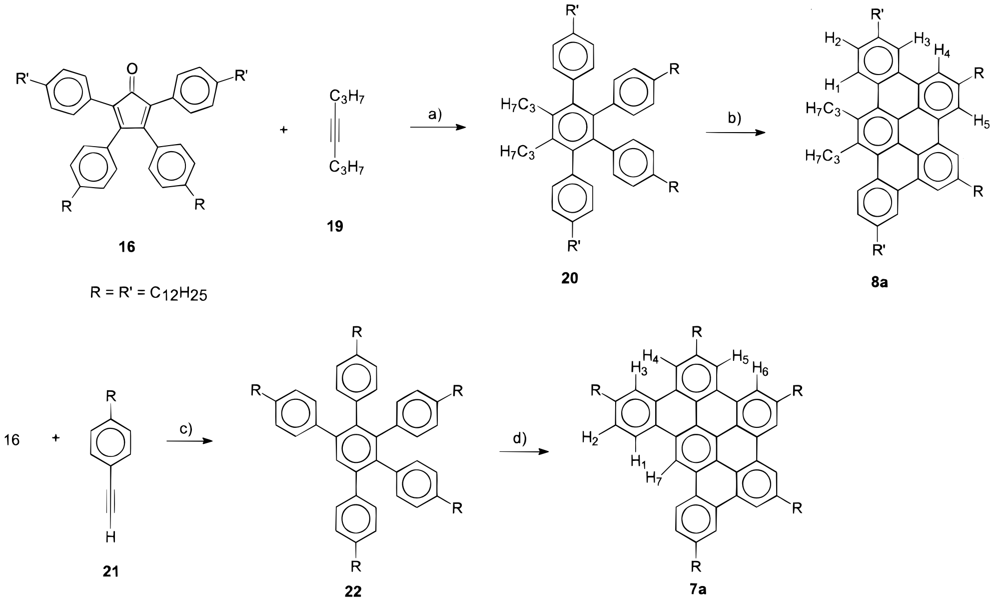
Another example of a moderately soluble PAH is the arrowlike molecule **9a** containing 54 core aromatic carbons (Scheme 3). Introduction of four alkyl chains improves solubility to such an extent that characterization could be achieved not only by LD-TOF mass spectrometry and UV/visible spectroscopy but also by NMR spectroscopy. The synthesis involves four steps.

Starting from 1,3,5-tribromobenzene (**23**), Pd(0)-catalyzed Hagihara reaction with phenylacetylene afforded 3,5-dibromodiphenylacetylene (**24**) in 77% yield. The alkyne **25** was obtained via Pd(0)-catalyzed Suzuki coupling of **24** with phenylboronic acid, which was then converted into the oligophenylene precursor **26** in a Diels−Alder cycloaddition with tetraphenylcyclopentadienone (**26**, 77%; **26a**, 92%). Cyclode-

---

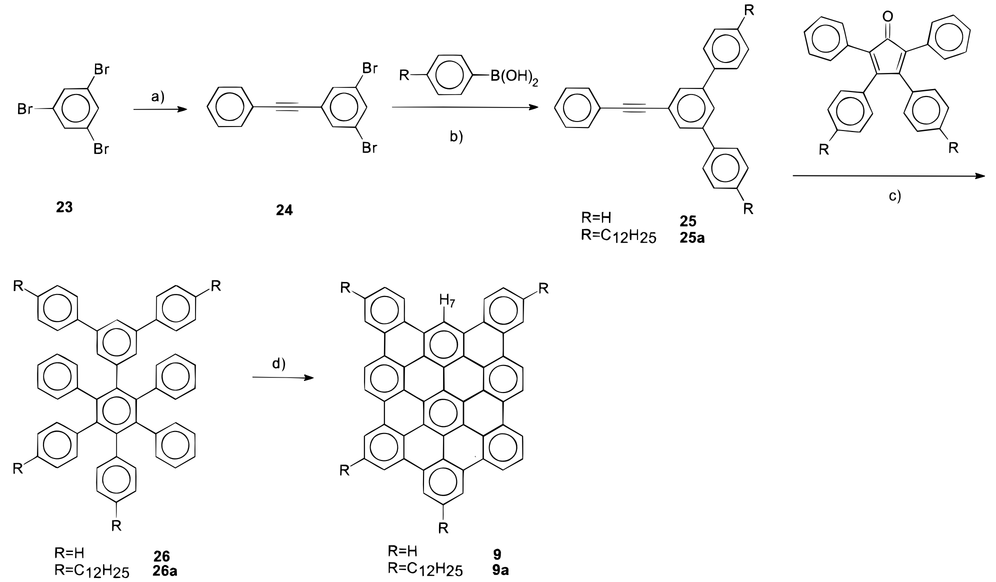
[15] Vollhardt, K. P. C. *Acc. Chem. Res.* **1970**, *10*, 1.
[16] Dilthey, W.; Hurtig, G. *Chem. Ber.* **1934**, *67*, 495.
[17] Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357.

Scheme 2. Synthesis of PAHs **7a** and **8a**[a]



[a] Conditions: (a) diphenyl ether, reflux, 24 h; 44% (b) $FeCl_3$, CH_2Cl_2, 25 °C, 30 min, 24%; (c) *o*-xylene, reflux, 24 h, 99%; (d) $FeCl_3$, CH_2Cl_2, 25 °C, 30 min, 53%.

Scheme 3. Synthesis of Arrowlike PAHs **9** and **9a**[a]

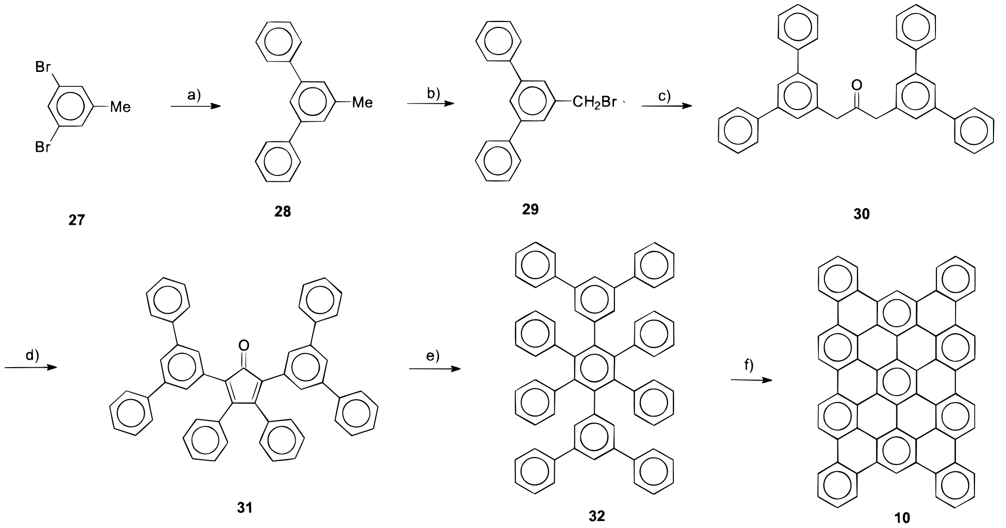


[a] (a) phenylacetylene, $Pd(PPh_3)_4$, CuI, piperidine, 25 °C, 24 h, 77%; (b) $Pd(PPh_3)_4$, toluene, K_2CO_3, EtOH, H_2O, reflux, 24 h, 99%; (c) tetraphenylcyclopentadienone, diphenyl ether, reflux, 16 h, 77%; (d) $Cu(OSO_2CF_3)_2$, $AlCl_3$, CS_2, 25 °C, 24 h, 75%.

hydrogenation of **26** with copper(II)trifluoromethanesulfonate/aluminum(III) chloride and **26a** with iron(III) chloride yielded the desired PAHs **9** and **9a**, respectively, as a brownish orange powder (**9**, 75%; **9a**, 73%). The four dodecyl chains of **9a** provide sufficient solubility for characterization so that the proposed structure could be proven unambiguously. A ^{1}H NMR spectrum was recorded at 140 °C. As expected, due to lack of symmetry, the spectrum is complex and difficult to interpret. Strong $\pi-\pi$-interactions between single molecules favor aggregation leading to broad resonance signals in the NMR spectrum and disallow complete assignment of all signals. Mass spectrometry and elemental analysis gave satisfying results and were in full accordance with the theoretically expected values. This example demonstrates again the problems of structure elucidation of PAHs with insufficient solubility and processability, where a molecule as small as **9a** is on the verge of being unprocessable. Whereas the unsubstituted analogue **9** is completely insoluble, the poor solubility of **9a** allows purification by column chromatography.

A comparison of the proton NMR shifts of the structurally related compounds **7a**, **8a**, and **9a** reveals interesting information. The observed chemical shifts result from a complex interplay of ring size, perimeter type, and aggregation. A complete assignment of all signals was achieved by a combination of 1D NOE difference and H,H COSY measurements. As expected from the deshielding effects induced by stronger ring current, protons inside a bay (e.g., H_1, Scheme 2) absorb at lower field than those offside a bay (H_2). This becomes clear when comparing the shifts for H_1 and H_2 in **7a** and **8a**, respectively (**7a**: H_1, $\delta = 8.97$ ppm; H_2, $\delta = 7.64$ ppm. **8a**: H_1, $\delta = 8.40$ ppm; H_2, $\delta = 7.42$ ppm). A comparison between the two slightly different bay types in **7a** and **8a** (**8a** contains a propyl group

Scheme 4. Synthesis of PAH **10**[a]



[a] Conditions: (a) phenylboronic acid, $Pd(PPh_3)_4$, toluene, K_2CO_3, EtOH, H_2O, reflux, 24 h, 91%; (b) NBS, CCl_4, reflux, 18 h, 94%; (c) $Fe(CO)_5$, NaOH, PTC, CH_2Cl_2, H_2O, reflux, 18 h, 31%; (d) benzil, *n*Bu_4NOH, 1,4-dioxane, reflux, 1 h, 47%; (e) diarylacetylene, diphenyl ether, reflux, 16 h, 95%; (f) $Cu(OSO_2CF_3)_2$, $AlCl_3$, CS_2, 25 °C, 24 h, 87%.

where **7a** bears a proton, H_7) clearly demonstrates that both ring current-induced deshielding and van der Waals shielding effects influence chemical shifts. However, both resonances for H_1 and H_2 appear at lower field in **7a** whereas the strongest ring current-induced deshielding is seen for the cove-type proton H_7 in **7a**. Surprisingly, the analogous proton in **9a** (Scheme 3) resonates at significantly higher field. However, the broad signals in the proton NMR spectrum of **9a** suggest that ring protons could be placed in the shielding region of a neighboring disk-type π-system due to aggregation effects and would, therefore, lead to an absorption at higher field.

At this point it should be noted that we have been able to perform a detailed NMR analysis of the parent compound **7** since it had been sufficiently soluble in tetrachloroethane at 80 °C. Also, we could subject **7** to X-ray crystal structure analysis.[18] It should be mentioned that **7** is planar within the limit of accuracy, which is important since one might have anticipated that a steric interaction of protons in the cove (H_1, H_7) might cause a bending of the π-system and would also influence chemical shifts.

Extending the π-system in only one direction by adding two additional phenyl rings to **9** leads to the "cove"-type PAH **10** (Scheme 4). 3,5-Diphenyltoluene (**28**) was prepared by Suzuki coupling of 3,5-dibromotoluene (**27**) with phenylboronic acid in 91% yield. NBS bromination of **28** afforded the benzyl bromide derivative **29,** which was converted into bis(3,5-diphenylbenzyl) ketone (**30**) under the use of iron pentacarbonyl. Knoevenagel condensation of **30** with benzil gave cyclopentadienone **31**, which was then subjected to Diels–Alder cycloaddition with diphenylacetylene to yield the oligophenylene **32** (95%). Oxidative cyclodehydrogenation under conditions mentioned above resulted in the PAH **10** as a brown powder (87%). An alternative route leading to **10** will be published elsewhere.[10]

The synthesis of the starlike PAH **6** with a "cove"-type periphery required an unsymmetrically substituted diketone, which was synthesized via Hagihara coupling of 3-bromobiphenyl (**33**) with phenylacetylene and subsequent oxidation of the resulting acetylene **34** to the benzil derivative **35** (Scheme 5). Condensation to the cyclopentadienone **36** and subsequent Diels–Alder addition with dienophile **34** afforded an inseparable mixture of the regioisomers **37a** and **37b** in 95% yield. Nevertheless, cyclodehydrogenation of the isomers resulted in the PAH **6** because oxidative formation of 12 carbon–carbon bonds led to the same target molecule in both cases.

The next higher homologue of HBC is the C_{114} compound **5**. The intended synthesis involves three steps starting from the brominated *o*-terphenyl **38** (Scheme 6):[19] Pd(0)-catalyzed coupling to the diarylacetylene **39** (78%) was followed by trimerization with dicobaltoctacarbonyl, which afforded the precursor **40**. Unexpectedly, subsequent cyclodehydrogenation afforded not only the desired PAH **5** but also species of slightly higher molecular weight, as will be discussed later.

A brief discussion of the physical properties of the PAHs **5**, **6**, **9**, and **10** clearly points out the difficulties in investigating the chemistry and proving the structure of such extended aromatic systems. All four compounds are completely insoluble; purification was therefore limited to extensive washing and extraction, and structure elucidation was restricted to mass spectrometry, UV spectroscopy, and elemental analysis. UV spectra could only be recorded by smearing the sample onto a quartz substrate, as will be discussed later. Due to their poor processability, unsubstituted PAHs more extended than the perylene derivative **7** exceed the limits of conventional techniques of characterization, which requires the development of new sophisticated methods of structure proof. The most powerful tool for identifying extended PAHs has turned out to be LD-TOF or MALDI-TOF mass spectrometry. PAHs **6**, **9**, and **10** have been investigated by LD-TOF mass spectrometry and the obtained highly resolved spectra gave unambiguous evidence for a complete cyclization since the formation of each chemical bond between adjacent phenyl rings reduces the molecular weight by two mass units.[13a] The observed isotopic distribution pattern was in all cases in good correspondence to the theoretically expected distribution (Figure 1).

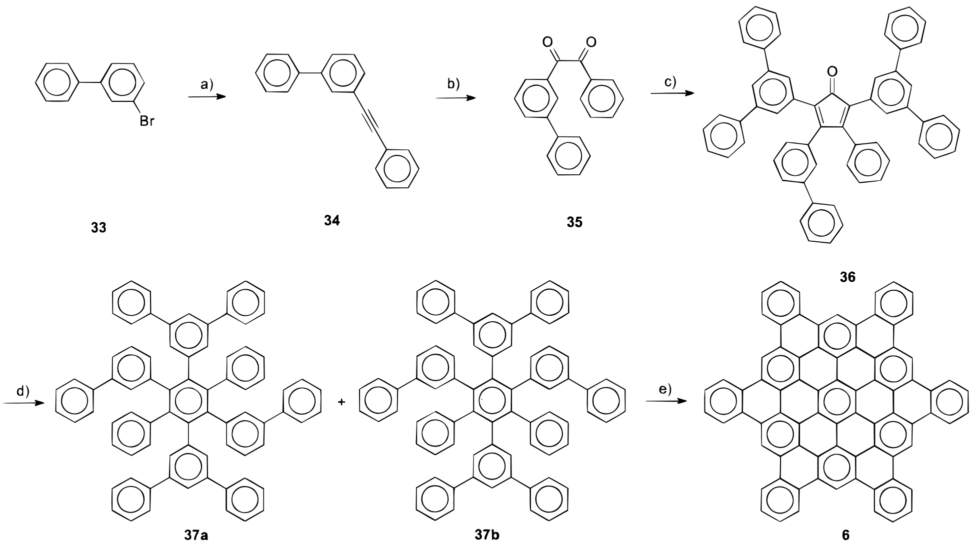
However, LD-TOF mass spectrometry also suffers from a severe problem: Probably due to their dominating π–π-interactions, more extended PAHs require high laser power for desorption of the analyte molecules, which easily leads to unfavorable side reactions such as fragmentation or hydrogen

---

(18) Kübel, C.; Eckhardt, K.; Enkelmann, V.; Wegner, G.; Müllen, K. *J. Mater. Chem.* **2000**, *10*, 879.

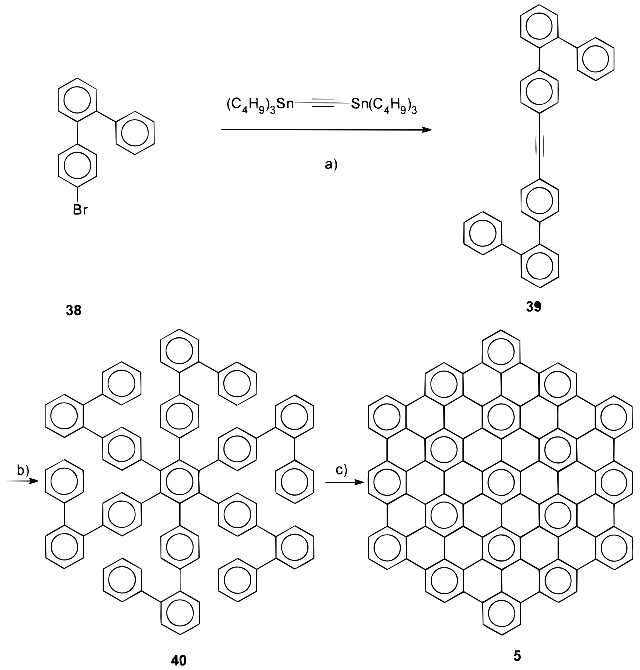
(19) Sato, T.; Shimada, S.; Hata, K. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 6.

Scheme 5. Synthesis of Star-like PAH **6**[a]



[a] Conditions: (a) phenylacetylene, Pd(PPh$_3$)$_4$, CuI, piperidine, 25 °C, 24 h, 94%; (b) I$_2$, DMSO, reflux, 18 h, 81%; (c) **30**, nBu$_4$NOH, 1,4-dioxane, reflux, 15 min, 59%; (d) **34**, diphenyl ether, reflux, 2 h, 68%; (e) Cu(OSO$_2$CF$_3$)$_2$, AlCl$_3$, CS$_2$, 25 °C, 24 h, 89%.

Scheme 6. Synthesis of PAH **5**[a]



[a] Conditions: (a) Pd(PPh$_3$)$_4$, toluene, 120 °C, 72 h, 78%; (b) Co$_2$(CO)$_8$, 1,4-dioxane, 100 °C, 14 h, 36%; (c) Cu(OSO$_2$CF$_3$)$_2$, AlCl$_3$, CS$_2$, 25 °C, 24 h, 89%.

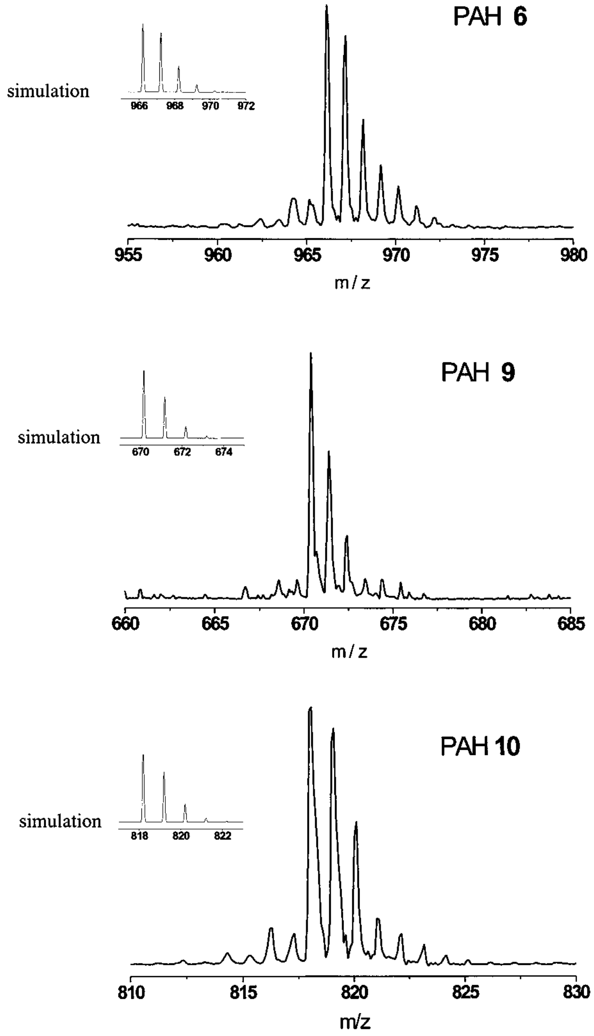
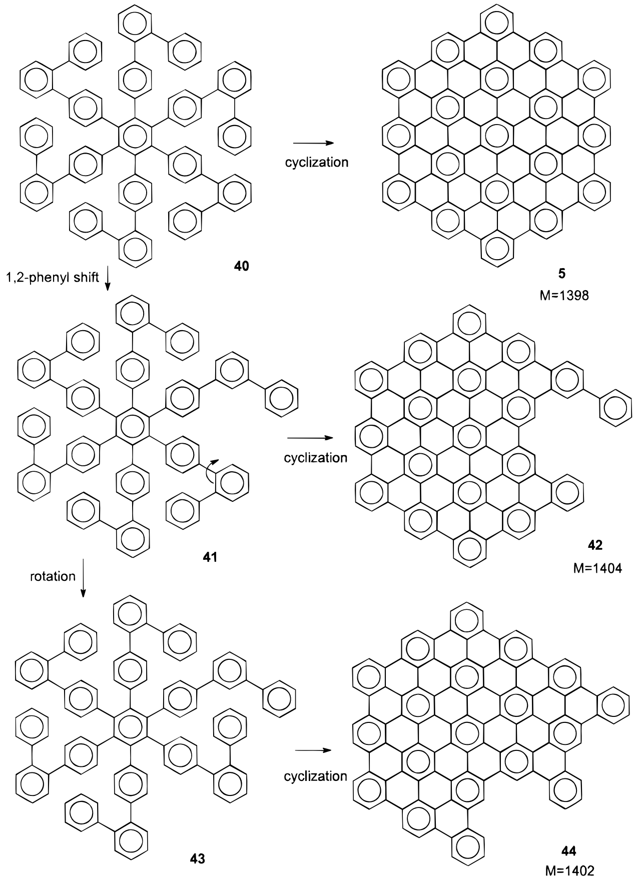


Figure 1. LD-TOF spectra of PAHs **6**, **9**, and **10**. Samples were suspended in tetrachloroethane and ultrasonificated to prevent formation of aggregates.

elimination. As a consequence, the obtained spectra get more complex and tedious to interpret. These difficulties can be clearly demonstrated when large PAHs are investigated with LD techniques.[13] The results of the MALDI-TOF measurements will be discussed later. LD characterization of the PAH **5** containing 114 carbons revealed yet a further unforeseen problem: Contrary to PAHs **6**, **9**, and **10**, the LD spectrum shows not only the desired molecular peak at $m/z = 1398$, but also two other peaks of comparable intensity which are four and six mass units higher. These two additional peaks cannot be explained satisfactorily by partially cyclized or chlorinated species because extension of reaction time only led to increased chlorination and the observed peaks remained unchanged, which suggests that they do not originate from incomplete cyclization. From a thermodynamic point of view, incomplete cyclization would also be unfavorable because only the formation of a fully dehydrogenated system gains a major increase of resonance energy. On

Scheme 7. Rearrangement and Formation of the PAHs **42** and **44**



the other hand, chlorination would result in peaks corresponding with molecular weights several mass units higher. We therefore tentatively attribute these two peaks to the PAHs **42** and **44** which are formed by rearrangement of the precursor **40** and subsequent cyclization (Scheme 7).

A prerequisite to the formation of the oligophenylenes **41** and **43** is a 1,2-phenyl shift and a rotation around a biphenyl bond. We suggest that the 1,2-phenyl shift is catalyzed by the strong Lewis acid aluminum(III) chloride, a reaction that has precedence in the observations of Allen and Pingert in the case of *o*-terphenyl.[20] Rearrangement at low temperature led to *m*- and *p*-terphenyl, whereas at high temperature, triphenylene was yielded. However, the rearrangement of *o*-terphenyl to *p*-terphenyl via the meta derivative occurred under relatively drastic conditions, i.e., refluxing benzene and extended reaction times. Complete conversion of the ortho to a mixture of meta and para isomers was observed after 3 days and after 11 days only *p*-terphenyl was found. Therefore, it can be concluded that rearrangement of the meta to the para derivative requires several days and elevated temperatures even for a small aromatic molecule if a stepwise mechanism is assumed. The precursor of the extended PAH **5**, the oligophenylene compound **40**, also contains *o*-terphenyl units, which makes the proposed 1,2-phenyl shift most probable.[13a] Since the other extended, unsubstituted PAHs **6**, **9**, and **10** show only the desired molecular peak in the LD spectrum, hypothetical rearrangements, i.e., 1,2-phenyl shifts, would have to result in species with exactly the same molecular weight to be indistinguishable by mass spectrometry. For PAHs **9** and **10**, this would require a phenyl shift in the opposite direction; i.e., a *m*-terphenyl unit rearranges into an *o*-terphenyl unit. However, such a hypothesis is not in accordance with Allen and Pingert's results. In the case of the starlike PAH **6**, rearrangement of a *m*-terphenyl unit into an *o*-terphenyl unit is possible in general. On the other hand, the cyclodehydrogenation was completed in 24 h at room temperature, which makes such a phenyl shift less probable. Therefore, the possibility of rearrangements under our reaction conditions seems to be restricted to oligophenylenes that bear *o*-terphenyl units.

The assumed rotation in the precursor molecule **41** around a biphenyl bond is not sterically hindered. Quantification of the relative amounts of the target molecule **5** and the two rearranged species is rather difficult, since desorption and ionization probabilities strongly depend on the molecules' structure. However, close similarity of the molecular structure and LD peak intensities suggest that all three species are formed in comparable amounts, which means that our cyclodehydrogenation route does not selectively lead to the desired PAH **5**.

To prove this hypothesis and to offer an additional approach to an extended PAH containing 114 carbons, the synthesis of a polyalkylated derivative of **5** containing 12 alkoxy chains is now underway. Since the cyclization product is expected to provide sufficient solubility for detailed characterization, insight should be provided into the cyclization mechanism of large oligophenylenes that bear *o*-terphenyl units.

The above-mentioned LD technique for the characterization of large, insoluble PAHs is supplemented by a complementary method, MALDI-TOF spectrometry, which induces desorption of the sample more smoothly by distributing the analyte molecules in an appropriate matrix.[13] PAHs **5**, **6**, **9**, and **10** were also investigated by MALDI-TOF spectrometry and found to contain traces of partially cyclized as well as monochlorinated compounds. Quantification of these impurities is still a challenge since desorption and ionization probabilities of the impurities and the target molecule are usually different. Nevertheless, considering both techniques, LD- and MALDI-TOF spectrometry, the amount of the organic side products can be estimated to be less than 2% in an even more extended PAH containing 222 carbon atoms.[13b]

Mass spectrometry can quantify organic side products in the final cyclization reaction, whereas inorganic impurities such as aluminum, copper, and chlorine were found to be less than 1% according to energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS).[21]

All the results obtained so far by mass spectrometry provide reliable proof for the structure of extended PAHs. Since our interest focuses not only on the synthesis and characterization of large PAHs but also on their optical properties, UV/visible spectroscopy remains an important method to deliver information in this field. However, nearly all of the large PAHs investigated in this study show extremely low solubility, insufficient to record their optical absorption spectra in solution. Even high-boiling solvents as xylene could not break up aggregation. For example, PAHs **6**, **9**, and **10** were refluxed in *o*-xylene for several days and no UV/visible spectra were obtained from these solutions.[22] Thus, the only possibility to determine these properties for large unsubstituted PAHs is measurement in thin films (solid-state characterization). Thin films may be prepared mechanically by simply smearing samples on a quartz substrate. Model studies were first conducted to ensure the reliability of the solid-state method;

---

(20) Allen, C. F. H.; Pingert, F. P. *J. Am. Chem. Soc.* **1942**, *64*, 1365.

(21) Kübel, C. Ph.D. Thesis, Johannes Gutenberg-University, Mainz, 1998.

(22) Brand, J. D.; Ph.D. Thesis, Johannes Gutenberg-University, Mainz, 1999.

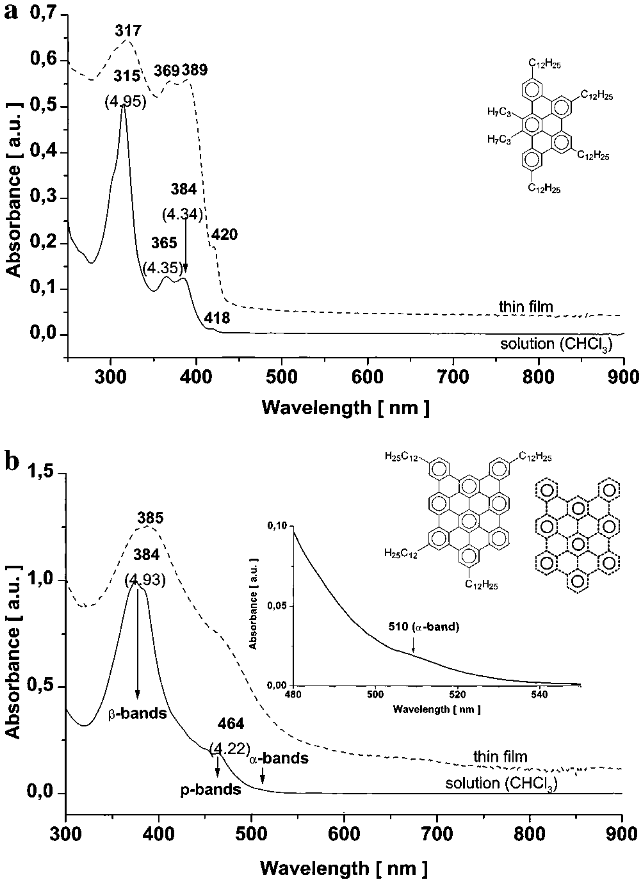


Figure 2. UV/visible spectra of PAHs **8a** (**a**) and **9a** (**b**): solution and thin-film (quartz substrate) spectra displaying the same optical properties. Arbitrary units were chosen for the ordinate because no extinction coefficients could be determined for the thin-film measurements. For solution spectra, extinction coefficients are given in parentheses.

i.e., smaller analogues (e.g., **7a**, **8a, 9a**) with solubilizing substituents were characterized both in solution and as thin film and good correlation was seen between the two methods.

We have observed similar peaks in the thin-film UV−visible spectra, although the optical absorption bands in the solid state are broad and weakly red shifted (2−3 nm), compared to the corresponding solution spectra of the alkyl-substituted analogue compounds (Figure 2).

The UV/visible spectra of **7a** and **8a** clearly show three types (groups) of bands (α, β, p) which are typical of aromatic hydrocarbons, in solution as well as in film.[2a] The spectra of **8a** are given as an example in Figure 2a. The detection of the α-band (510 nm) of **9** is difficult because of the extremely low intensity of this band, but both spectra (solution and film) distinctly show the β-bands (~385 nm) and p-bands (~460 nm).

Having established its reliability, we applied this method to the larger hydrocarbons. With extending size of the π-system, the spectra are progressively red shifted and this trend is most easily observed in the stronger absorption bands, the β-bands. More specifically, this absorption peak is steadily shifted from 387 nm for **9** to 440 nm for **6** as the size of the chromophore increases as shown in Figure 3. Similar investigations of the optical behavior of other PAHs and a detailed discussion of the obtained results will be published elsewhere.[14]

Conclusions and Outlook

In this paper, we have introduced a new series of PAHs with different perimeter types, which have been designed based on symmetry and size considerations. The synthetic route follows a two-step protocol involving the buildup of appropriate precursor molecules and subsequent cyclodehydrogenation to planar all-benzenoid hydrocarbons. In principle, this route can be extended to even larger PAHs than presented here provided that planarization is still sterically possible. However, nonalkyl-substituted PAHs suffer from meager solubility so that characterization and purification still remain a challenge. Therefore, structure elucidation basically focuses on sophisticated techniques of laser desorption time-of-flight mass spectrometry as well as UV/visible spectroscopy. Although LD-TOF mass spectrometry can definitely prove the success of the final cyclodehydrogenation, the question of rearrangements concerning the most extended PAH of the presented series, **5**, still has to be elucidated further. Nevertheless, they seem to be restricted to oligophenylenes with *o*-terphenyl units; the other members of the PAH family reported herein could be synthesized in moderate to high yields. The UV spectra recorded for thin films consistently exhibit a significant bathochromic shift of the β-bands, and current research on the optical properties of even more extended PAHs is still going on in our laboratories. These investigations should be the key to increase our knowledge on large aromatic compounds, which are considered to be the still missing link between benzene and macroscopic graphite.

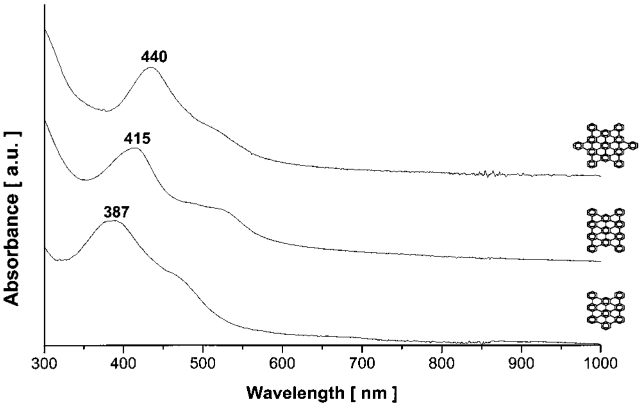


Figure 3. UV/visible spectra of thin films (quartz substrate) of PAHs **6**, **9**, and **10**: Note the bathochromic shift of the β-bands, a consequence of extending the π-system of PAHs. Arbitrary units were chosen for the ordinate because no extinction coefficients could be determined for the thin film measurements.

Experimental Section

1,2,3,4-Tetrakis(4-dodecyl)phenyl-5,6-dipropylbenzene (20). 4-Octyne (**19;** 0.95 g, 8.62 mmol) and 2,3,4,5-tetrakis(4-dodecylphenyl)-cyclopentadienone (**16**; 2.02 g, 1.91 mmol) were dissolved in diphenyl ether (14 mL) under an argon atmosphere and the resultant mixture was refluxed for 16 h. Solvent was removed in vacuo, and the obtained residue was purified by column chromatography (petrolether/dichloromethane) to give a yellowish oil (0.96 g, 44%): ^{1}H NMR (250 MHz, $C_2D_2Cl_4$) δ 6.86 (d, $J = 8.2$ Hz, 4H), 6.81 (d, $J = 8.2$ Hz, 4H), 6.50 (d, $J = 8.2$ Hz, 4H), 6.44 (d, $J = 8.2$ Hz, 4H), 2.40 (t, $J = 7.3$ Hz, 8H, $\alpha CH_{2,dodecyl}$), 2.18 (t, $J = 7.4$ Hz, 4H, $\alpha CH_{2,propyl}$), 1.59−0.89 (m, 84H, H_{alkyl}), 0.80 (t, $J = 6.8$ Hz, 12 H, $CH_{3,dodecyl}$), 0.65 (t, $J = 7.3$ Hz, 3 H, $CH_{3,propyl}$); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 33 °C) δ 141.06, 139.83, 139.12, 139.06, 138.88, 138.63, 138.09 (all C_{aromat}), 131.49, 130.79, 127.18, 126.35 (all $C_{aromat}H$), 36.03, 35.78, 35.58, 33.45, 32.26, 31.65, 31.55, 30.07, 30.02, 29.85, 29.72, 29.28, 29.14, 25.03, 23.05 (all C_{alkyl}), 15.25, 14.55 (all CH_3); MS (FD, 8 kV) *m/z* (%) 1139.5 (100) [M^+] (calcd for $C_{84}H_{130}$, 1140.0). Anal. Calcd for $C_{84}H_{130}$: C, 88.51; H, 11.49. Found: C, 87.87; H, 11.38.

1,2,3,4,5-Pentakis(4-dodecyl)phenylbenzene (22). 4-(Dodecyl)-phenylacetylene (**21**; 1.00 g, 3.70 mmol) and **16** (4.31 g, 4.07 mmol) were dissolved in *o*-xylene (20 mL) under an argon atmosphere and refluxed for 16 h. Solvent was removed in vacuo, and the obtained residue was purified by column chromatography (petroleum ether/dichloromethane) to give a yellowish oil which crystallized upon standing (4.77 g, 99%): mp 29 °C; ^{1}H NMR (250 MHz, THF-d_8) δ 7.38 (s, 1H, H_{cove}), 6.93 (d, $J = 8.2$ Hz, 4H, $H_{cove.}$), 6.85 (d, $J = 7.9$ Hz, 4H, $H_{cove.}$), 6.64−6.59 (m, 8H), 6.56−6.52 (m, 8H), 2.48−2.36 (m, 4H, αCH_2), 2.36−2.22 (m, 6H, αCH_2), 1.52−1.27 (m, 10H, βCH_2), 1.26−0.97 (m, 90H, H_{alkyl}), 0.85−0.73 (m, 15H, CH_3); ^{13}C NMR (125 MHz, CD_2Cl_2, 33 °C) δ 142.88, 141.69, 141.40, 140.81, 140.45, 140.17, 140.09, 138.86, 138.53 (all C_{aromat}), 132.25, 132.19, 131.92, 130.62, 128.35, 127.69, 127.34 (all $C_{aromat}H$), 36.33, 36.18, 32.81, 32.25, 32.19, 32.15, 30.61, 30.56, 30.52, 30.41, 30.38, 30.25, 30.22, 30.15, 29.74, 23.55 (all C_{alkyl}), 14.73 (CH_3); MS (FD, 8 kV) *m*/*z* (%) 1299.4 (100) [M^+] (calcd for $C_{96}H_{146}$, 1300.2). Anal. Calcd for $C_{96}H_{146}$: C, 88.68; H, 11.32. Found: C, 88.11; H, 11.09.

PAH 7a. (Since the systematic names according to the IUPAC nomenclature do not contribute to the clarity of the molecular structure as can easily be seen for the smallest and the largest PAH presented herein, **8a** and **5**, respectively, we decided not to give the full IUPAC names, but just the numbers of compounds as shown in the schemes.)

PAH 8a: 3,6,9,12-Tetra(dodecyl)-15,16-dipropyl(tribenzo[*e*;*g*,*h*,*i*;*k*])-perylene.

PAH 5: Bisbenzo[5″,6″]naphthaceno[2″,1″,12″,11″,10″,9″:5′,6′,7′,8′,9′]-heptaceno[1′,18′,17′,16′,15′,14′,13′:3,4,5,6,7,8,9,10]hexaceno[2,1,16,15,14,13,12,11-*defghijklmno*:2′,1′,16′,15′,14′,13′,12′,11′-*stuvwxyz*$a_1b_1c_1d_1$]-heptacene

22 (1.03 g, 0.80 mmol) was dissolved in dichloromethane (200 mL) in a Schlenk flask under an argon atmosphere. Throughout the whole reaction, a constant stream of Ar was bubbled through the mixture to remove HCl formed in situ. A solution of iron(III) chloride (1.64 g, 10.11 mmol) in nitromethane was added dropwise, and the mixture stirred for 30 min at room temperature. Methanol (100 mL) was added, and a beige solid precipitated which was filtered, dried, and purified by column chromatography (petrolether/dichloromethane). Recrystallization from *n*-heptane yielded an orange solid (545 mg, 53%): NOE difference ^{1}H NMR; H,H COSY ^{1}H NMR (500 MHz,$C_2D_2Cl_4$) δ 10.11 (s, 1H, H_7), 8.97 (d, $J = 8.3$ Hz, 2H, H_1), 8.83 (s, 2H, H_6), 8.80 (s, 2H, H_5), 8.70 (s, 2H, H_4), 8.59 (s, 2H, H_3), 7.58 (d, $J = 8.3$ Hz, 2H, H_2), 3.15−3.0 (m, 6H, αCH_2), 3.0−2.85 (m, 4H, αCH_2), 2.0−1.70 (m, 10H, βCH_2), 1.60−0.95 (m, 90H, H_{alkyl}), 0.85−0.65 (m, 15H, CH_3); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 141.17, 140.43, 136.34, 131.53, 130.32, 129.61, 129.51 (all C_{aromat}), 129.31 ($C_{aromat}H$), 128.08 (C_{aromat}), 126.41 ($C_{aromat}H$), 123.46 ($C_{aromat}H$), 123.15 (C_{aromat}), 122.49 (C_{aromat}), 122.01 ($C_{aromat}H$), 121.53 ($C_{aromat}H$), 37.52, 36.74, 35.07, 32.61, 32.29, 31.98, 30.10, 30.04, 29.74, 25.91, 23.12 (all C_{alkyl}), 14.81, 14.41 (all CH_3); MS (LD-TOF) *m*/*z* (%) 1292.1 (100) [M^+] (calcd for $C_{96}H_{138}$, 1292.2). Anal. Calcd for $C_{96}H_{138}$: C, 89.24; H, 10.76. Found: C, 88.80; H, 10.59.

PAH 8a. 20 (768 mg, 0.67 mmol) was dissolved in dichloromethane (30 mL) in a Schlenk flask under an argon atmosphere. Throughout the whole reaction, a constant stream of argon was bubbled through the mixture to remove HCl formed in situ. A solution of iron(III) chloride (982 mg, 6.10 mmol) in nitromethane was added dropwise, and the mixture stirred for 30 min at room temperature. Methanol (100 mL) was added, and a yellow solid precipitated which was purified by column chromatography (petroleum ether/dichloromethane). Recrystallization from *n*-heptane yielded a yellow solid (184 mg, 24%): NOE difference ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ 8.75 (s, 2H, H_5), 8.61 (s, 2H, H_4), 8.46 (d, $J = 1.2$ Hz, 2H, H_3), 8.40 (d, $J = 8.3$ Hz, 2H, H_1), 7.42 (dd, $J = 8.3$ Hz, $J = 1.2$ Hz, 2H, H_2), 3.66−3.55 (m, 4H, $\alpha CH_{2,propyl}$), 3.09 (t, $J = 7.7$ Hz, 4H, $\alpha CH_{2,R}$), 2.87 (t, $J = 8.0$ Hz, 4H, $\alpha CH_{2,R'}$), 2.10−1.95 (m, 4H, βCH_2), 1.95−1.85 (m, 4H, βCH_2), 1.85−1.75 (m, 4H, βCH_2), 1.65−1.25 (m, 82H, H_{alkyl}), 1.05−0.87 (m, 18H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.75, 141.03, 136.79, 131.31, 130.30, 129.43, 128.05, 126.84, 123.52, 123.03, 122.30, 122.13, 121.76 (all C_{aromat}), 99.82, 37.38 (C_{alkyl}), 36.63, 35.15, 32.73, 32.25, 32.00, 30.00, 29.96, 29.93, 29.70, 25.98, 23.05 (all C_{alkyl}), 15.06 (CH_3), 14.57 (CH_3); MS (FD, 8 kV) *m*/*z* (%) 1134.3 (100) [M^+] (calcd for $C_{84}H_{124}$, 1133.9). Anal. Calcd for $C_{84}H_{124}$: C, 88.98; H, 11.02. Found: C, 88.20; H, 11.04.

3,5-Dibromodiphenylacetylene (24). To a solution of 1,3,5-tribromobenzene (**23**; 30.40 g, 96.57 mmol), palladium(0)−tetrakis(triphenylphosphine) (1.40 g, 1.21 mmol), and CuI (442.1 mg, 2.32 mmol) in piperidine (300 mL), phenylacetylene (5.21 mL, 4.85 g, 47.44 mmol) was added. The resulting mixture was stirred at room temperature for 24 h under an argon atmosphere. The reaction mixture was poured into NH_4Cl solution and extracted with dichloromethane. The organic layer was washed with NH_4Cl solution and water and then dried with $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by column chromatography (petroleum ether) to afford **24** (12.32 g, 77%) as colorless crystals: mp 107.0−107.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (t, $J = 1.8$ Hz, 1H), 7.59 (d, $J = 1.8$ Hz, 2H), 7.53−7.46 (m, 2H), 7.38−7.32 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.89, 132.99, 131.74, 128.96, 128.46, 126.76, 122.62, 122.27, 91.96, 86.38; MS (FD, 8 kV) *m*/*z* (%) 336.1 (100) [M^+] (calcd for $C_{14}H_8Br_2$, 335.90). Anal. Calcd for $C_{14}H_8Br_2$: C, 50.04; H, 2.40; Br, 47.56. Found: C, 49.84; H, 3.15.

3,5-Diphenyldiphenylacetylene (25). To a deoxygenated solution of phenylboronic acid (8.78 g, 71.99 mmol) and K_2CO_3 (41.5 g, 300.3 mmol) in water (150 mL) and ethanol (75 mL), a deoxygenated solution of **24** (6.00 g, 17.85 mmol) in toluene (300 mL) and palladium(0)−tetrakis(triphenylphosphine) (2.03 mg, 1.756 mmol) was added. The resulting mixture was heated at reflux for 24 h under an argon atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water and dried with $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by column chromatography (dichloromethane/petroleum ether) to afford **25** (5.84 g, 99%) as colorless crystals: mp 127.0−128.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (t, $J = 1.7$ Hz, 1H), 7.75 (d, $J = 1.7$ Hz, 2H), 7.66 (d, $J = 6.9$ Hz, 4H), 7.58 (dd, $J = 7.1$ Hz, 2.5 Hz, 2H), 7.47 (dd, $J = 7.4$ Hz, 6.9 Hz, 4H), 7.42−7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.00, 140.40, 131.69, 129.15, 128.86, 128.39, 127.72, 127.22, 126.13, 124.19, 123.20, 89.60, 89.36; MS (FD, 8 kV) *m*/*z* (%) 330.3 (100) [M^+] (calcd for $C_{26}H_{18}$, 330.43). Anal. Calcd for $C_{26}H_{18}$: C, 94.51; H, 5.49. Found: C, 95.14; H, 5.03.

(3,5-Diphenylphenyl)pentaphenylbenzene (26). A mixture of **25** (1.00 g, 3.03 mmol) and tetraphenylcyclopentadienone (1.20 g, 3.13 mmol) in diphenyl ether (10 mL) was heated at reflux for 16 h under an argon atmosphere. After cooling to room temperature, ethanol (100 mL) was added to the reaction mixture. The precipitated crystals were collected by filtration and purified by recrystallization from dichloromethane/ethanol to afford **26** (1.60 g, 77%) as colorless crystals: mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.19 (m, 11H), 7.108 (d, $J = 1.8$ Hz, 2H), 7.01−6.86 (m, 25H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.82, 140.63, 140.61, 140.51, 140.43, 139.98, 139.90, 139.80, 131.63, 131.47, 131.44, 129.91, 128.43, 127.05, 126.93, 126.80, 126.60, 125.49, 125.24, 123.04; MS (FD, 8 kV) *m*/*z* (%) 686.8 (100) [M^+] (calcd for $C_{54}H_{38}$, 686.30). Anal. Calcd for $C_{54}H_{38}$: C, 94.42; H, 5.58. Found: C, 94.83; H, 4.84.

PAH 9. (Due to incomplete combustion, elemental analyses for carbon-rich compounds often yield too low carbon contents which can be seen for the PAHs **5**, **6**, **9**, and **10.**)

To a mixture of copper(II)−trifluoromethanesulfonate (2.53 g, 6.93 mmol) and aluminum(III) chloride (981.5 mg, 7.361 mmol) in carbon disulfide (50 mL), **26** (100.0 mg, 0.15 mmol) was added. After stirring at room temperature for 1 h under an argon atmosphere, the mixture was poured into 10% HCl solution. The precipitated crystals were collected by filtration, washed with 10% NH_4OH solution, water, carbon disulfide, and dichloromethane, and dried in vacuo to afford **9** (73.2 mg, 75%) as an orange brown powder: mp >300 °C; MS (MALDI-TOF) *m*/*z* (%) 670.7 (100) [M^+] (calcd for $C_{54}H_{22}$, 607.17). Anal. Calcd for $C_{54}H_{22}$: C, 96.69; H, 3.31. Found: C, 83.51; H, 3.26.

4-Dodecylphenylboronic Acid. To a solution of 4-bromododecylbenzene (10.00 g, 30.74 mmol) in dry tetrahydrofuran (200 mL) at −78 °C, an *n*-butyllithium solution (1.6 M, 57.5 mL, 92.0 mmol) in hexane was added dropwise. After stirring at the same temperature for 1 h, trimethoxyborane (10.5 mL, 9.61 g, 92.46 mmol) was added to the mixture dropwise. After removing the dry ice acetone bath, the mixture was stirred for another 16 h. Then the mixture was poured into 2 N HCl (300 mL) and extracted with dichloromethane. The organic layer was washed with water, dried with Na_2SO_4, and concentrated under reduced pressure to afford the 4-dodecylphenylboronic acid as a pale yellow oil which was used without further purification.

3,5-Di(4-dodecylphenyl)diphenylacetylene (25a). To a deoxygenated solution of 4-dodecylphenylboronic acid (12.36 g, 42.59 mmol) and K_2CO_3 (27.6 g, 199.7 mmol) in water (100 mL) and ethanol (50 mL), a deoxygenated solution of **24** (4.00 g, 11.90 mmol) in toluene (200 mL) and palladium(0)−tetrakis(triphenylphosphine) (688.8 mg, 0.60 mmol) was added. The resulting mixture was heated at reflux for 24 h under an argon atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water and dried with $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by column chromatography (petrolether) to afford **25a** (1.77 g, 22%) as colorless crystals: mp 42.7−44.2 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (t, J = 1.7 Hz, 1H), 7.70 (d, J = 1.7 Hz, 2H), 7.59−7.54 (m, 6H), 7.38−7.32 (m, 3H), 7.26 (d, J = 8.0 Hz, 4H), 2.65 (t, J = 7.6 Hz, 4H), 1.65 (p, J = 7.6 Hz, 4H), 1.39−1.20 (m, 36H), 0.87 (t, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.59, 141.87, 137.75, 131.68, 128.90, 128.71, 128.35, 128.27, 127.02, 125.82, 124.01, 123.30, 89.58, 89.35, 35.64, 31.92, 31.46, 29.67, 29.64, 29.60, 29.53, 29.35, 22.68, 14.09; MS (FD, 8 kV) *m/z* (%) 666.7 (100) [M^+] (calcd for $C_{50}H_{66}$, 666.52). Anal. Calcd for $C_{50}H_{66}$: C, 90.03; H, 9.97. Found: C, 90.18; H, 9.82.

3,5-Di(4-dodecylphenyl)-4′′,4′′′-didodecylhexaphenylbenzene (26a). A mixture of **25a** (1.01 g, 1.52 mmol) and 3,4-di(4-dodecylphenyl)-2,5-diphenylcyclopentadienone (1.09 g, 1.51 mmol) in diphenyl ether (10 mL) was refluxed for 18 h under an argon atmosphere. After cooling to room temperature, ethanol (100 mL) was added to the reaction mixture. The solvent was decanted, and the residual oil was purified by column chromatography (petroleum ether) to afford **26a** (1.89 g, 92%) as a pale yellow oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, J = 1.5 Hz, 1H), 7.11 (d, J = 8.2 Hz, 4H), 7.07 (d, J = 8.2 Hz, 4H), 7.00 (d, J = 1.5 Hz, 2H), 6.93−6.82 (m, 15H), 6.72−6.72 (m, 8H), 2.576 (t, J = 7.4 Hz, 4H), 2.35 (t, J = 7.4 Hz, 2H), 2.34 (t, J = 7.4 Hz, 2H), 1.60 (p, J = 7.4 Hz, 4H), 1.43−1.06 (m, 76H), 0.88 (t, J = 6.9 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.71, 141.13, 141.07, 141.03, 140.92, 140.74, 140.70, 140.42, 140.16, 139.90, 139.65, 139.34, 139.32, 138.77, 137.94, 137.91, 131.72, 131.59, 131.33, 131.29, 129.56, 128.49, 126.85, 126.72, 126.67, 126.59, 126.50, 125.36, 125.26, 125.02, 122.63, 35.59, 35.32, 31.93, 31.52, 31.15, 29.73, 29.68, 29.64, 29.60, 29.53, 29.38, 29.36, 28.81, 22.69, 14.10; MS (FD, 8 kV) *m/z* (%) 1360.4 (100) [M^+] (calcd for $C_{102}H_{134}$, 1360.05). Anal. Calcd for $C_{102}H_{134}$: C, 90.07; H, 9.93. Found: C, 90.95; H, 9.24.

PAH 9a. To a stirred solution of **26a** (1.00 g, 0.74 mmol) in dichloromethane (200 mL), a solution of iron(III) chloride (11.85 g, 730.51 mmol) in nitromethane (30 mL) was added dropwise. An argon stream was bubbled through the mixture throughout the course of the reaction. After stirring for another 30 min, the reaction was quenched with methanol (60 mL). The resulting mixture was poured into water and extracted with hot toluene. The extract was purified by column chromatography (hot toluene/petroleum ether) to afford **9a** (723.3 mg, 73%) as an orange powder: ^{1}H NMR (500 MHz, $CDCl_2CDCl_2$, 140 °C) δ 9.03 (br, 1H), 8.21 (br, 14H), 7.54 (br, 3H), 3.14 (br, 8H), 2.16 (br, 8H), 1.89−1.36 (br m, 72H), 1.00 (br, 12H); MS (FD, 8 kV) *m/z* (%) 1342.9 (100) [M^+] (calcd for $C_{102}H_{118}$, 1343.92); MS (MALDI-TOF) *m/z* (%) 1342.7 (100) [M^+] (calcd for $C_{102}H_{118}$, 1343.92). Anal. Calcd for $C_{102}H_{118}$: C, 91.15; H, 8.85. Found: C, 91.16; H, 8.78.

3,5-Diphenyltoluene (28). To a deoxygenated solution of phenylboronic acid (19.51 g, 160.01 mmol) and K_2CO_3 (66.34 g, 480.01 mmol) in water (240 mL) and ethanol (120 mL), a deoxygenated solution of 3,5-dibromotoluene (**27**; 10.00 g, 40.01 mmol) in toluene (500 mL) and palladium(0)−tetrakis(triphenylphosphine) (4.62 g, 4.00 mmol) was added. The resulting mixture was heated at reflux for 4 days under an argon atmosphere. The reaction mixture was poured into water and extracted with toluene. The organic layer was washed with water and dried with $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by recrystallization from ethanol to afford **28** (8.88 g, 91%) as colorless crystals: mp 131.4−131.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 4H), 7.62 (s, 1H), 7.46 (dd, J = 7.6 Hz, 7.3 Hz, 4H), 7.41 (s, 2H), 7.36 (t, J = 7.3 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.80, 141.32, 138.75, 128.72, 127.28, 127.26, 126.96, 123.40, 21.58; MS (FD, 8 kV) *m/z* (%) 244.2 (100) [M^+] (calcd for $C_{19}H_{16}$, 244.13). Anal. Calcd for $C_{19}H_{16}$: C, 93.40; H, 6.60. Found: C, 93.51; H, 6.57.

3,5-Diphenylbenzyl Bromide (29). A mixture of **28** (8.80 g, 36.02 mmol) and NBS (7.05 g, 39.62 mmol) in carbon tetrachloride (300 mL) was heated at reflux for 18 h. After cooling to room temperature, precipitated crystals were removed by filtration. The filtrate was concentrated under reduced pressure. The residue was purified by recrystallization from ethanol to afford **29** (10.91 g, 94%) as colorless needles: mp 91.6−93.1 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (t, J = 1.5 Hz, 1H), 7.63 (d, J = 6.9 Hz, 4H), 7.59 (d, J = 1.5 Hz, 2H), 7.60 (dd, J = 7.3 Hz, 6.9 Hz, 4H), 7.36 (t, J = 7.3 Hz, 2H), 4.61 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.45, 140.55, 138.75, 128.85, 127.69, 127.25, 126.75, 126.26, 33.41; MS (FD, 8 kV) *m/z* (%) 321.1 (100) [M^+] (calcd for $C_{19}H_{15}Br$, 322.04). Anal. Calcd for $C_{19}H_{15}Br$: C, 70.60; H, 4.68; Br, 24.72. Found: C, 69.74; H, 4.85.

1,3-Bis(3,5-diphenylphenyl)acetone (30). To a mixture of **29** (11.80 g, 36.51 mmol), NaOH (8.98 g, 224.57 mmol), and benzyltriethylammonium chloride (318.5 mg, 1.40 mmol) in dichloromethane (120 mL) and water (6 mL), iron pentacarbonyl (3.6 mL, 5.36 g, 27.38 mmol) was added. The resulting mixture was refluxed for 18 h under an argon atmosphere. The reaction mixture was then poured into 6 N HCl solution and extracted with dichloromethane. The organic layer was washed with water, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography (dichloromethane/petroleum ether) to afford **30** (2.88 g, 31%) as colorless crystals: mp 213.8−215.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.54 (d, J = 7.9 Hz, 8H), 7.40 (dd, J = 7.9 Hz, 7.6 Hz, 8H), 7.34 (t, J = 7.6 Hz, 4H), 7.337 (s, 4H), 3.90 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.26, 142.36, 140.82, 134.97, 128.77, 127.52, 127.27, 125.02, 49.54; MS (FD, 8 kV) *m/z* (%) 514.5 (100) [M^+] (calcd for $C_{39}H_{30}O$, 514.23). Anal. Calcd for $C_{39}H_{30}O$: C, 91.02; H, 5.88; O, 3.11. Found: C, 90.26; H, 6.16.

2,5-(3,5-Diphenylphenyl)-3,4-diphenylcyclopentadienone (31). To a refluxing solution of **30** (1.00 g, 1.95 mmol) and diphenyl diketone (415.8 mg, 1.98 mmol) in 1,4-dioxane (2 mL), a tetrabutylammonium hydroxide solution (0.8 M, 1.2 mL, 0.96 mmol) in methanol was added. The resulting mixture was heated at reflux for 1 h under an argon atmosphere. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (dichloromethane/petroleum ether) to afford **31** (634.5 mg, 47%) as purple crystals: mp 225.4−227.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (t, J = 1.8 Hz, 2H), 7.50 (d, J = 1.8 Hz, 4H), 7.45 (d, J = 8.0 Hz, 8H), 7.41−7.25 (m, 18H), and 7.09 (d, J = 8.4 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.23, 155.18, 141.38, 140.90, 133.31, 131.46, 129.37, 128.66, 128.33, 128.00, 127.30, 127.15, 125.26, 125.19; MS (FD, 8 kV) *m/z* (%) 687.5 (100) [M^+] (calcd for $C_{53}H_{36}O$, 688.28). Anal. Calcd for $C_{53}H_{36}O$: C, 92.41; H, 5.27; O, 2.32. Found: C, 91.49; H, 6.59.

1,4-Bis(3,5-diphenylbenzene)−2,3,5,6-tetraphenylbenzene (32). A mixture of diphenylacetylene (131.4 mg, 0.74 mmol) and **31** (500.5 mg, 0.73 mmol) in diphenyl ether (5 mL) was heated at reflux for 16 h under an argon atmosphere. After cooling to room temperature, ethanol (100 mL) was added to the reaction mixture. The precipitated crystals were collected by filtration and purified by recrystallization from dichloromethane/ethanol to afford **32** (579.5 mg, 95%) as colorless crystals: mp >300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (t, J = 7.5 Hz, 8H), 7.33 (t, J = 1.5 Hz, 2H), 7.29 (t, J = 7.2 Hz, 8H), 7.22 (d, J = 7.2 Hz, 8H), 7.11 (d, J = 1.5 Hz, 4H), 7.03−6.96 (m, 16H), 6.93 (t, J = 6.7 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.37, 141.12, 140.82, 140.61, 140.22, 139.94, 131.68, 129.93, 128.44, 127.08, 126.95, 126.85, 125.56, 123.10; MS (FD, 8 kV) *m/z* (%) 837.7 (100) [M^+] (calcd for $C_{66}H_{46}$, 838.36). Anal. Calcd for $C_{66}H_{46}\cdot 4H_2O$: C, 87.00; H, 5.97; O, 7.02. Found: C, 87.31; H, 5.53.

PAH 10. To a mixture of copper(II)−trifluoromethanesulfonate (5.20 g, 14.37 mmol) and aluminum(III) chloride (2.00 g, 15.01 mol) in carbon disulfide (200 mL), **32** (200.4 mg, 0.24 mmol) was added. After stirring at room temperature for 24 h under an argon atmosphere, the resulting mixture was poured into 10% HCl solution. The precipitated crystals were collected by filtration, washed with 10% NH_4OH solution, water, carbon disulfide, and dichloromethane, and dried in vacuo to afford **10** (171.4 mg, 88%) as a brown powder: mp >300 °C; MS

(FD, 8 kV) *m*/*z* (%) (100) [M^+] (calcd for $C_{66}H_{26}$, 818.20). Anal. Calcd for $C_{66}H_{26}$: C, 96.80; H, 3.20. Found: C, 86.67; H, 3.26.

3-Phenyldiphenylacetylene (34). To a solution of 3-bromobiphenyl (**33**) (5.54 g, 23.79 mmol), palladium(0)−tetrakis(triphenylphosphine) (1.24 g, 1.07 mmol), and CuI (408.6 mg, 2.15 mmol) in piperidine (200 mL), phenylacetylene (4.7 mL, 4.39 g, 42.98 mmol) was added. The resulting mixture was stirred at 80 °C for 5 h under an argon atmosphere. The reaction mixture was poured into NH_4Cl solution and extracted with dichloromethane. The organic layer was washed with NH_4Cl solution and water and then dried with $MgSO_4$. After the solvent was removed in vacuo, the residue was purified by column chromatography (petroleum ether) to afford **34** (5.66 g, 94%) as a colorless oil: ^1H NMR (300 MHz, $CDCl_3$) δ 7.57 (t, $J = 1.5$ Hz, 1H), 7.41−7.10 (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.42, 140.36, 131.64, 130.34, 128.80, 128.78, 128.35, 128.29, 127.58, 127.10, 127.08, 123.74, 123.24, 89.52, 89.37; MS (FD, 8 kV) *m*/*z* (%) 254.3 (100) [M^+] (calcd for $C_{20}H_{14}$, 254.11).

3-Phenyl Diphenyl Diketone (35). A solution of **34** (3.00 g, 11.80 mmol) and iodine (1.53 g, 7.14 mmol) in DMSO (50 mL) was heated at reflux for 18 h under an argon atmosphere. The reaction mixture was poured into Na_2SO_3 solution and extracted with dichloromethane. The organic layer was washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (dichloromethane/petroleum ether) to give **35** (2.75 g, 81%) as yellow crystals: mp 71.5−72.1 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (t, $J = 1.7$ Hz, 1H), 8.02−7.85 (m, 4H), 7.69−7.33 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.48, 194.43, 142.29, 139.61, 134.90, 133.56, 133.48, 133.03, 129.94, 129.47, 129.03, 128.97, 128.79, 128.26, 128.05, 127.18; MS (FD, 8 kV) *m*/*z* (%) 286.5 (100) [M^+] (calcd for $C_{20}H_{14}O_2$, 286.10). Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93; O, 11.18. Found: C, 83.95; H, 4.86.

2,5-(3,5-Diphenylphenyl)-3-phenyl-4-(3-biphenyl)cyclopentadienone (36). To a refluxing solution of **30** (1.50 g, 2.92 mmol) and 3-phenyl diphenyl diketone[35] (840.8 mg, 2.94 mmol) in 1,4-dioxane (3 mL), a tetrabutylammonium hydroxide solution (0.8 M, 1.8 mL, 1.44 mmol) in methanol was added. The resulting mixture was heated at reflux for 15 min under an argon atmosphere. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, dried with $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (dichloromethane/petroleum ether) to afford **36** (1.32 g, 59%) as purple crystals: mp 148.4−150.2 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (t, $J = 1.6$ Hz, 1H), 7.68 (t, $J = 1.6$ Hz, 1H), 7.56 (d, $J = 1.6$ Hz, 2H), 7.53 (d, $J = 1.6$ Hz, 2H), 7.50−7.43 (m, 8H), 7.41−7.26 (m, 22H), 7.21−7.09 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.21, 155.15, 154.92, 141.51, 141.41, 141.20, 140.90, 140.49, 133.55, 133.49, 131.54, 131.42, 129.46, 128.75, 128.70, 128.67, 128.56, 128.47, 128.22, 128.03, 127.47, 127.44, 127.32, 127.17, 126.97, 125.47, 125.35, 125.30, 125.22; MS (FD, 8 kV) *m*/*z* (%) 763.6 (100) [M^+] (calcd for $C_{59}H_{40}O$, 764.31). Anal. Calcd for $C_{59}H_{40}O$: C, 92.64; H, 5.27; O, 2.09. Found: C, 91.84; H, 5.76.

1,4-Bis(3,5-diphenylbenzene)−2,5-Di(3-phenylbenzene)−3,6-Diphenylbenzene (37a) and 1,4-Bis(3,5-diphenylbenzene)−3,5-Di(3-phenylbenzene)−2,6-Diphenylbenzene (37b). A mixture of **34** (343.8 mg, 1.35 mmol) and **36** (1.00 g, 1.31 mmol) in diphenyl ether (5 mL) was heated at reflux for 2 h under an argon atmosphere. After cooling to room temperature, ethanol (100 mL) was added to the reaction mixture. The precipitated crystals were collected by filtration and purified by recrystallization from dichloromethane/ethanol to afford **37a** and **37b** (882.8 mg, 68%) as colorless crystals: mp 287.5−288.4 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37−6.94 (m, 54H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.42, 141.36, 141.33, 141.25, 141.13, 141.05, 140.82, 140.67, 140.64, 140.57, 140.54, 140.47, 140.42, 140.35, 140.23, 140.03, 139.88, 139.87, 131.85, 131.80, 131.75, 131.72, 131.32, 131.26, 130.61, 130.53, 130.29, 130.16, 129.97, 129.87, 129.85, 129.73, 128.46, 127.37, 127.22, 127.15, 127.10, 127.04, 127.00, 126.88, 125.81, 125.79, 124.44, 123.25, 123.21; MS (FD, 8 kV) *m*/*z* (%) 991.1 (100) [M^+] (calcd for $C_{78}H_{54}$, 990.42). Anal. Calcd for $C_{78}H_{54}$: C, 94.51; H, 5.49. Found: C, 93.70; H, 6.08.

PAH 6. To a mixture of copper(II)−trifluoromethanesulfonate (5.26 g, 14.55 mmol) and aluminum(III) chloride (2.25 g, 16.84 mol) in carbon disulfide (200 mL), the mixture of **37a** and **37b** (200.0 mg, 0.20 mmol) was added. After stirring at room temperature for 24 h under an argon atmosphere, the resulting mixture was poured into 10% HCl solution. The precipitated crystals were collected by filtration, washed with 10% NH_4OH solution, water, carbon disulfide, and dichloromethane, and dried in vacuo to afford **6** (174.2 mg, 89%) as a brown powder: mp >300 °C; MS (MALDI-TOF) *m*/*z* (%) 965.9 (100) [M^+] (calcd for $C_{78}H_{30}$, 966.23). Anal. Calcd for $C_{78}H_{30}$: C, 96.87; H, 3.13. Found: C, 92.07; H, 3.46.

Bis(4,1′:2′,1″terphen-1-yl)acetylene (39). To a deoxygenated solution of 4-bromo-1,1′:2′,1″-terphenyl (**38**; 4.50 g, 14.60 mmol)[19] in toluene (60 mL), palladium(0)−tetrakis(triphenylphosphine) (1.52 g, 1.32 mmol) and bis(tributylstannyl)acetylene (5.86 g, 9.70 mmol) were added under an argon atmosphere and refluxed for 62 h. After the solvent was removed in vacuo, the residue was purified by column chromatography (petroleum ether/dichloromethane)) to afford **39** (2.74 g, 78%) as colorless crystals: mp 253 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42−7.41 (m, 8H); 7.33 (d, $J = 8.6$ Hz, 4H), 7.24−7.18 (m, 6H), 7.14−7.11 (m, 4H), 6.36 (d, $J = 8.6$ Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.59, 141.27, 140.61, 139.86, 131.12, 130.68, 130.39, 129.88, 129.86, 127.99, 127.76, 127.54, 126.60, 121.34, 89.69; MS (FD, 8 kV) *m*/*z* (%) 482.1 (100) [M^+] (calcd for $C_{38}H_{26}$, 482.20);

1,2,3,4,5,6-Hexakis(4,1′:2′,1″terphen-1-yl)benzene (40). To a deoxygenated solution of **39** (500 mg, 1.03 mmol) in 1,4-dioxane (100 mL), dicobaltoctacarbonyl (118 mg, 0.35 mmol) was added under an argon atmosphere and the resultant mixture refluxed for 14 h. After the solvent was removed in vacuo, the obtained residue was purified by column chromatography (petroleum ether/dichloromethane)) to afford **40** (180 mg, 36%) as colorless crystals: mp 335 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45−7.29 (m, 18H); 7.25−7.19 (m, 6H), 6.03 (t, $J = 7.6$ Hz, 12H), 6.85 (d, $J = 7.9$ Hz, 12H), 6.80 (t, $J = 7.3$ Hz, 6H), 6.61 (d, $J = 8.4$ Hz, 12H), 6.50 (d, $J = 8.4$ Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.54, 140.64, 140.50, 140.09, 139.10, 138.20, 131.72, 131.00, 130.90, 130.09, 128.44, 127.91, 127.59, 127.52, 126.63; MS (FD, 8 kV) *m*/*z* (%) 1446.7 (100) [M^+] (calcd for $C_{114}H_{78}$, 1446.6). Anal. Calcd for $C_{114}H_{78}$: C, 94.57; H, 5.43. Found: C, 94.40; H, 5.51.

PAH 5. To a mixture of copper(II)−trifluoromethanesulfonate (3.51 g, 9.70 mmol) and aluminum(III) chloride (1.30 g, 9.71 mol) in carbon disulfide (100 mL), **40** (50 mg, 0.033 mmol) was added. After stirring at room temperature for 14 days under an argon atmosphere, the resulting mixture was poured into methanol (50 mL). The precipitated crystals were collected by filtration and washed with 10% NH_4OH solution, 10% HCl solution, and water. After drying, the residue was washed again with ethanol, carbon disulfide, and hot toluene. The obtained black solid (42 mg, 91%) was dried in vacuo: mp >300 °C; MS (MALDI-TOF) *m*/*z* (%) 1398.4 (100) [M^+] (calcd for $C_{114}H_{30,}$ 1398.3). Anal. Calcd for $C_{114}H_{30}$: C, 97.84; H, 2.16. Found: C, 79.79; H, 2.37.

Acknowledgment. Financial support by the Volkswagenstiftung, the European Commission (TMR-Program SISITOMAS), and Sony International (Europe) is gratefully acknowledged. S.I. thanks the Humboldtstiftung for a scholarship; the authors thank Dr. M. Watson for valuable insight toward the preparation of this paper.

JA000832X