Liquid Crystalline Triptycene Derivatives

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A route to triptycenes substituted with one, two, five, and six paraffinic chains was developed using the Diels–Alder reaction as the key reaction. 1,4,5,8-Tetrakis(dodecyloxy)-11-hydroxy-14-(dodecanoyloxy)triptycene, 1,4,5,8-tetrakis(dodecyloxy)-11,14-bis(dodecanoyloxy)triptycene, and 1,4,5,8,-11,14-hexakis(dodecyloxy)triptycene were obtained in a nine-step procedure starting from diaminoanthrarufin. The five-chain derivative demonstrates original mesomorphic properties.

Introduction

Triptycene substituted with five long paraffinic chains in α positions **9** has been synthesized (Figure 1). This molecule presents liquid crystalline properties. The X-ray diffraction patterns indicate a layered arrangement (smectic) with a hexagonal packing of the triptycenes.[1-3] **9** presents moreover a disordered smectic A phase. It is the first smectogen derived from a rigid core belonging to the D_{3h} symmetry.

I present here the main results concerning the mesomorphic properties of **9** and the detailed synthesis of compounds **9** and **10** (see Scheme II) substituted with, respectively, five and six chains of dodecyl length.

Since the first synthesis of triptycene by Bartlett,[4] numerous chemical methods have been described for its preparation.[5] The Diels–Alder reaction involving a 1,4,5,8-substituted anthracene with *p*-benzoquinone offered an easy access to α-functionalized triptycenes. Schemes I and II describe the synthesis of the substituted anthracene and triptycene, respectively.

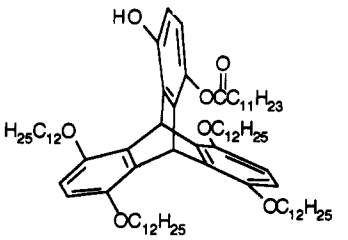

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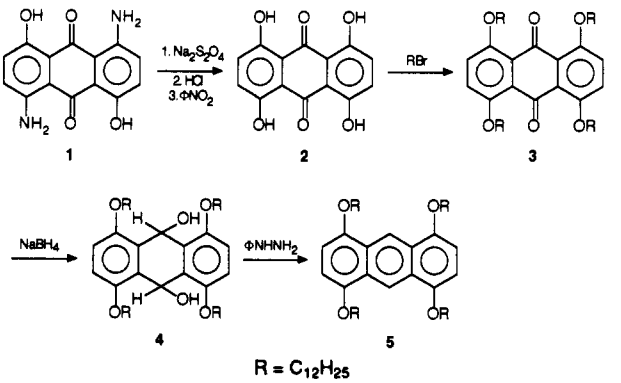
Figure 1. Triptycene derivative **9** demonstrates liquid crystalline properties.

Scheme I. Synthesis of Substituted Anthracene



Results and Discussion

Synthesis of Substituted Anthracene. 1,4,5,8-Tetrakis(dodecyloxy)anthracene (**5**) was obtained starting from the commercially available diaminoanthrarufin (**1**). Conversion of **1** into 1,4,5,8-tetrahydroxyanthraquinone (**2**) has already been described.[6]

For the reaction of phenols with long-chain bromoalkanes, two methods are particularly efficient.[7] The first is Bram's method of phase-transfer catalysis without solvent, which uses KOH as base,[8,9] and the second is the reaction in DMF with K_2CO_3 as base.[10] For the synthesis of 1,4,5,8-tetrakis(dodecyloxy)anthraquinone (**3**), both methods proved to be quite unsuccessful with yields of about 10%. Each time a large amount of partially alkylated products was obtained. This lack of reactivity of *peri*-hydroxyanthraquinones is well known.[11] It is due to the formation of chelates between the carbonyl and the neighboring hydroxyl groups. The use of Cs_2CO_3 instead of K_2CO_3 gave better yield (80%), since the cesium salt enhanced the nucleophility of the phenate, making it more freely accessible to alkylation. Cesium salts of phenolic compounds have been successfully used in crown ether synthesis.[12]

Although several reductive systems may be used for the conversion of the 9,10-anthraquinone into anthracene,[13] only a few are efficient for the *peri*-alkoxyanthraquinones.[14,15] The following two-step procedure proved to be successful for the reduction of polymethoxy-9,10-an-

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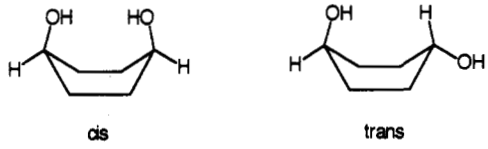


Figure 2. Cis and trans isomers of 9,10-dihydro-9,10-anthracenediol. Only the central cycle is represented.

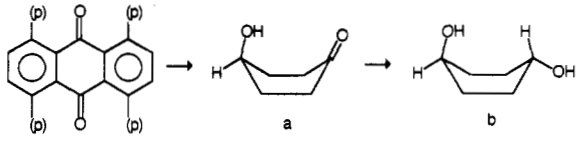
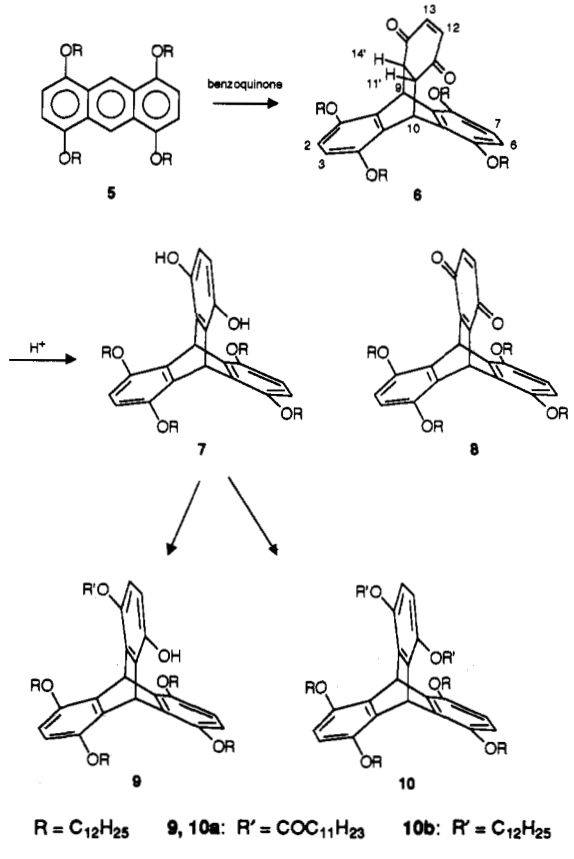


Figure 3. Intermediate oxanthrone **a** leads first to the trans isomer **b**.

Scheme II. Synthesis of Triptycene Derivatives



$R = C_{12}H_{25}$ **9, 10a**: $R' = COC_{11}H_{23}$ **10b**: $R' = C_{12}H_{25}$

thraquinones:[16] a first reduction by $NaBH_4$ in MeOH led to the corresponding 9,10-dihydro-9,10-anthracenediol, and a second reduction process with phenylhydrazine in CH_3CO_2H gave the anthracene derivative. Many difficulties arose from the first step because of the low solubility of the anthraquinone **3** in protic solvents. The reaction was carried out in THF, with a small amount of MeOH (10%), giving **4** in theoretical yield. ^1H NMR measurements for **4** indicate the presence of two doublets at 6.45 and 6.20 ppm and two OH peaks at 3.45 and 2.65 ppm. The latter disappeared when D_2O was added, whereas the doublets at 6.45 and 6.20 ppm became singlets, because of the removal of coupling with the hydroxyl protons. Integration data are in agreement with a 1:1 cis–trans mixture of isomers (Figure 2).

This result may be explained by the mechanism of

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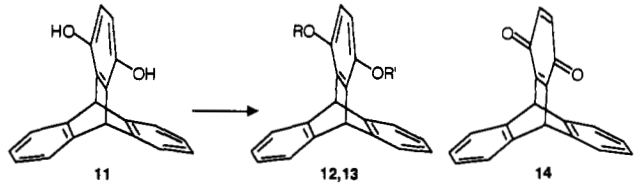
Scheme III. Synthesis of Mono- and Dialkylated Triptycene Derivatives



12: $R' = H$, $R = C_{12}H_{25}$ **13a**: $R = R' = COC_{11}H_{23}$
13b: $R = R' = C_{12}H_{25}$

formation of dihydroanthracenediol.[17] Because of the steric hindrance of peri-substituents, the hydrides attack the intermediate oxanthrone **a** axially. This leads to the trans-diol **b** (Figure 3), which partially isomerizes into the cis isomer because of the unfavorable interaction between the equatorial hydroxyl group and the peri-substituents (p).

Synthesis of Triptycene Derivatives. The Diels–Alder reaction of the substituted anthracene **5** with *p*-benzoquinone first led to the adduct **6**. The yield of the reaction was improved by using an excess of benzoquinone[18,19] and reducing the solvent quantity. However, high concentrations also allowed the formation of degradation products. Consequently, the reaction was stopped when the first byproduct appeared in TLC; nevertheless, **6** was obtained in satisfactory yield (70%).

6 was isomerized into the triptycenediphenol **7** with HBr in CH_3CO_2H.[4] This reaction must be quenched before the monoacetylation of the compound **7**.

The final alkylation or alcoylation steps have been attempted with the unsubstituted parent compound **11** (Scheme III). The alkylation of the triptycenediphenol **11** was carried out under mild conditions (rt, 20 min),[20] resulting in a mixture of mono- and disubstituted compounds **12** and **13b**. Another byproduct was identified as the triptycenequinone **14**. The hexasubstituted derivative **10b** was obtained with the Bram's method. Unexpectedly, this product is almost insoluble in usual solvents at rt. Its characterization by ^1H NMR measurements had to be carried out at high temperature. Alcoylation of compound **11** led to the expected disubstituted compound **13a**. Using the same reactional conditions ($C_{11}H_{23}COCl$/pyridine/toluene) with **7** mainly gave the monoalcoylated compound **9**. The hexasubstituted derivative **10a** can be obtained in high yield (80%) by using the carboxylic acid activated with DCC.[2,21]

Mesomorphic Properties. Both anthraquinone **3** and anthracene **5** demonstrate liquid crystalline properties. Their mesophases, according to the microscopic textures and the X-ray diffraction patterns, proved to be smectic A phases.[2] Structural data and results obtained by differential scanning calorimetry (DSC) are given in Table I.

The DSC thermogram (Figure 4) of the triptycene substituted with five chains **9** shows the existence of several phase transitions. X-ray diffraction measurements for each phase are reported in Table II.

The diffraction patterns show a lamellar structure in all cases. The corresponding interreticular distance *d* is

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Table I. Thermal Behavior and Structural Data for the Anthraquinone and Anthracene Derivatives[a]

		T_1 (ΔH)		T_2 (ΔH)		d (Å)
3	C	112 (50)	S_A	132 (13)	I	30
5	C	96.6 (75.3)	S_A	101.4 (17.4)	I	31

[a] T_1 melting point, T_2 clearing point (°C); ΔH transition enthalpy (J/g); C crystal, S_A smectic A (liquid crystalline phase), I isotropic phase; d interreticular distance in the S_A phase.

$$M_4 \xrightarrow{153°C} M_3 \xrightarrow{156°C} M_2 \xrightarrow{163°C} M_1 \xrightarrow{169°C} \text{Isotropic}$$

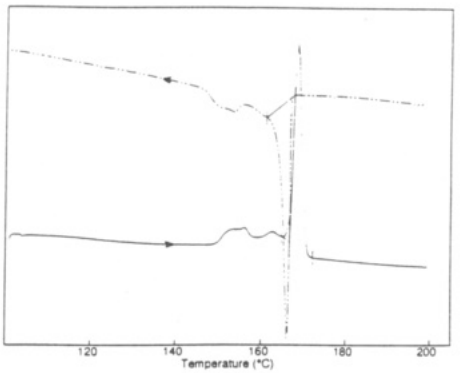

Figure 4. DSC thermogram of **9** at 10 °C/mn.

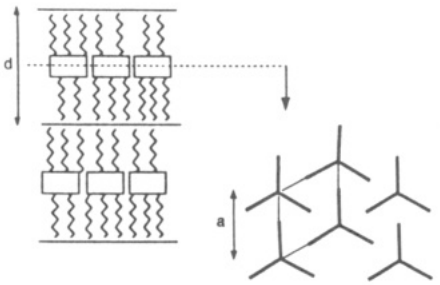

Figure 5. Structural model for the smectic phase, with a hexagonal ordering of the triptycene cores within the layers.

approximately the length of the molecule (30 Å). The disordered mesophase M_1 can be identified by microscopic observations (conic-focals texture) as a smectic A phase. With decreasing temperature, the greater rigidity of the paraffinic chains leads to a larger interlamellar distance. Moreover, a hexagonal ordering appears, which has been associated with a p31m arrangement of the triptycene cores within the layers (Figure 5).

At room temperature, the hexagonal cell parameter a is equal to the van der Waals distance of the triptycene cores (8 Å), as estimated by CPK models (Figure 6). X-ray measurements indicate that a increases with increasing temperature; this probably corresponds to a greater motion of the rigid cores. In the disordered phase, the triptycene cores are disorganized and no long-range positional order can be observed. Solid NMR measurements are in progress to understand the organization of both the rigid and aliphatic tails in these lamellar mesophases.

A difference in mesomorphic behavior between the five-chain and six-chain derivatives was observed: whereas the five-chain derivative shows mesomorphic properties, the six-chain derivatives present only highly ordered lamellar phases. This behavior was explained by the area allowed for the chains in the condensed phases.[1-3] The closest packing of the triptycene cores (a = 8 Å) leads to a 55.4 Å^2 cell area. For the pentasubstituted derivative, 22.2 Å^2 is then allowed per paraffinic chain. This value

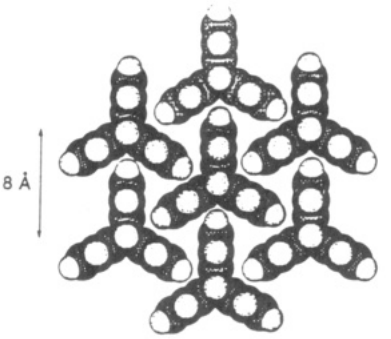

Figure 6. Illustration of the intralamellar ordering with the CPK models.

Table II. Structural Data of 9

phase	T (°C)	interlamellar distance d (Å)	intralamellar distance a (Å)	chains (Å)
M_1	166	30	disordered	halo (4.5)
M_2	159	30.8	8.3	halo (4.5)
M_3	154	31.5	8.3	halo (4.5)
M_4	20	35.3	8.0	4.2_8

is compatible with a disordered state of the chain, leading to a mesophase. For the hexasubstituted derivative, 18.5 Å^2 only are available for each chain, which leads to a crystalline state.

Because of the remarkable compatibility between the aromatic and aliphatic moieties, we proposed for this new type of compound the name "epitaxygens".[1]

Conclusion

Triptycene derivatives substituted with five and six paraffinic chains were synthesized following a nine-step procedure. The main difficulties arose from the low solubility of the high molecular weight products and intermediates.

The mesomorphic behavior of the five-chain triptycene derivative makes the triptycene a new mesogen core. It has the unique property to allow the synthesis of smectogenic molecules whose rigid core belongs to the D_{3h} symmetry. Moreover, the shape of the triptycene leads specifically to a p31m organization within the plane. The use of the triptycene subunit may allow the obtainment of defect-free thin films.

Experimental Section

General. The abbreviations ar and cyh indicate, respectively, aromatic and cyclohexane. Calorimetric measurements were performed with a Perkin-Elmer DSC7 differential scanning calorimeter at 10 °C/mn. X-ray diffraction patterns were recorded under vacuum, with a monochromatic (Cu Kα) X-ray radiation. IR spectra were performed with a Perkin-Elmer 1600 FTIR spectrophotometer and UV-spectra with a UVIKON 860 spectrophotometer. NMR spectra were recorded in $CDCl_3$ using Varian E390 and Bruker AM250 spectrometers. Silica gel was used for column chromatographies (Merck 7734, 0.063–0.200 mm), PTLC ($60F_{254+366}$, Merck 5637, 2 mm) and TLC ($60F_{254}$, Merck 5735, 0.2 mm). Elemental analyses were performed in the Centre de Recherche sur les Macromolécules, Strasbourg. Diaminoanthrarufin (1) is available from Lancaster, purity 97%.

Synthesis of the Substituted Anthracene. 1,4,5,8-Tetrahydroxy-9,10-anthraquinone (2). Leuco-1,4,5,8-tetrahydroxyanthraquinone. A mixture of 20 g (0.075 mol) of 1 and 40 g (1 mol) of sodium hydroxide was heated in 1 L of water. When the temperature reached 70 °C, 40 g (0.23 mol) of sodium dithionite was added portionwise. The mixture, which became rapidly reddish, was boiled for 2 h until ammonia was no longer

evolved. At rt, the sodium salt of the leuco compound was filtered off, washed with water and dried under vacuum (P_2O_5) (19.2 g of dark crystals with bronze green reflex, 65%). The free leuco compound was obtained in theoretical yield by suspending the sodium salt in hot water and acidifying with dilute HCl up to pH = 1. The brown precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid: ^{1}H NMR δ 9.9 (s, OH, disappears when D_2O is added), 7.15 (s, 2, ar), 3 (s, 4, aliphatic). Anal. Calcd for $C_{14}H_{10}O_6$, MW 274.23: C, 61.32; H, 3.67; N, 0. Found: C, 60.53; H, 3.48; N, 0.8.

Deshydrogenation. The free leuco compound (13.3 g) in 104 mL of nitrobenzene was stirred at 195 °C. Around 180 °C, the brown solution took a crimson color and the heat of reaction caused the mixture to boil. The reflux condenser was removed for 15 min to expel water. The mixture was allowed to stand for 12 h. The solid product was isolated by filtration and washed with nitrobenzene (100 mL) and thoroughly with ether. Compound **2** was obtained as dark-blue crystals (12 g, 92%): MS(EI) *m/e* 272. Anal. Calcd for $C_{14}H_8O_6$ MW 272.21: C, 61.77; H, 2.96; N, 0. Found: C, 61.88; H, 2.87; N, 0.48. Residual product containing nitrogen was probably unchanged diaminoanthrarufin[6] or 8-amino-1,4,5-trihydroxyanthraquinone.[22] Purifications were unsuccessful because of the poor solubility of **2** in usual solvents.

1,4,5,8-Tetrakis(dodecyloxy)anthraquinone (3). To a mixture of 1 g (3.67 mmol) of **2** and 4.8 g (14.7 mmol) of Cs_2CO_3 was added 3.6 mL (14.9 mmol) of $C_{12}H_{25}Br$ and 3 mL of DMF. The mixture was stirred at 100 °C for 15 h, allowed to cool to rt, diluted with CH_2Cl_2, and briefly filtered over silica gel (40 g, CH_2Cl_2). The organic filtrate was concentrated and chromatographed (SiO_2 250 g; CH_2Cl_2–ether (98:2)). The fractions containing the yellow spot (R_f (CH_2Cl_2–cyh (80:20)) 0.1) were collected and recrystallized from acetone (gold yellow crystals, 2.81 g, 81%): IR (KBr) 1681.7 cm^{-1} (C=O); ^{1}H NMR δ 7.1 (s, 4, ar), 4.0 (t, 8, OCH_2), 1.25 (m, 80, CH_2), 0.85 (t, 12, CH_3); ^{13}C NMR δ 163 (q, C=O), 151.5 (q, CO), 126.6 (q, C ar), 120.6 (t, CH ar), 71 (s, OCH_2), 32 (s, CH_2, in $CH_3\beta$ or $OCH_2\beta$ positions), 29.5 (s, CH_2), 26 (s, CH_2, $OCH_2\gamma$), 22.7 (s, CH_2, $CH_3\alpha$), 14 (s, CH_3); clearing point: 132 °C. Anal. Calcd for $C_{62}H_{104}O_6$ MW 945.5: C, 78.76; H, 11.08. Found: C, 78.08; H, 10.95.

1,4,5,8-Tetrakis(dodecyloxy)-9,10-dihydro-9,10-anthracenediol (4). To 410 mg (0.43 mmol) of **3** dissolved in a mixture of methanol (5 mL) and THF (50 mL) was added gradually 480 mg (12.6 mmol) of freshly ground $NaBH_4$. The orange solution boiled gently and decolored rapidly to pale yellow. After 2.5 h, the mixture was poured into 300 mL of ice–water. The white precipitate was filtered off and dried under vacuum (P_2O_5) (white powder, 410 mg, theoretical yield). The dihydrodiol **4** showed no residual carbonyl absorption in its IR spectra: ^{1}H NMR δ 6.83; 6.78 (2s, 4, ar), 6.45; 6.20 (2d, 2, benzylic), 4.0 (m, OCH_2), 3.45; 2.65 (br d, 2 OH), 1.3 (m, CH_2), 0.9 (t, CH_3). The melting point was not reproducible, probably due to various cis–trans proportions. Anal. Calcd for $C_{62}H_{108}O_6$ MW 949.5: C, 78.43; H, 11.46. Found: C, 73.24; H, 10.57. The dihydrodiol was used with no further purification because attempted recrystallizations led to reoxydation products. This instability of 9,10-dihydro-9,10-anthracenediols is well known.[15]

1,4,5,8-Tetrakis(dodecyloxy)anthracene (5). To 2.16 g (2.27 mmol) of **4** was added 2.23 mL (22.7 mmol) of phenylhydrazine and 11.4 mL of glacial acetic acid. The mixture, placed under nitrogen, was immerged into an oil bath at 60 °C, warmed at 90–100 °C for 15 min, and then refluxed for 15 min. After the mixture was allowed to cool for 2 h, the crude product was filtered, washed with acetic acid, methanol, and acetone, and dried under vacuum. Purification was performed by chromatography (CH_2Cl_2–cyh (20:80)). Compound **5** was eluted first (characteristic fluorescent spot at 254 nm) (76%). The pale yellow crystals were recrystallized from EtOAc: UV (CH_2Cl_2) λ_{max} 263, 317, 335, 350, 367, 393, 416. ^{1}H NMR δ 9.2 (s, H9, H10), 6.6 (s, 4, ar), 4.15 (m, OCH_2), 1.25 (m, CH_2), 0.85 (t, CH_3); clearing point 102.3 °C. Anal. Calcd for $C_{62}H_{106}O_4$ MW 915.5: C, 81.34; H, 11.67. Found: C, 81.44; H, 11.65.

Synthesis of Triptycene Derivatives. 1,4,5,8-Tetrakis(dodecyloxy)-11,14-dioxo-11′,14′-dihydrotriptycene (6). To 650 mg (0.7 mmol) of substituted anthracene **5** was added 760 mg (7 mmol) of *p*-benzoquinone, purified by filtration on silica gel (CH_2Cl_2), and 1 mL of dry toluene. The mixture was stirred at 105 °C. The evolution was followed by TLC (CH_2Cl_2–cyh (80:20)): R_f 1 (**5**), R_f 0.57 (**6**), R_f 0.47 (benzoquinone). The heating was stopped as soon as the first byproduct (R_f 0.83) appeared (1.5 h < *t* < 6 h). After standing for 1 h, the crude mixture was filtered, washed thoroughly with hot water until benzoquinone was removed, and dried (P_2O_5). Chromatography afforded pure **6** (SiO_2 75 g; CH_2Cl_2–cyh (60:40)) (518 mg, 71%). Pale yellow crystals were obtained by recrystallization from acetone: IR (KBr) 1675 cm^{-1} (C=O); ^{1}H NMR δ 6.6, 6.55 (s, s, H2, H3, H6, H7), 6.2 (s, H12, H13), 5.7 (s, H9, H10), 3.9 (m, OCH_2), 2.95 (s, H11′, H14′), 1.75 (m, $OCH_2\beta$), 1.25 (m, CH_2), 0.85 (t, CH_3). **6** melted at 133.4 °C and decomposed above 150 °C. After several cycles, the thermogram of anthracene **5** was obtained. This demonstrates the thermal instability of compound **6**, involved in a retro-Diels–Alder reaction. Anal. Calcd for $C_{68}H_{110}O_6$ MW 1023.6: C, 79.79; H, 10.83. Found: C, 79.16; H, 10.81.

1,4,5,8-Tetrakis(dodecyloxy)-11,14-dihydroxytriptycene (7). Compound **6** (340 mg, 0.33 mmol), suspended in 1.5 mL of glacial acetic acid, was heated rapidly at 120 °C. After **6** was dissolved, 200 μL of dilute HBr (0.48%) was added drop by drop. This caused the separation of a yellow solid, which slowly whitened. After 30 min at 120 °C, the mixture was allowed to cool to rt, filtered off, washed with acetic acid, and dried under vacuum (P_2O_5) to afford almost pure product (reddish white powder, 330 mg, 97%): TLC R_f (CH_2Cl_2–cyh (50:50)) 0.92 (**5**), 0.57 (**8**), 0.3 (**6**), 0.1 (**7**). A small amount of anthracene **5** appeared again, significant of a retro-Diels–Alder reaction of **6**. Chromatography (CH_2Cl_2–cyh (80:20)) afforded a white product, which must be protected from air to avoid the partial oxidation of **7** into the corresponding red triptycenequinone **8**: ^{1}H NMR δ 6.6 (s, H9, H10), 6.5 (s, H2, H3, H6, H7), 6.35 (s, H12, H13), 4.9 (br, OH), 3.9 (t, 8, OCH_2), 1.3 (m, CH_2), 0.85 (t, CH_3); mp 190.5 °C. Anal. Calcd for $C_{68}H_{110}O_6$ MW 1023.6: C, 79.79; H, 10.83. Found: C, 78.41; H, 10.76.

1,4,5,8-Tetrakis(dodecyloxy)triptycenoquinone (8) was also obtained as a byproduct during the esterification of **7**. Recrystallization from a mixture of acetone/toluene afforded red crystals: UV (THF) λ_{max} (ϵ) 248 (11 560), 294 (6730), 408 (400); ^{1}H NMR δ 6.65 (s, 2, H9, H10 or H12, H13), 6.55 (s, 2, H9, H10 or H12, H13), 6.5 (s, H2, H3, H6, H7), 3.9 (t, 8, OCH_2), 1.3 (m, CH_2), 0.85 (t, CH_3); mp 209 °C. Anal. Calcd for $C_{68}H_{108}O_6$ MW 1021.6: C, 79.95; H, 10.65. Found: C, 79.50; H, 10.89.

1,4,5,8-Tetrakis(dodecyloxy)-11-hydroxy-14-(dodecanoyloxy)triptycene (9). Triptycenediphenol **7** (130 mg, 0.127 mmol), $C_{11}H_{23}COCl$ (80 μL, 0.345 mmol), and dry pyridine (20 μL, 0.25 mmol) in 17 mL of dry toluene were stirred at 60 °C for 48 h (TLC R_f (CH_2Cl_2–cyh (80:20)) 0.77 (**8** + **10a**) 0.35 (**9**) 0.08 (**7**)). After evaporation of the solvent, preparative TLC ($CHCl_3$–ether (98:2)) afforded **9** (85 mg, 55%), which is recrystallized from toluene (white powder): IR (KBr) 3471 (OH) 1744.7 cm^{-1} (OC=O); UV (ether) λ_{max} 293 (ϵ) 340 (ϵ/20); ^{1}H NMR (250 MHz) δ 6.60 (s, 1, H9 or H10), 6.61, 6.57, 6.46, 6.44 (AB, *J* = 8.5 Hz, H12, H13), 6.48 (br s, H2, H3, H6, H7), 6.44 (s, 1, H9 or H10), 3.91 (t, 8, OCH_2), 2.67 (t, 2, $OCOCH_2$), 1.3 (m, CH_2), 0.9 (t, CH_3). The AB structure was evidenced by adding C_6D_6: ^{1}H NMR ($CDCl_3$ + C_6D_6) δ 6.96 (s, H9 or H10), 6.73 (s, H9 or H10), 6.54 (AB, *J* = 8.5 Hz, 1 H), 5.97 (AB, *J* = 8.5 Hz, 1 H); ^{13}C NMR δ 171.95 (q, C=O), 149.03 (q, C_1 or C_4), 148.61 (q, C_1 or C_4), 147.91 (q, C_{14} or C_{11}), 139.74 (q, $C_{11'}$ or $C_{14'}$), 139.50 (q, $C_{11'}$ or $C_{14'}$), 136.05 (q, $C_{1'}$ or $C_{4'}$), 135.54 (q, $C_{1'}$ or $C_{4'}$), 133.41 (q, C_{11} or C_{14}), 119.23 (t, C_{12} or C_{13}), 113.46 (t, C_{12} or C_{13}), 111.56 (t, C_2 or C_3), 111.10 (t, C_2 or C_3), 70.29 (s, OCH_2), 69.75 (s, OCH_2), 35.64 (t, C_9 or C_{10}), 34.48 (t, C_9 or C_{10}), 34.48 (s, α ester), 31.95 (s, β ether or β CH_3), 29.88 (s, γ ester + γ CH_3), 29.7 (CH_2 core), 29.39 (s, δ ether + δ ester + δ CH_3), 26.17 (s, γ ether), 26.13 (s, γ ether), 25.25 (s, β ester), 22.69 (s, α CH_3), 14.06 (p, CH_3); clearing point 169 °C; MS (CI(NH_3)) *m/e* 1205, (*m* + 18)/*e* 1222. Anal. Calcd for $C_{80}H_{132}O_7$ MW 1205.9: C, 79.68; H, 11.03. Found: C, 78.67; H, 11.29.

1,4,5,8-Tetrakis(dodecyloxy)-11,14-bis(dodecanoyloxy)triptycene (10a). The procedure described above afforded **10a** after further chromatography: fractions containing **10a** and **8** were gathered and separated by PTLC (EtOAc–cyh (50:50)) R_f 1 (**8**, 10%), 0 (**10a**, 3%). After filtration on Celite, the hexa-

(22) Bayer, O. In *Methoden der organischen Chemie*; Houben-Weyl-Müller, 4.Aufl., Bd VII/3c; Thieme: Stuttgart, 1979; p 170.

substituted derivative was obtained as white crystals: UV (CH_2Cl_2) λ_{max} 298 (ϵ) 350 (ϵ/20); ^1H NMR δ 6.7 (s, 2, H9, H10 or H12, H13), 6.45 (s, 6, ar + H9, H10 or H12, H13), 3.85 (t, 8, OCH_2), 2.65 (t, 4, $OCOCH_2$), 1.3 (m, CH_2), 0.9 (t, CH_3); mp 150.2 °C. Anal. Calcd for $C_{92}H_{154}O_8$ MW 1388.2: C, 79.60; H, 11.18. Found: C, 79.01; H, 11.12.

1,4,5,8,11,14-Hexakis(dodecyloxy)triptycene (10b). Triptycenediphenol 7 (100 mg, 0.097 mmol), $C_{12}H_{25}Br$ (400 μL, 1.67 mmol), KOH (100 mg, 1.78 mmol), and a few drops of Aliquat 336 were stirred without solvent at 80 °C for 1.5 h. After extraction with CH_2Cl_2/H_2O, a highly insoluble solid was isolated by filtration from the organic phase, dried, and recrystallized after Soxhlet extraction (toluene) (white solid, 60%): ^1H NMR (250 MHz) δ 6.77 (s, 2, H9, H10), 6.46 (s, 6, ar), 3.90 (t, 12, OCH_2); ^1H NMR (90 MHz, toluene-d_7, 95 °C) δ 6.35 (s, 6, ar), 3.9 (t, 12, OCH_2), 1.3 (m, CH_2), 0.95 (t, CH_3). The chemical shift of bridge protons was masked into the solvent signal; mp 180.1 °C; MS-(CI(NH_3)) *m/e* 1359; (*m* + 18)/*e* 1377; *m*/2*e* 680. Anal. Calcd for $C_{92}H_{158}O_6$ MW 1360.3: C, 81.23; H, 11.71. Found: C, 80.97; H, 11.88.

Alkylation of 11,14-Dihydroxytriptycene (11). To 0.77 g of KOH (13.75 mmol) dissolved in DMSO (4 mL) was added 0.5 g (1.74 mmol) of compound 11, synthesized by Bartlett's procedure,[4] and $C_{12}H_{25}Br$ (1.7 mL, 7.1 mmol). The orange mixture was stirred at rt for 20 min. Chromatography (CH_2Cl_2–cyh (25:75), then CH_2Cl_2) afforded successively anthracene (small amount), diether **13b** (48%), triptycenequinone **14** (16%), monoether **12** (23%), and remaining 11.

11-Hydroxy-14-(dodecyloxy)triptycene (12) was recrystallized from heptane–toluene (75:25) (white powder): ^1H NMR δ 7.35, 6.9 (AA'BB', 8, ar), 6.25 (AB, 2, H12, H13), 5.85 (s, 1, H9 or H10), 5.8 (s, 1, H9 or H10), 5.15 (br s, OH), 3.95 (t, 2, OCH_2), 1.3 (m, CH_2), 0.95 (m, CH_3); mp 165 °C. Anal. Calcd for $C_{32}H_{38}O_2$ MW 454.65: C, 84.54; H, 8.42. Found: C, 84.48; H, 8.61.

11,14-Bis(dodecyloxy)triptycene (13b): ^1H NMR δ 7.35, 6.95 (AA'BB', 8, ar), 6.5 (AB, 2, H12, H13), 5.85 (s, 2, H9, H10), 3.9 (t, 4, OCH_2), 1.3 (m, CH_2), 0.9 (m, CH_3); mp 95.5 °C. Anal. Calcd for $C_{44}H_{62}O_2$ MW 622.97: C, 84.83; H, 10.03. Found: C, 84.92; H, 10.10.

11,14-Bis(dodecanoyloxy)triptycene (13a). Triptycenediphenol 11 (0.5 g, 1.74 mmol), dodecanoyl chloride (800 μL, 3.47 mmol), and pyridine (280 μL, 3.4 mmol) were stirred in toluene (7 mL) at 75 °C for 22 h. The organic phase was washed several times with water, neutral, acid, and neutral. Evaporation afforded white crystals (0.57 g, 50%), recrystallized from heptane: ^1H NMR δ 7.35, 7.0 (AA'BB', 8, ar), 6.75 (AB, 2, H12, H13), 5.4 (s, 2, H9, H10), 2.7 (t, 4, $OCOCH_2$), 2.4 (m, 4, $CH_2\beta$), 1.3 (m, CH_2), 0.95 (m, CH_3); mp 122.6 °C. Anal. Calcd for $C_{44}H_{58}O_4$ MW 650.94: C, 81.18; H, 8.98. Found: C, 81.27; H, 9.18.

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