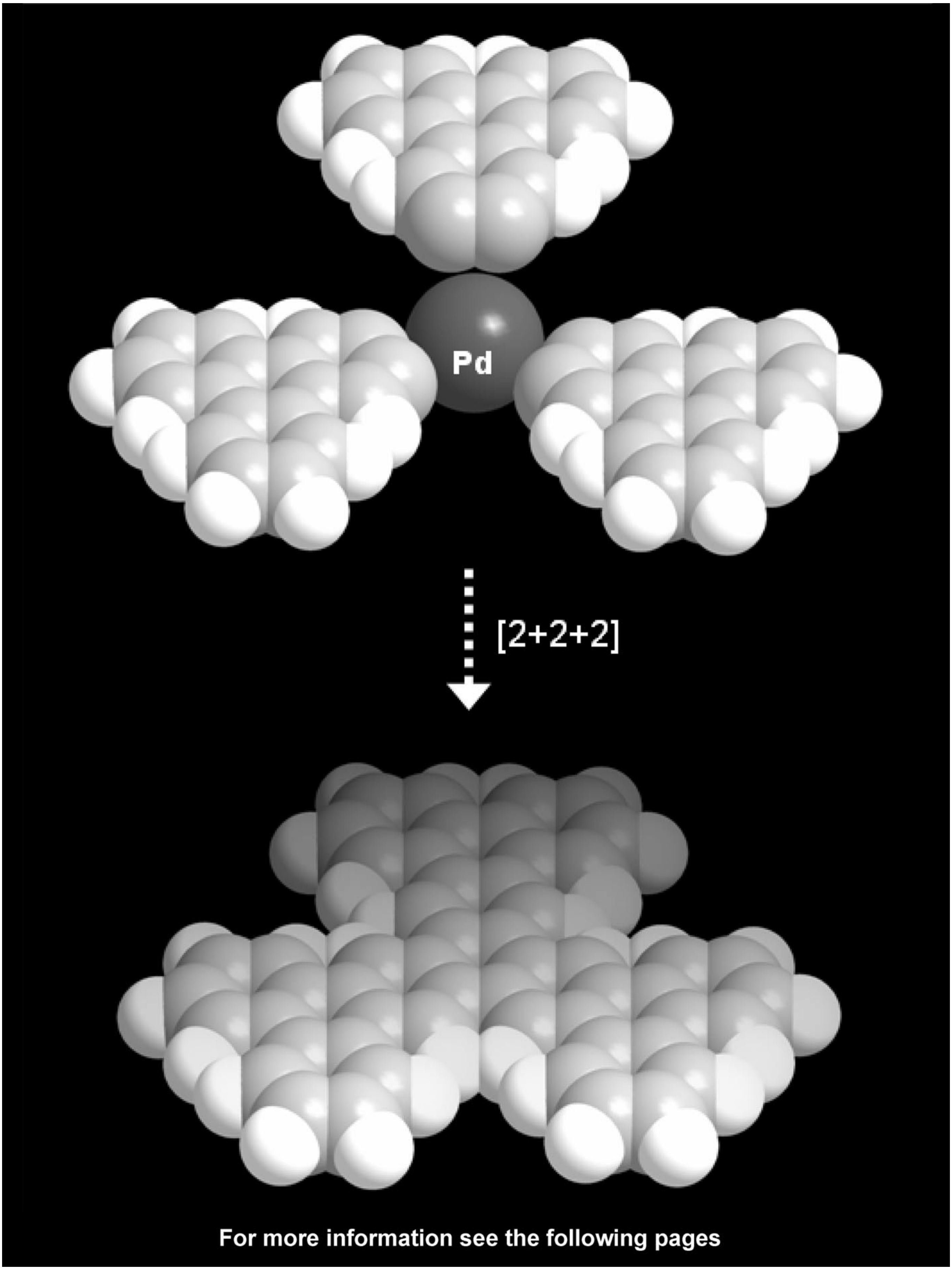
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Synthesis of Extended Triphenylenes by Palladium-Catalyzed [2+2+2] Cycloaddition of Triphenylynes

Carmen Romero, Diego Peña,* Dolores Pérez,* and Enrique Guitián[a]

Dedicated to Professor K. Peter C. Vollhardt on the occasion of his 60th birthday

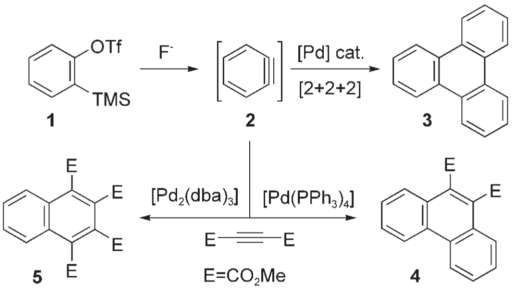
Abstract: The synthesis of *ortho*-(trimethylsilyl)triphenylenyl triflates **7** is described. Fluoride-induced decomposition of these triflates leads to the generation of didehydrotriphenylenes (triphenylynes) **6**. These arynes undergo [4+2] cycloadditions with dienes to afford the corresponding Diels–Alder adducts or palladium-catalyzed formal [2+2+2] cycloadditions to afford extended triphenylenes.

Keywords: arynes • catalysis • cyclotrimerization • palladium • triphenylenes

Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a broad family of organic compounds which have been extensively studied in the fields of materials science, environmental chemistry, and medicinal chemistry.[1] In recent years, graphite-like[1c,2] and sterically congested[3] PAHs have attracted special attention because of their unique structures and properties. Interest in triphenylenes has in fact been continuous since certain triphenylene derivatives were found to form discotic liquid crystals.[4] Thirty years of research on these compounds has shown that the formation of discotic mesophases is usually linked to the existence of a flat aromatic core surrounded by medium-sized aliphatic chains, and that the corresponding columnar mesophases can exhibit high-charge mobility in the direction of the columnar axis. Triphenylenes thus have great potential as the basis of optical and electronic devices. Although they can be prepared in many ways,[4c] the efficient, mild synthesis of asymmetric and extended derivatives is still challenging.

In recent years we have developed methods for the preparation of polycyclic arenes based on the palladium-catalyzed cyclotrimerization of arynes.[5,6] Initially we found that generating benzyne (**2**) in the presence of catalytic amounts of a palladium complex afforded triphenylene (**3**) in good yield (Scheme 1).[5] The extension of this formal [2+2+2] cycloaddition to substituted and polycyclic arynes has enabled us to synthesize substituted triphenylenes, sterically congested PAHs, such as helicenes,[7a–c] and compounds related to the [*N*] phenylenes.[7d] We have since shown that the same methods can be applied to the cocyclization of arynes and alkynes with high chemoselectivity. When benzyne was cocyclized with dimethylacetylenedicarboxylate (DMAD) in the presence of catalytic amounts of $[Pd(PPh_3)_4]$, phenanthrenedicarboxylate **4** was obtained as the major product in 84% yield. However, if $[Pd_2(dba)_3]$ was used as the catalyst, naphthalenetetracarboxylate **5** was isolated in 83% yield.[8a] Remarkably, the scope of this methodology was soon found to extend to metal-catalyzed cocyclization reactions of arynes with alkynes,[8b–g] allyl derivatives,[9a] CO,[9b] allenes,[9c] and strained bicyclic alkenes.[9d] We now report our efforts to



Scheme 1. Palladium-catalyzed [2+2+2] cycloaddition of benzyne.

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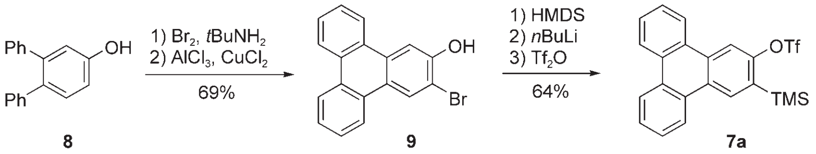
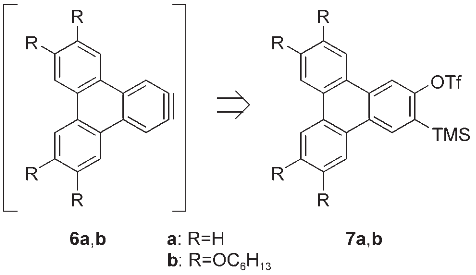
synthesize extended triphenylenes by palladium-catalyzed formal [2+2+2] cycloadditions of didehydrotriphenylenes **6** (Scheme 2).



Scheme 3. Synthesis of triflate **7a**.



Scheme 2. Triphenylynes **6** and their corresponding precursors **7**.

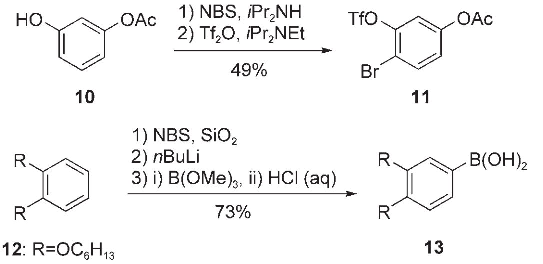
The success of metal-catalyzed reactions involving arynes does not only depend on the choice of a suitable metal complex as catalyst, but also on the generation of the aryne in a controlled fashion under mild reaction conditions. For this purpose, fluoride-induced decomposition of an *ortho*-(trimethylsilyl)aryl triflate, such as **1**, is an excellent method,[10] as the rate of aryne generation can be modulated by modifying the solubility of the fluoride source, and the required neutral, room temperature conditions are compatible with transition-metal-catalyzed reactions.[11,12] We accordingly chose triflates **7** as our triphenylyne precursors (Scheme 2). Specifically, we prepared triflates generating both unsubstituted triphenylyne **6a**, which was used for exploration of triphenylyne reactions, and the alkoxy-substituted derivative **6b**, which we envisaged would afford more soluble products able to form columnar mesophases.

Results and Discussion

Synthesis of aryne precursors: The precursor of 2,3-didehydrotriphenylene (**6a**) was prepared from 1,1′:2′,1″-terphenyl-4′-ol (3,4-diphenylphenol, **8**).[13] *ortho*-Bromination of compound **8**, catalyzed by tBuNH$_2$ in toluene, followed by metal-mediated oxidative cyclodehydrogenation in CS_2 afforded triphenylenol **9** in 69% yield (Scheme 3). Triflate **7a** was obtained from *ortho*-bromohydroxyarene **9** by means of the one-pot methodology developed by our group for the synthesis of *ortho*-(trimethylsilyl)aryl triflates:[10b] treatment of compound **9** with hexamethyldisilazane (HMDS) in refluxing THF gave a quantitative yield of the corresponding trimethylsilyl ether, which was transformed into triflate **7a** in 64% yield by successive treatment with nBuLi and Tf_2O at −100°C.

Abstract in Spanish: *Se describe la síntesis de los triflatos de orto-(trimetilsilil)trifenilenilo **7**. La descomposición inducida por ión fluoruro de estos triflatos da lugar a la generación de los dideshidrotrifenilenos (trifenilinos) **6**. Estos arinos pueden participar en cicloadiciones [4+2] con dienos para obtener los correspondientes aductos de Diels-Alder o en cicloadiciones formales [2+2+2] catalizadas por paladio para dar lugar a trifenilenos extendidos.*

The alkoxy-substituted triflate **7b** was synthesized from commercially available resorcinol monoacetate (**10**) and 1,2-bis(hexyloxy)benzene (**12**, Scheme 4). Acetate **10** was *ortho*-brominated by reaction with *N*-bromosuccinimide (NBS) in the presence of catalytic amounts of iPr$_2$NH in CH_2Cl_2, and subsequent reaction with Tf_2O and iPr$_2$NEt in CH_2Cl_2 at 0°C afforded triflate **11** in 49% overall yield from **10**. Compound **12** was used to obtain boronic acid **13** in 73% yield by a modified version of a previously reported procedure.[14]

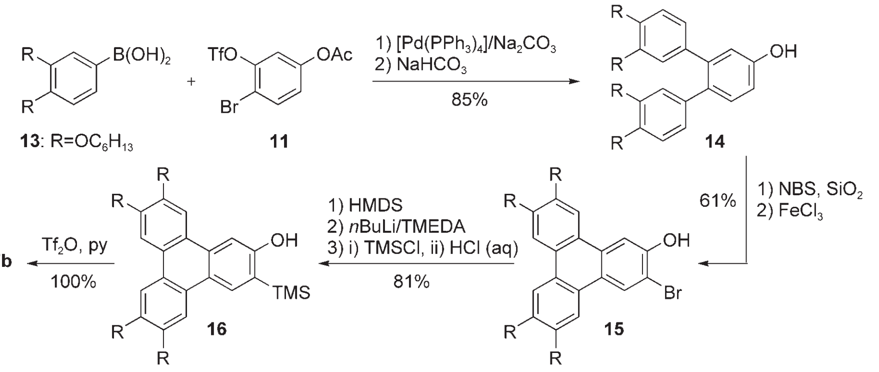


Scheme 4. Synthesis of triflate **11** and boronic acid **13**.

Palladium-catalyzed double Suzuki coupling of triflate **11** with boronic acid **13** in THF at 85°C, followed by hydrolysis of the resulting acetate by addition of an aqueous solution of $NaHCO_3$ afforded terphenylol **14** in 85% yield (Scheme 5). *ortho*-Bromination of compound **14** by NBS in the presence of silica gel in CH_2Cl_2, followed by oxidative cyclodehydrogenation promoted by $FeCl_3$ in CH_2Cl_2 afforded triphenylenol **15** in 61% overall yield from **14**.

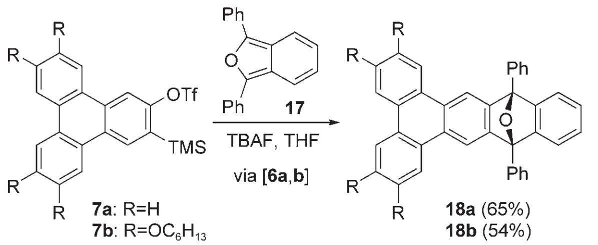
To our surprise, the one-pot procedure used for **7a** failed to afford compound **7b** in good yield from *ortho*-bromohydroxyarene **15**. However, **7b** was successfully prepared by conversion of **15** to *ortho*-(trimethylsilyl)hydroxyarene **16** in 81% yield, which required the use of tetramethylethylenediamine (TMEDA) to ensure complete halogen-metal exchange by nBuLi. This step was followed by quantitative reaction of **16** with Tf_2O in the presence of pyridine.

Cycloaddition reactions of arynes: The ability of triflates **7** to form arynes **6** through fluoride-induced decomposition was confirmed when treatment of **7** with tetrabutylammoni-



Scheme 5. Synthesis of alkoxy-substituted triflate **7b**.

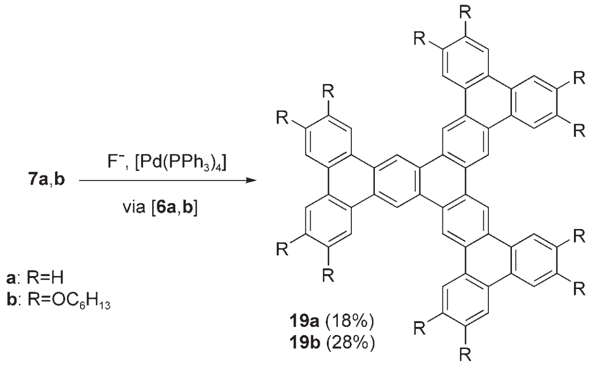
um fluoride (TBAF) in the presence of 1,3-diphenylisobenzofuran (**17**) afforded the polycyclic compounds **18** in good yields by means of [4+2] cycloaddition (Scheme 6).



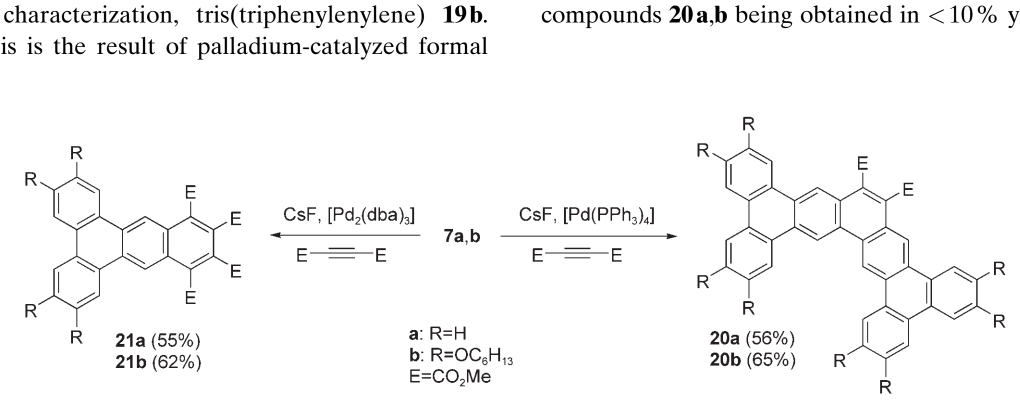
Scheme 6. [4+2] Cycloaddition of arynes **6**.

According to our previous experience with respect to Pd-catalyzed cyclotrimerizations of arynes,[5–7] we treated triflate **7a** with TBAF (1.5 equiv) and [Pd(PPh$_3$)$_4$] (0.1 equiv) in THF at room temperature.[15] The greyish solid filtered from the reaction mixture was highly insoluble in all common organic solvents, as is typical for unsubstituted graphite-like PAHs. Although this extreme insolubility precluded full characterization of this compound, the results of mass spectrometry (FAB) and ^{1}H NMR spectroscopy (750 MHz) were consistent with the expected tris(triphenylenylene) **19a** (Scheme 7). Analogous treatment of hexyloxy-substituted aryne precursor **7b** with CsF (3 equiv) and [Pd(PPh$_3$)$_4$] (0.1 equiv) in CH$_3$CN/CH$_2$Cl$_2$ 3:1[16] gave a 28% yield of a more soluble polycyclic arene amenable to full spectroscopic characterization, tris(triphenylenylene) **19b**. Presumably this is the result of palladium-catalyzed formal [2+2+2] cycloaddition of aryne **6b**. Compound **19b** is a *supertriphenylene*, which has previously been isolated by Müllen and co-workers, who studied its interesting mesomorphic properties.[17]

When arynes are generated in the presence of Pd^0 catalysts and electron-deficient alkynes, [2+2+2] cocycloaddition products can be obtained chemoselectively.[8a,d] Arynes **6** are no exception. Treatment of triflates **7a,b** with CsF in the presence of DMAD and 10 mol% of [Pd(PPh$_3$)$_4$] led to the cocycloaddition of two molecules of the aryne and one of the alkyne (Scheme 8), as shown by the isolation of extended triphenylenes **20a** and **b** in 56 and 65% yields, respectively.[18] In this reaction, polycyclic arenes **21a** and **b**, resulting from the reaction of one aryne and two alkynes, were obtained as minor products in 16 and 18% yields, respectively. By contrast, when 5 mol% of the [Pd$_2$(dba)$_3$] catalyst and an excess of DMAD were used, the major products were **21a** (55%) and **b** (62%), compounds **20a,b** being obtained in <10% yield.



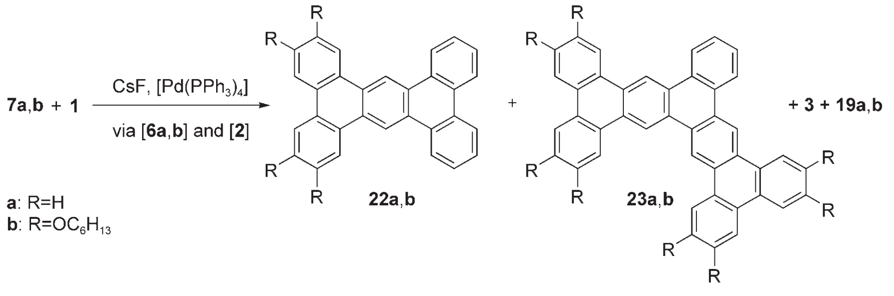
Scheme 7. Cyclotrimerization of arynes **6** to afford tris(triphenylenylene)s **19**. Reaction conditions for **7a**: [Pd(PPh$_3$)$_4$] (0.1 equiv), Bu$_4$NF (1.5 equiv), THF, 1 h. For **7b**: [Pd(PPh$_3$)$_4$] (0.1 equiv), CsF (3 equiv), CH$_3$CN/CH$_2$Cl$_2$ 3:1, 14 h.



Scheme 8. Cocycloaddition of arynes **6** with DMAD.

Significantly, the ^{1}H NMR chemical shifts of the polycyclic arene **20b** showed strong concentration dependence. The flat shape of this large polycyclic aromatic hydrocarbon and the presence of donor and acceptor substituents in different regions of the molecule suggest that aromatic π-stacking interactions could be responsible for this effect.[19] Most likely, these interactions might provide columnar mesomorphic properties for this polycyclic arene. Studies on the behavior of **20b** as a liquid crystal are in progress.

Another approach to large PAHs by this methodology is the cocyclotrimerization of different arynes. In view of the large number of arynes that have been reported in recent years,[6] this combinatorial approach could lead to a great variety of structurally diverse polycyclic arenes. In this work, generation of triphenylynes **6** and benzyne (**2**) in the same reaction vessel in the presence of catalytic amounts of the Pd(0) catalyst afforded mixtures of the four possible cyclotrimerization products, homotrimers **3** and **19** and heterotrimers **22** and **23** (Scheme 9). In the case of **6a**, treatment of triflate **7a** under the standard cyclotrimerization conditions in the presence of an excess of benzyne precursor **1** (ratio 1:4) led to the isolation of a highly insoluble solid, mainly composed of polycyclic arene **22a**, resulting from the [2+2+2] cocycloaddition of one molecule of triphenylyne **6a** with two molecules of benzyne.[20] Similarly, simultaneous generation of arynes **6b** and **2** (ratio 1:4) in the presence of 10 mol% of [Pd(PPh$_3$)$_4$] afforded a 42% yield of alkoxy-substituted polyarene **22b** together with triphenylene (**3**) and small amounts of polyarene **23b** (9%) and tris(triphenylenylene) **19b** (2%).[21]



Scheme 9. Cocycloaddition of arynes **6** with benzyne (**2**).

Conclusion

Fluoride-induced generation of 2,3-didehydrotriphenylenes **6** from 3-(trimethylsilyl)triphenylenyl 2-triflates **7**, enables their palladium-catalyzed cyclotrimerization and chemoselective formal [2+2+2] cocycloaddition with alkynes and with other arynes to afford extended triphenylenes. Some of these large polycyclic arenes can probably behave as liquid crystals. Studies on the mesomorphic properties of these compounds are in progress and the results will be reported in due course.

Experimental Section

General methods: All reactions were carried out under argon by using oven-dried glassware. Solvents were dried by distillation from a drying agent: THF from Na/benzophenone; toluene and benzene from Na; CH_3CN and CH_2Cl_2 from CaH_2. TMSCl, iPr$_2$NEt, iPr$_2$NH, TMEDA and tBuNH$_2$ were distilled from CaH_2 prior to use. 2-Trimethylsilylphenyl triflate (**1**),[10b] 1,1′:2′,1″-terphenyl-4′-ol (3,4-diphenylphenol, **8**),[13] and Pd(PPh$_3$)$_4$[22] were prepared by following published procedures. Commercial reagents were purchased from ABCR, Aldrich, or Strem Chemicals, and were used without further purification, except resorcinol monoacetate (**10**), which was purified by column chromatography before use. nBuLi and Bu$_4$NF (TBAF) were used as solutions in hexane (2.40 M) and THF (1 M), respectively. TLC was performed on Merck silica gel 60 F$_{254}$; chromatograms were visualized with UV light (254 and 360 nm). Flash-column chromatography was performed on Merck silica gel 60 (ASTM 230–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded at 250 and 63 MHz (Bruker DPX-250 instrument) or 300 and 75 MHz (Varian Mercury-300 instrument), respectively. High- or low-temperature NMR spectra were recorded on either a Bruker AMX-500 or a Varian Inova-750 instrument. Low-resolution electron impact mass spectra (EI-LRMS) were determined at 70 eV on a HP-5988 A instrument. High-resolution mass spectra (HRMS) and FAB (positive FAB in 3-nitrobenzyl alcohol) were obtained on a Micromass Autospec spectrometer. MALDI-TOF spectra were determined on a Bruker Autoflex instrument. IR spectra were recorded on a Mattson Cygnus 100 spectrophotometer. Melting points were measured on a Gallenkamp instrument. UV/Vis spectra were obtained on a Varian Cary 100 Bio or a Jasco V-530 spectrophotometer.

For the synthesis of aryne precursors **7a–b** see the Supporting Information.

Cycloaddition reactions of arynes derived from triflates 7a,b

10,15-Epoxy-10,15-diphenyl-10,15-dihydrodibenzo[*a*,*c*]naphthacene (18a): Bu$_4$NF (80 µL, 1 M, 0.080 mmol) was added dropwise to a solution of **7a** (25 mg, 0.056 mmol) and 1,3-diphenylisobenzofuran (**17**, 23 mg, 0.084 mmol) in THF (1 mL) at 0°C, and the mixture was stirred at room temperature for 1 h. After this time, H_2O (2 mL) and Et_2O (2 mL) were added, the phases were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel; CH_2Cl_2/hexane 1:3), affording **18a** (18 mg, 65%) as a white solid. M.p. 245°C (dec); ^{1}H NMR (300 MHz, CDCl$_3$): δ=8.59 (m, 2H), 8.57 (s, 2H), 8.50 (m, 2H), 8.13 (d, J=7.5 Hz, 4H), 7.71 (dd, J=7.7 Hz, 4H), 7.63–7.56 (m, 6H), 7.47 (m, 2H), 7.09 ppm (m, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ=149.9 (2C), 148.7 (2C), 134.9 (2C), 129.8 (2C), 129.7 (2C), 129.0 (4CH), 128.5 (2CH), 127.9 (2C), 127.1 (4CH), 127.02 (2CH), 126.99 (2CH), 126.1 (2CH), 123.3 (2CH), 123.2 (2CH), 120.6 (2CH), 115.1 (2CH), 90.7 ppm (2C); EI-MS: m/z (%): 496 (75); EI-HRMS: m/z: calcd for $C_{38}H_{23}O$: 496.1827; found: 496.1831; UV/Vis (CH_2Cl_2): λ_{max} (ε)=352 (4000), 314 (sh, 10000), 301 (sh, 14000), 270 (68300), 263 nm (sh, 54800 mol^{-1} dm^{3}cm^{-1}).

10,15-Epoxy-2,3,6,7-tetrakis(hexyloxy)-10,15-diphenyl-10,15-dihydrodibenzo[*a*,*c*]naphthacene (18b): Bu$_4$NF (140 µL, 1 M, 0.140 mmol) was added dropwise to a solution of **7b** (93 mg, 0.11 mmol) and 1,3-diphenylisobenzofuran (**17**, 45 mg, 0.165 mmol) in THF (2 mL) at 0°C, and the mixture was stirred at room temperature for 1 h. After this time, H_2O (2 mL) and Et_2O (2 mL) were added, the phases were separated and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel; hexane, then Et_2O/hexane 1:9 to 1:3), affording **18b**

(53 mg, 54 %) as a white solid. M.p. 114–116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.38$ (s, 2H), 8.12 (d, $J = 7.1$ Hz, 4H), 7.88 (s, 2H), 7.79 (s, 2H), 7.68 (dd, $J = 7.4$ Hz, 4H), 7.58 (m, 2H), 7.46 (m, 2H), 7.07 (m, 2H), 4.24–4.16 (m, 8H), 1.98–1.86 (m, 8H), 1.59–1.52 (m, 8H), 1.42–1.37 (m, 16H), 0.97–0.90 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.1$ (2C), 149.6 (2C), 148.9 (2C), 147.3 (2C), 135.1 (2C), 128.9 (4CH), 128.5 (2CH), 127.3 (4CH), 126.8 (2C), 126.0 (2CH), 124.5 (2C), 123.8 (2C), 120.6 (2CH), 114.8 (2CH), 107.8 (2CH), 106.7 (2CH), 90.8 (2C), 69.7 ($2CH_2$), 69.5 ($2CH_2$), 31.7 ($4CH_2$), 29.35 ($2CH_2$), 29.31 ($2CH_2$), 25.8 ($4CH_2$), 22.7 ($4CH_2$), 14.0 ppm ($4CH_3$); MS (FAB$^+$): *m*/*z* (%): 898 (100), 897 (83); MALDI-TOF HRMS: *m*/*z*: calcd for $C_{62}H_{73}0_5$: 897.5453; found: 897.5488; UV/Vis ($CHCl_3$): λ_{max} (ε) = 352 (7800), 326 (sh, 13100), 311 (22900), 286 (96700), 276 (sh, 76100), 265 (59700), 252 nm (50600 mol^{-1} dm^3 cm^{-1}).

Hexabenzo[*a*,*c*,*k*,*m*,*u*,*w*]trinaphthylene (19a): Bu_4NF (150 µL, 1 M, 0.15 mmol) was added dropwise to a solution of **7a** (45 mg, 0.10 mmol) and [$Pd(PPh_3)_4$] (11.6 mg, 0.010 mmol) in THF (0.5 mL), and the mixture was stirred at room temperature for 1 h. The resulting suspension was filtered to give a residue, which was subsequently washed with hexane (3 mL), EtOH (3 mL), and CH_2Cl_2 (2×3 mL) to afford **19a** (4.0 mg, 18 %) as a highly insoluble greyish solid. M.p. >275 °C; ^{1}H NMR (750 MHz, 363 K, $C_2D_2Cl_4$): $\delta = 10.08$ (s, 6H), 9.07 (d, $J = 7.6$ Hz, 6H), 8.76 (d, $J = 8.0$ Hz, 6H), 7.91 (dd, $J = 8.5$ Hz, 6H), 7.83 ppm (dd, $J = 8.5$ Hz, 6H); MS (FAB$^+$): *m*/*z* (%): 678 (45), 339 (22); HRMS (FAB$^+$): *m*/*z* calcd for $C_{54}H_{30}$: 678.2348; found: 678.2343; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 352 (12500), 334 (19400), 320 (20800), 286 (20200), 264 (19900), 234 nm (16300 mol^{-1} dm^3 cm^{-1}).

2,3,6,7,12,13,16,17,22,23,26,27-Dodecakis(hexyloxy)hexabenzo-[*a*,*c*,*k*,*m*,*u*,*w*]-trinaphthylene (19b):[17] Finely powdered anhydrous CsF (27 mg, 0.18 mmol) was added to a solution of **7b** (50 mg, 0.059 mmol) and [$Pd(PPh_3)_4$] (6.9 mg, 6 µmol) in CH_3CN/CH_2Cl_2 3:1 (6 mL), and the mixture was stirred vigorously at room temperature for 14 h. After this time, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography (silica gel; CH_2Cl_2/hexane 1:2 to 3:1), affording **19b** (10.5 mg, 28 %) as a yellow solid. M.p. 104–177 °C;[23] ^{1}H NMR (300 MHz, 298 K, $CDCl_3$, 4.3 mM): $\delta = 9.63$ (s, 6H), 8.27 (s, 6H), 7.81 (s, 6H), 4.37 (t, $J = 5.9$ Hz, 12H), 4.25 (t, $J = 6.5$ Hz, 12H), 2.02–1.95 (m, 24H), 1.67–1.60 (m, 24H), 1.48–1.36 (m, 48H), 1.00–0.88 ppm (m, 36H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.9$ (6C), 149.0 (6C), 128.1 (6C), 128.0 (6C), 124.6 (6C), 123.7 (6C), 116.8 (6CH), 107.8 (6CH), 107.0 (6CH), 69.5 ($6CH_2$), 69.4 ($6CH_2$), 32.0 ($6CH_2$), 31.8 ($6CH_2$), 29.7 ($12CH_2$), 26.2 ($6CH_2$), 26.0 ($6CH_2$), 22.8 ($12CH_2$), 14.11 ($6CH_3$), 14.08 ppm ($6CH_3$); MALDI-TOF MS: *m*/*z*: 1880.6 (100); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 378 (49900), 357 (71400), 325 (68200), 315 (65800), 286 (65200), 279 (66300), 271 nm (sh, 64500 mol^{-1} dm^3 cm^{-1}).

Dimethyl tetrabenzo[*a*,*c*,*m*,*o*]pentaphene-10,11-dicarboxylate (20a): Finely powdered anhydrous CsF (140 mg, 0.92 mmol) was added to a solution of **7a** (103 mg, 0.23 mmol), DMAD (40 µL, 0.32 mmol), and [$Pd(PPh_3)_4$] (27 mg, 0.023 mmol) in CH_3CN/CH_2Cl_2 3:1 (6.5 mL), and the mixture was stirred at room temperature for 14 h. After this time, the solvent was removed under reduced pressure, CH_2Cl_2 was added to the residue, and the resulting suspension was filtered. The resulting residue was washed with $MeOH/H_2O$ 1:4 (5×2 mL) affording **20a** (77 mg, 56 %) as a yellow solid. M.p. 220 °C (dec); ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): $\delta = 9.87$ (s, 2H), 9.32 (s, 2H), 8.91 (d, $J = 7.9$ Hz, 2H), 8.60 (d, $J = 7.7$ Hz, 4H), 8.54 (d, $J = 7.1$ Hz, 2H), 7.86 (dd, $J = 7.4$ Hz, 2H), 7.77 (dd, $J = 7.3$ Hz, 2H), 7.72–7.66 (m, 4H), 4.23 ppm (s, 6H); ^{13}C NMR (125 MHz, 373 K, $C_2D_2Cl_4$): $\delta = 168.1$ (2C), 130.7 (2C), 130.4 (2C), 130.2 (2C), 129.9 (2C), 129.5 (4C), 129.4 (2C), 129.3 (2C), 128.2 (2CH), 127.9 (2CH), 127.6 (4CH), 126.0 (2C), 123.7 (2CH), 123.6 (4CH), 123.3 (2CH), 121.8 (2CH), 117.0 (2CH), 52.7 ppm ($2CH_3$); MS (FAB$^+$): *m*/*z* (%): 594 (25); HRMS (FAB$^+$): *m*/*z*: calcd for $C_{42}H_{26}O_4$: 594.1831; found: 594.1820; IR (KBr): $\tilde{\nu} = 1730$ cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 379 (10600), 353 (20100), 335 (26200), 320 (19300), 274 nm (27600 mol^{-1} dm^3 cm^{-1}).Column chromatography of the organic phase (silica gel; ether/CH_2Cl_2/hexane 2:1:1) afforded **21a** (19 mg, 16 %).

Tetramethyl benzo[*b*]triphenylene-10,11,12,13-tetracarboxylate (21a): Finely powdered anhydrous CsF (134 mg, 0.88 mmol) was added to a solution of **7a** (99 mg, 0.22 mmol), DMAD (130 µL, 1.1 mmol), and [$Pd_2(dba)_3$]·$CHCl_3$ (11.4 mg, 0.011 mmol) in CH_3CN/CH_2Cl_2 3:1 (4.4 mL), and the mixture was stirred at room temperature for 14 h. After this time, the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel; ether/CH_2Cl_2/hexane 2:1:1), affording **21a** (62 mg, 55 %) as a yellow solid. M.p. 271–274 °C; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 9.30$ (s, 2H), 8.64–8.55 (m, 4H), 7.73–7.63 (m, 4H), 4.15 (s, 6H), 3.97 ppm (s, 6H); ^{13}C NMR (62.8 MHz, $CDCl_3$): 167.4 (2C), 166.9 (2C), 133.7 (2C), 131.4 (2C), 130.6 (2C), 129.0 (2CH), 128.7 (2C), 128.0 (2C), 127.8 (2CH), 127.4 (2C), 124.1 (2CH), 123.5 (2CH), 120.6 (2CH), 53.3 ($2CH_3$), 53.2 ppm ($2CH_3$); EI-MS: *m*/*z* (%): 510 (100); EI-HRMS: *m*/*z*: calcd for $C_{30}H_{22}O_8$: 510.1315; found: 510.1317; IR (KBr): $\tilde{\nu} = 1732$, 1721 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 394 (6000), 371 (8600), 308 (73700), 296 (sh, 58500), 269 (sh, 37900), 257 nm (49000 mol^{-1} dm^3 cm^{-1}).

Dimethyl 2,3,6,7,14,15,18,19-octakis(hexyloxy)tetrabenzo[*a*,*c*,*m*,*o*]pentaphene-10,11-dicarboxylate (20b): Finely powdered anhydrous CsF (36 mg, 0.24 mmol) was added to a solution of **7b** (67 mg, 0.079 mmol), DMAD (14 µL, 0.11 mmol), and [$Pd(PPh_3)_4$] (9.1 mg, 7.9 µmol) in CH_3CN/THF 5:1 (2 mL), and the mixture was stirred at room temperature for 14 h and then poured on H_2O/CH_2Cl_2 1:2 (15 mL). The phases were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel; CH_2Cl_2/hexane 2:1, then CH_2Cl_2/ether/hexane 2:1:17 to 6:1:13), affording **20b** (36 mg, 65 %) and **21b** (13 mg, 18 %) as yellow solids. Data for **20b**: m.p. 103–260 °C;[23] ^{1}H NMR (500 MHz, 293 K, $CDCl_3$, 3.7 mM): $\delta = 9.78$ (s, 2H), 9.10 (s, 2H), 8.40 (s, 2H), 7.94 (s, 2H), 7.83 (s, 2H), 7.77 (s, 2H), 4.46 (t, $J = 5.9$ Hz, 4H), 4.28 (t, $J = 6.5$ Hz, 4H), 4.25–4.20 (m, 8H), 4.12 (s, 6H), 2.05–1.94 (m, 16H), 1.64–1.57 (m, 16H), 1.46–1.39 (m, 32H), 0.98–0.92 ppm (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.7$ (2C), 150.1 (2C), 149.1 (2C), 148.7 (2C), 148.5 (2C), 129.5 (2C), 128.4 (2C), 128.0 (2C), 127.4 (2C), 125.0 (2C), 124.4 (2C), 123.6 (2C), 123.2 (2C), 123.0 (2C), 120.7 (2CH), 115.8 (2CH), 108.3 (2CH), 106.2 (4CH), 106.0 (2CH), 69.4 ($2CH_2$), 69.2 ($2CH_2$), 69.1 ($2CH_2$), 68.4 ($2CH_2$), 52.2 ($2CH_3$), 32.0 ($2CH_2$), 31.8 ($6CH_2$), 29.7 ($4CH_2$), 29.5 ($4CH_2$), 26.4 ($2CH_2$), 26.0 ($2CH_2$), 25.9 ($4CH_2$), 22.8 ($4CH_2$), 22.7 ($4CH_2$), 14.1 ppm ($8CH_3$); MS (FAB$^+$): *m*/*z* (%): 1395 (100); MALDI-TOF HRMS: *m*/*z*: calcd for $C_{90}H_{122}O_{12}$: 1394.8931; found: 1394.8862; IR (CsI): $\tilde{\nu} = 2925$, 2856, 1717, 1264 cm^{-1}; UV/Vis ($CHCl_3$): λ_{max} (ε) = 415 (18000), 380 (53000), 362 (67500), 300 (85500), 279 (sh, 57100), 265 nm (57500 mol^{-1} dm^3 cm^{-1}).

Tetramethyl 2,3,6,7-tetrakis(hexyloxy)benzo[*b*]triphenylene-10,11,12,13-tetracarboxylate (21b): Finely powdered anhydrous CsF (59 mg, 0.39 mmol) was added to a solution of **7b** (70 mg, 0.083 mmol), DMAD (60 µL, 0.49 mmol), and [$Pd_2(dba)_3$]·$CHCl_3$ (4.3 mg, 4.2 µmol) in CH_3CN/THF 5:1 (2.4 mL), and the mixture was stirred at room temperature for 14 h and then poured on H_2O/CH_2Cl_2 (15 mL) 1:2. The phases were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel; CH_2Cl_2/hexane 2:1, then CH_2Cl_2/ether/hexane 2:1:17 to 6:1:13), affording **21b** (47 mg, 62 %) as a yellow solid. M.p. 137–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.11$ (s, 2H), 8.02 (s, 2H), 7.75 (s, 2H), 4.26–4.22 (m, 8H), 4.12 (s, 6H), 3.96 (s, 6H), 2.03–1.90 (m, 8H), 1.62–1.59 (m, 8H), 1.42–1.38 (m, 16H), 0.97–0.92 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.6$ (2C), 167.0 (2C), 150.9 (2C), 149.2 (2C), 133.6 (2C), 130.9 (2C), 127.3 (2C), 126.8 (2C), 125.3 (2C), 122.4 (2C), 119.8 (2CH), 108.2 (2CH), 107.2 (2CH), 69.6 ($2CH_2$), 69.5 ($2CH_2$), 53.1 ($2CH_3$), 53.0 ($2CH_3$), 31.6 ($4CH_2$), 29.3 ($4CH_2$), 25.83 ($2CH_2$), 25.81 ($2CH_2$), 22.65 ($2CH_2$), 22.64 ($2CH_2$), 14.0 ppm ($4CH_3$); MS (FAB$^+$): *m*/*z* (%): 910 (100); HRMS (FAB$^+$): *m*/*z*: calcd for $C_{54}H_{70}O_{12}$: 910.4867; found: 910.4862; IR (KBr): $\tilde{\nu} = 2951$, 2928, 2857, 1733, 1724 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 412 (6900), 345 (38600), 306 (38200), 298 (46800), 275 (75100), 268 nm (72200 mol^{-1} dm^3 cm^{-1}).

Phenanthro[9,10-*b*]triphenylene (22a):[24] Finely powdered anhydrous CsF (159 mg, 1.05 mmol) was added to a solution of **7a** (31 mg, 0.070 mmol), **1** (83 mg, 0.28 mmol), and $[Pd(PPh_3)_4]$ (40 mg, 0.035 mmol) in CH_3CN/THF 4:1 (1.4 mL), and the mixture was stirred at room temperature for 14 h. After this time, the resulting suspension was treated with CH_2Cl_2 (2 mL) and centrifuged. The pellet was washed with H_2O (2 mL) and CH_2Cl_2 (2×2 mL) and dried under vacuum. The resulting highly insoluble white solid (16 mg) was mainly composed of polycyclic arene **22a**.[20] ^1H NMR (750 MHz, 353 K, $C_2D_2Cl_4$): $\delta = 9.92$ (s, 2H), 8.98 (d, $J = 8.0$ Hz, 4H), 8.72 (d, $J = 8.0$ Hz, 4H), 7.81 (dd, $J = 7.4$ Hz, 4H), 7.76 ppm (dd, $J = 7.4$ Hz, 4H); MALDI-TOF MS: *m/z* (%): 678 (**3**, 40), 528 (**23a**, 100), 378 (**22a**, 48); UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon) = 332$ (6000), 294 (12100), 259 nm (9100 $mol^{-1}\,dm^3\,cm^{-1}$).

2,3,6,7-Tetrakis(hexyloxy)phenanthro[9,10-*b*]triphenylene (22b): Finely powdered anhydrous CsF (159 mg, 1.05 mmol) was added to a solution of **7b** (59 mg, 0.070 mmol), **1** (83 mg, 0.28 mmol), and $[Pd(PPh_3)_4]$ (40 mg, 0.035 mmol) in CH_3CN/CH_2Cl_2 3:1 (1.4 mL), and the mixture was stirred at room temperature for 14 h. After this time, the solvent was removed under reduced pressure and the resulting residue was purified by column chromatography (silica gel; hexane, then CH_2Cl_2/hexane 1:3 to 1:1), affording **22b** (23 mg, 42%) as a white solid, 2,3,6,7,16,17,20,21-octakis(hexyloxy)pentabenzo[*a*,*c*,*h*,*m*,*o*]pentaphene (**23b**, 4 mg, 9%) and **19b** (0.6 mg, 2%). Data for **22b**: M.p. 190–193 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 9.63$ (s, 2H), 8.87 (dd, $J = 8.1$, 1.1 Hz, 2H), 8.66 (dd, $J = 8.1$, 1.1 Hz, 2H), 8.26 (s, 2H), 7.85 (s, 2H), 7.77–7.66 (m, 4H), 4.36 (t, $J = 6.5$ Hz, 4H), 4.27 (t, $J = 6.6$ Hz, 4H), 2.07–1.92 (m, 8H), 1.71–1.59 (m, 8H), 1.49–1.38 (m, 16H), 1.00–0.93 ppm (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.0$ (2C), 149.2 (2C), 130.1 (2C), 130.0 (2C), 128.2 (2C), 127.8 (2C), 127.35 (2CH), 127.29 (2CH), 124.7 (2C), 123.7 (2C), 123.5 (2CH), 123.3 (2CH), 117.0 (2CH), 107.9 (2CH), 107.4 (2CH), 69.8 ($2CH_2$), 69.7 ($2CH_2$), 31.8 ($2CH_2$), 31.7 ($2CH_2$), 29.5 ($2CH_2$), 29.4 ($2CH_2$), 25.94 ($2CH_2$), 25.88 ($2CH_2$), 22.71 ($2CH_2$), 22.68 ($2CH_2$), 14.07 ppm ($2CH_3$); MS (FAB^+): *m/z* (%): 778 (100); HRMS (FAB^+): *m/z*: calcd for $C_{54}H_{66}O_4$ 778.4961; found: 778.4967; UV/Vis (CH_2Cl_2): λ_{max} $(\varepsilon) = 336$ (sh, 39900), 319 (52300), 301 (75700), 275 (sh, 50100), 266 nm (52900 $mol^{-1}\,dm^3\,cm^{-1}$). Data for **23b**: m.p. 95–217 °C;[23] ^1H NMR (300 MHz, 298 K, $CDCl_3$, 5.0 mM): $\delta = 9.51$ (s, 2H), 9.38 (s, 2H), 8.73 (m, 2H), 8.22 (s, 2H), 8.07 (s, 2H), 7.81 (s, 2H), 7.76 (s, 2H), 7.73 (m, 2H), 4.38 (t, $J = 6.1$ Hz, 4H), 4.31 (t, $J = 6.6$ Hz, 4H), 4.26 (t, $J = 6.7$ Hz, 4H), 4.22 (t, $J = 6.3$ Hz, 4H), 2.04–1.95 (m, 16H), 1.70–1.59 (m, 16H), 1.47–1.39 (m, 32H), 1.01–0.91 ppm (m, 24H); ^{13}C NMR (75 MHz, 298 K, $CDCl_3$, 15.1 mM): $\delta = 150.1$ (2C), 149.95 (2C), 149.88 (2C), 149.5 (2C), 148.9 (2C), 148.8 (2C), 130.2 (2C), 127.8 (2C), 127.6 (2C), 127.4 (2C), 127.0 (2CH), 124.7 (2C), 124.1 (2C), 123.5 (2C), 123.3 (2CH), 116.6 (2CH), 116.3 (2CH), 108.1 (2CH), 107.1 (2CH), 107.0 (2CH), 106.8 (2CH), 69.6 ($2CH_2$), 69.4 ($4CH_2$), 69.3 ($2CH_2$), 31.95 ($2CH_2$), 31.85 ($2CH_2$), 31.80 ($4CH_2$), 29.9 ($2CH_2$), 29.6 ($2CH_2$), 29.54 ($2CH_2$), 29.48 ($2CH_2$), 29.2 ($2CH_2$), 26.03 ($2CH_2$), 25.98 ($2CH_2$), 25.90 ($2CH_2$), 22.75 ($4CH_2$), 22.71 ($4CH_2$), 14.11 ($4CH_3$), 14.08 ppm ($4CH_3$); MS (FAB^+): *m/z* (%): 1329 (62); MALDI-TOF HRMS: *m/z*: calcd for $C_{90}H_{120}O_8$: 1328.8978; found: 1328.8975; UV/Vis ($CHCl_3$): λ_{max} $(\varepsilon) = 380$ (sh, 34600), 350 (68900), 324 (sh, 73300), 310 (93900), 284 (87600), 257 nm (sh, 68500 $mol^{-1}\,dm^3\,cm^{-1}$).

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[1] a) E. Clar, *Polycyclic Hydrocarbons*, Academic Press, London, **1964**; b) R. G. Harvey, *Polycyclic Aromatic Hydrocarbons*, Wiley-VCH, Weinheim, **1997**; c) M. D. Watson, A. Fechtenkötter, K. Müllen, *Chem. Rev.* **2001**, *101*, 1267; d) R. G. Harvey, *Curr. Org. Chem.* **2004**, *8*, 303; e) M. Bendikov, F. Wudl, D. F. Perepichka, *Chem. Rev.* **2004**, *104*, 4891; f) A. C. Grimsdale, K. Müllen, *Angew. Chem.* **2005**, *117*, 5732; *Angew. Chem. Int. Ed.* **2005**, *44*, 5592.

[2] a) M. Müller, C. Kubel, K. Müllen, *Chem. Eur. J.* **1998**, *4*, 2099; b) Z. Wang, Ž. Tomović, M. Kastler, R. Pretsch, F. Negri, V. Enkelmann, K. Müllen, *J. Am. Chem. Soc.* **2004**, *126*, 7794.

[3] See for example: a) H. M. Duong, M. Bendikov, D. Steiger, Q. Zhang, G. Sonmez, J. Yamada, F. Wudl, *Org. Lett.* **2003**, *5*, 4433; b) D. Z. Wang, T. J. Katz, J. Golen, A. L. Rheingold, *J. Org. Chem.* **2004**, *69*, 7769; c) J. Lu, D. M. Ho, N. J. Vogelaar, C. M. Kraml, R. A. Pascal Jr., *J. Am. Chem. Soc.* **2004**, *126*, 11168; d) E. L. Elliott, A. Orita, D. Hasegawa, P. Gantzel, J. Otera, J. S. Siegel, *Chem. Commun.* **2004**, 581.

[4] a) S. Chandrasekhar, B. K. Sadashiva, K. A. Suresh, *Pramana* **1977**, *9*, 471; b) S. Chandrasekhar, *Liq. Cryst.* **1993**, *14*, 3; c) for a recent review of the synthesis of triphenylenes see: D. Pérez, E. Guitián, *Chem. Soc. Rev.* **2004**, *33*, 274–283.

[5] D. Peña, S. Escudero, D. Pérez, E. Guitián, L. Castedo, *Angew. Chem.* **1998**, *110*, 2804; *Angew. Chem. Int. Ed.* **1998**, *37*, 2659.

[6] For a recent review of palladium-catalyzed cycloaddition reactions of arynes see: E. Guitián, D. Pérez, D. Peña in *Topics in Organometallic Chemistry, Vol. 14* (Ed.: J. Tsuji), Springer, Weinheim, **2005**, pp. 109–146.

[7] a) D. Peña, D. Pérez, E. Guitián, L. Castedo, *Org. Lett.* **1999**, *1*, 1555; b) D. Peña, A. Cobas, D. Pérez, E. Guitián, L. Castedo, *Org. Lett.* **2000**, *2*, 1629; c) D. Peña, A. Cobas, D. Pérez, E. Guitián, L. Castedo, *Org. Lett.* **2003**, *5*, 1863; d) B. Iglesias, A. Cobas, D. Pérez, E. Guitián, K. P. C. Vollhardt, *Org. Lett.* **2004**, *6*, 3557.

[8] a) D. Peña, D. Pérez, E. Guitián, L. Castedo, *J. Am. Chem. Soc.* **1999**, *121*, 5827; b) K. V. Radhakrishnan, E. Yoshikawa, Y. Yamamoto, *Tetrahedron Lett.* **1999**, *40*, 7533; c) E. Yoshikawa, K. V. Radhakrishnan, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, *122*, 7280; d) D. Peña, D. Pérez, E. Guitián, L. Castedo, *J. Org. Chem.* **2000**, *65*, 6944. For some partially intramolecular examples see: e) D. Peña, D. Pérez, E. Guitián, L. Castedo, *Eur. J. Org. Chem.* **2003**, 1238; f) Y. Sato, T. Tamura, M. Mori, *Angew. Chem.* **2004**, *116*, 2490; *Angew. Chem. Int. Ed.* **2004**, *43*, 2436; g) J.-C. Hsieh, C.-H. Cheng, *Chem. Commun.* **2005**, 2459.

[9] a) E. Yoshikawa, Y. Yamamoto, *Angew. Chem.* **2000**, *112*, 185; *Angew. Chem. Int. Ed.* **2000**, *39*, 173; b) N. Chatani, A. Kamitani, M. Oshita, Y. Fukumoto, S. Murai, *J. Am. Chem. Soc.* **2001**, *123*, 12686; c) J.-C. Hsieh, D. K. Rayabarapu, C.-H. Cheng, *Chem. Commun.* **2004**, 532; d) T.-T. Jayanth, M. Jeganmohan, C.-H. Cheng, *J. Org. Chem.* **2004**, *69*, 8445.

[10] a) Y. Himeshima, T. Sonoda, H. Kobayashi, *Chem. Lett.* **1983**, 1211; b) D. Peña, A. Cobas, D. Pérez, E. Guitián, *Synthesis* **2002**, 1454.

[11] For recent examples of palladium-catalyzed reactions involving arynes besides cycloadditions see: a) H. Yoshida, J. Ikadai, M. Shudo, J. Ohshita, A. Kunai, *J. Am. Chem. Soc.* **2003**, *125*, 6638; b) H. Yoshida, K. Tanino, J. Ohshita, A. Kunai, *Angew. Chem.* **2004**, *116*, 5162; *Angew. Chem. Int. Ed.* **2004**, *43*, 5052; c) Z. Liu, X. Zhang, R. C. Larock, *J. Am. Chem. Soc.* **2005**, *127*, 15716.

[12] For recent examples of uncatalyzed reactions involving this aryne generation method see: a) H. Yoshida, E. Shirakawa, Y. Honda, T. Hiyama, *Angew. Chem.* **2002**, *114*, 3381; *Angew. Chem. Int. Ed.* **2002**, *41*, 3247; b) H. Yoshida, H. Fukushima, J. Ohshita, A. Kunai, *Angew. Chem.* **2004**, *116*, 4025; *Angew. Chem. Int. Ed.* **2004**, *43*, 3935; c) U. K. Tambar, B. M. Stoltz, *J. Am. Chem. Soc.* **2005**, *127*, 5340; d) Z. Liu, R. C. Larock, *J. Am. Chem. Soc.* **2005**, *127*, 13112, and references [3a,b].

[13] For the preparation of 1,1′:2′,1″-terphenyl-4′-ol (3,4-diphenylphenol, **8**) see: A. Kawamoto, H. Uda, N. Harada, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3279.

[14] For the synthesis of boronic acid **13** see: a) H. Meier, B. Rose, *J. Prakt. Chem.* **1998**, *340*, 536. For a convenient method of monobromination of bis(alkoxy)benzenes by using NBS/silica gel see: b) H. Konishi, K. Aritomi, T. Okano, J. Kiji, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 591.

[15] The use of a soluble fluoride source (TBAF) was preferred to avoid coprecipitation of trimer **19a** with an inorganic fluoride source, such as CsF.

[16] The use of CsF, a fluoride that is only sparingly soluble in the solvent mixture, slowed down the rate of aryne generation, thus preventing an undesirably high concentration of the reactive species in the reaction mixture.

[17] T. Yatabe, M. A. Harbison, J. D. Brand, M. Wagner, K. Müllen, P. Samori, J. P. Rabe, *J. Mater. Chem.* **2000**, *10*, 1519.

[18] Due to the poor solubility of triflates **7** in CH_3CN, CH_2Cl_2 or THF were employed as cosolvents in cocycloaddition reactions with DMAD. For **7a** the solvent mixture was CH_3CN/CH_2Cl_2 3:1 and for **7b** CH_3CN/THF 5:1.

[19] A. S. Shetty, J. Zhang, J. S. Moore, *J. Am. Chem. Soc.* **1996**, *118*, 1019.

[20] Although the ^1H NMR spectrum of this solid in $C_2D_2Cl_4$ at 80 °C showed mainly signals expected from compound **22a**, the presence of the less soluble polycyclic arenes **23a** and **19a** was shown by mass spectrometry (MALDI). Due to the poor solubility of these three polycyclic arenes, it was not possible to determine their precise molar ratio in the mixture.

[21] Like **20b**, polycyclic arene **23b** and trimer **19b** have concentration-dependent ^1H NMR chemical shifts.

[22] L. S. Hegedus, *Palladium in Organic Synthesis, Organometallics in Synthesis: A Manual* (Ed.: M. Schlosser), Wiley, New York, **1994**.

[23] A broad melting transition is probably due to liquid crystal behaviour.

[24] J. P. Anhalt, E. H. White, *Tetrahedron* **1972**, *28*, 2921.

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