Preparation of 1,2,5,6,9,10-Hexaalkoxyhexahelicenes

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1,2,5,6,9,10-Hexaalkoxyhexahelicenes **3** represent [3]star compounds with a helical core. A multi-step synthetic concept for **3** is discussed, in which the final step **16** → **3** is a twofold oxidative photocyclization. The linearly conjugated compounds **16** contain stilbene and vinylnaphthalene units.

Key words: Helicenes, Photocyclization, Wittig–Horner Reaction, Siegrist Reaction

Introduction

[3]Star compounds, which consist of conjugated aromatic cores and three, six or nine alkoxy groups, represent interesting structures for materials science [1]. 2,3,6,7,10,11-Hexaalkoxytriphenylenes (**1**) are prominent examples (Fig. 1). From their first preparations [2, 3] till our days [4 – 9], a large variety of compounds **1** have been thoroughly studied. Much less is known about 1,2,5,6,9,10-hexaalkoxycoronenes (**2**) [10, 11], and nothing is known about 1,2,5,6,9,10-hexaalkoxyhexahelicenes (**3**). In contrast to **1** and **2**, compound **3** has a non-planar, chiral polycyclic core. Many mesophases are known for compounds **1**, some for systems **2**. This arises the question: Do chiral thermotropic liquid crystalline phases (LC) exist for **3**? Due to the lack of symmetry, the usual synthesis of hexahelicenes on the basis of 2,7-distyrylnaphthalenes [12], is not useful in this case. We conceived a multi-step procedure, which starts from benzene and naphthalene derivatives.

Results and Discussion

Scheme 1 summarizes the preparation of the 2-{2-[4-(2-phenylvinyl)phenyl]vinyl}naphthalenes **16a**, **b**, which were chosen as precursors for the desired hexahelicenes **3**.

3-Methylbenzene-1,2-diol (**4**) was alkylated twice under phase transfer conditions [13, 14]. We used long alkyl chains to get high solubilities throughout the whole reaction sequence. The obtained 3-methyl-1,2-dialkoxybenzenes **6a**, **b** were subjected to a Bouveault formylation to **7a**, **b**. The formylation was neither regioselective nor chemoselective; the CH_3 group was also attacked by DMF [15, 16]. Consequently the yields of **7a**, **b** were low. In a second reaction se-

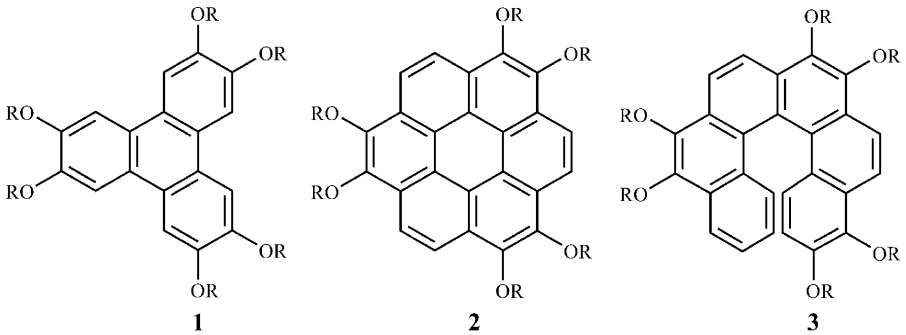
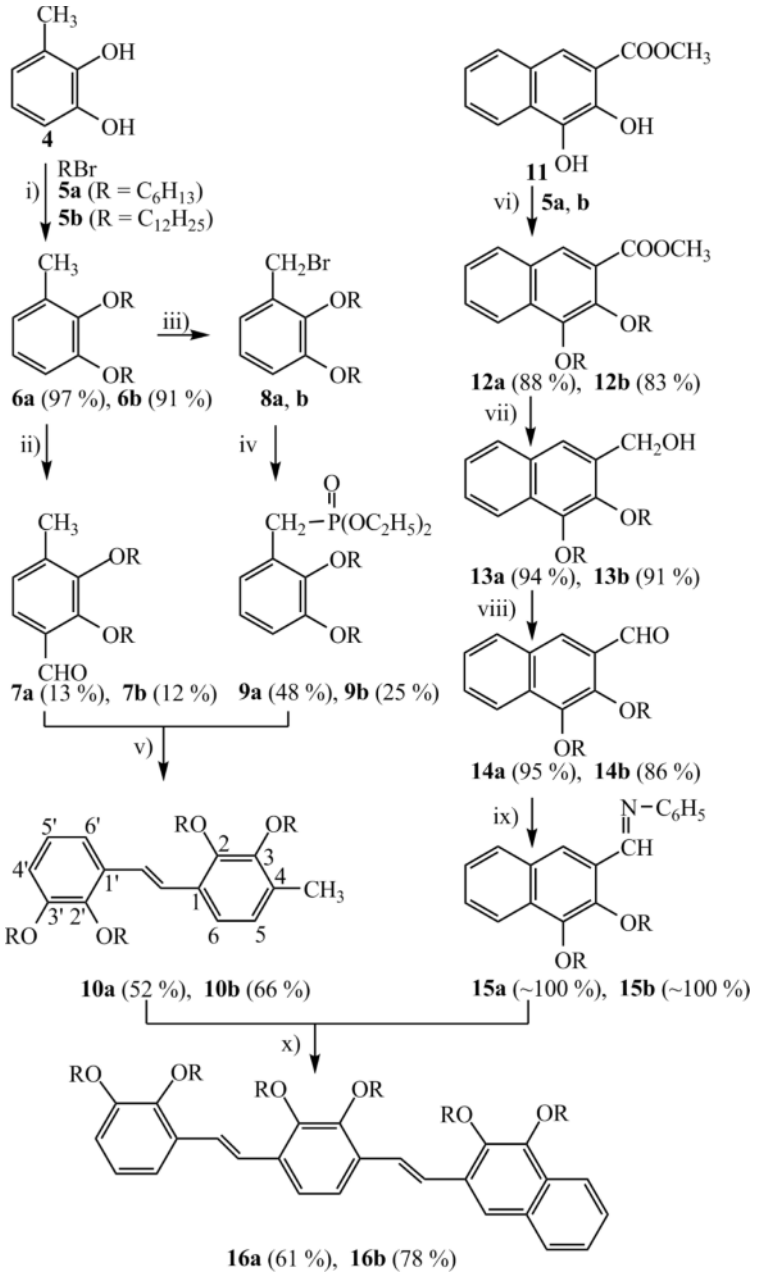


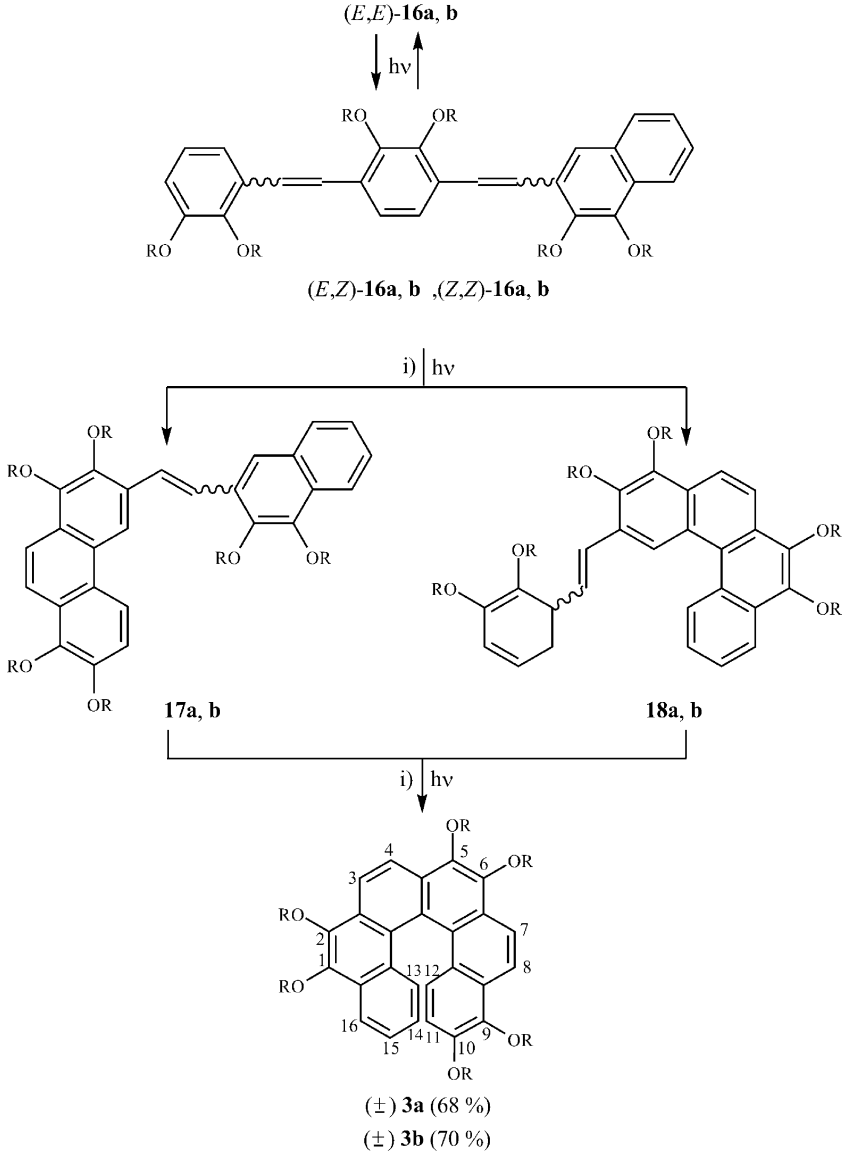
Fig. 1.



Scheme 1. Preparation of the 2-{(*E*)-2-[4-((*E*)-2-phenylvinyl)phenyl]vinyl}naphthalenes **16a**, **b**: i) KOH, Aliquat 336, 1,4-dioxane; ii) 1. BuLi, TMEDA, 2. DMF; iii) NBS, CCl_4; iv) $P(OC_2H_5)_3$, 160 °C; v) NaH, DME; vi) K_2CO_3, acetone; vii) $LiAlH_4$; viii) DDQ, 1,4-dioxane; ix) C_6H_5-NH_2, $CHCl_3$; x) $KOC(CH_3)_3$, DMF.

quence, **6a**, **b** were transformed to the phosphonates **9a**, **b** *via* the bromides **8a**, **b** [14]. Wittig–Horner reactions **7a+9a** and **7b+9b** gave the (*E*)-configured stilbenes **10a** and **10b**, respectively.

The naphthalene moiety of **16a**, **b** was synthesized on the basis of the ester **11** [17, 18], which was alkylated with the bromoalkanes **5a**, **b** to obtain **12a**, **b**. Reduction with $LiAlH_4$ yielded the alcohols **13a**,



Scheme 2. Photoisomerization of (*E*,*E*)-**16a**, **b** and subsequent cyclizations and oxidations to the hexahelicenes **3a**, **b**: i) I_2, .

b, which were gently oxidized by 2,3-dicyano-5,6-dichloro-1,4-benzoquinone (DDQ) to the aldehydes **14a**, **b**. The reaction with aniline gave then the Schiff bases **15a**, **b**. In contrast to the left branch of the synthetic Scheme 1, all yields in the right branch are very high. The four steps from **11** to **15a** have for example an overall yield of $88 \times 0.94 \times 0.95 \times 100 = 78.6\,\%$. Siegrist reactions [19] of **10a**+**15a** and **10b**+**15b** gave then **16a** and **16b**, respectively. The stereoselectivity in favor of the (*E*)-configuration is so high that the (*Z*)-isomers could not be detected in the NMR spectra of the crude reaction products **16a**, **b** [20].

Irradiation of (*E*,*E*)-**16a**, **b** led to the formation of the two possible (*E*,*Z*)-isomers and the (*Z*,*Z*)-isomer, which subsequently underwent cyclization and oxidation to **17a**, **b** and/or **18a**, **b** (Scheme 2). The second photocyclization and oxidation gave **3a** and **3b**, respectively, in good overall yields. In principle, an

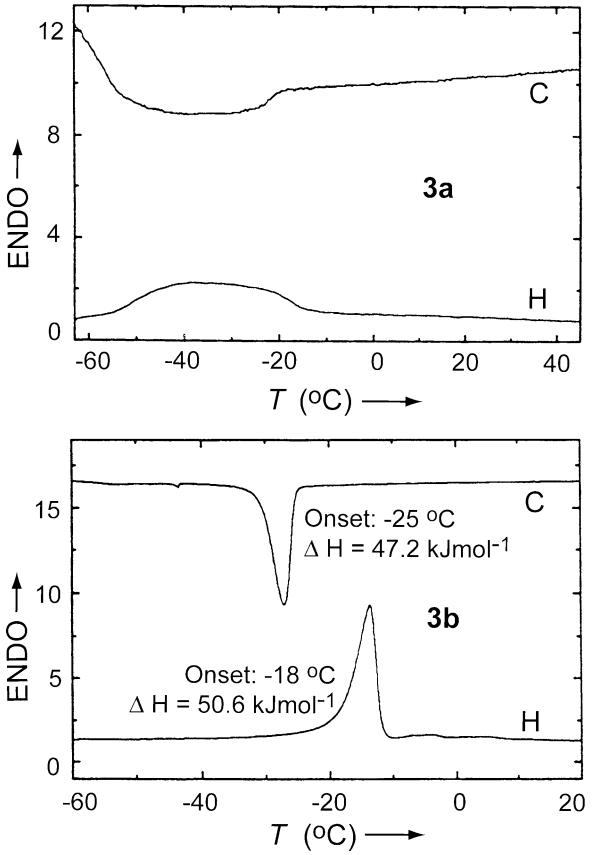


Fig. 2. DSC curves of **3a** and **3b**, measured at a rate of 10 K min^{-1}: H heating curve, C cooling curve.

unsubstituted system **16** would have four cyclization modes, which can lead to four different condensed benzenoid aromatics; however, the alkoxy groups in **16a**, **b** block three cyclization routes, so that only the route **16a**, **b**→**3a**, **b** remains. Iodine served as oxidant and methyloxirane as scavenger for the generated hydrogen iodide [21]. At the stage of the not isolated intermediates **17** and/or **18**, photoisomerizations have to be assumed.

The racemates **3a** and **3b** are pale-yellow oils which solidify below −20 °C. Both compounds exhibit very different DSC curves (Fig. 2); however, the formation of thermotropic mesophases could be excluded by polarization microscopy. Liquid crystals are very rare in the series of hexahelicenes [22, 23]. The broad peak in the heating and cooling curve of **3a** is unusual. It can be possibly due to a superposition of several close-lying phase transitions in the solid state. Impurities and of course any decomposition between −20 and −55 °C could be excluded.

Table 1. ^{1}H NMR spectra of **3a** and **3b** in $CDCl_3$, TMS as internal standard. (δ values in ppm, coupling constants J in Hz)

Proton (spin system)	**3a**	**3b**
3-H / 4-H (AB)	8.27 / 8.29	8.26 / 8.30
^3J	8.7	8.8
7-H / 8-H (AB)	8.35 / 8.39	8.32 / 8.38
^3J	8.8	8.8
11-H (A)	6.33	6.32
^3J	9.3	9.2
12-H (B)	7.15	7.13
13-H (A)	7.49	7.48
^3J	8.5	8.5
14-H (B)	6.60	6.58
15-H (C)	7.17	7.16
16-H (D)	8.13	8.11
^3J	7.9	8.0
10-OCH_2 (t)	3.86	3.83
1-, 2-, 5-, 6-, 9-OCH_2 (m)	3.84–4.43	3.95–4.45
β-CH_2 (m)	1.86–2.03	1.80–2.06
γ-CH_2 (m)	1.55–1.75	1.51–1.80
δ-CH_2 (m) and higher	1.20–1.48	1.15–1.51
CH_3 (m)	0.84–0.97	0.81–1.00

The hexahelicenes **3a**, **b** belong to the point group C_1, they are chiral. Consequently they show ten aromatic CH signals, ten C_q and six C_qO signals in the ^{13}C NMR spectra. Most characteristic are their ^{1}H NMR signals (Table 1). The aromatic protons give three AB and one ABCD spin patterns. The signals at highest field in the aromatic region were found for 11-H at $\delta = 6.33$ and 6.32 ppm, respectively. The overlap of the terminal benzene rings and the high electron density, induced by the 10-OR groups, are the reason for the resonance at unusually high field.

Conclusion

The hexahelicenes **3a** and **3b** are the first examples of [3]star compounds with a helical core consisting of a hexahelicene structure. Their preparation in a multistep synthesis was based on the twofold oxidative photocyclization of the linearly conjugated 2-(4-styryl-styryl)naphthalenes **16a** and **16b** (Schemes 1 and 2).

Experimental Section

NMR spectra were recorded on a Bruker AM 400 spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C.

FD MS (5 kV) and EI MS (70 eV) measurements were performed with a Finnigan MAT 95 spectrometer. UV/Vis spectra were obtained with a Zeiss MCS 320/340 diode array spectrometer. Melting points were taken on a Büchi apparatus and are uncorrected. A Perkin-Elmer DSC 7 instrument served for the differential scanning calorimetry (DSC). Polarization microscopy was performed with a Leitz Ortholux II microscope. Elemental analyses were determined in the microanalytical laboratory of the Chemistry Department of the University of Mainz.

The synthetic sequence **4**→**6a**, **b**→**8a**, **b** → **9a**, **b** is described elsewhere [14].

It was not necessary to isolate the intermediate bromo compounds **8a**, **b**. However, the oily compound 2,3-bis(hexyloxy)benzylbromide (**8a**) was checked for its purity by NMR control. – ^{1}H NMR ($CDCl_3$): $\delta = 0.88-1.01$ (m, 6 H, CH_3), 1.25 – 1.45 (m, 8 H, CH_2), 1.45 – 1.61 (m, 4 H, CH_2), 1.75 – 1.94 (m, 4 H, CH_2), 3.95 (t, $^3J = 6.3$ Hz, 2 H, OCH_2), 4.13 (t, $^3J = 6.6$ Hz, 2 H, OCH_2), 6.83 (dd, $^3J = 6.8$ Hz, $^4J = 2.9$ Hz, 1 H, 4-H), 6.89 – 7.02 (m, 2 H, 5-H, 6-H). – ^{13}C NMR ($CDCl_3$): $\delta = 13.9$, 14.0 (CH_3), 22.5, 22.6, 25.7, 25.8, 29.7, 30.3, 31.5, 31.7 (CH_2), 28.3 (CH_2Br), 113.7 (C-4), 122.3, 123.7 (C-5, C-6), 131.9 (C-1), 146.7, 152.3 (C-2, C-3). The only visible impurity was the starting compound **6a**, which does not react with triethyl phosphite.

*Bouveault formylation of **6a, b** to **7a, b***

Benzene derivative **6a**, **b** (22.0 mmol) and *N*,*N*′-tetramethylethylendiamine (TMEDA, 3.0 mL, 33.0 mmol) were dissolved in 100 mL of dry and deoxygenated diethyl ether. A 2.7 M solution of *n*-butyllithium in hexane (21.0 mL, 33.0 mmol) was added and the mixture stirred for 3 h at ambient temperature, before dimethylformamide (DMF, 2.3 mL, 33.0 mmol) was added. After a further hour at room temperature, first H_2O (10 mL) and then 2 M HCl (10 mL) were slowly dropped into the mixture. The organic layer and the extract of the water layer (50 mL diethyl ether) were unified, neutralized ($NaHCO_3$), dried ($MgSO_4$) and evaporated. The residue was purified by column filtration (5×40 cm SiO_2, toluene or CH_2Cl_2).

*2,3-Bis(hexyloxy)-4-methylbenzaldehyde (**7a**)*

Colorless oil, yield 0.92 g (13 %). – ^{1}H NMR ($CDCl_3$): $\delta = 0.85-0.95$ (m, 6 H, CH_3), 1.23 – 1.40 (m, 8 H, CH_2), 1.40 – 1.55 (m, 4 H, CH_2), 1.70 – 1.90 (m, 4 H, CH_2), 2.28 (s, 3 H, CH_3), 3.92 (t, $^3J = 6.5$ Hz, 2 H, OCH_2), 4.08 (t, $^3J = 6.4$ Hz, 2 H, OCH_2), 6.95/7.45 (AB, $^3J = 8.6$ Hz, 2 H, 5-H, 6-H), 10.31 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta =$ 14.0, 16.4 (CH_3, partly superimposed), 22.5, 22.6, 25.7, 25.7, 29.0, 30.2, 31.4, 31.6 (CH_2), 73.3, 75.3 (OCH_2), 122.6 (C-5), 125.1 (C-6), 129.0 (C-1), 140.3 (C-4), 150.9 (C-3), 155.8 (C-2), 189.5 (CHO). – MS (FD): m/z (%) = 320 (100) $[M]^+$. – $C_{20}H_{32}O_3$ (320.5): calcd. C 74.96, H 10.06; found C 74.79, H 9.82.

*2,3-Bis(dodecyloxy)-4-methylbenzaldehyde (**7b**)*

Colorless oil, yield 1.29 g (12 %). – ^{1}H NMR ($CDCl_3$): $\delta = 0.84-0.95$ (m, 6 H, CH_3), 1.15 – 1.40 (m, 32 H, CH_2), 1.40 – 1.53 (m, 4 H, CH_2), 1.68 – 1.84 (m, 4 H, CH_2), 2.27 (s, 3 H, CH_3), 3.92 (t, $^3J = 6.4$ Hz, 2 H, OCH_2), 4.07 (t, $^3J =$ 6.4 Hz, 2 H, OCH_2), 6.94/7.45 (AB, $^3J = 8.0$ Hz, 2 H, 5-H, 6-H), 10.32 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 14.0$, 16.6 (CH_3, partly superimposed), 22.6, 26.0, 26.1, 29.3, 29.4, 29.6, 30.1, 30.4, 31.9 (CH_2, partly superimposed), 73.1, 75.2 (OCH_2), 122.4 (C-5), 125.9 (C-6), 128.8 (C-1), 140.3 (C-4), 150.9 (C-3), 155.6 (C-2), 189.6 (CHO). – MS (EI): m/z (%) = 488 (14) $[M]^+$, 152 (100). – $C_{32}H_{56}O_3$ (488.8): calcd. C 78.63, H 11.55; found C 78.51, H 11.60.

*Wittig–Horner reaction of **7a, b** and **9a, b** for the preparation of **10a, b***

Phosphonic acid ester **9a**, **b** (2.1 mmol) in 40 mL of dry dimethoxyethane (DME) was dropped under nitrogen to NaH (420 mg, 10.5 mmol, 60 % in paraffin) suspended in 120 mL of dry DME. Aldehyde **7a**, **b** (2.1 mmol) was slowly added and the reaction mixture heated to reflux for 6 h. Then 40 g crushed ice was added and the aqueous phase extracted with 100 mL of diethyl ether. The unified organic phases were dried ($MgSO_4$) and evaporated. The residue was purified by column chromatography (3×40 cm SiO_2, petroleum ether, b. p. 40 – 70 °C / CH_2Cl_2 2 : 1).

*1-{(E)-2-[2,3-Bis(hexyloxy)phenyl]vinyl}-2,3-bis(hexyloxy)-4-methylbenzene (**10a**)*

Yield 650 g (52 %), viscous oil. – ^{1}H NMR ($CDCl_3$): $\delta = 0.82-0.94$ (m, 12 H, CH_3), 1.20 – 1.38 (m, 16 H, CH_2), 1.38 – 1.56 (m, 8 H, CH_2), 1.63 – 1.88 (m, 8 H, CH_2), 2.26 (s, 3 H, 4-CH_3), 3.95 – 4.02 (m, 8 H, OCH_2), 6.78 (d, $^3J =$ 7.9 Hz, 1 H, 4′-H), 6.89 (d, $^3J = 8.1$ Hz, 1 H, 5-H), 7.00 (t, $^3J = 7.9$ Hz, 1 H, 5′-H), 7.24 (d, $^3J = 7.6$ Hz, 1 H, 6′-H), 7.25 (′s′, 2 H, olefin. H), 7.31 (d, $^3J = 8.0$ Hz, 1 H, 6-H). – ^{13}C NMR ($CDCl_3$): $\delta = 14.1$, 16.2 (CH_3, partly superimposed), 22.7, 22.8, 25.9, 30.5, 31.7, 31.8 (CH_2, partly superimposed), 68.7, 73.0, 73.7, 73.9 (OCH_2), 112.3, 117.5, 120.3, 123.1, 123.7, 123.8, 125.8 (aromat. and olefin. CH), 130.5, 131.8, 132.4 (aromat. C_q), 146.4, 150.3, 151.1, 152.7 (C_qO). – MS (FD): m/z (%) = 594 (100) $[M]^+$. – $C_{39}H_{62}O_4$ (594.9): calcd. C 78.74, H 10.50; found C 78.84, H 10.43.

*1-{(E)-2-[2,3-Bis(dodecyloxy)phenyl]vinyl}-2,3-bis(dodecyloxy)-4-methylbenzene (**10b**)*

Yield 1.29 g (66 %), viscous oil. – ^{1}H NMR ($CDCl_3$): $\delta = 0.83-0.94$ (m, 12 H, CH_3), 1.15 – 1.44 (m, 64 H, CH_2),

1.44 – 1.58 (m, 8 H, CH_2), 1.72 – 1.88 (m, 8 H, CH_2), 2.25 (s, 3 H, 4-CH_3), 3.90 – 4.03 (m, 8 H, OCH_2), 6.78 (d, ^3J = 7.9 Hz, 1 H, 4′-H), 6.89 (d, ^3J = 8.1 Hz, 1 H, 5-H), 6.99 (t, ^3J = 7.9 Hz, 1 H, 5′-H), 7.24 (d, ^3J = 7.8 Hz, 1 H, 6′-H), 7.31 (d, ^3J = 8.1 Hz, 1 H, 6-H), 7.41 (′s′, 2 H, olefin. H). – ^{13}C NMR ($CDCl_3$): δ = 14.1, 16.1 (CH_3, partly superimposed), 22.7, 26.2, 26.4, 29.4, 29.7, 30.4, 30.5, 31.9 (CH_2, partly superimposed), 68.6, 73.0, 73.7, 73.9 (OCH_2), 112.1, 117.4, 120.2, 122.6, 123.7, 123.7, 125.7 (aromat. and olefin. CH), 130.4, 131.7, 132.3 (aromat. C_q), 146.3, 150.2, 151.0, 152.6 (C_qO). – MS (FD): m/z (%) = 931 (100) $[M]^+$. – $C_{63}H_{110}O_4$ (931.6): calcd. C 81.23, H 11.90; found C 81.14, H 11.81.

*Alkylation of 3,4-dihydroxynaphthalene-2-carboxylic acid methyl ester (**11**)*

To ester **11** [17, 18] (1.30 g, 5.96 mmol), K_2CO_3 (2.00 g, 14.5 mmol) and a trace of KI in 60 mL of dry acetone, 1-bromoalkane **5a**, **b** (14.0 mmol) was added. The vigorously stirred mixture was heated to reflux under nitrogen for 3 d. After filtration the solvent was evaporated and the residue purified by column chromatography (4 × 50 cm SiO_2, toluene).

*3,4-Bis(hexyloxy)naphthalene-2-carboxylic acid methyl ester (**12a**)*

Yield 2.03 g (88 %), viscous oil. – ^{1}H NMR ($CDCl_3$): δ = 0.83 – 0.92 (m, 6 H, CH_3), 1.20 – 1.36 (m, 8 H, CH_2), 1.36 – 1.52 (m, 4 H, CH_2), 1.68 – 1.86 (m, 4 H, CH_2), 3.94 (s, 3 H, OCH_3), 4.06 – 4.18 (m, 4 H, OCH_2), 7.35 – 7.55 (m, 2 H, 6-H, 7-H), 7.80 (d, ^3J = 8.0 Hz, 1 H, aromat. H), 8.07 (s, 1 H, 1-H), 8.10 (d, ^3J = 8.4 Hz, 1 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3, superimposed), 22.6, 25.7, 25.8, 30.2, 30.4, 31.7 (CH_2, partly superimposed), 52.2 (OCH_2), 74.1, 74.7 (OCH_2), 121.7, 125.6, 126.9, 127.7, 128.6 (aromat. CH), 125.9 (C-4a), 130.0 (C-2), 131.4 (C-4a), 146.6, 147.6 (C-3, C-4), 166.8 (CO). – MS (EI): m/z (%) = 386 (21) $[M]^+$, 186 (100). – $C_{24}H_{34}O_4$ (386.5): calcd. C 74.58, H 8.87; found C 74.27, H 8.57.

*3,4-Bis(dodecyloxy)naphthalene-2-carboxylic acid methyl ester (**12b**)*

Yield 2.81 g (85 %), viscous oil. – ^{1}H NMR ($CDCl_3$): δ = 0.83 – 0.92 (m, 6 H, CH_3), 1.20 – 1.42 (m, 32 H, CH_2), 1.42 – 1.60 (m, 4 H, CH_2), 1.75 – 1.92 (m, 4 H, CH_2), 3.94 (s, 3 H, OCH_3), 4.06 – 4.20 (m, 4 H, OCH_2), 7.39 – 7.58 (m, 2 H, 6-H, 7-H), 7.79 (d, ^3J = 8.1 Hz, 1 H, aromat. H), 8.07 (s, 1 H, 1-H), 8.11 (d, ^3J = 8.3 Hz, 1 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3, superimposed), 22.7, 26.1, 26.2, 29.3, 29.6, 30.3, 30.5, 31.9 (CH_2, partly superimposed), 52.2 (OCH_3), 74.1, 74.7 (OCH_2), 121.8, 125.6, 127.0, 127.7, 128.7 (aromat. CH), 125.9 (C-4a), 130.0 (C-2), 131.4 (C-8a), 146.7, 147.7 (C-3, C-4), 166.8 (CO). – MS (EI): m/z (%) = 554 (44) $[M]^+$, 186 (100). – $C_{36}H_{58}O_4$ (554.8): calcd. C 77.93, H 10.54; found C 78.20, H 10.75.

*Reduction of the esters **12a**, **b** to the alcohols **13a**, **b***

To $LiAlH_4$ (190 mg, 5.0 mmol) in 50 mL of dry diethyl ether, ester **12a**, **b** (5.0 mmol) in 20 mL of diethyl ether was slowly added at a rate, so that the mixture was gently boiling. After heating to reflux for 2 h, 10 mL of H_2O and 20 mL of 2 M HCl were added. The separated organic layer was treated with aqueous $NaHCO_3$, washed with H_2O, dried ($MgSO_4$) and evaporated. The residue was purified by column filtration (4 × 30 cm SiO_2, CH_2Cl_2).

*[3,4-Bis(hexyloxy)naphthalen-2-yl]methanol (**13a**)*

Yield 1.69 g (94 %), colorless solid, which melted at 63 – 64 °C. – ^{1}H NMR ($CDCl_3$): δ = 0.85 – 0.97 (m, 6 H, CH_3), 1.28 – 1.44 (m, 8 H, CH_2), 1.44 – 1.61 (m, 4 H, CH_2), 1.73 – 1.93 (m, 4 H, CH_2), 4.07 (t, ^3J = 6.7 Hz, 2 H, OCH_2), 4.13 (t, ^3J = 6.6 Hz, 2 H, OCH_2), 4.81 (s, 2 H, CH_2OH), 7.33 – 7.48 (m, 2 H, aromat. H), 7.51 (s, 1 H, 1-H), 7.71 (d, ^3J = 8.1 Hz, 1 H, aromat. H), 8.09 (d, ^3J = 8.6 Hz, 1 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 13.9 (CH_3, superimposed), 22.5, 25.7, 25.8, 30.4, 31.6 (CH_2, partly superimposed), 62.0 (CH_2OH), 73.5, 73.6 (OCH_2), 121.4, 122.0, 124.9, 125.5, 127.6 (aromat. CH), 129.2, 130.8, 134.7 (aromat. C_q), 145.8, 146.4 (C_qO). – MS (EI): m/z (%) = 358 (22) $[M]^+$, 172 (100). – $C_{23}H_{34}O_3$ (358.5): calcd. C 77.05, H 9.56; found C 77.27, H 9.73.

*[3,4-Bis(dodecyloxy)naphthalen-2-yl]methanol (**13b**)*

Yield 2.52 g (91 %), colorless solid, which melted at 54 – 56 °C. – ^{1}H NMR ($CDCl_3$): δ = 0.85 – 0.96 (m, 6 H, CH_3), 1.20 – 1.40 (m, 32 H, CH_2), 1.40 – 1.60 (m, 4 H, CH_2), 1.73 – 1.93 (m, 4 H, CH_2), 4.04 – 4.19 (m, 4 H, OCH_2), 4.82 (s, 2 H, CH_2OH), 7.36 – 7.48 (m, 2 H, aromat. H), 7.52 (s, 1 H, 1-H), 7.75 (d, ^3J = 8.1 Hz, 1 H, aromat. H), 8.07 (d, ^3J = 8.5 Hz, 1 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (CH_3, superimposed), 22.7, 26.1, 26.2, 29.4, 29.6, 30.5, 31.9 (CH_2, partly superimposed), 62.7 (CH_2OH), 73.7, 73.8 (OCH_2), 121.5, 122.3, 125.1, 125.7, 127.7 (aromat. CH), 129.4, 131.0, 134.7 (aromat. C_q), 146.0, 146.7 (C_qO). – MS (EI): m/z (%) = 526 (35) $[M]^+$, 172 (100). – $C_{35}H_{58}O_3$ (526.9): calcd. C 79.79, H 11.10; found C 80.10, H 10.75.

*Oxidation of the alcohols **13a**, **b** to the aldehydes **14a**, **b***

4.0 mmol of **13a**, **b** and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 908 mg, 4.0 mmol) were stirred under Ar in 20 mL of 1,4-dioxane at room temperature for 12 h. The filtered reaction mixture was concentrated and purified by column chromatography (3 × 50 cm SiO_2, CH_2Cl_2).

*3,4-Bis(hexyloxy)naphthalene-2-carbaldehyde (**14a**)*

Yield 1.35 g (95 %), colorless solid, which melted at 43 – 45 °C. – ^{1}H NMR ($CDCl_3$): $\delta = 0.82 - 0.93$ (m, 6 H, CH_3), 1.20 – 1.42 (m, 8 H, CH_2), 1.42 – 1.62 (m, 4 H, CH_2), 1.75 – 1.96 (m, 4 H, CH_2), 4.14 (t, $^3J = 6.6$ Hz, 2 H, OCH_2), 4.17 (t, $^3J = 6.6$ Hz, 2 H, OCH_2), 7.41 – 7.62 (m, 2 H, 6-H, 7-H), 7.89 (d, $^3J = 8.1$ Hz, 1 H, 8-H), 8.11 (d, $^3J = 8.5$ Hz, 1 H, 5-H), 8.11 (s, 1 H, 1-H), 10.50 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 13.9$ (CH_3, superimposed), 22.5, 25.6, 25.7, 30.0, 30.3, 31.5 (CH_2, partly superimposed), 73.9, 74.9 (OCH_2), 121.7, 125.0, 125.7, 128.4, 129.8 (aromat. CH), 129.2, 130.0, 132.8 (aromat. C_q), 145.8, 146.4 (C_qO), 190.3 (CHO). – MS (FD): m/z (%) = 356 (100) $[M]^+$. – $C_{23}H_{32}O_3$ (356.5): calcd. C 77.48, H 9.05; found C 77.37, H 8.83.

*3,4-Bis(dodecyloxy)naphthalene-2-carbaldehyde (**14b**)*

Yield 1.81 g (86 %), colorless solid, which melted at about 30 °C. – ^{1}H NMR ($CDCl_3$): $\delta = 0.82 - 0.92$ (m, 6 H, CH_3), 1.20 – 1.49 (m, 32 H, CH_2), 1.49 – 1.65 (m, 4 H, CH_2), 1.75 – 2.00 (m, 4 H, CH_2), 4.10 (t, $^3J = 6.6$ Hz, 2 H, OCH_2), 4.22 (t, $^3J = 6.5$ Hz, 2 H, OCH_2), 7.40 – 7.60 (m, 2 H, aromat. H), 7.89 (d, $^3J = 8.1$ Hz, 1 H, aromat. H), 8.11 (d, $^3J = 8.6$ Hz, 1 H, aromat. H), 8.13 (s, 1 H, 1-H), 10.51 (s, 1 H, CHO). – ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3, superimposed), 22.6, 26.1, 26.2, 29.4, 29.5, 29.6, 30.2, 30.4, 31.9 (CH_2, partly superimposed), 74.1, 75.1 (OCH_2), 121.8, 125.2, 125.9, 128.5, 129.9 (aromat. CH), 129.3, 130.1, 133.0 (aromat. C_q), 146.9, 148.7 (C_qO), 190.6 (CHO). MS (EI): m/z (%) = 524 (13) $[M]^+$, 188 (100). – $C_{35}H_{56}O_3$ (524.8): calcd. C 80.10, H 10.75; found C 80.21, H 10.80.

*Formation of the Schiff bases **15a, b***

Aldehyde **14a**, **b** (3.40 mmol) and aniline (400 mg, 4.30 mmol) were dissolved in 60 mL of $CHCl_3$ and heated to reflux for 1 d, so that the formed H_2O was continuously removed. The volatile parts were distilled off and the residue dried at 0.1 kPa. The obtained oily products were analytically pure.

*{1-[3,4-Bis(hexyloxy)naphthalen-2-yl]methylidene}-phenylamine (**15a**)*

Quantitative yield: 1.46 g, pale-yellow oil. – ^{1}H NMR ($CDCl_3$): $\delta = 0.82 - 0.98$ (m, 6 H, CH_3), 1.20 – 1.42 (m, 8 H, CH_2), 1.42 – 1.65 (m, 4 H, CH_2), 1.65 – 1.96 (m, 4 H, CH_2), 4.13–4.23 (m, 4 H, OCH_2), 7.23 – 7.57 (m, 7 H, aromat. H), 7.90 (d, $^3J = 8.2$ Hz, 1 H, aromat. H), 8.11 (d, $^3J = 8.3$ Hz, 1 H, aromat. H), 8.44 (s, 1 H, 1-H), 8.97 (s, 1 H, CHN). – ^{13}C NMR ($CDCl_3$): $\delta = 14.4$ (CH_3, superimposed), 23.0, 26.2, 30.6, 30.8, 32.0 (CH_2, partly superimposed), 74.3, 76.7 (OCH_2), 121.4, 122.0, 123.1, 125.8, 126.3, 127.4, 129.5 (aromat. CH, partly superimposed), 129.6, 130.4, 131.1 (aromat. C_q), 146.4, 147.8 (C_qO), 152.3 (C_qN), 157.3 (CHN). – MS (FD): m/z (%) = 431 (100) $[M]^+$. – $C_{29}H_{37}NO_2$ (431.6): calcd. C 80.70, H 8.64, N 3.25; found C 80.65, H 8.80, N 3.24.

*{1-[3,4-Bis(dodecyloxy)naphthalen-2-yl]methylidene}-phenylamine (**15b**)*

Quantitative yield: 2.04 g, pale-yellow oil. – ^{1}H NMR ($CDCl_3$): $\delta = 0.84 - 1.00$ (m, 6 H, CH_3), 1.20 – 1.44 (m, 32 H, CH_2), 1.44 – 1.68 (m, 4 H, CH_2), 1.68 – 1.96 (m, 4 H, CH_2), 4.11 – 4.22 (m, 4 H, OCH_2), 7.23 – 7.57 (m, 7 H, aromat. H), 7.90 (d, $^3J = 8.2$ Hz, 1 H, aromat. H), 8.12 (d, $^3J = 8.3$ Hz, 1 H, aromat. H), 8.45 (s, 1 H, 1-H), 8.98 (s, 1 H, CHN). – ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3, superimposed), 22.7, 26.2, 29.4,29.5, 29.7, 30.3, 30.5, 31.9 (CH_2, partly superimposed), 74.0, 76.4 (OCH_2), 121.1, 121.7, 122.8, 125.5, 126.0, 127.1, 129.1 (aromat. CH, partly superimposed), 129.6, 130.7, 131.3 (aromat. C_q), 146.5, 147.9 (C_qO), 152.5 (C_qN), 157.0 (CHN). – MS (EI): m/z (%) = 599 (17) $[M]^+$, 507 (100). – $C_{41}H_{61}NO_2$ (599.9): calcd. C 82.08, H 10.25, N 2.33; found C 82.05, H 10.27, N 2.40.

*Siegrist reaction of the Schiff bases **15a, b** and the methylstilbenes **10a, b***

Methylstilbene **10a**, **b** (3.0 mmol) and Schiff base **15a**, **b** (3.3 mmol) were treated in 150 mL of dry DMF with 3.8 g (34.0 mmol) $KOC(CH_3)_3$ at room temperature. After 0.5 h the reaction mixture was heated to 90 °C and stirred for 1.5 h. Then 30 mL of H_2O and 50 mL of 2 M HCl were slowly added. The mixture was extracted with 3 × 120 mL of diethyl ether. The neutralized ($NaHCO_3$) ether solution was dried ($MgSO_4$) and evaporated. The residue was purified by column filtration (4 × 40 cm SiO_2, toluene).

*1,2-Bis(hexyloxy)-3-((E)-2-{2,3-bis(hexyloxy)-4-[(E)-2-(2,3-bis(hexyloxy)phenyl)vinyl]phenyl}vinyl)naphthalene (**16a**)*

Stilbene **10a** (1.8 g, 3.0 mmol) and Schiff base **15a** (1.4 g, 3.3 mmol) yielded 1.71 g (61 %) **16a** as yellow oil. – ^{1}H NMR ($CDCl_3$): $\delta = 0.83 - 0.96$ (m, 18 H, CH_3), 1.20 – 1.40 (m, 24 H, CH_2), 1.44 – 1.59 (m, 12 H, CH_2), 1.75 – 1.90 (m, 12 H, CH_2), 3.95 – 4.16 (m, 12 H, OCH_2), 6.80 (d, $^3J = 8.1$ Hz, 1 H), 7.00 (t, $^3J = 8.0$ Hz, 1 H), 7.26 (d, $^3J = 8.0$ Hz, 1 H, aromat. H), 7.34 – 7.48 (m, 5 H, aromat. and olefin. H), 7.53 (d, $^3J = 16.5$ Hz, 1 H, olefin. H), 7.56/7.62 (AB, $^3J = 16.5$ Hz, olefin. H), 7.77 (d, $^3J = 8.3$, 1 H, aromat. H), 7.87 (s, 1 H, aromat. H), 8.06 (d, $^3J = 7.9$, 1 H, aromat. H). – ^{13}C NMR ($CDCl_3$): $\delta = 14.1$ (CH_3, superimposed), 22.8, 25.9, 26.1,29.4, 29.7, 30.4, 31.6, 31.8, 32.8 (CH_2, partly superimposed), 68.7, 73.8, 73.9, 74.0, 74.1, 74.2 (OCH_2), 112.4, 117.4, 119.9, 120.7, 120.7, 121.7, 123.4, 123.8 123.8, 123.9, 124.4, 125.2, 125.5, 127.8 (aromat. and olefin. CH), 129.2, 131.1, 131.6, 131.9, 132.2, 132.5 (aromat. C_q), 146.5,

146.6, 146.7, 150.6, 150.7, 152.7 (aromat. C_qO). – MS (FD): m/z (%) = 933 (100) $[M]^+$. – $C_{62}H_{92}O_6$ (933.4): calcd. C 79.78, H 9.93; found C 79.91, H 10.03.

*1,2-Bis(dodecyloxy)-3-((E)-2-{2,3-bis(dodecyloxy)-4-[(E)-2-(2,3-bis(dodecyloxy)phenyl)vinyl]phenyl}vinyl) naphthalene (**16b**)*

Stilbene **10b** (2.8 g, 3.0 mmol) and Schiff base **15b** (2.0 g, 3.3 mmol) yielded 3.36 g (78 %) **16b** as pale-yellow crystals, which melted at 49 – 51 °C. – ^{1}H NMR ($CDCl_3$): δ = 0.85 – 0.98 (m, 18 H, CH_3), 1.20 – 1.50 (m, 96 H, CH_2), 1.50 – 1.70 (m, 12 H, CH_2), 1.83 – 1.96 (m, 12 H, CH_2), 4.00 – 4.24 (m, 12 H, OCH_2), 6.83 (d, ^3J = 8.2 Hz, 1 H), 7.05 (t, ^3J = 8.1 Hz, 1 H), 7.32 (d, ^3J = 7.8 Hz, 1 H), 7.43 (t, ^3J = 8.0 Hz, 1 H, aromat. H), 7.46 – 7.62 (m, 5 H, aromat. and olefin. H), 7.59 (s, 1 H, aromat. H), 7.64/7.70 (AB, ^3J = 16.6, 2 H, olefin. H), 7.82 (d, ^3J = 7.5 Hz, 1 H, aromat. H), 7.93 (s, 1 H, aromat. H), 8.14 (d, ^3J = 7.9 Hz, 1 H, aromat. H). – ^{13}C NMR ($CDCl_3$): δ = 14.1 (superimposed), 22.7, 26.3, 26.4, 26.5, 29.4, 29.5, 29.7, 29.8, 30.5, 30.6, 31.8, 32.0 (CH_2, partly superimposed), 68.7, 73.7, 73.9, 74.0, 74.1, 74.2 (OCH_2), 112.6, 117.7, 120.0, 120.8, 120.9, 121.7, 123.6, 123.7, 124.0, 124.1, 124.6, 125.2, 125.5, 127.8 (aromat. and olefin. CH), 129.3, 131.2, 131.7, 132.0, 132.3, 132.6 (aromat. C_q), 146.7, 146.8, 147.8, 150.7, 150.8, 152.8 (aromat. C_qO). – MS (FD): m/z (%) = 1438 (100) $[M]^+$. – $C_{98}H_{164}O_6$ (1438.4): calcd. C 81.83, H 11.49; found C 81.88, H 11.45.

*Preparation of the phenanthro[3,4-c]phenanthrenes **3a**, **b***

A solution of 0.7 mmol **16a**, **b** and 0.35 g (1.4 mmol) I_2 in 2 L of dry benzene was purged by a stream of oxygen-free nitrogen for 0.5 h. Methyloxirane (4.9 mL, 70 mmol) was added and the mixture irradiated with a Hanovia-450 W medium-pressure lamp equipped with a Pyrex filter. The red solution bleaches in the course of the reaction which takes 10 – 12 h. The N_2 stream was maintained till the process came to an end. The reaction mixture was treated with aqueous $NaHCO_3$, dried ($MgSO_4$) and evaporated. The crude product was purified by a twofold column chromatography (3 × 50 cm SiO_2, petroleum ether, b. p. 40 – 70 °C / CH_2Cl_2 5 : 1 to 2 : 1).

*1,2,5,6,9,10-Hexakis(hexyloxy)phenanthro[3,4-c] phenanthrene (**3a**)*

Yield 440 mg (68 %), light-yellow oil. – ^{1}H NMR ($CDCl_3$): δ = 14.0, 14.1 (CH_3, superimposed), 22.7, 25.7, 26.0, 29.4, 29.5, 29.7, 30.5, 31.6, 31.8, 31.9 (CH_2, partly superimposed), 69.5, 73.8, 73.9, 74.0, 74.1, 74.1 (OCH_2), 114.3, 120.1, 120.8, 120.9, 121.0, 121.6, 123.6, 124.1, 125.4, 128.0 (aromat. CH), 121.8, 125.4, 125.7, 126.1, 126.7, 127.3, 128.0, 128.1, 128.4, 129.3 (aromat. C_q), 142.4, 142.9, 143.5, 143.6, 144.1, 147.1 (C_qO). – MS (FD): m/z (%) = 929 (100) $[M]^+$. – $C_{62}H_{88}O_6$ (929.4): calcd. C 80.13, H 9.54; found C 80.15, H 9.86.

*1,2,5,6,9,10-Hexakis(dodecyloxy)phenanthro[3,4-c] phenanthrene (**3b**)*

Yield 700 mg (70 %), light-yellow oil. – ^{1}H NMR ($CDCl_3$): δ = 14.0, 14.1 (CH_3, superimposed), 22.7, 26.1, 26.4, 29.4, 29.5, 29.7, 30.6, 32.0 (CH_2, partly superimposed), 69.4, 73.7, 73.8, 74.0 (OCH_2, partly superimposed), 113.8, 120.1, 120.7, 120.8, 120.9, 121.5, 123.6, 124.0, 125.4, 128.0 (aromat. CH), 121.7, 125.3, 125.6, 126.0, 126.6, 127.3, 128.0, 128.1, 128.4, 129.2 (aromat. C_q), 142.2, 142.8, 143.5, 143.5, 144.1, 147.4 (C_qO). – MS (FD): m/z (%) = 1434 (100) $[M]^+$. – $C_{98}H_{160}O_6$ (1434.4): calcd. C 82.06, H 11.24; found C 82.07, H 11.27.

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[1] H. Detert, M. Lehmann, H. Meier, *Materials* **2010**, *3*, 3218–3330.
[2] F.-H. Marquardt, *J. Chem. Soc.* **1965**, 1517–1518.
[3] M. Piatelli, E. Fatturusso, R. A. Nicolaus, S. Magno, *Tetrahedron* **1965**, *21*, 3229–3236.
[4] V. Bhalla, H. Arora, H. Singh, M. Kumar, *Dalton Trans.* **2013**, *42*, 969–974.
[5] F. Yang, X. Bai, H. Guo, C. Li, *Tetrahedron Lett.* **2013**, *54*, 409–413.
[6] Y.-F. Zhu, X.-L. Guan, Z. Shen, X.-H. Fen, Q.-F. Zhou, *Macromolecules* **2012**, *45*, 3346–3355.
[7] K. R. Leight, B. E. Esarey, A. E. Murray, J. J. Reczek, *Chem. Mater.* **2012**, *24*, 3318–3328.
[8] Z. Li, X. Chen, Y. Zhang, J. Zhang, Z. Hu, *Chem. Lett.* **2012**, *41*, 1588–1590.
[9] D. Wu, H. Zhang, J. Liang, H. Ge, S. H. Liu, J. Yin, C. Chi, J. Wu, *J. Org. Chem.* **2012**, *77*, 11319–11324.
[10] R. Rieger, V. Enkelmann, K. Müllen, M. Kastler, *Chem. Eur. J.* **2008**, *14*, 6322–6325.
[11] H.-P. Jia, S.-X. Liu, S. Decurtins, L. Sanguinet, E. Levillain, *J. Org. Chem.* **2009**, *74*, 5727–5729.
[12] F. B. Mallory, C. W. Mallory, *Org. React.* **1984**, *30*, 1–456.
[13] H. Meier, H. Kretzschmann, H. Kolshorn, *J. Org. Chem.* **1992**, *57*, 6847–6852.

[14] M. Schwertel, S. Hillmann, H. Meier, *Helv. Chim. Acta,* in print.
[15] C. Huang, N. Ghavtadze, B. Chattopadhyay, V. Gevorgyan, *J. Am. Chem. Soc.* **2011**, *133*, 17630–17633.
[16] See also: S. Werle, T. Fey, J. M. Neudoerfl, H.-G. Schmalz, *Org. Lett.* **2007**, *9*, 3555–3558.
[17] R. Mählau, F. Kriebel, *Ber. Dtsch. Chem. Ges.* **1895**, *28*, 3092.
[18] S. Desai, *J. Ind. Chem. Soc.* **1951**, *28*, 213–217.
[19] A. F. Siegrist, *Helv. Chim. Acta* **1967**, *50*, 906–957.
[20] See also: H. Meier, *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1399–1420.
[21] L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **1991**, *56*, 3769–3775.
[22] C. Nuckolls, T. J. Katz, *J. Am. Chem. Soc.* **1998**, *120*, 9541–9544.
[23] L. Vyklicky, S. H. Eichhorn, T. J. Katz, *Chem. Mater.* **2003**, *15*, 3594–3601.