Synthesis of Areno-Condensed [24]Annulenes

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[24]Annulenes condensed with three phenanthrene units (**11a–d**) or with three chrysene ring systems (**22**) were prepared by multi-step syntheses. The cyclic condensation reaction in the final step led to highly symmetrical compounds. Long flexible alkoxy groups attached to the periphery enhance the solubility and give rise to a strong aggregation of the molecules which was observed in solution by NMR and fluorescence excitation spectroscopy, and in the pure state by the detection of liquid crystalline phases in differential scanning calorimetry and polarization microscopy.

Introduction

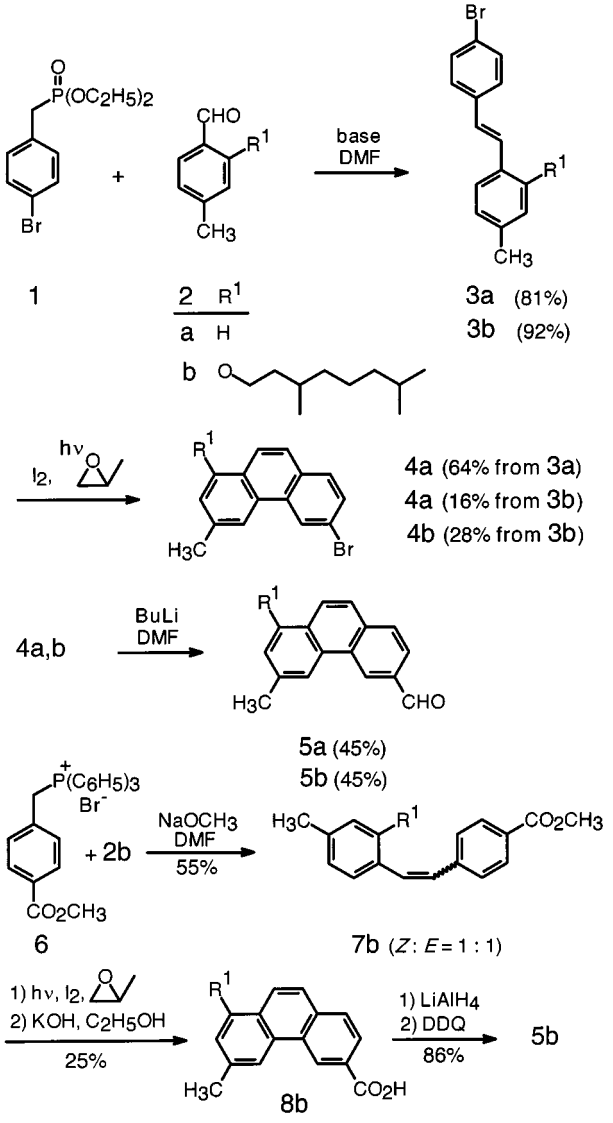
Annulenes are a fascinating class of compounds in theoretical as well as in synthetic chemistry.[1] Higher [*n*]annulenes ($n \geq 10$), however, are not suitable for applications in materials science because their thermal stability is much too low. Condensation of the macrocyclic conjugated ring with several aromatic ring systems, such as benzene,[2–4] naphthalene,[5] phenanthrene[5–10] or pyrene[11] stabilizes the compounds to such an extent that the decomposition temperature often rises above 300 °C.

Provided that the nonplanar macrocyclic rings in the tri- or tetraarenoannulenes show a fast ring inversion, these molecules represent discotic mesogens for the generation of columnar phases of liquid crystals. Previously, we concentrated on this topic by the preparation and investigation of triareno[18]annulenes. The hitherto obtained tetraareno[24]annulenes proved to adopt an S_4 conformation, did not show ring inversion and did not form LC phases.[6] Thus, we decided to synthesize and study [24]annulenes condensed with three arene units.

Results and Discussion

Syntheses

The synthetic sequence for the preparation of the triphenanthro[3,4,4a,4b,5,6-*abcde*:3,4,4a,4b,5,6-*ijklm*:3,4,4a,4b,5,6-*qrstu*]cyclotetraeicosenes (**11a–d**) started with diethyl 4-bromobenzylphosphonate (**1**) and the substituted benzaldehydes **2a,b**. Long, flexible alkoxy side chains guarantee an enhanced solubility and, moreover, they are a precondition for the formation of mesophases. The Wittig-Horner reaction of **1** and **2a,b** gave high yields of the stilbenes **3a,b** which, at thermodynamic equilibrium, are present with more than 95% of the (*E*) configuration. Irradiation ($\lambda \geq 270$ nm) led to the phenanthrenes **4a,b** via the photochemical $E \rightarrow Z$ isomerization and a subsequent oxidative cyclization. Iodine was used as the oxidant and methyloxirane as a scavenger for hydrogen iodide.[12] A ring closure **3b** → **4a** by the elimination of 3,7-dimethyloctanol competes with the reaction **3b** → **4b**. The yields shown in Scheme 1 reveal a low regioselectivity of the photocyclization.



Scheme 1. Preparation of the phenanthrene carbaldehydes **5a,b**

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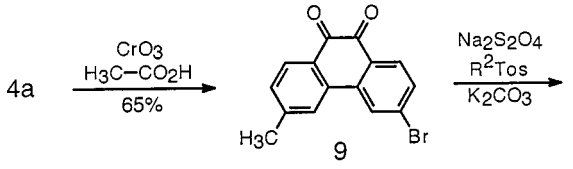
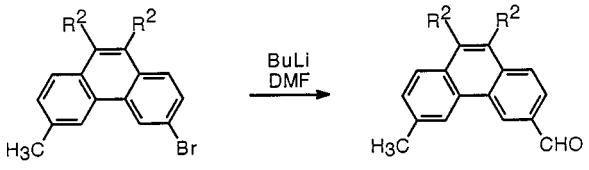
The bromo compounds **4a,b** were transformed to the aldehydes **5a,b** by a Bouveault reaction. The overall yield for **1** → **5** amounted to 23.3% for **5a** and 11.6% for **5b** We therefore tried another route for the preparation of **5b** starting with the phosphonium salt **6** and the aldehyde **2b**. The Wittig reaction yielded a 1:1 mixture of (*Z*)- and (*E*)-stilbene **7b**. Subsequent photocyclization and ester hydrolysis gave the carboxylic acid **8b**, which was reduced with $LiAlH_4$ to the primary alcohol and oxidized in situ with DDQ to the aldehyde **5b**. Due to the low yield of the photocyclization, the overall yield of this variant was virtually the same as in the original procedure (11.8%).

A larger number of alkoxy groups could be introduced by the oxidation of **4a** to the 9,10-phenanthrenequinone **9** and reductive alkylation of **9** to **4c,d** (Scheme 2) Replacement of the bromo substituent by the formyl group gave the phenanthrene carbaldehydes **5c,d**.



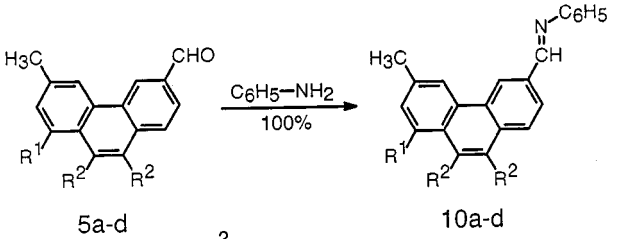


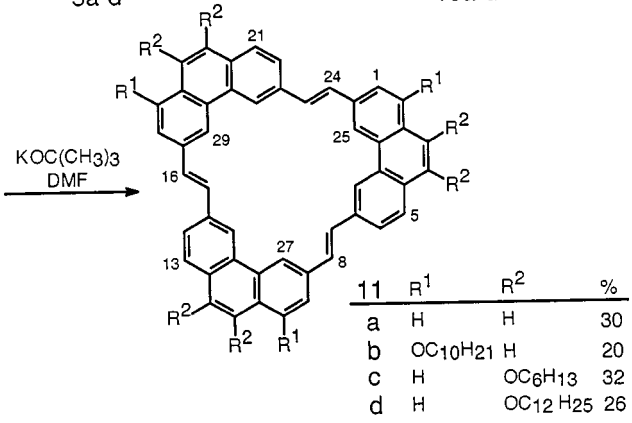
4	R^2	%
c	OC_6H_{13}	22
d	$OC_{12}H_{25}$	33

Scheme 2. Preparation of the phenanthrene carbaldehydes **5c,d**

The aldehydes **5a−d** were transformed in a quantitative reaction with aniline to the *N*-phenyl imines **10a−d**. Finally, the target compounds **11a−d** were obtained by a threefold cyclic condensation of **10a−d** in a strongly alkaline medium (Scheme 3). The process is highly *trans* selective; there were no indications of a *cis* configuration in the ^1H NMR spectra of the triphenanthro[24]annulenes **11a−d**.

The synthesis of a [24]annulene condensed with three chrysene units is shown in Scheme 4. The aldehyde **12** was transformed via the alcohol **13** to the phosphonium salt **14**. Bromination of 2-bromo-1-methylnaphthalene (**15**) with NBS gave the dibromide **16**, which yielded the naphthaldehyde **17** upon reaction with 2-nitropropane in an alkaline medium. The Wittig reaction of **14** and **17** gave the 1,2-diarylpropene **18** in high yields. The *Z*/*E* ratio of 1:3 was inconsequential because the following oxidative photocyclization **18** → **19** is based on the photoisomerization of *E* → *Z*. The obtained chrysene **19** was subjected to a Bouveault formylation to the aldehyde **20**. The quantitatively formed *N*-phenylimine **21** gave the target compound **22** in the final step. The yield of the threefold cyclocondensation, a variant of the Siegrist reaction,[13] was poor; nevertheless, the process represents an easy access to the 24-membered





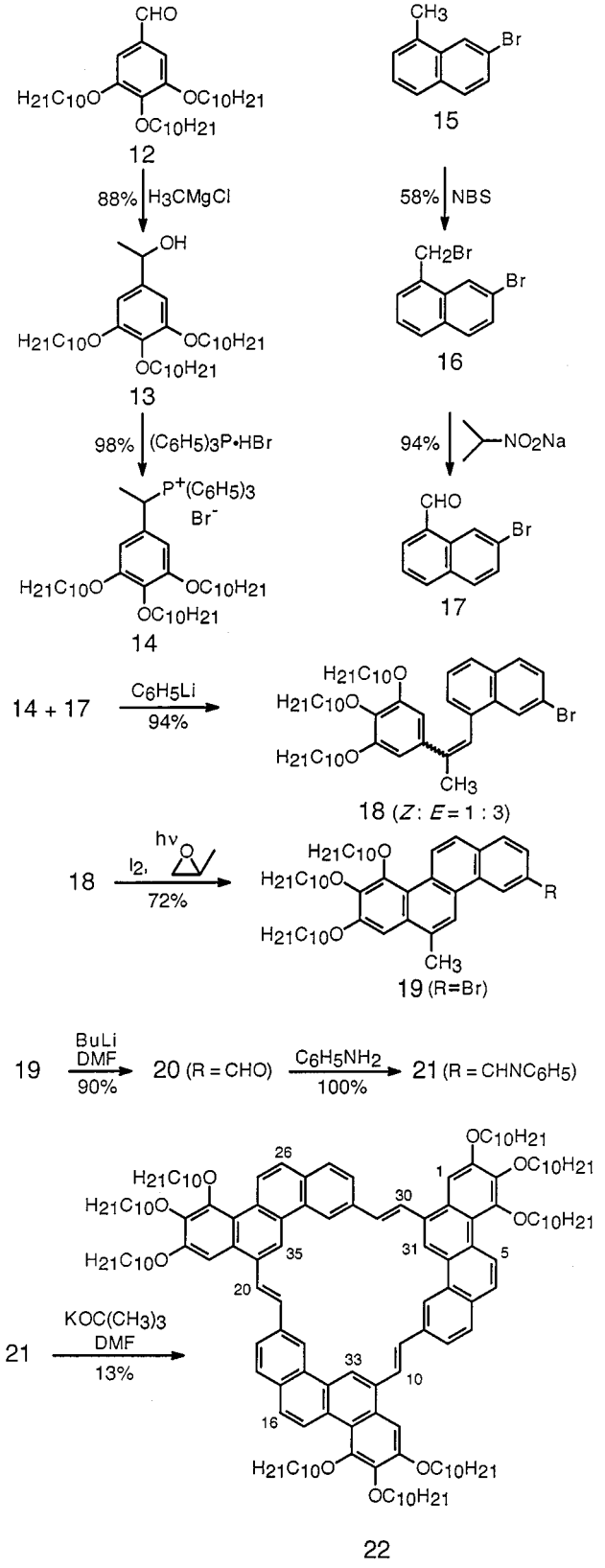
11	R^1	R^2	%
a	H	H	30
b	$OC_{10}H_{21}$	H	20
c	H	OC_6H_{13}	32
d	H	$OC_{12}H_{25}$	26

Scheme 3. Preparation of the triphenanthro[24]annulenes **11a−d**

ring. Linear condensation products could be easily separated by chromatography on a column filled with a layer of SiO_2 and a layer of basic Al_2O_3 as they contain polar *N*-phenylimine end groups.

Characterization of the [24]Annulenes

According to the synthetic procedure, the compounds **11a−d** and **22** have C_3 axes. Moreover, **11a**, **11c** and **11d** have — due to the conformational dynamics — three C_2 axes perpendicular to C_3. The ring systems of all five molecules appear to be planar on the NMR timescale: the *gem* OCH_2 protons of **11a,c,d** and **22** are enantiotopic in the ^1H NMR spectra at room temperature. We have not yet been able to detect a frozen nonplanar structure as in the tetraphenanthro[24]annulenes studied before.[6] Obviously, nonplanar C_3 conformations, which have to be accepted according to earlier force field calculations,[6] show an inversion of the central 24-membered ring and a rotation around the C−C bonds between the aromatic and the olefinic moieties. Both processes are fast in terms of the NMR timescale. Consequently, the olefinic protons 7-H and 8-H (Scheme 3) are as chemically equivalent as the proton pairs 1-H/ 6-H, 2-H/ 5-H and 25-H/ 26-H are in **11a,c,d**. The unsymmetrical substitution of the ring system in **11b** and **22** reduces the de-facto symmetry from D_{3h} to C_{3h}. Moreover, the side chains of **11b** contain asymmetric C atoms so that the molecules **11b** finally have C_3 or C_1 symmetry. The *gem* OCH_2 protons of **11b** are isochronous by chance. The low solubility permitted the measurement of ^{13}C NMR spectra only for **11b**, **11d** and **22**. The results given in the Experimental Section are in accordance with the symmetry statements.



Scheme 4. Preparation of the trichryseno[24]annulene **22**

The molecules **11a–d** and **22** can be regarded as aromatic "islands" which are combined by olefinic "bridges". The *trans* configuration of the olefinic group is proved by the symmetry — a threefold *cis* configuration can be excluded for steric reasons. Moreover, the less symmetrical compounds **11b** and **22** exhibit olefinic AB spin patterns in the ^{1}H NMR spectra with ^3J = 16.0 ± 0.1 Hz. There is no indication of a macrocyclic ring current. The outer and inner olefinic protons exchange quickly (δ = 7.65 ± 0.35). The aromatic protons are fixed in outer or inner positions, but their chemical shifts correspond to the aromatic system. The protons 25-H in **11a–d** and 31-H in **22**, for example, have their resonances at δ = 8.9 ± 0.5, a value which is typical for the bay region of phenanthrenes (chrysenes).

The aggregation of the disk-like molecules is a point of special interest. The aggregation in solution is shown here by the dependence of the NMR and fluorescence excitation spectra on the concentration. A 6×10^{-4} M solution of **11c** in $CDCl_3$, for example, gives a normally resolved ^{1}H NMR spectrum, whereas the corresponding measurement in a 6×10^{-3} M solution leads to broad, unresolved resonance signals; the singlet signal for 25-H at δ = 9.31 has, for example, a half-width of 4.9 Hz in the 6×10^{-4} M solution and a half width of 121.5 Hz in the 6×10^{-3} M solution (400 MHz, 21 °C). Even more striking are the fluorescence excitation spectra. That for **11c** is shown in Figure 1. The measurement in the apolar solvent cyclohexane, which is particularly prone to the formation of aggregates, leads to completely different spectra for 10^{-4}, $10^{-5}$and 10^{-6} M solutions. The spectrum of the 10^{-6} M solution corresponds to the absorption spectrum (λ_{max} = 365 nm, ε = 190000 L·mol^{-1}·cm^{-1}). The spectra at 10^{-5} and 10^{-4} mol·L^{-1} are totally different and reveal that the aggregation is more complex than a mere monomer-dimer equilibrium (the maximum at 378 nm for 10^{-5} mol·L^{-1} is not present either at 10^{-4} or at 10^{-6} mol·L^{-1}).

The parent system **11a** and the compound **11b** with three alkoxy chains do not form LC phases. Differential scanning calorimetry of **11c** shows phase transitions at 5.3, 65.5, 142.6 and 155 °C (onset temperatures) in the second heating curve. An isotropic phase could not be detected until 300 °C was reached, at which point decomposition occurs. The textures observed in polarization microscopy at 88, 162 and 260 °C reveal the generation of LC phases; their exact characterization will be provided by small angle X-ray scattering experiments. Compound **11d** has a single mesophase between 26.2 and 69.0 °C and compound **22** shows an LC phase above 24.7 °C that starts to decompose above 300 °C.

Conclusions

The triphenanthro[24]annulenes **11a–d** and the trichryseno[24]annulene **22** can be prepared by threefold cyclic condensation reactions of the corresponding arenes **10a–d** and **21**, which bear *N*-phenylimino groups and methyl groups, respectively. Apart from π-π interactions, these disk-like compounds exhibit strong tendencies to aggregate in solution as well as in the pure state (thermotropic LC phases), provided that six long, flexible alkoxy chains (OC_6H_{13}, $OC_{10}H_{21}$, $OC_{12}H_{25}$) are attached to the periphery.

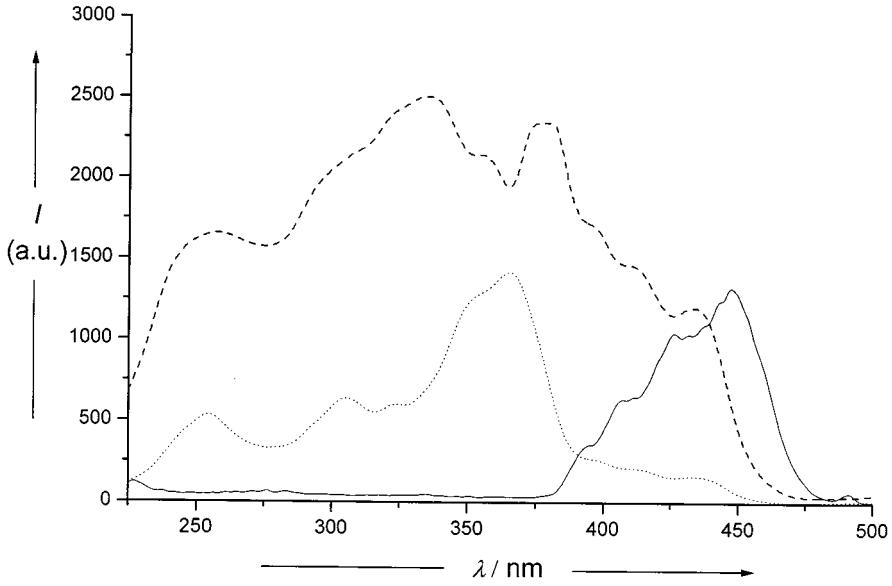


Figure 1. Fluorescence excitation spectra of **11c** ($\lambda_{observ.}$ = 505 nm) in cyclohexane: ····· 10^{-6} M, ---- 10^{-5} M, –– 10^{-4} M solution

Experimental Section

General: Melting points (uncorrected): Büchi apparatus. – IR: Beckman Acculab 4, KBr pellets or neat film. – Fluorescence: Hitachi spectrometer. – NMR: Bruker AM 400, $CDCl_3$ with TMS as internal standard. – MS: Varian MAT CH 7A and Finnigan MAT 95. – Differential scanning calorimetry: Perkin–Elmer DSC 7. – Polarization microscopy: Leitz Ortholux II, Mettler FP-52.

Diethyl 4-bromobenzylphosphonate (1): Prepared according to the literature.[14–16]

2-(3,7-Dimethyloctyloxy)-4-methylbenzaldehyde (2b): 1-Bromo-3,7-dimethyloctane (11.61 g, 52.5 mmol) was slowly dropped into a mixture of 4-methylsalicylaldehyde (6.81 g, 50.0 mmol),[17] KOH (2.81 g, 42.6 mmol), K_2CO_3 (1.03 g, 7.5 mmol), KI (100 mg) and Aliquat 336 (1.0 g) in ethylene glycol dimethyl ether (200 mL). The stirred mixture was kept under argon and refluxed for 1 day. The mixture was filtered and evaporated and the residue purified by column chromatography (8 × 8 cm SiO_2, CH_2Cl_2). Yield: 13.61 g (98%), viscous oil. – ^{1}H NMR ($CDCl_3$): δ = 0.85 (d, 6 H, CH_3), 0.94 (d, 3 H, CH_3), 1.23 (m, 6 H, CH_2), 1.55 (m, 3 H, CH_2 and CH), 1.85 (m, 1 H, CH), 2.37 (s, 3 H, CH_3), 4.07 (m, 2 H, OCH_2), 6.76 (d, 1 H, 3-H), 6.79 (dd, 1 H, 5-H), 7.70 (d, 1 H, 6-H), 10.41 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$): δ = 19.6, 22.2, 22.5, 22.6 (CH_3), 24.6, 35.9, 37.2, 39.1 (CH_2), 27.9, 29.8 (CH), 66.6 (OCH_2), 112.9 (C-3), 121.4 (C-5), 122.6 (C-1), 128.0 (C-6), 147.2 (C-4), 161.5 (C-2), 189.3 (CHO). – EI MS (70 eV): *m/z* (%) = 276 (98) [$M^{+\cdot}$], 136 (100), 108 (55), 57 (38), 43 (52). – $C_{18}H_{28}O_2$ (276.4): calcd. C 78.21, H 10.21; found C 78.00, H 10.07.

(*E*)-1-(4-Bromophenyl)-2-(4-methylphenyl)ethene (3a): Prepared according to the literature.[18] Yield 81%, m.p. 211 °C (literature: m.p. 211 °C).

(*E*)-1-(4-Bromophenyl)-2-[2-(3,7-dimethyloctyloxy)-4-methylphenyl]-ethene (3b): Aldehyde **2b** (9.95 g, 36.0 mmol) and **1** (11.06 g, 36.0 mmol) dissolved in DMF (200 mL) were dropped into a suspension of KOH (23.76 g, 423 mmol) in DMF (150 mL). After 12 h stirring at ambient temperature, the mixture was kept for 1 h at 50 °C and then poured into 200 g ice/200 mL diethyl ether. The layers were separated and the aqueous layer was extracted with diethyl ether (2 × 100 mL). The combined organic phases were washed with saturated NaCl, dried over $MgSO_4$ and concentrated. The oily residue was purified by column chromatography (6 × 10 cm SiO_2, toluene). Yield 14.18 g (92%) of a light yellow oil, which crystallized after a few days at 5 °C. – ^{1}H NMR ($CDCl_3$): δ = 0.88 (d, 6 H, CH_3), 0.99 (d, 3 H, CH_3), 1.27 (m, 6 H, CH_2), 1.63 (m, 3 H, CH_2 and CH), 1.91 (m, 1 H, CH), 2.36 (s, 3 H, CH_3), 4.05 (m, 2 H, OCH_2), 6.72 (d, 1 H), 6.77 (dd, 1 H), 7.40 (m, 1 H, aromat., ABC spin pattern), 7.03 (d, ^3J = 16.5 Hz, 1 H), 7.40 (d, 1 H, olefin, AB system), 7.40 (m, 4 H, aromat., AA′BB′ system). – ^{13}C NMR ($CDCl_3$): δ = 19.7, 21.7, 22.6, 22.7 (CH_3), 24.8, 36.3, 37.4, 39.2 (CH_2), 28.0, 30.1 (CH), 66.7 (OCH_2), 112.8, 121.3, 124.6, 126.5, 126.6, 127.8, 131.6 (aromat. CH), 120.6, 123.2, 137.2, 139.1, 156.5 (aromat. and olefin. C_q). – EI MS (70 eV): *m/z* (%) = 430, 428 (35) [$M^{+\cdot}$] Br pattern, 290 (33), 288 (34), 108 (100). – $C_{25}H_{33}BrO$ (429.4): calcd. C 69.92, H 7.75; found C 69.69, H 7.72.

3-Bromo-6-methylphenanthrene (4a): Prepared and identified according to the literature.[19]

6-Bromo-1-(3,7-dimethyloctyloxy)-3-methylphenanthrene (4b): Compound **3b** (3.78 g, 8.8 mmol), iodine (2.35 g, 9.26 mmol) and methyloxirane (50 mL, 41.5 g, 714.5 mmol) were irradiated with a 450 W Hanovia middle pressure lamp with a Corex filter in 1900 mL of dry and degassed cyclohexane. Filtration through silica gel (8 × 8 cm) with toluene yielded a mixture of **4a** and **4b**, which was separated by column chromatography [40 × 3 cm SiO_2, petroleum ether (40–70 °C)]. The first fraction consisted of 0.38 g (16%) of **4a**, the second fraction of 1.04 g (28%) **4b** as a colorless oil. – ^{1}H NMR ($CDCl_3$): δ = 0.94 (d, 6 H, CH_3), 1.04 (d, 3 H, CH_3), 1.32 (m, 6 H, CH_2), 1.60 (m, 1 H, CH), 1.77 (m, 2 H, CH_2), 1.99 (m, 1 H, CH), 2.59 (s, 3 H, CH_3), 4.16 (m, 2 H, OCH_2), 6.83 (d, 1 H, 2-H), 7.58 (d, 1 H, 9-H), 7.63 (dd, 1 H, 7-H), 7.70 (d, 1 H, 8-H), 7.91 (d, 1 H, 4-H), 8.21 (d, 1 H, 10-H), 8.75 (d, 1 H, 5-H). – ^{13}C NMR ($CDCl_3$): δ = 19.8, 22.6, 22.6, 22.7 (CH_3), 24.7, 36.3, 37.4, 39.3 (CH_2), 28.0, 30.1 (CH), 66.8 (OCH_2), 109.0, 114.4, 121.1, 124.2, 125.9, 129.4, 129.9 (aromat. CH), 120.2, 121.7, 130.4, 130.9, 131.3, 137.0, 155.3 (aromat. C_q). – FD MS: *m/z* (%) = 428, 426 (100) [$M^{+\cdot}$] Br pattern. – HR-MS ($^{12}C_{25}{}^1H_{31}{}^{81}Br^{16}O$): calcd. 428.1538; found 428.1537.

6-Methylphenanthrene-3-carbaldehyde (5a): *n*-Butyllithium (32 mL, 80 mmol, 2.5 M in hexane) was added within 15 min. to **4a** (17.0 g, 63.0 mmol) in dry THF (300 mL) at −15 °C. After stirring for 1 h at 0 °C, 25 mL of DMF (23.6 g, 731 mmol) was added and the reaction was quenched with 50 mL of water after a further hour. The diethyl ether extract was carefully washed with the equivalent amount of water, dried and evaporated. Column chromatography (20 × 10 cm SiO_2, toluene) afforded 6.29 g (45%) of colorless needles; m.p. 126 °C. The identification of the product was performed by comparison with an authentic sample (m.p. 114−116 °C).[20]

8-(3,7-Dimethyloctyloxy)-6-methylanthracene-3-carbaldehyde (5b) by Bouveault reaction from 4b: This compound was prepared according to the procedure reported for **4b** above; yield 45%, m.p. 72 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.89 (d, 6 H, CH_3), 1.01 (d, 3 H, CH_3), 1.29 (m, 6 H, CH_2), 1.56 (m, 1 H, CH), 1.75 (m, 2 H, CH_2), 1.98 (m, 1 H, CH), 2.59 (s, 3 H, CH_3), 4.15 (m, 2 H, OCH_2), 6.83 (d, 1 H, 7-H), 7.62 (d, 1 H, 10-H), 7.88 (d, 1 H, 1-H), 7.98 (dd, 1 H, 2-H), 8.02 (d, 1 H, 5-H), 8.30 (d, 1 H, 9-H), 9.01 (d, 1 H, 4-H), 10.18 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 19.7, 22.6, 22.7, 22.7 (CH_3), 24.7, 36.1, 37.3, 39.2 (CH_2), 27.9, 30.0 (CH), 66.6 (OCH_2), 108.9, 114.2, 124.1, 124.5, 127.8, 129.1 (aromat. CH), 121.4, 129.3, 131.5, 133.7, 136.2, 137.8, 155.2 (aromat. C_q), 192.3 (CHO). − EI MS: *m*/*z* (%) = 376 (50) [$M^{+\cdot}$], 236 (100). − $C_{26}H_{32}O_2$ (376.6): calcd. C 82.93, H 8.57; found C 82.93, H 8.57.

Methyl (*Z*)- and (*E*)-4-{2-[2-(3,7-Dimethyloctyloxy)-4-methylphenyl]ethenyl}benzoate (7b): Phosphonium bromide **6**[21] (6.29 g, 12.8 mmol) and **2b** (3.62 g, 13.1 mmol) dissolved in 100 mL of DMF and 50 mL of methanol were treated at room temperature with Na (0.69 g, 30.0 mmol) in 100 mL of methanol. After 1 h stirring, the solvent was evaporated and the residue extracted with boiling hexane. The crude product was purified by column chromatography (12 × 8 cm SiO_2, toluene) to give 2.89 g (55%) of a colorless oil which consisted of a 1:1 mixture of (*E*)- and (*Z*)-**7b**. − FD-MS: *m*/*z* (%) = 408 (100) [$M^{+\cdot}$]. − $C_{27}H_{36}O_3$ (408.6): calcd. C 79.37, H 8.88; found C 79.31, H 8.88. Treatment of the mixture with I_2 in boiling toluene led to the thermodynamic equilibrium in which the (*E*) configuration strongly predominates.
(*E*)-**7b:** ^{1}H NMR ($CDCl_3$): δ = 0.84 (d, 6 H, CH_3), 0.96 (d, 3 H, CH_3), 1.24 (m, 6 H, CH_2), 1.58 (m, 3 H, CH_2 and CH), 1.90 (m, 1 H, CH), 2.34 (s, 3 H, CH_3), 3.90 (s, 3 H, OCH_3), 4.04 (m, 2 H, OCH_2), 6.71 (1 H), 6.76 (1 H), 7.46 (1 H, aromat. ABM spin pattern), 7.11 (1 H), 7.54 (1 H, olefin. AB system, ^3J = 16.5 Hz), 7.52 (2 H), 7.98 (2 H, aromat. AA′BB′ system). − ^{13}C NMR ($CDCl_3$): δ = 19.7, 21.7, 22.6, 22.7 (CH_3), 24.8, 36.3, 37.3, 39.2 (CH_2), 27.9, 30.1 (CH), 51.9 (OCH_3), 66.7 (OCH_2), 112.9, 121.4, 126.1, 126.4, 126.6, 126.7, 129.9 (aromat. and olefin. CH), 123.0, 128.7, 139.6, 142.9, 156.7 (aromat. C_q), 166.9 (CO, ester).

8-(3,7-Dimethyloctyloxy)-6-methylphenanthrene-3-carboxylic Acid (8b): The oxidative photocyclization was performed as described for the transformation **3b** → **4b** above Alkaline workup (KOH, ethanol) yielded 25% of carboxylic acid **8b**, which was directly transformed to the aldehyde **5b** by reduction to the primary alcohol with $LiAlH_4$ and subsequent oxidation with DDQ.[22] The yield of the process **8b** → **5b** was 86%. The total yield on the ester route **2b** → **7b** → **8b** → **5b**, however (11.8%) was not much higher than on the route **2b** → **3b** → **4b** → **5b** (11.6%).

3-Bromo-6-methyl-9,10-phenanthrenequinone (9): Compound **4a** (10.0 g, 37.0 mmol) was treated in 100 mL of acetic acid (100%) with CrO_3 (10.0 g, 66.0 mmol) in 60 mL of aqueous acetic acid (60%). The mixture was stirred for 15 min. at room temperature and then kept for 1 h at 60 °C. After addition of water (200 mL), the precipitate was filtered off, washed with water, dried and recrystallized from toluene. Yield 7.15 g (65%), orange needles, m.p. 220 °C (decomposition). − ^{1}H NMR ($CDCl_3$): δ = 2.47 (s, 3 H, CH_3), 7.26 (d, 1 H), 7.54 (d, 1 H), 7.64 (d, 1 H), 8.00 (m, 3 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ =22.4 (CH_3), 124.6, 127.1, 130.9, 131.2, 131.7, 132.6 (aromat. CH), 129.0, 129.7, 131.8, 134.3, 137.3, 147.6 (aromat. C_q), 179.0, 179.6 (CO). − EI-MS (70 eV): *m*/*z* (%) = 302, 300 (27) [$M^{+\cdot}$], Br isotope pattern, 274 (97), 272 (100). − $C_{15}H_9BrO_2$ (301.1): calcd. C 59.83, H 3.01; found C 60.11, H 3.51.

3-Bromo-9,10-dihexyloxy-6-methylphenanthrene (4c): Quinone **9** (4.0 g, 13.3 mmol), $Na_2S_2O_4$ (4.0 g, 23.0 mmol), K_2CO_3 (4.0 g), KI (100 mg) and hexyl *p*-toluenesulfonate (6.8 g, 26.6 mmol) were refluxed under argon in 80 mL of acetone for 7 days. Evaporation of the solvent led to a residue, which was purified by column chromatography (40 × 4 cm SiO_2, petroleum ether (40−70)/toluene 4:1). The first fraction contained 1.36 g (22%) of **4c**, m.p. 67 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.91 (t, 6 H, CH_3), 1.33−1.60 (m, 12 H, CH_2), 1.87 (m, 4 H, CH_2), 2.60 (s, 3 H, CH_3), 4.15 (m, 4 H, OCH_2), 7.45 (d, 1 H), 7.65 (d, 1 H), 8.06 (d, 1 H), 8.11 (d, 1 H), 8.30 (d, 1 H), 8.71 (d, 1 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 14.1, 21.9 (CH_3), 22.7, 26.0, 30.5, 31.8 (CH_2, superimposed), 73.6, 73.7 (OCH_2), 122.3, 124.1, 125.3, 129.1, 129.7, 135.7 (aromat. CH), 119.8, 122.4, 127.7, 127.9, 128.5, 129.8, 142.1, 143.7 (aromat. C_q). − FD-MS: *m*/*z* (%) = 472, 470 (100) [$M^{+\cdot}$], Br isotope pattern. − $C_{27}H_{35}BrO_2$ (471.5): calcd. C 68.78, H 7.48; found C 68.70, H 8.04.

3-Bromo-9,10-didodecyloxy-6-methylphenanthrene (4d): Prepared and purified as for the transformation **9** → **4c** above. Yield 33%, colorless oil. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (m, 6 H, CH_3), 1.20−1.70 (m, 36 H, CH_2), 1.75−1.95 (m, 4 H, CH_2), 2.59 (s, 3 H, CH_3), 4.10−4.25 (m, 4 H, OCH_2), 7.45 (d, 1 H), 7.65 (dd, 1 H), 8.08 (d, 1 H), 8.11 (d, 1 H), 8.31 (d, 1 H), 8.71 (d, 1 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 21.9 (CH_3), 22.7−32.0 (CH_2, superimposed), 73.6, 73.7 (OCH_2), 122.4, 124.1, 125.3, 129.1, 129.7, 135.7 (aromat. CH), 119.7, 122.3, 127.7, 127.9, 128.5, 129.7, 142.1, 143.6 (aromat. C_q). − FD MS: *m*/*z* (%) = 640, 638 (100) [$M^{+\cdot}$], Br isotope pattern. − $C_{39}H_{59}BrO_2$ (639.8): calcd. C 73.21, H 9.29; found C 73.40, H 9.14.

9,10-Dihexyloxy-6-methylphenanthrene-3-carbaldehyde (5c): Prepared as for the transformation **4a,b** → **5a,b**. The raw product was purified by column chromatography (SiO_2, toluene). Yield 66%; colorless waxy solid, m.p. 34 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (m, 6 H, CH_3), 1.20−1.60 (m, 12 H, CH_2), 1.80−2.00 (m, 4 H, CH_2), 2.61 (s, 3 H, CH_3), 4.15 (t, 2 H, OCH_2), 4.25 (t, 2 H, OCH_2), 7.49 (d, 1 H), 8.04 (d, 1 H), 8.16 (d, 1 H), 8.30 (d, 1 H), 8.47 (s, 1 H), 9.07 (s, 1 H, aromat. H), 10.21 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 21.9 (CH_3), 22.7, 25.9, 26.9, 30.4, 30.5, 31.7, 31.8 (CH_2, partly superimposed), 73.8, 73.8 (OCH_2), 122.5, 122.6, 123.1, 125.3, 126.9, 129.2 (aromat. CH), 127.7, 127.8, 129.0, 133.2, 134.1, 136.5, 142.0, 146.5 (aromat. C_q), 192.3 (CHO). − FD MS: *m*/*z* (%) = 420 (100) [$M^{+\cdot}$]. − $C_{28}H_{36}O_3$ (420.6): calcd. C 79.96, H 8.63; found C 79.99, H 8.53.

9,10-Didodecyloxy-6-methylphenanthrene-3-carbaldehyde (5d): Prepared and purified as for **5c** above. Yield 48%, colorless waxy solid, m.p. 65 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (m, 6 H, CH_3), 1.20−1.70 (m, 36 H, CH_2), 1.75−1.95 (m, 4 H, CH_2), 2.62 (s, 3 H, CH_3), 4.15 (t, 2 H, OCH_2), 4.25 (t, 2 H, OCH_2), 7.49 (d, 1 H), 8.04 (d, 1 H), 8.17 (d, 1 H), 8.31 (d, 1 H), 8.50, "s", 1 H, 9.09, "s", 1 H (aromat. CH), 10.23 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 22.0 (CH_3), 22.7−32.0 (CH_2), 73.8, 73.8 (OCH_2), 122.5, 122.6, 123.1, 125.4, 126.8, 129.2 (aromat. CH, superimposed),

127.7, 127.8, 129.0, 133.2, 134.1, 136.5, 142.0, 146.5 (aromat. C_q), 192.3 (CHO). − FD MS: *m/z* (%) = 588 (100) [$M^{+\cdot}$]. − $C_{40}H_{60}O_3$ (588.9): calcd. C 81.58, H 10.27; found C 81.50, H 10.15.

6-Methylphenanthrene-3-(*E*)-*N*-phenylcarbaldimine (10a): Aldehyde **5a** (617 mg, 2.8 mmol) and aniline (326 mg, 3.5 mmol) were kept at 75 °C for 6 h. A vacuum of 10^4 Pa aided the removal of the generated water. At the end of the reaction the pressure was reduced to 10^2 Pa to remove excess aniline. The residue consisted of analytically pure imine, a colorless waxy solid (827 mg, 100%). − ^{1}H NMR ($CDCl_3$): δ = 2.64 (s, 3 H, CH_3), 7.24 (m, 1 H, *p*-H, Phenyl), 7.32 (m, 2 H, *o*-H, Phenyl), 7.44 (m, 2 H, Phenyl), 7.65−7.83 (m, 4 H, 7-H, 8-H, 9-H, 10-H), 7.93 (d, 1 H, 1-H), 8.17 (dd, 1 H, 2-H), 8.56 (s, 1 H, 5-H), 8.70 (s, 1 H, CHN), 9.10 (s, 1 H, 4-H). − $C_{22}H_{17}N$ (295.4): calcd. C 89.46, H 5.80; found C 89.55, H 5.89.

8-(3,7-Dimethyloctyloxy)-6-methylphenanthrene-3-(*E*)-*N*-phenylcarbaldimine (10b): Prepared according to the procedure described for **10a**. Yield 100%; viscous oil which was used directly for the next step. − ^{1}H NMR ($CDCl_3$): δ = 0.87 (d, 6 H, CH_3), 1.00 (d, 3 H, CH_3), 1.37 (m, 6 H, CH_2), 1.77 (m, 3 H, CH_2 and CH), 1.98 (m, 1 H, CH), 2.61 (s, 3 H, CH_3), 4.18 (m, 2 H, OCH_2), 6.86 (d, 1 H, 7-H), 7.27 (m, 3 H, *o*-H and *p*-H, phenyl), 7.43 (m, 2 H-H, phenyl), 7.68 (d, 1 H, 10-H), 7.93 (d, 1 H, 1-H), 8.14 (d, 1 H, 5-H), 8.17 (dd, 1 H, 2-H), 8.26 (d, 1 H, 9-H), 8.70 (s, 1 H, CHN), 9.06 (d, 1 H, 4-H).

9,10-Dihexyloxy-6-methylphenanthrene-3-(*E*)-*N*-phenylcarbaldimine (10c): Prepared as for **10a** above. Yield 100%, viscous oil which was used directly for the next step. − ^{1}H NMR ($CDCl_3$): δ = 0.95 (m, 6 H, CH_3), 1.30−1.70 (m, 12 H, CH_2), 1.93 (m, 4 H, CH_2), 2.63 (s, 3 H, CH_3), 4.20 (t, 2 H, OCH_2), 4.26 (t, 2 H, OCH_2), 7.18−7.51 (m, 6 H, 7-H and Phenyl), 8.18 (d, 2 H, 1-H, 8-H), 8.31 (d, 1 H, 2-H), 8.54 (s, 1 H, 5-H), 8.70 (s, 1 H, CHN), 9.08 (s, 1 H, 4-H).

9,10-Didodecyloxy-6-methylphenanthrene-3-(*E*)-*N*-phenylcarbaldimine (10d): Prepared as for **10a** above; yield 100% viscous oil which was used directly for the next step. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (m, 6 H, CH_3), 1.20−1.70 (m, 36 H, CH_2), 1.91 (m, 4 H, CH_2), 2.62 (s, 3 H, CH_3), 4.18 (t, 2 H, OCH_2), 4.24 (t, 2 H, OCH_2), 7.22−7.50 (m, 6 H, 7-H and Phenyl), 8.15 (d, 1-H, 8-H), 8.18 (d, 1 H, 1-H), 8.53 (s, 1 H, 5-H), 8.70 (s, 1 H, CHN), 9.09 (s, 1 H, 4-H).

(7*E*,15*E*,23*E*)-Triphenanthro[3,4,4a,4b,5,6-*abcde*:3,4,4a,4b,5,6-*ijklm*:3,4,4a,4b,5,6-*qrstu*]cyclotetraeicosene (11a): Imine **10a** (780 mg, 2.64 mmol) was warmed under argon to 85 °C in dry DMF (100 mL), before KO*t*Bu (3.0 g, 2.67 mmol) was added quickly with vigorous stirring. After 3 h the reaction was quenched with of ice-cold water (200 mL). The ochre precipitate was filtered off and recrystallized from *p*-xylylene. − 162 mg (30%) of a yellow solid was obtained, m.p. > 230 °C. − ^{1}H NMR ($CDCl_3$): δ = 7.66 (s, 6 H, 7-H, 8-H, 15-H, 16-H, 23-H, 24-H), 7.80 (d, 6 H, 1-H, 6-H, 9-H, 14-H, 17-H, 22-H), 7.82 (s, 6 H, 3-H, 4-H, 11-H, 12-H, 19-H, 20-H), 7.86 (d, 6 H, 2-H, 5-H, 10-H, 13-H, 18-H, 21-H), 9.36 (s, 6 H, 25-H, 26-H, 27-H, 28-H, 30-H). − FD MS: *m/z* (%) = 606 (100) [$M^{+\cdot}$], 303 (56) [$M/2^+$]. − $C_{48}H_{30}$ (606.8): calcd. C 95.02, H 4.98; found C 94.85, H 4.72.

(7*E*,15*E*,23*E*)-2,10,18-Tris(3,7-dimethyloctyloxy)triphenanthro[3,4,4a,4b,5,6-*abcde*:3,4,4a,4b,5,6-*ijklm*:3,4,4a,4b,5,6-*qrstu*]cyclotetraeicosene (11b): Prepared as described above for **11a**, reaction time: 1 h. Yield: 20%, yellow solid which starts to decompose at 160 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.93 (d, 18 H, CH_3), 1.04 (d, 9 H, CH_3), 1.35 (m, 18 H, CH_2), 1.60 (m, 6 H), 1.77 (m, 3 H), 1.89 (m, 3 H, CH_2 and CH), 4.01 (m, 6 H, OCH_2), 6.88 (d, 3 H, 1-H, 9-H, 17-H), 7.35 (3 H), 7.48 (3 H, AB, ^3J = 16.1 Hz, 7-H, 8-H, 15-H, 16-H, 23-H, 24-H), 7.42 (d, 3 H, 4-H, 12-H, 20-H), 7.56 (dd, 3 H, 6-H, 14-H, 22-H), 7.65 (d, 3 H, 5-H, 13-H, 21-H), 7.90 (d, 3 H, 3-H, 11-H, 19-H), 8.52 (d, 3 H, 25-H, 27-H, 29-H), 9.00 (d, 3 H, 26-H, 28-H, 30-H). − ^{13}C NMR ($CDCl_3$): δ = 19.9, 22.7, 22.8 (CH_3), 24.8, 36.4, 37.5, 39.4 (CH_2), 28.1, 30.2 (CH), 66.6 (OCH_2), 104.3 (C-1), 114.3 (C-25), 120.7 (C-3), 120.9 (C-26), 123.6 (C-2a), 125.6 (C-6), 125.6 (C-4), 128.1 (C-7), 128.8 (C-5), 129.0 (C-8), 130.5, 131.6, 132.2, 135.1, 135.5 (C-4a, C-6a, C-24a, C-25a, C-25b), 155.5 (C-2). − FD MS: *m/z* (%) = 1076 (100) [M + H^+], 538 (43) [$M/2^+$]. − $C_{78}H_{90}O_3$ (1076): calcd. C 87.10, H 8.43; found C 86.83, H 8.39

(7*E*,15*E*,23*E*)-3,4,11,12,19,20-Hexahexyloxytriphenanthro[3,4,4a,4b,5,6-*abcde*:3,4,4a,4b,5,6-*ijklm*:3,4,4a,4b,5,6-*qrstu*]cyclotetraeicosene (11c): Prepared as described above for **11a**, reaction time: 10 min. The crude product was purified by chromatography (40 × 4 cm SiO_2, petroleum ether (40−70)/toluene, 2:1) and subsequent recrystallization from petroleum ether (40−70) to which acetone was added until the solution became turbid. Yield: 32%, yellow, fluorescent solid, m.p. 10.7 °C (DSC), clearing point >300 °C (decomposition). − ^{1}H NMR ($CDCl_3$): δ = 0.93 (t, 18 H, CH_3), 1.35−1.45 (m, 12 H, CH_2), 1.50−1.65 (m, 24 H, CH_2), 1.85−1.95 (m, 12 H, CH_2), 4.21 (t, 12 H, OCH_2), 7.80 (s, 6 H, 7-H, 8-H, 15-H, 16-H, 23-H, 24-H), 7.81 (d, 6 H, 1-H, 6-H, 9-H, 14-H, 17-H, 22-H), 8.19 (d, 6 H, 2-H, 5-H, 10-H, 13-H, 18-H, 21-H), 9.31 (s, 6 H, 25-H, 26-H, 27-H, 28-H, 29-H, 30-H). − FD MS: *m/z* (%) = 1208 (100) [M + H^+]. − $C_{84}H_{102}O_6$ (1207.7): calcd. C 83.54, H 8.51; found C 83.61, H 8.72.

(7*E*,15*E*,23*E*)-3,4,11,12,19,20-Hexadodecyloxytriphenanthro[3,4,4a,4b,5,6-*abcde*:3,4,4a,4b,5,6-*ijklm*:3,4,4a,4b,5,6-*qrstu*]cyclotetraeicosene (11d): Prepared as described above for **11a**, reaction time and purification as described for **11c**. Yield: 26% yellow, fluorescent solid, m.p. 27.2 °C (DSC), clearing point 70.0 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 18 H, CH_3), 1.20−1.50 (m, 96 H, CH_2), 1.50−1.65 (m, 24 H, CH_2), 1.85−1.95 (m, 12 H, CH_2), 4.18 (t, 12 H, OCH_2), 7.75 (s, 6 H, 7-H, 8-H, 15-H, 16-H, 23-H, 24-H), 7.76 (d, 6 H, 1-H, 6-H, 9-H, 14-H, 17-H, 22-H), 8.13 (d, 6 H, 2-H, 5-H, 10-H, 13-H, 18-H, 21-H), 9.25 (s, 6 H, 25-H, 26-H, 27-H, 28-H, 29-H, 30-H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.7−32.0 (CH_2), 73.7 (OCH_2), 120.8, 122.9, 125.3, 128.4, 129.0, 129.6, 134.5, 143.7. − FD MS: *m/z* (%) = 1714 (100) [M + H^+]. − $C_{120}H_{174}O_6$ (1713): calcd. C 84.15, H 10.24; found C 84.01, H 9.98.

1-(3,4,5-Tridecyloxyphenyl)ethanol (13): A solution (30 mL) of methylmagnesium chloride (20% in THF, 90.0 mmol) was added slowly at room temperature with stirring to a solution of 3,4,5-tri(decyloxy)benzaldehyde (16.1 g, 28.0 mmol) (**12**) in dry diethyl ether. After refluxing for 1 h, 100 g crushed ice was added and the layers were separated. The organic phase was extracted with diethyl ether (100 mL). The combined organic solutions were washed with saturated NaCl solution and dried over $MgSO_4$. Evaporation of the solvent yielded a colorless oil (14.56 g, 88%). − ^{1}H NMR ($CDCl_3$): δ = 0.86 (t, 9 H, CH_3), 1.25 (m, 42 H, CH_2), 1.44 (d, ^3J = 6.4 Hz, 3 H, CH_3), 1.77 (m, 6 H, CH_2), 3.93 (m, 6 H, OCH_2), 4.77 (q, ^3J = 6.4 Hz, 1 H, CH), 6.53 (s, 2 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 22.6, 26.1, 29.3, 29.3, 29.4, 29.5, 29.5, 29.6, 29.7, 30.3, 31.9 (CH_2, partly superimposed), 25.0 (CH_3), 69.2, 73.4 (OCH_2), 70.5 (CH), 104.0 (aromat. CH), 137.6, 141.1, 153.2 (aromat. C_q). − EI MS: *m/z* (%) = 590 (100) [$M^{+\cdot}$], 450 (32), 170 (25), 127 (46), 85 (25), 71 (55), 57 (75), 43 (82). − $C_{38}H_{70}O_4$ (591.0): calcd. C 77.23, H 11.94; found C 76.99, H 11.97.

1-(3,4,5-Tridecyloxyphenyl)ethyltriphenylphosphonium Bromide (14): Triphenylphosphine hydrobromide (4.53 g, 13.2 mmol) and **13**

(7.92 g, 13.4 mmol) were refluxed in chloroform (250 mL) for 10 h and the generated water was continuously removed by azeotropic distillation. Evaporation of the solvent led to an oily residue which was extracted with petroleum ether/diethyl ether (1:1). Separation of the volatile components at 20 °C and 10 Pa yielded the raw product (11.82 g, 98%) which could be used for the next reaction step without further purification. − − ^{1}H NMR ($CDCl_3$): δ = 0.85 (t, 9 H, CH_3), 1.24 (m, 42 H, CH_2), 1.62 (m, 4 H, CH_2), 1.70 (m, 2 H, CH_2), 1.79 [dd, ^3J(H,P) = 19.2 Hz, ^3J(H,H) = 7.0 Hz, 3 H, CH_3], 3.57 (m, 4 H, OCH_2), 3.85 (m, 2 H, OCH_2), 6.36 [d, ^4J(H,P) = 1.9 Hz, 2 H, aromat. H], 6.57 (m, 1 H, CH), 7.62 (m, 6 H), 7.73 (m 9 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ = 13.6, 13.6, 16.8 (CH_3), 22.2, 25.6, 28.7, 28.9, 29.1, 29.2, 29.8, 31.4 (CH_2, superimposed), 35.2 [d, ^1J(C,P) = 42.2 Hz, CH], 68.3, 72.8 (OCH_2), 108.0 [d, ^3J(C,P) = 5.3 Hz, aromat. CH], 117.3 [d, ^1J(C,P) = 82.4 Hz, C_q], 127.6 [d, ^2J(C,P) = 5.8 Hz, C_q], 129.6, 134.3, 134.4 (aromat. CH), 137.4 (C_qO), 152.6 [d, ^4J(C,P) = 2.6 Hz, C_qO].

7-Bromo-1-bromomethylnaphthalene (16): 7-Bromo-1-methylnaphthalene (**15**) (7.96 g, 36.0 mmol), NBS (6.41 g, 36.0 mmol), azobisisobutyronitrile (100 mg) and dibenzoylperoxide (100 mg) were refluxed in CCl_4 (50 mL) for 10 h. The precipitated succinimide was filtered off at 0 °C and the solution concentrated until colorless crystals were formed; yield 6.29 g (58%), m.p. 108 °C. − ^{1}H NMR ($CDCl_3$): δ = 4.88 (s, 2 H, CH_2), 7.40 (dd, 1 H, 3-H), 7.56 (m, 2 H, 2-H, 6-H), 7.76 (m, 2 H, 4-H, 5-H), 8.28 (d, 1 H, 8-H). − ^{13}C NMR ($CDCl_3$): δ = 31.0 (CH_2), 121.0 (C-7), 125.8, 126.2, 128.6, 129.6, 129.7, 130.4 (aromat. CH), 132.2, 132.4, 132.6 (aromat. C_q). − EI MS (70 eV): *m/z* (%) = 302/300/298 (15) [$M^{+\cdot}$], Br_2 pattern, 221 (97), 219 (100), 139 (53). − $C_{11}H_8Br_2$ (300.0): calcd. C 44.04, H 2.69; found C 44.08, H 2.59.

7-Bromo-1-naphthaldehyde (17): To a solution of sodium (0.40 g, 17.4 mmol) in dry methanol (20 mL) was added 2-nitropropane (1.5 mL, 1.49 g, 16.7 mmol) with stirring. A suspension of **16** (3.30 g, 11.0 mmol) in methanol (120 mL) was added and the mixture stirred for 6 days at room temperature in the dark. The solvent was removed and the residue treated with 100 mL of water and 100 mL of diethyl ether. The phases were separated and the water layer extracted with 50 mL of diethyl ether. The combined organic phases were extracted with sodium hydroxide (20 mL of 10% solution), washed with a saturated solution of NaCl and dried over $MgSO_4$. Concentration of the solution yielded 2.42 g (94%) of yellowish crystals, m.p. 112 °C. − ^{1}H NMR ($CDCl_3$): δ = 7.64 (dd, 1 H, 3-H), 7.66 (dd, 1 H, 6-H), 7.77 (d, 1 H, 5-H), 7.99 (dd, 1 H, 2-H or 4-H), 8.05 (dd, 1 H, 2-H or 4-H), 9.48 (d, 1 H, 8-H), 10.30 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 124.1 (C-7), 125.2, 127.5, 129.7, 130.5, 135.0, 137.7 (aromat. CH), 130.3, 131.1, 132.0 (aromat. C_q), 193.0 (CHO). − EI MS (70 eV): *m/z* (%) = 236/234 (69) [$M^{+\cdot}$], Br pattern, 208 (28), 206 (28), 155 (43), 127 (100). − $C_{11}H_7BrO$ (235.1): calcd. C 56.20, H 3.00, Br 33.99; found C 56.41, H 2.99, Br 33.69.

(*Z*/*E*)-1-(7-Bromonaphth-1-yl)-2-(3,4,5-tridecyloxyphenyl)propene (18): Phenyllithium (6.5 mL, 13.0 mmol, 2 M in THF) was added with a syringe to **14** (11.76 g, 12.8 mmol) dissolved in dry THF (100 mL) at 0 °C under argon. The deep red solution was warmed to room temperature and stirred for 10 min. before **16** (2.28 g, 9.7 mmol) in THF (50 mL) was added dropwise. After refluxing for 2 h, water (10 mL) was added, the solvent evaporated and the residue dissolved in diethyl ether (100 mL). The solution was washed with water (100 mL), dried over $MgSO_4$ and concentrated. Column filtration (10 × 12 cm silica gel, petroleum ether 50−80 °C/toluene 3:1) yielded 7.88 g (94%) of a colorless oil which started to crystallize after a few days at 0 °C. The *Z*/*E* ratio of 1:3 was determined by ^{1}H NMR spectroscopy. − FD MS: *m/z* (%) = 793/791 (96) [$M^{+\cdot}$], Br pattern, 574 (100). − $C_{49}H_{75}BrO_3$ (792.0): calcd. C 74.31, H 9.54, Br 10.09; found C 74.20, H 9.55, Br 10.53.

(*E*)-18: ^{1}H NMR ($CDCl_3$): δ = 0.89 (m, 9 H, CH_3), 1.28 (m, 42 H, CH_2), 1.82 (m, 6 H, CH_2), 2.10 (d, 3 H, CH_3), 4.08 (m, 6 H, OCH_2), 6.84 (s, 2 H, aromat. H), 7.14 (m, 1 H, olefin. H), 7.19 (dd, 1 H), 7.58 (m, 4 H), 8.17 (d, 1 H, aromat. H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 17.6 (CH_3), 22.7, 26.1, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 30.4, 31.9 (CH_2 partly superimposed), 69.3, 73.5 (OCH_2), 105.1 (aromat. CH), 120.1 (C_q), 123.9, 125.7, 127.0, 127.5, 127.6, 129.1, 130.0 (aromat. and olefin. CH), 132.0, 133.3, 135.1, 138.0, 138.3, 139.7, 153.0 (C_q).

9-Bromo-2,3,4-tridecyloxy-12-methylchrysene (19): Compound **18** (7.11 g, 8.98 mmol) and iodine (2.64 g, 10.4 mmol) were dissolved in a mixture of cyclohexane (1900 mL) and methyloxirane (50 mL) and irradiated with a 450 W Hanovia middle pressure lamp through a Corex filter. After 50 h the solution was filtered through a column filled with Al_2O_3 (4 × 10 cm, CH_2Cl_2). Recrystallization of the residue from petroleum ether (40−70)/ethanol (1:1) yielded 5.08 g (72%) of a colorless solid, m.p. 64 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, 9 H, CH_3), 1.28 (m, 42 H, CH_2), 1.90 (m, 6 H, CH_2), 2.79 (s, 3 H, CH_3), 4.03 (t, 2 H, OCH_2), 4.16 (m, 4 H, OCH_2), 7.22 (s, 1 H, 1-H), 7.63 (dd, 1 H, 8-H), 7.78 (d, 1 H, 7-H), 7.79 (d, 1 H, 6-H), 8.36 (s, 1 H, 11-H), 8.85 (d, 1 H, 10-H), 9.70 (d, 1 H, 5-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 21.3 (CH_3), 22.7, 26.3, 29.4, 29.5, 29.6, 29.7, 29.8, 30.4, 30.6, 31.9 (CH_2, superimposed), 68.6, 74.1, 74.2 (OCH_2), 101.8, 121.2, 125.0, 125.8, 126.2, 128.9, 129.6 (aromat. CH), 120.1, 120.2, 126.4, 128.0, 130.0, 130.2, 131.5, 132.5, 142.7, 152.1, 152.7 (aromat. C_q). − FD MS: *m/z* (%) = 791/789 (100) [$M^{+\cdot}$], Br pattern. − $C_{49}H_{73}BrO_3$ (790.0): calcd. C 74.50, H 9.31, Br 10.11; found C 74.54, H 9.22, Br 9.84.

8,9,10-Tridecyloxy-6-methylchrysene-3-carbaldehyde (20): A solution of **19** (4.90 g, 6.2 mmol) in diethyl ether (200 mL) was purged with argon and cooled to − 10 °C before a solution of *n*-butyllithium (6.0 mL, 9.6 mmol, 1.6 M in hexane) was added. After stirring for 0.5 h, dry DMF (3 mL, 39.0 mmol) was added and the reaction mixture slowly warmed to room temperature. Neutralization was performed with H_2O (50 mL), 2 M HCl (50 mL) and subsequent treatment with a saturated aqueous $NaHCO_3$ solution (50 mL). The organic layer was dried over $MgSO_4$ and purified by column filtration (6 × 8 cm SiO_2, toluene). The obtained yellow compound was recrystallized from petroleum ether (40−70)/ethanol (10:1). Yield 4.12 g (90%), m.p. 54 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 9 H, CH_3), 1.27 (m, 42 H, CH_2), 1.91 (m, 6 H, CH_2), 2.82 (s, 3 H, CH_3), 4.06 (t, 2 H, OCH_2), 4.18 (m, 4 H, OCH_2), 7.24 (s, 1 H, 7-H), 7.88 (d, 1 H, 12-H), 7.99 (d, 1 H, 1-H), 8.04 (dd, 1 H, 2-H), 8.53 (s, 1 H, 5-H), 9.21 (d, 1 H, 4-H), 9.85 (d, 1 H, 11-H), 10.26 (s, 1 H, CHO). − ^{13}C NMR ($CDCl_3$): δ = 14.2, 21.4 (CH_3), 22.7, 26.3, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 30.5, 30.6, 32.0 (CH_2, partly superimposed), 68.5, 74.3 (OCH_2), 101.7, 121.1, 123.9, 125.1, 128.5, 129.0, 129.2 (aromat. CH), 120.0, 128.0, 128.0, 129.5, 130.2, 133.3, 133.8, 135.2, 142.8, 152.0, 152.8 (aromat. C_q), 192.7 (CHO). − FD MS: *m/z* (%) = 739 (100) [$M^{+\bullet}$]. − $C_{50}H_{74}O_4$ (739.1): calcd. C 81.25, H 10.09; found C 80.99, H 10.28.

(*E*)-8,9,10-Tridecyloxy-6-methylchrysene-3-*N*-phenylcarbaldimine (21): Aldehyde **20** (3.70 g, 5.0 mmol) and aniline (0.70 g, 7.5 mmol) were stirred for 2 h at 60 °C. The generated water was removed several times by applying a vacuum of 0.1 Pa. The reaction mixture was then dissolved in boiling ethanol/chloroform (10:1). On cooling, beige crystals precipitated (4.07 g, 100%), m.p. 82 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.90 (t, 9 H, CH_3), 1.29 (m, 42 H, CH_2), 1.93

(m, 6 H, CH_2), 2.82 (s, 3 H, CH_3), 4.08 (t, 2 H, OCH_2), 4.18 (m, 4 H, OCH_2), 7.24 (s, 1 H, 7-H), 7.31 (m, 3 H, *o*-H, *p*-H, Phenyl), 7.45 (m, 2 H, Phenyl), 7.89 (d, 1 H, 12-H), 8.00 (d, 1 H, 1-H), 8.20 (dd, 1 H, 2-H), 8.57 (s, 1 H, 5-H), 8.74 (s, 1 H, CHN), 9.14 (d, 1 H, 4-H), 9.79 (d, 1 H, 11-H). − ^{13}C NMR ($CDCl_3$): δ = 14.1, 21.3 (CH_3), 22.7, 26.2, 29.4, 29.5, 29.6, 29.7, 30.4, 30.5, 31.9 (CH_2, partly superimposed), 68.4, 74.2 (OCH_2), 101.6, 121.0, 121.4, 124.5, 125.3, 125.9, 127.4, 128.6, 129.2 (aromat. CH), 120.1, 127.7, 127.8, 129.8, 130.0, 132.6, 133.4, 133.7, 142.5, 152.0, 152.3, 152.5 (aromat. C_q), 161.0 (CHN). − FD MS: *m/z* (%) = 814 (100) [M^+]. − $C_{56}H_{79}NO_3$ (814.3): calcd. C 82.61, H 9.78, N 1.72; found C 82.64, H 9.85, N 1.69.

(9*E*,19*E*,29*E*)-2,3,4,12,13,14,22,23,24-Nonakis(decyloxy)trichryseno[3,4,4a,4b,5,6-*abcde*:3,4,4a,4b,5,6-*ijklm*:3,4,4a,4b,5,6-*qrstu*]cyclotetraeicosene (22): Imine **21** (2.04 g, 2.50 mmol) in degassed DMF (350 mL) was heated under argon to 80−90 °C; KO*t*Bu (2.81 g, 25.04 mmol) was added to the vigorously stirred solution. After 30−40 min. the mixture was cooled to 0 °C and water (400 mL) was added. The brown-yellow precipitate was collected, washed with water and methanol, dried and filtered with petroleum ether (40−70)/dichloromethane (1:1) through a column containing SiO_2 (6 × 8 cm) and basic Al_2O_3 (2 × 8 cm). Recrystallization from acetone/dichloromethane/*n*-hexane (30:3:1) yielded 243 mg (13%) of a yellow solid, which formed an LC phase at 24.7 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.89 (m, 27 H, CH_3), 1.30 (m, 114 H, CH_2), 1.64 (m, 12 H, CH_2), 1.93 (m, 18 H, CH_2), 3.95 (t, 6 H, 4-OCH_2), 4.10 (t, 6 H, 2-OCH_2), 4.21 (t, 6 H, 3-OCH_2), 7.30 (s, 3 H, 1-H, 11-H, 21-H), 7.66 (d, 3 H, 6-H, 16-H, 26-H), 7.79 (d, ^3J = 15.9 Hz, 3 H, 10-H, 20-H, 30-H), 7.93 (d, 3 H, 7-H, 17-H, 27-H), 8.00 (d, ^3J = 15.9 Hz, 3 H, 9-H, 19-H, 29-H), 8.06 (dd, 3 H, 8-H, 18-H, 28-H), 8.98 (d, 3 H, 32-H, 34-H, 36-H), 9.17 (s, 3 H, 31-H, 33-H, 35-H), 9.40 (d, 3 H, 5-H, 15-H, 25-H); the signal correlation is based on NOE measurements. − ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3), 22.7, 22.7, 26.3, 26.4, 26.5, 29.4, 29.5, 29.6, 29.7, 29.7, 29.8, 29.8, 29.9, 29.9, 30.5, 30.8, 31.9, 32.0 (CH_2, partly superimposed), 68.2 (2-OCH_2), 73.7 (4-OCH_2), 74.1 (3-OCH_2), 100.5 (C-1), 117.6 (C-31), 120.3 (C-4a), 121.8 (C-8), 124.4 (C-32), 125.3 (C-10), 125.7 (C-5), 126.0 (C-6), 128.7 (C-7), 130.4 (C-9), 127.2, 128.6, 128.6, 130.9, 131.1, 131.2, 135.5 (C-4b, C-6a, C-8a, C-10a, C-10b, C-31a, C-31b), 142.3 (C-3), 151.7, 152.0 (C-2, C-4); the signal correlation is based on 2 D ^{1}H,^{13}C shift correlation measurements. − FD MS: *m/z* (%) = 2163 (100) [M + H^+]. − $C_{150}H_{216}O_9$ (2163): calcd. C 83.28, H 10.06; found C 82.74, H 10.04.

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