

Synthesis of Tripyreno[2,3,4-*abc* : 2,3,4-*ghi* : 2,3,4-*mno*][18]annulenes

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Dedicated to Prof. Dr. H. Kunz on the Occasion of his 60th Birthday

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Abstract. The title compounds were prepared in a multi-step synthesis in which primarily the pyrene building blocks were formed (**1,2** → **11a,b**). The final reaction step **11a,b** → **12a,b** consisted of a threefold *trans* selective cyclocondensation

process that generated the central 18-membered ring. Hexyloxy or dodecyloxy sidechains attached on the periphery led to the formation of liquid crystalline phases.

Annulenes are an important class of chemical compounds which deserves great interest in synthetic respect as well as in theoretical respect [1, 2]. However, [n]annulenes ($n \geq 10$) are not suitable for applications in materials science, because their chemical stability is much too low. Aromatic ring systems as benzene [3–5], naphthalene [6], phenanthrene [6–11] or chrysene [12], condensed with the annulene perimeter, enhance strongly the thermal stability of these compounds. Moreover, these disc-like systems represent discotic mesogens which are a precondition for the formation of liquid crystals with discotic nematic or columnar phases [6–11, 13]. The photochemistry of these compounds provides an access to belt cyclophanes [4, 5, 7, 8, 13]; the major applications in materials science are in the field of imaging techniques and photoconductivity [9, 10, 13–15].

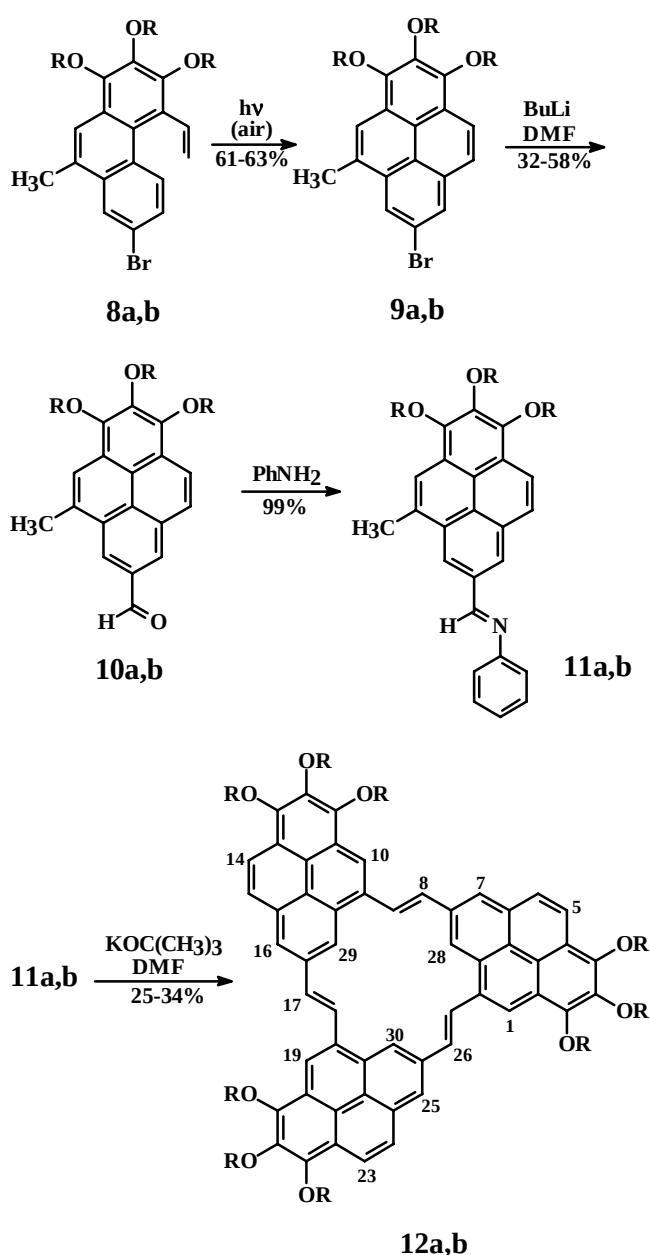
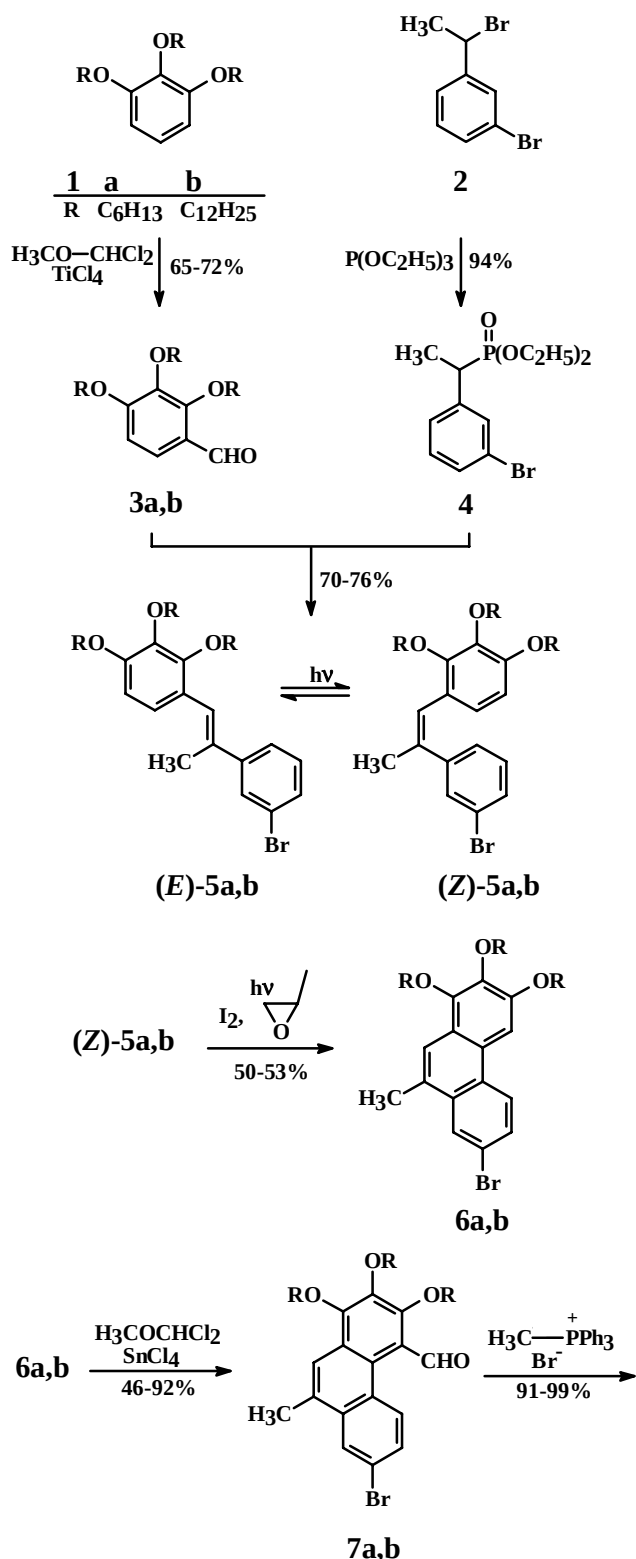
Many areno-condensed annulenes exhibit a high tendency of aggregation in solution as well as in the neat phase [4, 6, 7, 8, 11]. Thus, bimolecular photoreactions are efficient even in highly diluted solutions, because light is being absorbed by aggregates (dimers *etc.*). Pyrene on the other hand is a classic example for the formation of excimers which exist in the electronically excited singlet state S_1 and decay on deactivation to the ground state S_0 [16]. The objective of our project is to investigate the photophysics and the photochemistry of excimers which are formed by irradiation of (dimeric) aggregates and decompose to aggregates (clusters) without dissociation. The present paper contains the synthetic access to [18]annulenes which are condensed with three pyrene ring systems.

Synthesis

The 1,2,3-trialkoxybenzenes **1a,b** and 3-(1-bromoethyl)bromobenzene **2** served as starting materials for

the synthesis of the tripyreno[18]annulenes **12a,b**. Regioselective formylation of **1a,b** to the 2,3,4-trialkoxybenzaldehydes **3a,b** could be achieved with the Rieche-Gross [17, 18] or with the Vilsmeier method. Dibromide **2** was transformed in an Arbusov rearrangement with triethyl phosphite to the monophosphonate **4**. The Wittig-Horner reaction of **3a,b** and **4** yielded the substituted stilbenes **5a,b**. The modest stereoselectivity did not play a role, because an *E/Z* photoisomerization was induced in the consecutive step, in which an oxidative cyclization to the phenanthrene derivatives **6a,b** was performed. The cyclization is regioselective; the isomeric 5-bromo-1,2,3-trialkoxy-9-methylphenanthrenes could be observed as by-product in the ^1H NMR spectrum of the raw material. Iodine served as oxidant and methyloxirane as scavenger for the generated hydrogen iodide [19]. The regioselective formylation of **6a,b** in the sterically hindered 4-position was obtained with the Rieche-Gross reaction; however, tin tetrachloride as Lewis acid had to be used instead of titanium tetrachloride, in order to get high yields of the 1,2,3-trialkoxy-7-bromo-9-methylphenanthrene-4-carbaldehydes **7a,b**. The formyl group was then displaced by the vinyl group in an almost quantitative Wittig reaction (**7a,b** → **8a,b**). A second oxidative photocyclization yielded the pyrene derivatives **9a,b**. The bromo substituent in 7-position could be exchanged in a Bouveault reaction and the generated aldehydes **10a,b** transformed to the corresponding *N*-phenylimines **11a,b**. The latter compounds contain the appropriate functional groups for a cyclocondensation reaction, namely the imino group and the activated methyl group. In a threefold highly (*E*)-selective [15] cyclocondensation the desired tripyreno[18]annulenes **12a,b** could be obtained. Of course, linear condensation products could not be avoided, but they contained polar endgroups and were easily separated by column chromatography. Thus, the Siegrist reaction [20] **11a,b** → **12a,b** represented a convenient cyclization process,

although the yields were moderate. Due to minor (*E*)-selectivities, other formations of CC double bonds proved to be less suitable, since (*Z*)-configured double bonds do not permit a cyclic process leading to an 18-membered central ring. The multi-step procedure for the preparation of **12a,b** is summarized in Scheme 1.



Scheme 1 Preparation of the tripyreno[18]annulenes **12a,b**

Characterization of the Tripyreno[18]annulenes

In contrast to the unsubstituted [18]annulene [21], the areno-condensed [18]annulenes are not planar [4, 6, 11]. They can be regarded as aromatic "islands" which are combined by *trans* configured olefinic "bridges". There is no indication for a macrocyclic ring current effect. The inner protons 9-H, 18-H, 27-H and 28-H, 29-H, 30-H exhibit NMR signals at 8.55 ± 0.06 ppm and 9.12 ± 0.08 ppm, respectively. The outer protons 8-H, 17-H and 26-H show signals at higher field, namely at 7.72 ± 0.08 ppm. Moreover, the coupling constant 3J (8-H, 9-H) amounts to 15.8 Hz, a value that proves the olefinic character and the *trans* configuration of the "bridges".

The geminal OCH₂ protons of the sidechains at 4.25–4.40 ppm provide a simple proof for the fast inversion of the central 18-membered ring. The diastereotopic protons in the C₃ conformation become enantiotopic by a ring inversion process which is fast in the NMR time scale. Like in the corresponding triphenanthro[18]annulenes [6], **12a** and **12b** have C_{3h} symmetry on average. All these NMR results were obtained by room temperature measurements of diluted solutions (about 1.5 × 10^{−3} M) of **12a,b** in CDCl₃. The ¹H NMR signals become broad and unresolved with increasing concentration. The aggregation tendency is particularly high in nonpolar solvents like cyclohexane.

The aggregation of **12a,b** in the pure state leads to discotic liquid crystals. The second heating curves in the differential scanning calorimetry (DSC) show mesophases between 57.0 and 104.8 °C for **12a** and between −11.9 and 125.0 °C for **12b** (onset temperatures). The Δ*H* values for the transition of the crystalline states to the LC phases amount to 8.14 and 13.7 J/g, respectively. The phase transformations at 104.8 and 125.0 °C have very small Δ*H* values (1.24 J/g for **12a** and 0.3 J/g for **12b**) and lead to birefringent mesophases which start to decompose above 250 °C. Thus, the transition temperatures to the isotropic melts cannot be determined. A detailed characterization of the LC phases will be subject to X-ray small angle scanning measurements.

Conclusion and Outlook

The symmetrical tripyreno[18]annulenes **12a,b** could be obtained by a multi-step synthesis, in which the pyrene building blocks were generated first, and then their linkage was achieved by a threefold condensation. The major synthetic challenge consisted in the elaboration of three regioselective steps (**1** → **3**, **5** → **6** and **6** → **7**) and one highly stereoselective and cyclic process (**11** → **12**). Nine hexyloxy or dodecyloxy chains attached on the periphery enhance the solubility and are a precondition for the formation of liquid crystalline phases. The nonplanar discotic mesogens exhibit at room temperature an inversion of the central 18-membered ring which is fast on the NMR time scale.

Preliminary measurements [22] of the time-resolved fluorescence reveal that the electronically excited aggregates do not dissociate into single molecules within a ns time scale – a process which is typical for excimers. Thus, the pyrene systems **12a,b** provide the molecular basis for an extension of the excimer theory in photophysics and photochemistry.

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Experimental

The melting points were measured on a Büchi melting point apparatus and are uncorrected. The ¹H and ¹³C NMR spectra were recorded on Bruker spectrometers AM 400 and AC 200; the mass spectra were obtained on a Finnigan MAT 95. A Beckman Acculab 4 spectrometer served for the measurements of the IR spectra. DSC measurements were performed on a Perkin-Elmer DSC 7 apparatus.

2,3,4-Trihexyloxybenzaldehyde (**3a**) and 2,3,4-Tridodecyloxybenzaldehyde (**3b**)

Preparation and spectroscopic identification according to the literature [11, 23, 24].

Diethyl 1-(3-bromophenyl)ethylphosphonate (**4**)

Preparation and spectroscopic identification according to the literature [11].

2-(3-Bromophenyl)-1-(2,3,4-trihexyloxyphenyl)propene (**5a**)

The phosphonate **4** (7.22 g, 20.2 mmol) was dissolved in 80 ml of DMF and cooled to 0 °C in an argon atmosphere; 3.41 g (32.0 mmol) KO^tBu was added in small portions under stirring, so that the temperature was kept below 5 °C. After the ylide formation the solution was allowed to come to room temperature, and 8.23 g (20.2 mmol) **3a** in 80 ml DMF was slowly added under stirring within 1 h. The reaction mixture was stirred for another hour before 3.0 g NH₄Cl in 70 ml of water was added. The vigorously stirred mixture was then extracted several times with equal amounts of toluene. The toluene solution was washed three times with water, dried with MgSO₄ and evaporated. In order to remove remaining traces of DMF, the raw product was heated *in vacuo* to 50 °C. The purification was performed by column chromatography (60 × 4 cm silica gel/toluene). Yield 8.1 g (70%), almost colourless oil. The yield obtained with this modified procedure was about twice as high as in the original procedure [11]. The product was identified by comparison with an authentic sample [11].

2-(3-Bromophenyl)-1-(2,3,4-tridodecyloxyphenyl)propene (**5b**)

The preparation was performed as described for **5a**; the *E/Z* ratio of the raw product was 3 : 1. The data presented below refer to the pure (*E*)-configuration. 4.16 g (12.96 mmol) **4** and 7.69 g (11.67 mmol) **3b** yielded 7.33 g (76%) colourless oil. – IR (neat): ν/cm^{−1} = 2900, 1580, 1480, 1460, 1290, 1090, 780. – ¹H NMR (CDCl₃): δ/ppm = 0.87 (t, 9H, CH₃), 1.20–1.55 (m, 54H, CH₂), 1.60–1.80 (m, 6H, CH₂), 2.16 (s, 3H, CH₃), 3.95–4.15 (m, 6H, OCH₂), 6.64 (d, ³*J* = 8.8 Hz, 1H, 5-H), 6.88 (s, 1H, olefin. H), 6.95 (d, 1H, ³*J* = 8.8 Hz, 6-H), 7.20 (m, 1H, aromat. H), 7.40 (m, 2H, aromat. H), 7.65 (s, 1H, aromat. H). – MS (FD): *m/z* (%) = 827/825 (100), [M⁺, Br isotope pattern].

C₅₁H₈₅O₃Br Calcd.: C 74.15 H 10.37
(826.15) Found: C 74.13 H 10.41.

2-Bromo-6,7,8-trihexyloxy-10-methylphenanthrene (**6a**)

Preparation according to the literature [11]. The product was identified by comparison with an authentic sample.

2-Bromo-6,7,8-tridodecyloxy-10-methylphenanthrene (6b)

A solution of 4.17 g (5.05 mmol) of **5b** and 1.3 g iodine (5.1 mmol) in 2 l cyclohexane was saturated with a strong stream of argon gas for 30 min. Then 20 ml (16.63 g, 286 mmol) of methyloxirane were added and the solution was irradiated with a 450 W-Hanovia middle pressure mercury lamp through a Corex filter. After about 12 h the colour of the iodide vanished and another portion of 4.17 g (5.05 mmol) of **5b** and 1.3 g (5.1 mmol) of iodine was added and the irradiation continued. After about 24 h the solution had a light orange colour; it was washed with aqueous sodium thiosulfate and water, dried over MgSO_4 and evaporated. The raw product was dissolved in toluene and purified by column chromatography (60×4 cm silica gel toluene/petrol ether 1 : 4). Yield 4.20 g (50%), colourless waxy solid; *m.p.* 38 °C. – IR (neat): $\nu/\text{cm}^{-1} = 2920, 1580, 1460, 1360, 1270, 995, 760$. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 0.87$ (t, 9H, CH_3), 1.20–1.60 (m, 54H, CH_2), 1.70–2.00 (m, 6H, CH_2), 2.67 (s, 3H, CH_3), 4.00–4.40 (m, 6H, OCH_2), 7.61 (dd, $^4J = 2.0$ Hz, $^3J = 8.8$ Hz, 1H, 6-H), 7.91 (d, $^3J = 8.8$ Hz, 1H, 5-H), 7.95 (s, 1H, 10-H), 8.17 (d, $^4J = 2.0$ Hz, 1H, 7-H), 10.43 (s, 1H, CHO). – ^{13}C NMR (CDCl_3): $\delta/\text{ppm} = 14.1$ (CH_3), 20.0 (CH_3), 22.7–32.0 (CH_2), 74.3, 74.6, 74.6 (OCH_2), 121.3, 127.0, 128.5, 130.7 (aromat. CH), 121.6, 124.1, 125.1, 126.1, 127.3, 131.5, 134.8, 143.5, 151.8, 154.5 (C_q), 191.3 (CHO). – MS (FD): m/z (%) = 851/853 (100) [M^+ , Br isotope pattern].
 $\text{C}_{52}\text{H}_{83}\text{BrO}_4$ Calcd.: C 73.30 H 9.82
 (852.14) Found: C 73.41 H 9.73.

7-Bromo-1,2,3-trihexyloxy-9-methylphenanthrene-4-carbaldehyde (7a)

A solution of 6.0 g (10.4 mmol) **6a** in 600 ml dichloromethane was cooled to 0 °C; under stirring 15.0 ml (34.95 g, 134 mmol) of SnCl_4 were added slowly so that the temperature was kept below 5 °C. A precipitate was formed and the solution was stirred for another 30 min while the temperature raised to 10 °C. At this temperature 15 ml (19.06 g, 219 mmol) of dichloromethyl methyl ether was slowly added under stirring. The reaction mixture was continued at 0 °C for 1 h and then warmed slowly to room temperature; 300 ml of ice water were added and the mixture stirred over night. The organic phase was washed with water, aqueous NaHCO_3 and water, dried over MgSO_4 and evaporated. The raw product was recrystallized from methanol/acetone (1 : 1). Yield 5.8 g (92%), colourless crystals; *m.p.* = 41 °C. – IR (neat): $\nu/\text{cm}^{-1} = 2920, 1670, 1420, 1330, 1220, 1100, 1050, 980, 810$. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 0.93$ (t, 9H, CH_3), 1.20–1.60 (m, 18H, CH_2), 1.70–2.00 (m, 6H, CH_2), 2.70 (s, 3H, CH_3), 4.00–4.40 (m, 6H, OCH_2), 7.61 (dd, $^3J = 8.8$ Hz, $^4J = 1.9$ Hz, 1H, 6-H), 7.91 (d, $^3J = 8.8$ Hz, 1H, 5-H), 7.95 (s, 1H, 10-H), 8.17 (d, $^4J = 1.9$ Hz, 1H, 8-H), 10.43 (s, 1H, CHO). – ^{13}C NMR (CDCl_3): $\delta/\text{ppm} = 14.0$ (CH_3), 20.0 (CH_3), 22.6, 25.8, 30.3, 31.7 (CH_2), 74.3, 74.5, 74.5 (OCH_2), 121.3, 127.0, 128.5, 130.7 (aromat. CH), 121.6, 124.1, 125.1, 126.1, 127.3, 131.5, 134.8, 143.5, 151.8, 154.5 (C_q), 191.3 (CHO). – MS (FD): m/z (%) = 600/598 (100) [M^+ , Br isotope pattern].
 $\text{C}_{34}\text{H}_{47}\text{BrO}_4$ Calcd.: C 68.10 H 7.90
 (599.66) Found: C 68.19 H 7.78.

7-Bromo-1,2,3-tridodecyloxy-9-methylphenanthrene-4-carbaldehyde (7b)

Preparation as described for **7a**. The raw product was purified by column chromatography (40×5 cm silica gel/toluene). Yield 46% colourless crystals; *m.p.* = 58 °C. – IR (KBr):

$\nu/\text{cm}^{-1} = 2920, 1670, 1460, 1440, 1360, 1120, 1070, 820$. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 0.87$ (t, 9H, CH_3), 1.20–1.60 (m, 54H, CH_2), 1.70–2.00 (m, 6H, CH_2), 2.70 (s, 3H, CH_3), 4.00–4.40 (m, 6H, OCH_2), 7.61 (dd, $^4J = 2.0$ Hz, $^3J = 8.8$ Hz, 1H, 6-H), 7.91 (d, $^3J = 8.8$ Hz, 1H, 5-H), 7.95 (s, 1H, 10-H), 8.17 (d, $^4J = 2.0$ Hz, 1H, 7-H), 10.43 (s, 1H, CHO). – ^{13}C NMR (CDCl_3): $\delta/\text{ppm} = 14.1$ (CH_3), 20.0 (CH_3), 22.7–32.0 (CH_2), 74.3, 74.6, 74.6 (OCH_2), 121.3, 127.0, 128.5, 130.7 (aromat. CH), 121.6, 124.1, 125.1, 126.1, 127.3, 131.5, 134.8, 143.5, 151.8, 154.5 (C_q), 191.3 (CHO). – MS (FD): m/z (%) = 851/853 (100) [M^+ , Br isotope pattern].

$\text{C}_{52}\text{H}_{83}\text{BrO}_4$ Calcd.: C 73.30 H 9.82
 (852.14) Found: C 73.41 H 9.73.

2-Bromo-6,7,8-trihexyloxy-10-methyl-5-vinylphenanthrene (8a)

4.0 g (15.0 mmol) of methyltriphenylphosphonium bromide dissolved in 30 ml THF was cooled to 0 °C before 1.35 g (12.0 mmol) KOtBu was slowly added, so that the temperature was kept below 10 °C. The orange reaction mixture was treated at 0 °C with a solution of 2.4 g (4.0 mmol) of **7a** in 20 ml THF under strong stirring for a few minutes. The mixture was permitted to come to room temperature and then treated with a solution of 5.0 g NH_4Cl in 50 ml of water. The organic layer was separated, washed with the same volume of concentrated aqueous NaCl solution, dried over MgSO_4 and evaporated. The raw product was filtered over 5×10 cm of silica gel with toluene. Yield 2.34 g (99%) of a colourless oil. – IR (neat): $\nu/\text{cm}^{-1} = 2960, 1610, 1580, 1430, 1370, 1340, 1120, 1080, 980, 910, 860, 820$. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 0.80$ –1.00 (m, 9H, CH_3), 1.20–1.60 (m, 18H, CH_2), 1.70–2.00 (m, 6H, CH_2), 2.67 (s, 3H, CH_3), 3.93 (t, 2H, OCH_2), 4.10–4.25 (m, 4H, OCH_2), 5.60–5.80 (m, 2H, olefin. H), 7.03 (dd, $^3J = 18.0$ Hz, $^3J = 11.2$ Hz, 1H, olefin. H), 7.54 (d, $^3J = 9.3$ Hz, 1H, 3-H), 7.92 (s, 1H, 9-H), 8.10 (s, 1H, 1-H), 8.92 (d, $^3J = 9.3$ Hz, 1H, 4-H). – ^{13}C NMR (CDCl_3): $\delta/\text{ppm} = 14.1$ (CH_3), 20.1 (CH_3), 22.7, 25.9, 30.5, 31.7 (CH_2), 73.5, 74.0, 74.4 (OCH_2), 119.1 (CH_2 , vinyl), 121.6, 126.6, 127.3, 130.9, 134.6 (aromat. and olefin. CH), 120.1, 124.8, 125.2, 125.6, 129.7, 130.3, 134.8, 144.3, 147.2, 150.9 (C_q). – MS (FD): m/z (%) = 596/598 (100) [M^+ , Br isotope pattern].
 $\text{C}_{35}\text{H}_{49}\text{O}_3\text{Br}$ Calcd.: C 70.34 H 8.26
 (597.68) Found: C 70.43 H 8.13.

2-Bromo-6,7,8-tridodecyloxy-10-methyl-5-vinylphenanthrene (8b)

Preparation and purification as described for **8a**. Yield 91% of a colourless oil which solidifies to a wax after a few days; *m.p.* = 42 °C. – IR (KBr): $\nu/\text{cm}^{-1} = 2920, 1590, 1430, 1380, 1340, 1120, 1080, 990, 820$. – ^1H NMR (CDCl_3): $\delta/\text{ppm} = 0.87$ (t, 9H, CH_3), 1.20–1.60 (m, 54H, CH_2), 1.70–2.00 (m, 6H, CH_2), 2.67 (s, 3H, CH_3), 3.92 (t, 2H, OCH_2), 4.05–4.20 (m, 4H, OCH_2), 5.60–5.80 (m, 2H, olefin. H), 7.03 (dd, $^3J = 17.6$ Hz, $^3J = 11.3$ Hz, 1H, olefin. H), 7.54 (d, $^3J = 9.3$ Hz, 1H, 3-H), 7.92 (s, 1H, 9-H), 8.10 (s, 1H, 1-H), 8.92 (d, $^3J = 9.3$ Hz, 1H, 4-H). – ^{13}C NMR (CDCl_3): $\delta/\text{ppm} = 14.1$ (CH_3), 20.1 (CH_3), 22.7–32.0 (CH_2), 73.4, 74.0, 74.4 (OCH_2), 119.1 (CH_2 , vinyl), 121.6, 126.6, 127.3, 130.9, 134.5 (aromat. and olefin. CH), 120.1, 124.8, 125.2, 125.6, 129.7, 130.3, 134.8, 144.3, 147.2, 150.9 (C_q). – MS (FD): m/z (%) = 849/851 (100) [M^+ , Br isotope pattern].

$C_{53}H_{85}BrO_3$ Calcd.: C 74.88 H 10.08
(850.17) Found: C 74.85 H 10.00.

2-Bromo-6,7,8-trihexyloxy-4-methylpyrene (9a)

2.0 g (3.3 mmol) of **8a**, dissolved in 200 ml benzene, was irradiated with a 450W-Hanovia middle pressure mercury lamp through a Duran glass filter. During the irradiation a weak stream of dry air was bubbled through the solution. After 1 h the solvent was evaporated and the residue purified by column chromatography (40 × 4 cm silica gel, cyclohexane/toluene 5 : 1). Yield 1.23 g (61%) colourless oil. – IR (neat): ν/cm^{-1} = 2900, 1560, 1390, 1340, 1280, 1040, 845 – 1H NMR ($CDCl_3$): δ/ppm = 0.93 (m, 9H, CH_3), 1.20–1.75 (m, 18H, CH_2), 1.80–2.20 (m, 6H, CH_2), 2.80 (s, 3H, CH_3), 4.10–4.34 (m, 6H, OCH_2), 7.83 (d, 3J = 9.3 Hz, 1H, 10-H), 8.14 (s, 1H, 5-H), 8.17, d, 4J = 1.5 Hz, 1H/ 8.23, d, 4J = 1.5 Hz, 1H (1-H, 3-H), 8.29 (d, 3J = 9.3 Hz, 1H, 9-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.1 (CH_3), 20.2 (CH_3), 22.7, 25.9, 30.5, 31.8 (CH_2), 74.3, 75.1, 75.1, (OCH_2), 121.9, 122.5, 123.4, 124.8, 126.4 (aromat. CH), 119.9, 120.9, 121.4, 121.5, 123.6, 130.9, 133.1, 133.2, 144.2, 147.8, 148.0. – MS (FD): m/z (%) = 594/596 (100) [M^+ , Br isotope pattern].
 $C_{35}H_{47}O_3Br$ Calcd.: C 70.57 H 7.95
(595.67) Found: C 70.51 H 8.01.

2-Bromo-6,7,8-tridodecyloxy-4-methylpyrene (9b)

Preparation as described for **9a**, column chromatography on silica gel (40 × 4 cm) with cyclohexane/toluene 13 : 1. Yield 1.76 g (63%) colourless oil. – IR (neat): ν/cm^{-1} = 2920, 1550, 1460, 1420, 1360, 1305, 1130, 1060, 870. – 1H NMR ($CDCl_3$): δ/ppm = 0.87 (t, 9H, CH_3), 1.20–1.60 (m, 54H, CH_2), 1.72–2.00 (m, 6H, CH_2), 2.80 (s, 3H, CH_3), 4.10–4.30 (m, 6H, OCH_2), 7.83 (d, 3J = 9.3 Hz, 1H, 10-H), 8.14 (s, 1H, 5-H), 8.17 (d, 4J = 1.5 Hz, 1H/8.23, d, 4J = 1.5 Hz, 1H (1-H, 3-H), 8.29 (d, 3J = 9.3 Hz, 1H, 9-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.1 (CH_3), 20.3 (CH_3), 22.1–32.0 (CH_2), 74.3, 75.1, 75.1 (OCH_2), 121.9, 122.5, 123.4, 124.8, 126.4 (aromat. CH), 119.9, 120.9, 121.4, 121.5, 123.6, 130.9, 133.1, 133.2, 144.2, 147.8, 148.0 (C_q). – MS (FD): m/z (%) = 847/849 (100) [M^+ , Br isotope pattern].
 $C_{53}H_{83}BrO_3$ Calcd.: C 75.06 H 9.86
(848.15) Found: C 74.94 H 9.91.

6,7,8-Trihexyloxy-4-methylpyrene-2-carbaldehyde (10a)

To 714 mg (1.2 mmol) of **9a**, dissolved in 20 ml dry ether, 1.0 ml of butyllithium solution in hexane (2.7 M) was slowly added under stirring at 0 °C in an argon atmosphere. The solution was then allowed to reach room temperature before 1.0 ml (0.95 g, 1.3 mmol) of dry DMF was added. After vigorous stirring for 2 h the reaction was stopped by adding 20 ml of water. The organic layer was separated, washed with concentrated aqueous NaCl solution, dried over $MgSO_4$ and evaporated. The raw product was purified by column chromatography (40 × 4 cm silica gel, toluene). Yield 384 mg (58%) of a yellow fluorescent oil. – IR (neat): ν/cm^{-1} = 2920, 1680, 1580, 1440, 1360, 1260, 1090. – 1H NMR ($CDCl_3$): δ/ppm = 0.80–1.11 (m, 9H, CH_3), 1.20–1.75 (m, 18H, CH_2), 1.80–2.20 (m, 6H, CH_2), 2.89 (s, 3H, CH_3), 4.15–4.35 (m, 6H, OCH_2), 8.01 (d, 3J = 9.3 Hz, 1H, 10-H), 8.17 (s, 1H, 5-H), 8.33 (d, 3J = 9.3 Hz, 1H, 9-H), 8.51, s, 1H/8.61, s, 1H (1-

H, 3-H), 10.39 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.1 (CH_3), 20.2 (CH_3), 22.7, 26.0, 30.5, 31.8 (CH_2), 74.4, 75.1, 75.2 (OCH_2), 121.3, 121.8, 122.4, 125.5, 126.3 (aromat. CH), 120.8, 122.6, 122.7, 128.3, 131.6, 131.8, 132.4, 132.8, 145.3, 147.7, 147.9 (C_q), 193.2 (CHO). – MS (FD): m/z (%) = 544 (100) [M^+].

$C_{36}H_{48}O_4$ Calcd.: C 79.37 H 8.88
(544.78) Found: C 79.84 H 8.83.

6,7,8-Tridodecyloxy-4-methylpyrene-2-carbaldehyde (10b)

Preparation as described for **10a**. Yield 32% of a yellow fluorescent oil. – IR (neat): ν/cm^{-1} = 2920, 1690, 1460, 1310. – 1H NMR ($CDCl_3$): δ/ppm = 0.88 (t, 9H, CH_3), 1.20–1.75 (m, 54H, CH_2), 1.80–2.10 (m, 6H, CH_2), 2.91 (s, 3H, CH_3), 4.21–4.35 (m, 6H, OCH_2), 8.02 (d, 3J = 9.3 Hz, 1H, 10-H), 8.19 (s, 1H, 5-H), 8.36 (d, 3J = 9.3 Hz, 1H, 9-H), 8.51, s, 1H/ 8.62 s, 1H (1-H, 3-H), 10.39 (s, 1H, CHO). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.1 (CH_3), 20.3 (CH_3), 22.7–32.0 (CH_2), 74.3, 74.3, 75.1 (OCH_2), 121.4, 121.8, 122.4, 125.5, 126.3 (aromat. CH), 120.8, 122.6, 122.7, 128.4, 131.7, 131.9, 132.4, 132.9, 145.3, 147.7, 147.9 (C_q), 193.3 (CHO). – MS (FD): m/z (%) = 797 (100) [M^+].

$C_{54}H_{84}O_4$ Calcd.: C 81.35 H 10.62
(797.26) Found: C 81.30 H 10.55.

(E)-6,7,8-Trihexyloxy-4-methylpyrene-2-(N-phenyl)carbaldehyde (11a)

Aniline (186 mg, 2.0 mmol) and 544 mg (1.0 mmol) of **10a** were heated for 6 h to 75 °C. A vacuum of 100 mbar was applied during the heating to remove the water generated in the reaction. Then a vacuum of 1 mbar was applied to remove the excess aniline. Yield 614 mg (99%) of an analytically pure semisolid compound. – IR (neat): ν/cm^{-1} = 2940, 1620, 1580, 1460, 1340, 1305, 1060, 760. – 1H NMR ($CDCl_3$): δ/ppm = 0.80–1.10 (m, 9H, CH_3), 1.30–1.75 (m, 18H, CH_2), 1.80–2.10 (m, 6H, CH_2), 2.93 (s, 3H, CH_3), 4.22–4.40 (m, 6H, OCH_2), 7.20–7.50 (m, 5H, phenyl), 8.01 (d, 3J = 8.8 Hz, 1H, 10-H), 8.18 (s, 1H, 5-H), 8.33 (d, 3J = 8.8 Hz, 1H, 9-H), 8.58, s, 1H/8.67, s, H, (1-H, 3-H), 8.85 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.1 (CH_3), 20.5 (CH_3), 22.7, 26.0, 30.6, 31.8 (CH_2), 74.3, 75.0, 75.1 (OCH_2), 121.0, 121.1, 121.2, 121.4, 121.9, 122.2, 122.3, 124.6, 126.0, 126.3, 126.8, 129.3, 131.8, 131.8, 132.3, 133.0, 144.7, 147.5, 147.7, 152.4 (aromat. C), 161.3 (CHN). – MS (FD): m/z (%) = 620 (100) [M^+].

$C_{42}H_{53}O_3N$ Calcd.: C 81.38 H 8.62 N 2.26
(619.89) Found: C 81.45 H 8.68 N 2.31.

6,7,8-Tridodecyloxy-4-methylpyrene-2-(N-phenyl)carbaldehyde (11b)

Preparation as described for **11a**. Yield 99% of an analytically pure semisolid compound. – 1H NMR ($CDCl_3$): δ/ppm = 0.80–1.00 (m, 9H, CH_3), 1.21–1.75 (m, 54H, CH_2), 1.80–2.10 (m, 6H, CH_2), 2.94 (s, 3H, CH_3), 4.15–4.40 (m, 6H, OCH_2), 7.20–7.50 (m, 5H, phenyl), 8.02 (d, 3J = 8.8 Hz, 1H, 10-H), 8.17 (s, 1H, 5-H), 8.32 (d, 3J = 8.8 Hz, 1H, 9-H), 8.60, s, 1H/8.69, s, 1H, (1-H, 3-H), 8.87 (s, 1H, CHN). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.1 (CH_3), 20.3 (CH_3), 22.7–32.0 (CH_2), 74.3, 75.0, 75.1 (OCH_2), 121.0, 121.1, 121.2, 121.4, 122.0, 122.2, 122.3, 124.6, 126.0, 126.3, 126.9, 129.3, 131.8, 131.8, 132.3, 133.0, 144.7, 147.5, 147.6, 152.3 (aromat. C), 161.4 (CHN). – MS (FD): m/z (%) = 872 (100) [M^+].

$C_{60}H_{89}NO_3$ Calcd.: C 82.61 H 10.28
(872.38) Found: C 82.58 H 10.25.

(8*E*,17*E*,26*E*)-2,3,4,11,12,13,20,21,22-Nonahexyloxytri-
pyreno[2,3,4-*abc* : 2,3,4-*ghi* : 2,3,4-*mno*]cyclooctadecene
(12a)

A solution of 619 mg (1.0 mmol) of **11a** in 100 ml DMF was degassed by use of an argon stream, potassium *tert*-butylate (1.12 g, 10.0 mmol) was added under vigorous stirring at 85 °C. After 10 min the dark reaction mixture was quickly cooled under stirring to 0 °C. At this temperature 100 ml ice water was slowly added so that the temperature was kept below 5 °C. The yellow suspension was stored over night at 5 °C, the precipitate collected by filtration over celite and washed with water. The raw product was dissolved in toluene and purified by column chromatography (40 × 3 cm silica gel, toluene/cyclohexane 1 : 1). The solution should be well protected from light. The first bright yellow fluorescent fraction contained the desired product. It was further purified by crystallization from petrol ether (*b.p.* 40–70 °C), to which acetone was added, till the solution became turbid. Yield 177 mg (34%) bright yellow solid, *m.p.* 57.0 °C (DSC). – IR (neat): ν/cm^{-1} = 2920, 1420, 1350, 1060. – 1H NMR ($CDCl_3$): δ/ppm = 0.85–1.05 (m, 27H, CH_3), 1.25–1.80 (m, 54H, CH_2), 1.85–2.10 (m, 18H, CH_2), 4.25–4.35 (m, 18H, OCH_2), 7.64 (d, 3J = 15.8 Hz, 3H, 8-H, 17-H, 26-H), 7.74 (d, 3J = 9.2 Hz, 3H, 6-H, 15-H, 24-H), 7.84 (s, 3H, 7-H, 16-H, 25-H), 8.17 (d, 3J = 9.2 Hz, 3H, 5-H, 14-H, 23-H), 8.49 (d, 3J = 15.8 Hz, 3H, 9-H, 18-H, 27-H), 8.55 (s, 3H, 1-H, 10-H, 19-H), 9.05 (s, 3H, 28-H, 29-H, 30-H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 14.1, 14.2 (CH_3), 22.8, 22.8, 26.1, 26.3, 30.8, 30.9, 31.9, 32.0 (CH_2), 74.3, 75.0 (OCH_2), 115.5, 117.0, 121.1, 121.4, 121.6, 121.7, 124.7, 125.1, 125.9, 125.9, 129.8, 130.0, 130.7, 131.7, 134.9, 144.0, 147.7, 147.9. – MS (FD): m/z (%) = 1581 (100) [$M+H^+$].
 $C_{108}H_{138}O_9$ Calcd.: C 82.09 H 8.80
(1580.29) Found: C 82.13 H 8.77.

(8*E*,17*E*,26*E*)-2,3,4,11,12,13,20,21,22-Nonadodecyl-
oxytripyrreno[2,3,4-*abc* : 2,3,4-*ghi* : 2,3,4-*mno*]cycloocta-
decene (12b)

Preparation as described for **12a**. Yield 25%, bright yellow solid; *m.p.* = –11.9 °C (DSC). – IR (neat): ν/cm^{-1} = 2920, 1460, 1350, 1050. – 1H NMR ($CDCl_3$): δ/ppm = 0.81 (t, 9H, CH_3), 0.88 (t, 18H, CH_3), 1.15–1.75 (m, 162H, CH_2), 1.90–2.05 (m, 18H, CH_2), 4.30–4.40 (m, 18H, OCH_2), 7.79 (d, 3J = 15.8 Hz, 3H, 8-H, 17-H, 26-H), 7.85 (d, 3J = 8.9 Hz, 3H, 6-H, 15-H, 24-H), 7.98 (s, 3H, 7-H, 16-H, 25-H), 8.22 (d, 3J = 8.9 Hz, 3H, 5-H, 14-H, 23-H), 8.61 (d, 3J = 15.8 Hz, 3H, 9-H, 18-H, 27-H), 8.68 (s, 3H, 1-H, 10-H, 19-H), 9.20 (s, 3H, 28-H, 29-H, 30-H). – MS (FD): m/z (%) = 2338 (100) [$M+H^+$].
 $C_{162}H_{246}O_9$ Calcd.: C 83.23 H 10.61
(2337.75) Found: C 83.08 H 10.91.

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