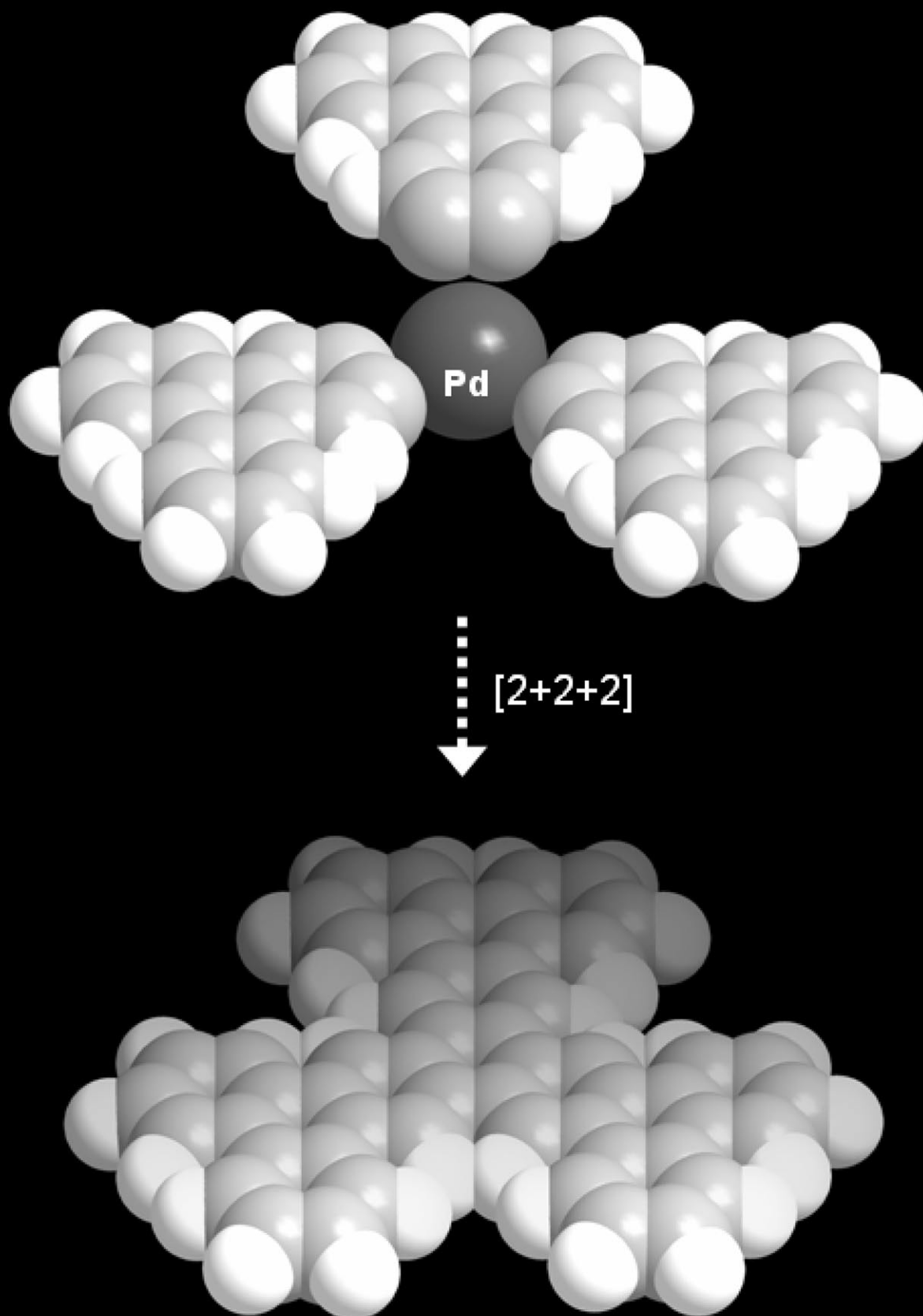




For more information see the following pages

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

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 (triphenylnes) **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.

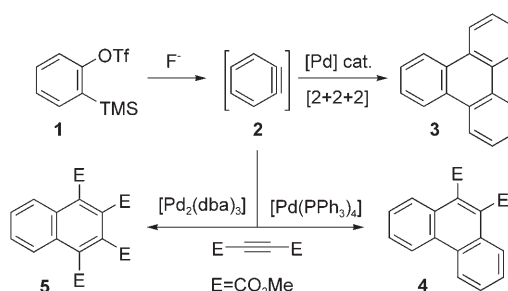
Keywords: arynes • catalysis • cyclotrimerization • palladium • triphenylenes

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 gen-

erating 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] cycload-



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

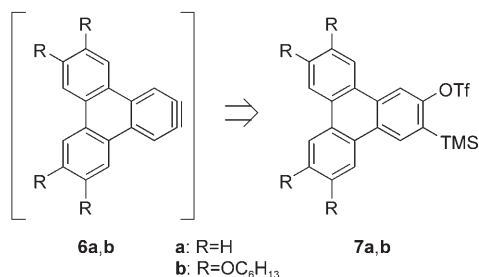
dition to substituted and polycyclic arynes has enabled us to synthesize substituted triphenylenes, sterically congested PAHs, such as helicenes,^[7a-c] and compounds related to the [N] phenylenes.^[7d] We have since shown that the same methods can be applied to the cocyclization of arynes and alkynes with high chemoselectivity. When benzyne was cocyclized with dimethylacetylenedicarboxylate (DMAD) in the presence of catalytic amounts of [Pd(PPh₃)₄], phenanthrene-dicarboxylate **4** was obtained as the major product in 84 % yield. However, if [Pd₂(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 cycloaddition 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

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

The success of metal-catalyzed reactions involving

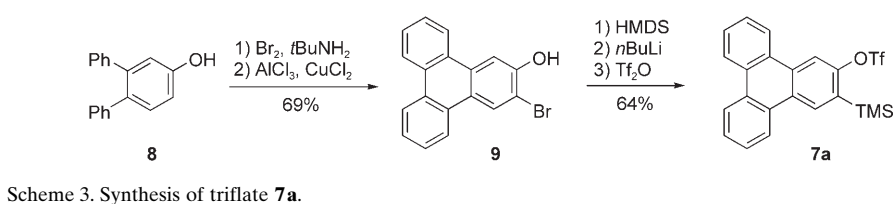


Scheme 2. Triphenylenes **6** and their corresponding precursors **7**.

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 triphenylene precursors (Scheme 2). Specifically, we prepared triflates generating both unsubstituted triphenylene **6a**, which was used for exploration of triphenylene reactions, and the alkoxy-substituted derivative **6b**, which we envisaged would afford more soluble products able to form columnar mesophases.

Results and Discussion

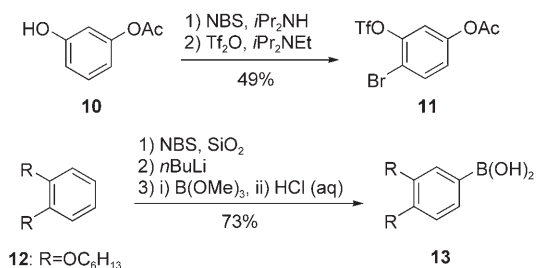
Synthesis of aryne precursors: The precursor of 2,3-didehydrotriphenylene (**6a**) was prepared from 1,1':2',1''-terphenyl-4'-ol (3,4-diphenylphenol, **8**).^[13] *ortho*-Bromination of compound **8**, catalyzed by *t*BuNH₂ in toluene, followed by metal-mediated oxidative cyclodehydrogenation in CS₂ afforded triphenylenol **9** in 69% yield (Scheme 3). Triflate **7a** was obtained from *ortho*-bromohydroxyarene **9** by means of



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

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 *n*BuLi and Tf₂O at –100 °C.

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*-



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

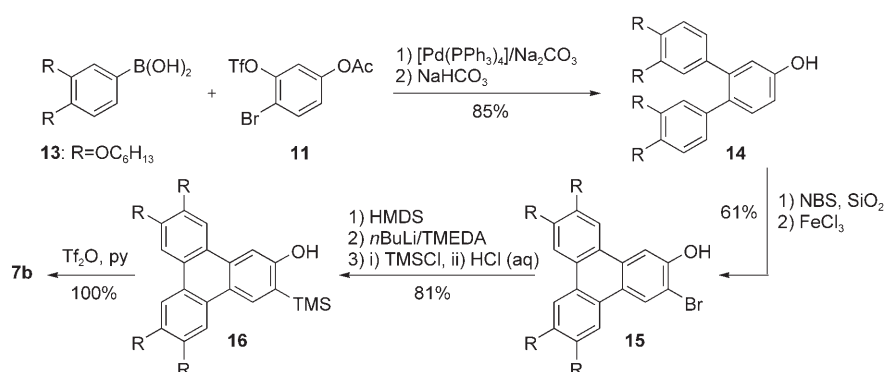
brominated by reaction with *N*-bromosuccinimide (NBS) in the presence of catalytic amounts of *i*Pr₂NH in CH₂Cl₂, and subsequent reaction with Tf₂O and *i*Pr₂NEt in CH₂Cl₂ at 0 °C afforded triflate **11** in 49% overall yield from **10**. Compound **12** was used to obtain boronic acid **13** in 73% yield by a modified version of a previously reported procedure.^[14]

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 NaHCO₃ afforded terphenylol **14** in 85% yield (Scheme 5). *ortho*-Bromination of compound **14** by NBS in the presence of silica gel in CH₂Cl₂, followed by oxidative cyclodehydrogenation promoted by FeCl₃ in CH₂Cl₂ 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 *n*BuLi. This step was followed by quantitative reaction of **16** with Tf₂O in the presence of pyridine.

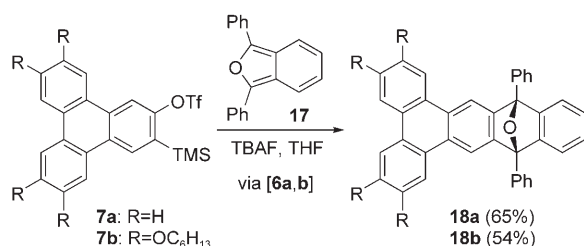
Cycloaddition reactions of arynes: The ability of triflates **7** to form arynes **6** through fluoride-induced decomposition was confirmed when treatment of **7** with tetrabutylammoni-

Abstract in Spanish: Se describe la síntesis de los triflatos de *orto*-(trimetilsilil)trifenileno **7**. La descomposición inducida por ión fluoruro de estos triflatos da lugar a la generación de los didehidrotrifenilenos (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.



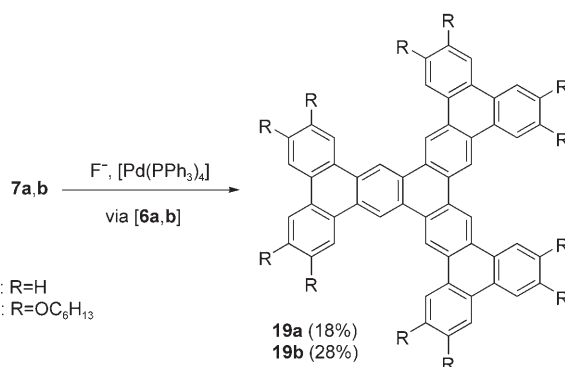
Scheme 5. Synthesis of alkoxy-substituted triflate **7b**.

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).



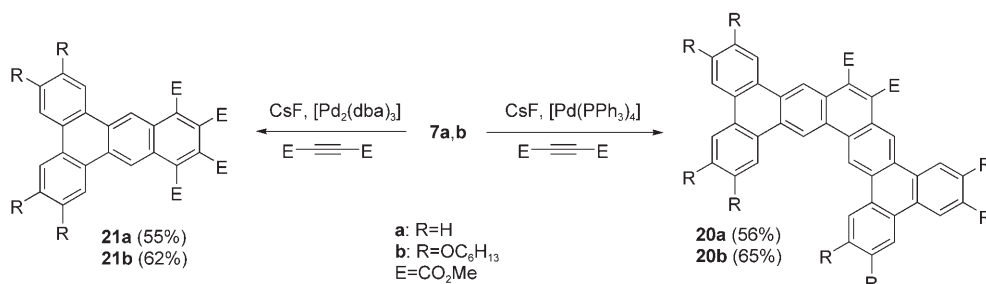
Scheme 6. [4+2] Cycloaddition of arynes **6**.

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(PPh₃)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 ¹H 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(PPh₃)₄] (0.1 equiv) in CH₃CN/CH₂Cl₂ 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



Scheme 7. Cyclotrimerization of arynes **6** to afford tris(triphenylenylene)s **19**. Reaction conditions for **7a**: [Pd(PPh₃)₄] (0.1 equiv), Bu₄NF (1.5 equiv), THF, 1 h. For **7b**: [Pd(PPh₃)₄] (0.1 equiv), CsF (3 equiv), CH₃CN/CH₂Cl₂ 3:1, 14 h.

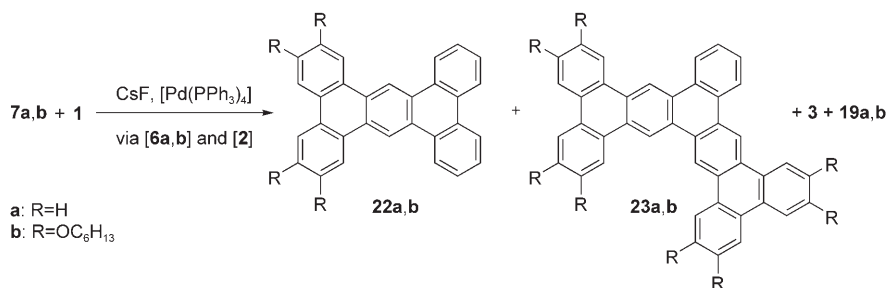
flates **7a,b** with CsF in the presence of DMAD and 10 mol% of [Pd(PPh₃)₄] led to the cocycloaddition of two molecules of the aryne and one of the alkyne (Scheme 8), as shown by the isolation of extended triphenylenes **20a** and **b** in 56 and 65% yields, respectively.^[18] In this reaction, polycyclic 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 [Pd₂(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 8. Cocycloaddition of arynes **6** with DMAD.

Significantly, the ^1H 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 triphenylenes **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 condi-



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

tions 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 triphenylene **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(triphenylene) **19b** (2%).^[21]

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_2NEt , iPr_2NH , 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_4NF (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). 1H 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_4NF (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); 1H 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_4NF (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; ^1H NMR (300 MHz, CDCl_3): δ = 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): δ = 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 (2CH₂), 69.5 (2CH₂), 31.7 (4CH₂), 29.35 (2CH₂), 29.31 (2CH₂), 25.8 (4CH₂), 22.7 (4CH₂), 14.0 ppm (4CH₃); MS (FAB⁺): m/z (%): 898 (100), 897 (83); MALDI-TOF HRMS: m/z : calcd for $\text{C}_{62}\text{H}_{30}\text{O}_5$: 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 ($50600 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).

Hexabenzo[*a,c,k,m,u,w*]triphenylene (19a): Bu_4NF (150 μL , 1 M, 0.15 mmol) was added dropwise to a solution of **7a** (45 mg, 0.10 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (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 $\times$ 3 mL) to afford **19a** (4.0 mg, 18%) as a highly insoluble greyish solid. M.p. > 275°C; ^1H NMR (750 MHz, 363 K, $\text{C}_2\text{D}_2\text{Cl}_4$): δ = 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 $\text{C}_{34}\text{H}_{30}$: 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 ($16300 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).

2,3,6,7,12,13,16,17,22,23,26,27-Dodecakis(hexyloxy)hexabenzo-*[a,c,k,m,u,w]*-triphenylene (19b):^[17] Finely powdered anhydrous CsF (27 mg, 0.18 mmol) was added to a solution of **7b** (50 mg, 0.059 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (6.9 mg, 6 μmol) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ 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; $\text{CH}_2\text{Cl}_2/\text{hexane}$ 1:2 to 3:1), affording **19b** (10.5 mg, 28%) as a yellow solid. M.p. 104–177°C;^[23] ^1H NMR (300 MHz, 298 K, CDCl_3 , 4.3 mm): δ = 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): δ = 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 (6CH₂), 69.4 (6CH₂), 32.0 (6CH₂), 31.8 (6CH₂), 29.7 (12CH₂), 26.2 (6CH₂), 26.0 (6CH₂), 22.8 (12CH₂), 14.11 (6CH₃), 14.08 ppm (6CH₃); 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, $64500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).

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 $[\text{Pd}(\text{PPh}_3)_4]$ (27 mg, 0.023 mmol) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ 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 $\times$ 2 mL) affording **20a** (77 mg, 56%) as a yellow solid. M.p. 220°C (dec); ^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$): δ = 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, $\text{C}_2\text{D}_2\text{Cl}_4$): δ = 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 (2CH), 123.7 (2CH), 123.6 (4CH), 123.3 (2CH), 121.8 (2CH), 117.0 (2CH), 52.7 ppm (2CH₃); MS (FAB⁺): m/z (%): 594 (25); HRMS (FAB⁺): m/z : calcd for $\text{C}_{42}\text{H}_{26}\text{O}_4$: 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 ($27600 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$). Column chromatography of the organic phase (silica gel; ether/ $\text{CH}_2\text{Cl}_2/\text{hexane}$ 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 $[\text{Pd}_2(\text{dba})_3]\cdot\text{CHCl}_3$ (11.4 mg, 0.011 mmol) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ 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/ $\text{CH}_2\text{Cl}_2/\text{hexane}$ 2:1:1), affording **21a** (62 mg, 55%) as a yellow solid. M.p. 271–274°C; ^1H NMR (250 MHz, CDCl_3): δ = 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 (2CH₃), 53.2 ppm (2CH₃); EI-MS: m/z (%): 510 (100); EI-HRMS: m/z : calcd for $\text{C}_{30}\text{H}_{22}\text{O}_8$: 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 ($49000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).

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 $[\text{Pd}(\text{PPh}_3)_4]$ (9.1 mg, 7.9 μmol) in $\text{CH}_3\text{CN}/\text{THF}$ 5:1 (2 mL), and the mixture was stirred at room temperature for 14 h and then poured on $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ 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; $\text{CH}_2\text{Cl}_2/\text{hexane}$ 2:1, then $\text{CH}_2\text{Cl}_2/\text{ether}/\text{hexane}$ 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] ^1H NMR (500 MHz, 293 K, CDCl_3 , 3.7 mM): δ = 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): δ = 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 (2CH₂), 69.2 (2CH₂), 69.1 (2CH₂), 68.4 (2CH₂), 52.2 (2CH₃), 32.0 (2CH₂), 31.8 (6CH₂), 29.7 (4CH₂), 29.5 (4CH₂), 26.4 (2CH₂), 26.0 (2CH₂), 25.9 (4CH₂), 22.8 (4CH₂), 22.7 (4CH₂), 14.1 ppm (8CH₃); MS (FAB⁺): m/z (%): 1395 (100); MALDI-TOF HRMS: m/z : calcd for $\text{C}_{90}\text{H}_{122}\text{O}_{12}$: 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 ($57500 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).

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 $[\text{Pd}_2(\text{dba})_3]\cdot\text{CHCl}_3$ (4.3 mg, 4.2 μmol) in $\text{CH}_3\text{CN}/\text{THF}$ 5:1 (2.4 mL), and the mixture was stirred at room temperature for 14 h and then poured on $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ (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; $\text{CH}_2\text{Cl}_2/\text{hexane}$ 2:1, then $\text{CH}_2\text{Cl}_2/\text{ether}/\text{hexane}$ 2:1:17 to 6:1:13), affording **21b** (47 mg, 62%) as a yellow solid. M.p. 137–140°C; ^1H NMR (300 MHz, CDCl_3): δ = 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): δ = 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 (2CH₂), 69.5 (2CH₂), 53.1 (2CH₃), 53.0 (2CH₃), 31.6 (4CH₂), 29.3 (4CH₂), 25.83 (2CH₂), 25.81 (2CH₂), 22.65 (2CH₂), 22.64 (2CH₂), 14.0 ppm (4CH₃); MS (FAB⁺): m/z (%): 910 (100); HRMS (FAB⁺): m/z : calcd for $\text{C}_{54}\text{H}_{70}\text{O}_{12}$: 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 ($72200 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).

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(PPh₃)₄] (40 mg, 0.035 mmol) in CH₃CN/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 CH₂Cl₂ (2 mL) and centrifuged. The pellet was washed with H₂O (2 mL) and CH₂Cl₂ (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, C₂D₂Cl₄): δ = 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 (CH₂Cl₂): λ_{max} (ε) = 332 (6000), 294 (12 100), 259 nm (9100 mol⁻¹ dm³ 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(PPh₃)₄] (40 mg, 0.035 mmol) in CH₃CN/CH₂Cl₂ 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 CH₂Cl₂/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)pentabenz[*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, CDCl₃): δ = 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); ¹³C NMR (75 MHz, CDCl₃): δ = 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 (2CH₂), 69.7 (2CH₂), 31.8 (2CH₂), 31.7 (2CH₂), 29.5 (2CH₂), 29.4 (2CH₂), 25.94 (2CH₂), 25.88 (2CH₂), 22.71 (2CH₂), 22.68 (2CH₂), 14.07 ppm (2CH₃); MS (FAB⁺): *m/z* (%): 778 (100); HRMS (FAB⁺): *m/z*: calcd for C₃₄H₆₆O₄ 778.4961; found: 778.4967; UV/Vis (CH₂Cl₂): λ_{max} (ε) = 336 (sh, 39 900), 319 (52 300), 301 (75 700), 275 (sh, 50 100), 266 nm (52 900 mol⁻¹ dm³ cm⁻¹). Data for **23b**: m.p. 95–217 °C;^[23] ¹H NMR (300 MHz, 298 K, CDCl₃, 5.0 mM): δ = 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); ¹³C NMR (75 MHz, 298 K, CDCl₃, 15.1 mM): δ = 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 (2CH₂), 69.4 (4CH₂), 69.3 (2CH₂), 31.95 (2CH₂), 31.85 (2CH₂), 31.80 (4CH₂), 29.9 (2CH₂), 29.6 (2CH₂), 29.54 (2CH₂), 29.48 (2CH₂), 29.2 (2CH₂), 26.03 (2CH₂), 25.98 (2CH₂), 25.90 (2CH₂), 22.75 (4CH₂), 22.71 (4CH₂), 14.11 (4CH₃), 14.08 ppm (4CH₃); MS (FAB⁺): *m/z* (%): 1329 (62); MALDI-TOF HRMS: *m/z*: calcd for C₉₀H₁₂₀O₈: 1328.8978; found: 1328.8975; UV/Vis (CHCl₃): λ_{max} (ε) = 380 (sh, 34 600), 350 (68 900), 324 (sh, 73 300), 310 (93 900), 284 (87 600), 257 nm (sh, 68 500 mol⁻¹ dm³ cm⁻¹).

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- [20] Although the ¹H NMR spectrum of this solid in C₂D₂Cl₄ 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.
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