Synthesis of Highly Substituted Hexahelicenes

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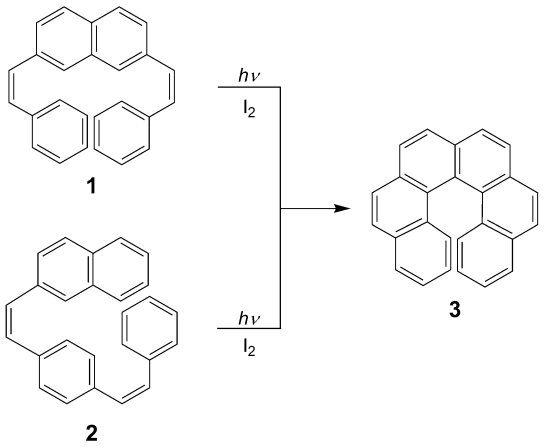
C_2-Symmetric hexahelicenes **3a**–**3g**, which bear four or six alkoxy chains, were prepared in eight-to-nine reaction steps in high overall yields. The final step consisted of a twofold oxidative photocyclization of the corresponding 2,7-bis(2-phenylethenyl)naphthalenes. Long (and branched) chains provide a good solubility and processability, which is a prerequisite for applications in organic synthesis and materials science.

1. Introduction. – Since their first preparation, helicenes attracted remarkable attention due to their outstanding properties [1–9]. In the previous years, an increasing number of applications of helicenes was reported; for example, in catalytic processes [10–17] or in materials science such as nonlinear optics (NLO) [18][19], molecular machines [20], liquid crystals [21][22], and thin-film transistors [23]. The majority of the here referred articles deals with carbo- or heterocyclic hexahelicenes. This prompted us to report our work on highly substituted hexahelicenes.

Photochemical generations of hexahelicenes (**3**), in the sense of twofold oxidative cyclizations, start either from 2,7-bis(2-phenylethenyl)naphthalenes (**1**) or from 2-{2-[4-(2-phenylethenyl)phenyl]ethenyl}naphthalene (**2**). The electrocyclic ring closures with subsequent dehydrogenation furnish good yields of these sterically hindered, chiral, benzenoid aromatics **3** (*Scheme 1*). In principle, **1** and **2** have more than one cyclization

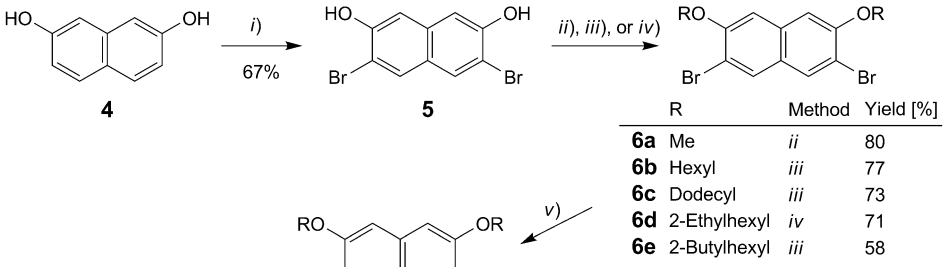
Scheme 1. *Photochemical Routes to Hexahelicenes*



route; however, according to theoretical predictions, the alternative routes play a minor role [24][25]. We applied the process **1** → **3** for the formation of highly substituted hexahelicenes **3**, which have a C_2 axis of symmetry. To achieve good solubilities, we introduced preferentially long and/or branched alkoxy groups. A certain background of this study was the question: 'Do such compounds form liquid crystals, or can such components change the mesophase properties of known discotic systems.'

2. Results and Discussion. – We started the synthetic route **1** → **3** with naphthalene-2,7-diol (**4**) and introduced first Br-substituents at C(3) and C(6) (*Scheme 2*). The use of excess Br_2 led to the 1,3,6,8-tetrabromo derivative, from which the present Sn powder removed the Br-substituents at C(1) and C(8) [26]. Three slightly different methods were then applied for the twofold *O*-alkylation **5** → **6a** – **6e**. Phase-transfer catalysis is particularly recommended for longer and/or branched alkyl groups. The dialdehydes **7a** – **7e** were obtained by twofold *Bouveault* reactions.

Scheme 2. *Preparation of 3,6-Dialkoxynaphthalene-2,7-dicarbaldehydes* **7a** – **7e**



	R	Method	Yield [%]
6a	Me	*ii*	80
6b	Hexyl	*iii*	77
6c	Dodecyl	*iii*	73
6d	2-Ethylhexyl	*iv*	71
6e	2-Butylhexyl	*iii*	58

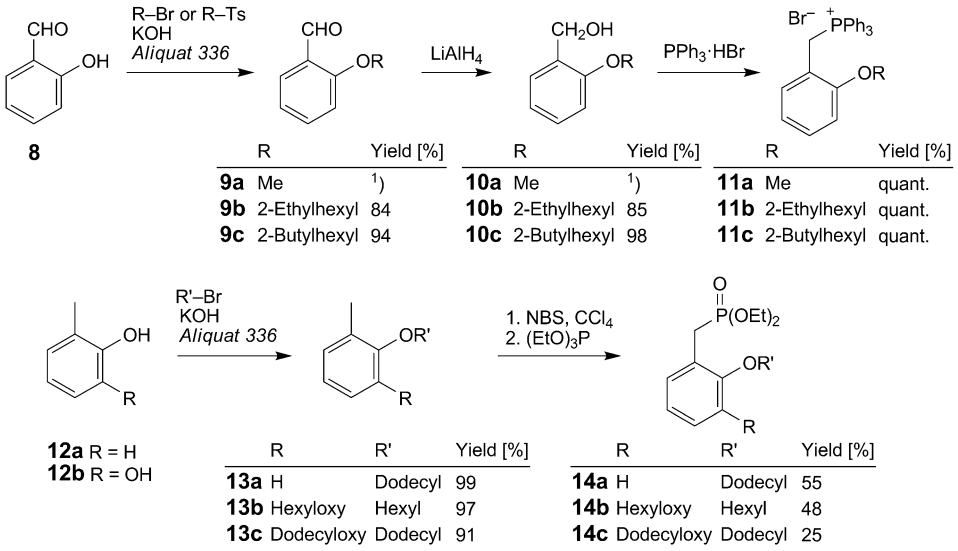
	R	Yield [%]
7a	Me	69
7b	Hexyl	77
7c	Dodecyl	75
7d	2-Ethylhexyl	68
7e	2-Butylhexyl	58

i) Br_2, Sn, AcOH. *ii*) KOH, Me_2SO_4. *iii*) RBr, KOH, *Aliquat 336*, 1,4-dioxane. *iv*) R–Ts, K_2CO_3, *Aliquat 336*, 1,4-dioxane. *v*) BuLi, THF/DMF.

In addition to the carbonyl components **7a** – **7e**, phosphonium salts for *Wittig* reactions or phosphonates for *Wittig–Horner* reactions were required. Salicylaldehyde **8** was alkylated to **9a** – **9c** for this purpose. Reduction with $LiAlH_4$ led to the benzyl alcohols **10a** – **10c**, which were directly transformed to the phosphonium bromides **11a** – **11c**, respectively, by the reaction with $Ph_3P \cdot HBr$. All these processes gave excellent-to-quantitative yields (*Scheme 3*).

2-Methylphenol (**12a**) and 3-methylcatechol (**12b**) were transformed to the ethers **13a** – **13c**. Bromination with *N*-bromosuccinimide (NBS) gave the corresponding benzyl bromides, which were *in situ* reacted with $(EtO)_3P$. *Arbusov* rearrangements yielded the phosphonates **14a** – **14c**.

Scheme 3. *Preparation of the Phosphonium Salts* **11a**–**11c** *and the Phosphonates* **14a**–**14c**



Wittig olefinations of **7a**, **7d**, **7e**, and **11a**–**11c**, and *Wittig–Horner* reactions of **7b**, **7c**, **7e**, and **14a**–**14c** led then to the 2,7-bis(2-phenylethenyl)naphthalenes **1a**–**1g** (*Scheme 4*). The generated double bonds had (*E*)-configurations in the case of the *Wittig–Horner* reactions. The *Wittig* reactions, however, yielded all three stereoisomers (*Z,E*)-**1**, (*E,E*)-**1**, and a small amount of (*Z,Z*)-**1**. The subsequent photocyclization **1** → **3** required (*Z*)-configurations, which were formed in any case by irradiation in the excited singlet state S_1. Therefore, stereoisomer mixtures of **1** could be directly used. The oxidation with I_2 was sustained by the addition of methyloxirane, which captured the formed HI [27][28]. The hexahelicenes **3a**–**3g** were obtained as racemic mixtures of (+)-(*P*)- and (−)-(*M*)-isomers.

The new compounds were characterized by 1D- and 2D-NMR spectroscopy. The data of the target compounds **3a**–**3g** are compiled in *Tables 1* and *2*. The hexahelicenes **3a**–**3g** belong to the point group C_2. Their CH_2 groups contain diastereotopic H-atoms. Different signals are particularly visible for the CH_2O H-atoms.

All hexahelicenes **3a**–**3g** have a good solubility in $CHCl_3$ and many other organic solvents such as THF or acetone. An exception is the tetramethoxy derivative **3a**, the solubility of which was not sufficient for recording a highly resolved ^{13}C-NMR spectrum. The *Figure* shows the differential scanning calorimetry (DSC) measurements of the tetrakis- and hexakis(dodecyloxy) compounds **3b** and **3f**, respectively. Both compounds form more than one crystalline but no thermotropic liquid crystalline phase. Moreover, **3b** exhibits an enormous undercooling effect for the crystallization.

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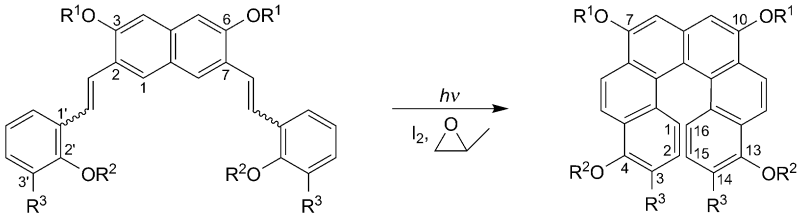
1) Commercially available.

Scheme 4. *Preparation of the 2,7-Bis(2-phenylethenyl)naphthalenes* **1a**–**1g** *and the Hexahelicenes* **3a**–**3g**

7a + **11a** —*i*)→ **1a**
7c + **14a** —*ii*)→ **1b**
7d + **11b** —*i*)→ **1c**
7e + **11c** —*i*)→ **1d**
7b + **14b** —*ii*)→ **1e**
7c + **14c** —*ii*)→ **1f**
7e + **14b** —*ii*)→ **1g**



	R^1	R^2	R^3	Yield [%]
1a	Me	Me	H	74
1b	Dodecyl	Dodecyl	H	78
1c	2-Etylhexyl	2-Etylhexyl	H	74
1d	2-Butylhexyl	2-Butylhexyl	H	89
1e	Hexyl	Hexyl	Hexyloxy	40
1f	Dodecyl	Dodecyl	Dodecyloxy	92
1g	2-Butylhexyl	Hexyl	Hexyloxy	77

	R^1	R^2	R^3	Yield [%]
3a	Me	Me	H	61
3b	Dodecyl	Dodecyl	H	82
3c	2-Etylhexyl	2-Etylhexyl	H	45
3d	2-Butylhexyl	2-Butylhexyl	H	37
3e	Hexyl	Hexyl	Hexyloxy	60
3f	Dodecyl	Dodecyl	Dodecyloxy	55
3g	2-Butylhexyl	Hexyl	Hexyloxy	19

i) BuLi, THF. *ii*) BuLi, THF, or alternatively NaH, dimethoxyethane.

3. Conclusions. – Hexahelicenes **3a**–**3g** with four or six alkoxy groups could be prepared by twofold oxidative cyclization of the corresponding 2,7-bis(2-phenylethenyl)naphthalenes **1a**–**1g**, which were synthesized by *Wittig* or *Wittig–Horner* reactions. Starting from commercially available compounds, altogether eight to nine steps were needed to obtain the C_2-symmetric hexahelicenes in high yields. The tetrakis(dodecyloxy) compound **3b**, for example, was obtained in eight steps in an average yield of 79% for each step. Long and/or branched alkoxy chains render the compounds a good solubility, which is a prerequisite for several applications in organic synthesis and materials science. The melting points of **3a**–**3f** range from $+218°$ to $-8°$; **3g** is an oil which forms a glassy state at $-50°$. None of the alkoxyhexahelicenes generates a liquid-crystalline phase. Further studies shall reveal whether known discotic mesophases can be transformed to chiral mesophases by doping with these alkoxyhexahelicenes.

We are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support.

Table 1. *^{1}H-NMR Data of the Hexahelicenes* **3a**–**3g**. Recorded in $CDCl_3$; δ in ppm, J in Hz.

	H–C(5/12), H–C(6/11)	H–C(8/9)	H–C(2/15), H–C(3/14)	H–C(1/16)	MeO or CH_2O	CH	CH_2	Me
3a	8.34, 8.35 (*AB*, J = 9.1, 4 H)	7.18 (*s*, 2 H)	6.55–6.59 (*m*, 4 H)	7.08–7.12 (*m*)	3.96 (*s*, 6 H), 4.17 (*s*, 6 H)			
3b	8.37, 8.39 (*AB*, J = 9.1, 4 H)	7.12 (*s*, 2 H)	6.56–6.60 (*m*, 4 H)	7.10–7.15 (*m*)	3.97–4.03 (*m*, 2 H), 4.12–4.19 (*m*, 2 H), 4.25–4.35 (*m*, 4 H)		1.26–1.50 (*m*, 64 H), 1.50–1.68 (*m*, 8 H)	0.86–0.92 (*m*, 12 H)
3c	8.37, 8.39 (*AB*, J = 9.2, 4 H)	7.17 (*s*, 2 H)	6.54–6.60 (*m*, 4 H)	7.10–7.16 (*m*)	3.86–3.91 (*m*, 2 H), 4.04–4.09 (*m*, 2 H), 4.16–4.26 (*m*, 4 H)	1.87–1.93 (*m*, 2 H), 1.93–2.00 (*m*, 2 H)	1.91–2.06 (*m*, 8 H), 1.32–1.50 (*m*, 16 H), 1.50–1.75 (*m*, 16 H)	0.88–1.09 (*m*, 24 H)
3d	8.37, 8.38 (*AB*, J = 9.1, 4 H)	7.16 (*s*, 2 H)	6.56–6.60 (*m*, 4 H)	7.12–7.14 (*m*)	3.86–3.89 (*m*, 2 H), 4.04–4.08 (*m*, 2 H), 4.17–4.24 (*m*, 4 H)	1.91–1.97 (*m*, 2 H), 1.97–2.04 (*m*, 2 H)	1.25–1.50 (*m*, 32 H), 1.50–1.71 (*m*, 16 H)	0.83–0.95 (*m*, 24 H)
3e	8.22, 8.40 (*AB*, J = 9.2, 4 H)	7.08 (*s*, 2 H)	6.38 (*d*, J = 9.3, 2 H)	7.27 (*d*, J = 9.3, 2 H)	3.83–3.90 (*m*, 4 H), 3.97–4.04 (*m*, 2 H), 4.20–4.33 (*m*, 6 H)		1.27–1.55 (*m*, 28 H), 1.55–1.84 (*m*, 12 H), 1.86–2.08 (*m*, 8 H)	0.89–1.00 (*m*, 18 H)
3f	8.17, 8.36 (*AB*, J = 9.1, 4 H)	7.09 (*s*, 2 H)	6.34 (*d*, J = 9.3, 2 H)	7.22 (*d*, J = 9.3, 2 H)	3.80–3.89 (*m*, 4 H), 3.93–4.01 (*m*, 2 H), 4.15–4.33 (*m*, 6 H)		1.25–1.50 (*m*, 100 H), 1.50–1.68 (*m*, 12 H)	0.84–0.91 (*m*, 18 H)
3g	8.17, 8.33 (*AB*, J = 9.2, 4 H)	7.10 (*s*, 2 H)	6.33 (*d*, J = 9.7, 2 H)	7.23 (*d*, J = 9.7, 2 H)	3.80–3.90 (*m*, 4 H), 3.90–4.01 (*m*, 2 H), 4.10–4.30 (*m*, 6 H)	1.84–2.07 (*m*, 2 H)	1.68–2.06 (*m*, 8 H), 1.10–1.84 (*m*, 56 H)	0.80–0.96 (*m*, 24 H)

Table 2. *^{13}C-NMR Data of the Hexahelicenes* **3b**–**3g**. Recorded in $CDCl_3$; δ in ppm.

	arom. CH	C_q	C_qO	CH_2O	CH	CH_2[a])	Me[a])
3b	104.0, 105.3, 118.9, 119.7, 120.9, 124.1	114.8, 123.4, 123.7, 129.8, 131.1, 134.7	153.9, 154.4	68.4, 68.5		22.7, 26.3, 26.4, 29.4, 29.5, 29.7, 31.9	14.1
3c	104.0, 105.3, 119.0, 119.8, 120.9, 124.2	114.9, 123.6, 123.9, 130.2, 131.2, 134.8	154.2, 154.7	70.9, 70.9	39.8	23.1, 24.3, 24.4, 29.2, 29.3, 29.7, 30.9, 31.0	11.3, 14.1
3d	103.8, 105.1, 118.8, 119.7, 120.7, 124.0	114.7, 123.4, 123.7, 129.8, 131.0, 134.7	154.0, 154.5	71.1, 71.1	38.2	23.0, 29.2, 29.6, 31.4	14.0
3e	103.3, 113.0, 113.0, 119.5, 119.9	114.0, 122.0, 124.9, 127.9, 130.0, 135.0	141.7, 147.7, 153.9	68.4, 69.2, 73.6		22.7, 25.9, 26.0, 29.4, 29.5, 30.4, 31.6, 31.9	14.1
3f	103.3, 113.0, 113.0, 119.5, 120.0	114.0, 122.0, 124.9, 127.9, 130.0, 135.0	141.7, 147.7, 153.9	68.4, 69.2, 73.7		22.7, 26.2, 26.3, 29.4, 29.5, 29.7, 31.9	14.1
3g	103.2, 113.1, 113.1, 119.5, 120.0	114.0, 122.2, 125.0, 128.0, 130.1, 135.1	141.7, 147.8, 154.1	69.2, 71.1, 73.7	38.2	22.7, 23.1, 26.0, 29.3, 29.4, 29.7, 31.6, 32.0	14.1

[a]) Superimposed signals.

Experimental Part

General. M.p.: *Büchi* melting-point apparatus. Differential scanning calorimetry (DSC): *DSC-7* from *Perkin-Elmer*, heating and cooling curves with a rate of 10°/min. ^{1}H- and ^{13}C-NMR spectra: *AM-400* spectrometer from *Bruker*; $CDCl_3$ as solvent if not otherwise stated, Me_4Si as internal standard; δ in ppm and J in Hz. FD-MS: *Finnigan-MAT-95* spectrometer, 5-kV ionization voltage. EI-MS: *Finnigan-MAT-95*, 70-eV ionization energy.

3,6-Dibromonaphthalene-2,7-diol (**5**). Preparation according to [29]. Yield: 67% ([29]: 70%). M.p. 189° ([26]: m.p. 189–190°).

2,7-Dibromo-3,6-dimethoxynaphthalene (**6a**). To **5** (10.0 g, 31.4 mmol) in 44 ml of 10% KOH (78.5 mmol), Me_2SO_4 (7.9 g, 62.6 mmol) was slowly dropped under N_2. The temp. should thereby not exceed 40°. The mixture was then heated for 45 min to *ca.* 100°, cooled, and extracted with 100 ml of Et_2O. The org. phase was washed with dil. KOH and H_2O, dried ($MgSO_4$), and evaporated. The residue was recrystallized from EtOH. Yield: 8.74 g (80%). M.p. 177° ([26]: m.p. 176.5–177°). ^{1}H-NMR ($CDCl_3$): 3.95 (*s*, 2 MeO); 7.02 (*s*, H–C(4), H–C(5)); 7.83 (*s*, H–C(1), H–C(8)). The compound was identical to an authentic sample [26].

2,7-Dibromo-3,6-bis(hexyloxy)naphthalene (**6b**). To a soln. of KOH (6.6 g, 0.12 mol), *Aliquat 336* (1.0 g), and **5** (15.0 g, 43 mmol) in 100 ml of dioxane, 1-bromohexane (21.5 g, 130 mmol) was dropped. The mixture was heated to 90° for 24 h, cooled, and filtered. The solvent was evaporated, and the residue was purified by column filtration (SiO_2 (6 × 30 cm); CH_2Cl_2). Yield: 16.1 g (77%). Colorless solid. M.p. 70–72°. ^{1}H-NMR ($CDCl_3$): 0.85–0.95 (*m*, J = 6.2, 2 Me); 1.30–1.40 (*m*, 4 CH_2); 1.40–1.60 (*m*, 2 CH_2); 1.82–1.95 (*m*, 2 CH_2); 4.06 (*t*, ^3J = 6.5, 2 CH_2O); 6.97 (*s*, H–C(4), H–C(5)); 7.83 (*s*, H–C(1), H–C(8)). ^{13}C-NMR ($CDCl_3$): 14.0 (Me); 22.6, 25.7, 28.9, 31.5 (CH_2); 69.1 (OCH_2); 106.4 (C(4), C(5)); 111.8 (C(2),

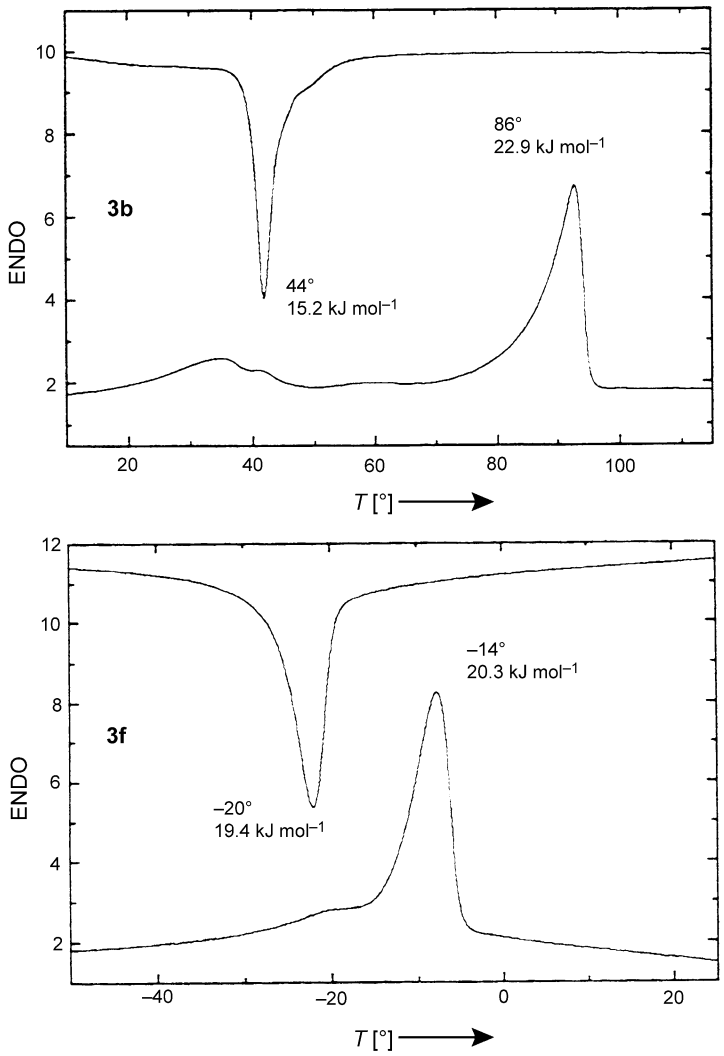


Figure. *DSC Heating and cooling curves of* **3b** *and* **3f**, *measured with a rate of 10 K min*$^{-1}$. Onset temperatures in ° and phase transition enthalpies ΔH in kJ mol^{-1}

C(7)); 125.0 (C(8a)); 130.8 (C(1), C(8)); 133.9 (C(4a)); 153.7 (C(3), C(6)). The compound was identical to an authentic sample [30].

2,7-Dibromo-3,6-bis(dodecyloxy)naphthalene (**6c**). Prepared as described for **6b**. Yield: 73%. Colorless solid. M.p. 63°. ^{1}H-NMR ($CDCl_3$): 0.81 – 0.91 (*m*, 2 Me); 1.20 – 1.24 (*m*, 18 CH_2); 1.40 – 1.55 (*m*, 2 CH_2); 1.81 – 1.93 (*m*, 2 CH_2); 4.05 (*t*, $^3J = 6.5$, 2 CH_2O); 6.96 (*s*, H–C(4), H–C(5)); 7.83 (*s*, H–C(1), H–C(8)). ^{13}C-NMR ($CDCl_3$): 14.1 (Me); 22.7, 26.0 29.0, 29.3, 29.6, 31.3 (CH_2, partly superimposed); 69.1 (CH_2O); 106.4 (C(4), C(5)); 111.8 (C(2), C(7)), 125.0 (C(8a)); 130.8 (C(1), C(8)); 133.9 (C(4a)); 153.7 (C(3), C(6)). EI-MS: 654 (30, M^+, Br_2 pattern), 57 (100). Anal. calc. for $C_{34}H_{54}Br_2O_2$ (654.6): C 62.38, H 8.31; found: C 62.25, H 8.24.

2,7-Dibromo-3,6-bis[(2-ethylhexyl)oxy]naphthalene (**6d**). To a soln of K_2CO_3 (5.3 g, 38.3 mmol), *Aliquat 336* (0.5 g), and **5** (5.0 g, 15.7 mmol) in 200 ml of 1,2-dimethoxyethane, 2-(2-ethylhexyl)-4-methylbenzenesulfonate (9.4 g, 33.0 mmol) was added. After 3-d boiling, the solvent was evaporated, and the residue was purified by column filtration (SiO_2 (6 × 30 cm); CH_2Cl_2/petroleum ether (PE; b.p. 40–70°) 1:1). Yield: 6.05 g (71%). Colorless oil. ^{1}H-NMR ($CDCl_3$): 0.92–1.01 (*m*, 4 Me); 1.20–1.40 (*m*, 4 CH_2); 1.40–1.65 (*m*, 4 CH_2); 1.78–1.95 (*m*, 2 CH); 3.95 (*d*, ^3J = 5.5, 2 OCH_2); 7.00 (*s*, H–C(4), H–C(5)); 7.82 (*s*, H–C(1), H–C(8)). ^{13}C-NMR ($CDCl_3$): 11.1, 14.0 (Me); 22.9, 23.9, 28.9, 30.4 (CH_2); 39.2 (CH); 71.2 (CH_2O); 106.1 (C(4), C(5)); 111.7 (C(2), C(7)); 124.8 (C(8a)); 130.6 (C(1), C(8)); 133.8 (C(4a)); 153.8 (C(3), C(6)). EI-MS: 542 (12, M^+, Br_2 pattern), 318 (100). Anal. calc. for $C_{26}H_{38}Br_2O_2$ (542.4): C 57.58, H 7.06; found: C 57.49, H 7.08.

2,7-Dibromo-3,6-bis[(2-butylhexyl)oxy]naphthalene (**6e**). Prepared as described for **6b**. Yield: 58%. Colorless oil. ^{1}H-NMR ($CDCl_3$): 0.75–0.90 (*m*, 4 Me); 1.15–1.35 (*m*, 8 CH_2); 1.35–1.50 (*m*, 4 CH_2); 1.75–1.93 (*m*, 2 CH); 3.97 (*d*, ^3J = 5.2, 2 CH_2O); 6.98 (*s*, H–C(4), H–C(5)); 7.81 (*s*, H–C(1), H–C(8)). ^{13}C-NMR ($CDCl_3$): 14.1 (Me); 23.1, 29.2, 31.2 (CH_2); 37.9 (CH); 72.0 (CH_2O); 106.4 (C(4), C(5)); 112.0 (C(2), C(7)); 125.1 (C(8a)); 130.8 (C(1), C(8)); 134.1 (C(4a)); 154.0 (C(3), C(6)). EI-MS: 598 (10, M^+), 318 (100). Anal. calc. for $C_{30}H_{46}Br_2O_2$ (598.5): C 60.20, H 7.75; found: C 60.01, H 7.92.

3,6-Dimethoxynaphthalene-2,7-dicarbaldehyde (**7a**). A 1.6M soln. of BuLi in hexane (37 ml, 59.0 mmol) was slowly dropped to **6a** (8.5 g, 24.6 mmol) dissolved in 200 ml of Et_2O. The temp. of the used cold bath (solid CO_2/PE (b.p. 40–70°)) was regulated, so that the magnetic stirring of the mixture worked sufficiently. The yellow-red soln. was then kept for 15 min at −78°. DMF (4.5 ml, 59 mmol) was added slowly at 0°. After 1 h stirring at r.t., the reaction was quenched first by the addition of 1 ml of H_2O and then 50 ml of 2M HCl. The formed precipitate was filtered, washed with H_2O, and treated with boiling acetone to give. **7a** (4.15 g, 69%). Light-yellow solid. M.p. 245° ([31]: m.p. 232–235°). ^{1}H-NMR ($CDCl_3$): 4.02 (*s*, 2 MeO); 7.06 (*s*, H–C(4), H–C(5)); 8.35 (*s*, H–C(1), H–C(8)); 10.47 (*s*, 2 CHO). The compound was identical to an authentic sample [31].

3,6-Bis(hexyloxy)naphthalene-2,7-dicarbaldehyde (**7b**). Prepared as described for **7a**. Yield: 77%. Colorless solid. M.p. 79°. ^{1}H-NMR ($CDCl_3$): 0.83–0.93 (*m*, 2 Me); 1.21–1.40 (*m*, 4 CH_2); 1.40–1.59 (*m*, 2 CH_2); 1.83–1.95 (*m*, 2 CH_2); 4.12 (*t*, ^3J = 6.4, 2 CH_2O); 6.97 (*s*, H–C(4), H–C(5)); 8.29 (*s*, H–C(1), H–C(8)); 10.48 (*s*, 2 CHO). ^{13}C-NMR ($CDCl_3$): 14.0 (Me); 22.5, 25.7, 28.9, 31.5 (CH_2); 68.6 (CH_2O); 105.6 (C(4), C(5)); 121.7 (C(8a)); 124.6 (C(2), C(7)); 132.6 (C(1), C(8)); 142.3 (C(4a)); 159.7 (C(3), C(6)); 189.3 (CHO). EI-MS: 384 (24, M^+), 216 (100). Anal. calc. for $C_{24}H_{32}O_4$ (384.5): C 74.97, H 8.39; found: C 74.94, H 8.29.

3,6-Bis(dodecyloxy)naphthalene-2,7-dicarbaldehyde (**7c**). Prepared as described for **7a**. Yield: 75%. Colorless crystals. M.p. 89–91°. ^{1}H-NMR ($CDCl_3$): 0.82–0.91 (*m*, 2 Me); 1.20–1.40 (*m*, 16 CH_2); 1.40–1.60 (*m*, 2 CH_2); 1.80–1.96 (*m*, 2 CH_2); 4.12 (*t*, ^3J = 6.4, 2 CH_2O); 6.98 (*s*, H–C(4), H–C(5)); 8.30 (*s*, H–C(1), H–C(8)); 10.48 (*s*, 2 CHO). ^{13}C-NMR ($CDCl_3$): 14.1 (Me); 22.6, 26.1, 28.9, 29.3, 29.6, 31.9 (CH_2, partly superimposed); 68.6 (CH_2O); 105.5 (C(4), C(5)); 121.7 (C(8a)); 124.7 (C(2), C(7)); 132.6 (C(1), C(8)); 142.3 (C(4a)); 159.7 (C(3), C(6)); 189.3 (CHO). EI-MS: 552 (66, M^+), 215 (100). Anal. calc. for $C_{36}H_{56}O_4$ (552.8): C 78.21, H 10.21; found: C 78.32, H 10.09.

3,6-Bis(2-ethylhexyl)naphthalene-2,7-dicarbaldehyde (**7d**). Prepared as described for **7a**. Yield 68%. Colorless oil. ^{1}H-NMR ($CDCl_3$): 0.83–0.99 (*m*, 4 Me); 1.20–1.42 (*m*, 4 CH_2); 1.42–1.60 (*m*, 4 CH_2); 1.73–1.91 (*m*, 2 CH); 4.00 (*d*, ^3J = 6.4, 2 CH_2O); 6.97 (*s*, H–C(4), H–C(5)); 8.18 (*s*, H–C(1), H–C(8)); 10.42 (*s*, 2 CHO). ^{13}C-NMR ($CDCl_3$): 11.1, 13.9 (Me); 22.9, 24.0, 29.0, 30.6 (CH_2); 39.3 (CH); 71.1 (CH_2O); 105.6 (C(4), C(5)); 121.7 (C(8a)); 124.8 (C(2), C(7)); 132.3 (C(1), C(8)); 142.3 (C(4a)); 159.8 (C(3), C(6)); 188.8 (CHO). EI-MS: 440 (12, M^+), 216 (100). Anal. calc. for $C_{28}H_{40}O_4$ (440.6): C 76.33, H 9.15; found: C 76.50, H 9.27.

3,6-Bis[(2-butylhexyl)oxy]naphthalene-2,7-dicarbaldehyde (**7e**). Prepared as described for **7a**. Yield: 58%. Colorless oil. ^{1}H-NMR ($CDCl_3$): 0.80–0.95 (*m*, 4 Me); 1.20–1.35 (*m*, 8 CH_2); 1.35–1.50 (*m*, 4 CH_2); 1.75–1.95 (*m*, 2 CH); 4.00 (*d*, ^3J = 5.2, 2 CH_2O); 7.00 (*s*, H–C(4), H–C(5)); 8.25 (*s*, H–C(1), H–C(8)); 10.46 (*s*, 2 CHO). ^{13}C-NMR ($CDCl_3$): 13.9 (Me); 22.9, 28.9, 31.0 (CH_2); 37.7 (CH); 71.2 (CH_2O); 105.5 (C(4), C(5)); 121.6 (C(8a)); 124.6 (C(2), C(7)); 132.3 (C(1), C(8)); 142.3 (C(4a)); 159.7 (C(3), C(6)); 188.9 (CHO). EI-MS: 496 (2, M^+), 216 (100). Anal. calc. for $C_{32}H_{48}O_4$ (496.7): C 77.38, H 9.74; found: C 77.16, H 9.58.

2-[(2-Ethylhexyl)oxy]benzaldehyde (**9b**). To a soln. of K_2CO_3 (6.9 g, 49.9 mmol), *Aliquat 336* (0.5 g), and *salicylaldehyde* (**8**) (5.0 g, 40.9 mmol) in 200 ml of dioxane, 2-ethylhexyl *p*-toluenesulfonate (11.7 g, 41.0 mmol) was added dropwise. After 3 d at 80°, the solvent was evaporated, and the product was purified by column filtration (SiO_2 (5 × 40 cm); CH_2Cl_2). Yield: 8.05 g (84%). Colorless oil. ^{1}H-NMR ($CDCl_3$): 0.80–0.91 (*m*, 2 Me); 1.19–1.30 (*m*, 2 CH_2); 1.30–1.50 (*m*, 2 CH_2); 1.65–1.80 (*m*, CH); 3.89 (*d*, ^3J = 5.3, CH_2O); 6.86–6.95 (*m*, H–C(3), H–C(5)); 7.40–7.60 (*m*, H–C(4)); 7.72–7.78 (*m*, H–C(6)); 10.46 (*s*, CHO). ^{13}C-NMR ($CDCl_3$): 11.0, 13.9 (Me); 22.8, 23.8, 28.9, 30.4 (CH_2); 39.2 (CH); 70.6 (CH_2O); 112.3 (C(3)); 120.2 (C(5)); 124.8 (C(1)); 127.9 (C(4)); 135.8 (C(6)); 161.6 (C(2)); 189.4 (CHO). EI-MS: 234 (22, M^+), 122 (100). Anal. calc. for $C_{15}H_{22}O_2$ (234.3): C 76.88, H 9.46; found: C 76.95, H 9.24.

2-[(2-Butylhexyl)oxy]benzaldehyde (**9c**). Prepareded as described for **9b**, using 1-bromo-2-butylhexane. The chromatographic purification was performed with PE (40–70°)/CH_2Cl_2 2:1. Yield: 94%. Colorless oil. ^{1}H-NMR ($CDCl_3$): 0.82–0.89 (*m*, 2 Me); 1.24–1.31 (*m*, 4 CH_2); 1.30–1.50 (*m*, 2 CH_2); 1.70–1.85 (*m*, CH); 3.90 (*d*, ^2J = 5.3, CH_2O); 6.87–6.97 (*m*, H–C(3), H–C(5)); 7.40–7.50 (*m*, H–C(4)); 7.75–7.84 (*m*, H–C(6)); 10.49 (*s*, CHO). ^{13}C-NMR ($CDCl_3$): 14.9 (Me); 22.9, 29.0, 31.1 (CH_2); 37.9 (CH); 71.2 (CH_2O); 12.4 (C(3)); 120.3 (C(5)); 125.1 (C(1)); 128.0 (C(4)); 135.7 (C(6)); 161.7 (C(2)); 189.4 (CHO). EI-MS: 262 (**8**), 43 (100). Anal. calc. for $C_{17}H_{26}O_2$ (262.4): C 77.82, H 9.99; found: C 77.65, H 9.71.

{2-[(2-Ethylhexyl)oxy]phenyl}methanol (**10b**). Aldehyde **9b** (7.0 g, 29.9 mmol) was slowly dropped to a soln. of $LiAlH_4$ (0.57 g, 15.0 mmol) in 200 ml of dry Et_2O, so that the Et_2O boiled gently. After 1 h heating to reflux, the reaction was quenched with H_2O. The formed precipitate was dissolved by the addition of 10% H_2SO_4, and the org. phase was separated, neutralized with a sat. aq. soln. of $NaHCO_3$, and washed with H_2O. The soln. was dried ($MgSO_4$) and evaporated. Purification by column filtration (SiO_2 (6 × 40 cm); CH_2Cl_2) gave **10b** (6.0 g, 85%). Colorless oil. ^{1}H-NMR ($CDCl_3$): 0.80–0.91 (*m*, 2 Me); 1.20–1.31 (*m*, 3 CH_2); 1.31–1.50 (*m*, CH_2); 1.63–1.77 (*m*, CH); 3.91 (*d*, ^3J = 5.4, CH_2O); 4.70 (*s*, CH_2OH); 6.86–6.93 (*m*, H–C(3), H–C(5)); 7.22–7.30 (*m*, H–C(4), H–C(6)). ^{13}C-NMR ($CDCl_3$): 11.9, 13.9 (Me); 22.8, 24.0, 29.0, 30.6 (CH_2); 39.1 (CH); 61.9 (CH_2OH); 70.0 (CH_2O); 110.7 (C(3)); 120.3 (C(5)); 128.2, 128.6 (C(4), C(6)); 129.2 (C(1)); 156.8 (C(2)). EI-MS: 236 (17, M^+), 106 (100). Anal. calc. for $C_{15}H_{24}O_2$ (236.4): C 76.23, H 10.23; found: C 76.05, H 10.42.

{2-[(2-Butylhexyl)oxy]phenyl}methanol (**10c**). Prepared as described for **10b**. Yield: 98%. Colorless oil. ^{1}H-NMR ($CDCl_3$): 0.88–0.96 (*m*, 2 Me); 1.22–1.50 (*m*, 6 CH_2); 1.73–1.86 (*m*, CH); 3.88 (*d*, ^3J = 5.4, CH_2O); 4.68 (*s*, CH_2OH); 6.81–7.00 (*m*, H–C(3), H–C(5)); 7.19–7.31 (*m*, H–C(4), H–C(6)). ^{13}C-NMR ($CDCl_3$): 13.9 (Me); 22.9, 25.4, 31.1 (CH_2); 38.9 (CH); 61.6 (CH_2OH); 70.3 (CH_2O); 110.6 (C(3)); 120.2 (C(5)); 128.5, 128.7 (C(4), C(6)); 129.1 (C(1)); 156.7 (C(2)). EI-MS: 264 (4, M^+), 73 (100). Anal. calc. for $C_{17}H_{28}O_2$ (264.4): C 77.22, H 10.67; found: C 77.05, H 10.57.

(2-Methoxybenzyl)(triphenyl)phosphonium Bromide (**11a**). Alcohol **10a** (26.4 g, 0.19 mol) and $Ph_3P \cdot HBr$ (65.6 g, 0.19 mol) were heated to reflux in 200 ml of dry $CHCl_3$ for 12 h. The formed H_2O was continuously separated. The solvent was evaporated, and the residue was recrystallized from Et_2O, to which EtOH was added until the whole bromide was dissolved. Yield: 88.0 g (*ca.* 100%). Colorless powder. M.p. 238–240°. ^{1}H-NMR ((D$_6$)DMSO): 3.17 (*s*, MeO); 4.95 (*d*, ^2J(H,P) = 14.8, CH_2); 6.75–6.85 (*m*, H–C(3), H–C(5)); 7.04–7.11 (*m*, H–C(6)); 7.23–7.33 (*m*, H–C(4)); 7.59–7.90 (*m*, Ph_3P). ^{13}C-NMR (CD_3OD): 26.2 (PCH_2, ^1J(C,P) = 49.1); 58.4 (MeO); 112.2 (C(3)); 117.0 (C_q, Ph); 118.6, 120.5, 122.0 (C(4), C(5), C(6)); 131.3, 135.3, 136.4 (CH, Ph_3P); 132.4 (C(1)); 158.9 (C(2)). FD-MS: 383 (100, [*M* – Br]$^+$), 384 (27). Anal. calc. for $C_{26}H_{24}BrOP$ (463.4): C 67.40, H 5.22; found: C 67.01, H 4.90.

{2-[(2-Ethylhexyl)oxy]benzyl}(triphenyl)phosphonium Bromide (**11b**). Prepared as described for **11a**. Yield: quant. Colorless powder. M.p. 192°. ^{1}H-NMR ($CDCl_3$): 0.70–0.78 (*m*, Me); 0.80–0.88 (*m*, Me); 1.05–1.25 (*m*, 4 CH_2); 2.01–2.11 (*m*, CH); 3.23 (*d*, ^3J = 4.3, CH_2O); 5.17 (*d*, ^2J(P,H) = 13.8, 2 H, PCH_2); 6.56–6.63 (*m*, H–C(2)); 6.70–6.80 (*m*, H–C(5)); 7.14–7.24 (*m*, H–C(4), H–C(6)); 7.50–7.80 (*m*, Ph_3P). ^{13}C-NMR (CD_3OD): 11.0, 14.0 (Me); 22.9, 23.5, 29.0, 30.3 (CH_2); 24.9 (PCH_2, ^1J(C,P) = 48.2); 39.1 (CH); 70.3 (CH_2O); 111.2 (C(3)); 115.3 (C_q, Ph); 117.1, 118.8, 121.0 (C(4), C(5), C(6)); 130.0, 134.0, 134.9 (CH, Ph); 132.1 (C(1)); 156.9 (C(2)). FD-MS: 481 (100 [*M* – Br]$^+$). Anal. calc. for $C_{33}H_{38}BrOP$ (561.6): C 70.58, H 6.82; found: C 70.70, H 6.94.

{2-[(2-Butylhexyl)oxy]benzyl}(triphenyl)phosphonium Bromide (**11c**). Prepared as described for **11a**. Yield: quant. Colorless powder. M.p. 188°. ^{1}H-NMR ((D$_6$)DMSO): 0.80–0.89 (*m*, 2 Me); 1.10–1.30 (*m*, 13 H, CH$_2$, CH); 3.38 (*m*, CH$_2$O); 4.87 (*d*, ^2J(P,H) = 15.0, PCH$_2$); 6.80–7.01 (*m*, H–C(3), H–C(4), H–C(5)); 7.25–7.35 (*m*, H–C(6)); 7.50–7.95 (*m*, Ph$_3$P). ^{13}C-NMR (CD$_3$OD): 14.4 (Me); 24.0, 30.2, 32.0 (CH$_2$); 25.6 (PCH$_2$, ^1J(C,P) = 49.7); 72.4 (CH$_2$O); 113.2 (C(3)); 116.5 (C$_q$, Ph); 118.9, 119.7, 121.9 (C(4), C(5), C(6)); 131.4, 135.1, 136.4 (CH, Ph); 131.8 (C(1)); 158.6 (C(2)). FD-MS: 509 (100 [*M* – Br]$^+$). Anal. calc. for C$_{35}$H$_{42}$BrOP (589.6): C 71.30, H 7.18; found: C 71.05, H 7.05.

Dodecyl 2-Methylphenyl Ether (**13a**). Prepared as described for **9b**, with **12a** (25.0 g, 0.23 mol) and 1-bromododecane (60.0 g, 0.24 mol). Yield: 62.9 g (99%). Colorless oil. ^{1}H-NMR (CDCl$_3$): 0.90–1.00 (*m*, Me); 1.30–1.55 (*m*, 9 CH$_2$); 1.78–1.95 (*m*, CH$_2$); 2.28 (*s*, Me); 3.99 (*t*, ^3J = 6.4, CH$_2$O); 6.81–6.92 (*m*, H–C(3), H–C(5)); 7.14–7.22 (*m*, H–C(4), H–C(6)). ^{13}C-NMR (CDCl$_3$): 14.1, 16.2 (Me); 22.7, 26.2, 28.2, 28.8, 29.4, 29.6, 31.9 (CH$_2$, partly superimposed); 67.8 (OCH$_2$); 110.8 (C(3)); 120.0 (C(5)); 126.6, 130.5 (C(4), C(6)); 126.8 (C(1)); 157.2 (C(2)). EI-MS: 276 (2, M^+), 135 (39), 57 (82), 43 (100). Anal. calc. for C$_{19}$H$_{32}$O (276.5): C 82.55, H 11.67; found: C 82.65, H 11.27.

1,2-Bis(hexyloxy)-3-methylbenzene (**13b**). Prepared as described in [32]. Yield: 97%. Pale-yellow oil.

1,2-Bis(dodecyloxy)-3-methylbenzene (**13c**). Prepared as described for **9b**. Yield: 91%. Pale-yellow oil. ^{1}H-NMR (CDCl$_3$): 0.85–0.95 (*m*, 2 Me); 1.20–1.41 (*m*, 16 CH$_2$); 1.41–1.60 (*m*, 2 CH$_2$); 1.71–1.88 (*m*, 2 CH$_2$); 2.25 (*s*, Me); 3.90–4.00 (*m*, 2 CH$_2$O); 6.71–6.79 (*m*, H–C(4), H–C(6)); 6.85–6.93 (*m*, H–C(5)). ^{13}C-NMR (CDCl$_3$): 14.1, 14.1, 16.0 (Me); 22.7, 26.2, 29.4, 29.5, 29.7, 30.5, 31.9 (CH$_2$, partly superimposed); 68.4, 72.6 (CH$_2$O), 111.8 (C(4)); 122.6, 123.2 (C(5), C(6)); 132.1 (C(1)); 146.8, 152.3 (C(2), C(3)). EI-MS: 460 (15, M^+), 124 (97), 56 (98), 54 (53), 43 (100). Anal. calc. for C$_{31}$H$_{56}$O$_2$ (460.8): C 80.81, H 12.25; found: C 81.02, H 12.16.

Diethyl [2-(Dodecyloxy)benzyl]phosphonate (**14a**). *N*-Bromosuccinimide (NBS; 25.5 g, 0.14 mol), **13a** (39.6 g, 0.14 mol), and azobisisobutyronitrile (AIBN; 0.2 g) were heated in 200 ml of dry CCl$_4$ to reflux for 4 h. The formed succinimide was filtered off and washed with CCl$_4$. The solvent was evaporated, and the residue was reacted with (EtO)$_3$P (21.9 g, 0.13 mol) at 160°. The formed bromoethane was continuously distilled off. After *ca.* 6 h, the reaction was complete. The purification of the product was performed by column filtration (SiO$_2$ (6 × 40 cm); Et$_2$O). Yield: 32.5 g (55%). Almost colorless oil. ^{1}H-NMR (CDCl$_3$): 0.80–0.89 (*m*, Me); 1.15 (*t*, ^3J = 5.7, 2 Me); 1.20–1.47 (*m*, 9 CH$_2$); 1.70–1.84 (*m*, CH$_2$); 3.22 (*d*, ^2J(P,H) = 21.6, PCH$_2$); 3.88–4.06 (*m*, 3 CH$_2$O); 6.76–6.89 (*m*, H–C(3), H–C(5)); 7.06–7.20 (*m*, H–C(4)); 7.25–7.33 (*m*, H–C(6)). ^{13}C-NMR (CDCl$_3$): 13.8, 16.0 (Me); 22.4, 25.8, 26.1 (^1J(PC) = 139.2); 29.0, 29.3, 31.6 (CH$_2$, partly superimposed); 61.5 (Me*C*H$_2$O); 67.9 (CH$_2$O); 111.0 (C(3)); 120.0, 120.0, 127.7 (C(4), C(5), C(6)); 130.8 (C(1)); 156.4 (C(2)). EI-MS: 412 (26, M^+), 244 (100). Anal. calc. for C$_{23}$H$_{41}$O$_4$P (412.6): C 66.96, H 10.02; found: C 66.80, H 10.15.

Diethyl [2,3-Bis(hexyloxy)benzyl]phosphonate (**14b**). Prepared as described for **14a**. Yield: 48%. Light-yellow oil. ^{1}H-NMR (CDCl$_3$): 0.80–0.90 (*m*, 2 Me); 1.10–1.50 (*m*, 6 CH$_2$, 2 OCH$_2$–*Me*); 1.65–1.80 (*m*, 2 CH$_2$); 3.20 (*d*, ^2J(P,H) = 21.8, PCH$_2$); 3.56–4.10 (*m*, 4 CH$_2$O); 6.68–6.75 (*m*, H–C(4)); 6.83–6.95 (*m*, H–C(5), H–C(6)). ^{13}C-NMR (CDCl$_3$): 14.0, 14.0, 16.3 (Me); 22.6, 22.6, 25.7, 25.8, 29.3, 30.3, 31.5, 31.7 (CH$_2$); 26.6 (^1J(P,C) = 139.7, PCH$_2$); 62.0 (Me*C*H$_2$O); 68.5, 73.1 (CH$_2$O); 112.1 (C(4)); 122.5, 123.3 (C(5), C(6)); 125.5 (C(1)); 146.7, 152.4 (C(2), C(3)). EI-MS: 427 (25, [*M* – H]$^+$), 108 (100). Anal. calc. for C$_{23}$H$_{41}$O$_5$P (428.6): C 64.46, H 9.64; found: C 64.70, H 9.75.

Diethyl [2,3-Bis(dodecyloxy)benzyl]phosphonate (**14c**). Prepared as described for **14a**. The CC was performed with CH$_2$Cl$_2$/AcOEt 4:1. Yield: 25%. Colorless solid. M.p. 37–38°. ^{1}H-NMR (CDCl$_3$): 0.82–0.90 (*m*, 2 Me); 1.19–1.50 (*m*, 18 CH$_2$, 2 *Me*CH$_2$O); 1.68–1.86 (*m*, 2 CH$_2$); 3.22 (*d*, ^2J(P,H) = 21.8, PCH$_2$); 3.89–4.10 (*m*, 4 CH$_2$O); 6.70–6.79 (*m*, H–C(4)); 6.88–7.00 (*m*, H–C(5), H–C(6)). ^{13}C-NMR (CDCl$_3$): 14.0, 16.3 (Me); 22.6, 26.0, 26.1, 29.3, 29.6, 30.3, 31.8 (CH$_2$, partly superimposed); 26.5 (*d*, ^1J(P,C) = 139.6, PCH$_2$); 61.8 (Me*C*H$_2$O); 68.4, 73.1 (CH$_2$O); 112.0 (C(4)); 122.4, 123.2 (C(5), C(6)); 125.5 (C(1)); 146.7, 152.2 (C(2), C(3)). EI-MS: 596 (23, M^+), 428 (100). Anal. calc. for C$_{35}$H$_{65}$O$_5$P (596.9): C 70.43, H 10.98; found: C 70.54, H 10.99.

*2,7-Dimethoxy-3,6-bis[(*E*)-2-(2-methoxyphenyl)ethenyl]naphthalene* (**1a**). BuLi in heptane (13.7 ml of a 2.7M soln.; 37.0 mmol) was slowly dropped at 0° to a soln. of **11a** (17.7 g, 38.2 mmol) in 110 ml of THF. The mixture turned red. After 15 min at r.t., **7a** (4.1 g, 16.8 mmol), suspended in 70 ml of THF, was

added. The red color disappeared, and a blue fluorescence could be observed. The mixture was heated to reflux for 5 h, before 50 ml of H_2O and 100 ml of 2M HCl were added. Et_2O was added in order to reach a good phase separation. The aq. phase was extracted two times with 100 ml of Et_2O each. The unified org. phases were dried ($MgSO_4$) and evaporated. The residue was purified by column filtration (SiO_2 (6 × 40 cm); PE (b.p. 40–70°)/$CHCl_3$ 1:4). Yield: 5.6 g (74%). Yellow product. Recrystallization from EtOH gave the pure (*E,E*)-isomer. M.p. 184–186°. ^{1}H-NMR ($CDCl_3$): 3.90 (*s*, 2 MeO); 3.96 (*s*, 2 MeO); 6.85–7.00 (*m*, 2 H–C(3′), 2 H–C(5′)); 7.01 (*s*, H–C(1), H–C(8)); 7.19–7.29 (*m*, 2 H–C(4′)); 7.52, 7.62 (*AB*, ^3J = 16.7, 4 olefin. H); 7.65–7.74 (*m*, 2 H–C(6′)); 8.03 (*s*, H–C(4), H–C(5)). ^{13}C-NMR ($CDCl_3$): 55.4, 55.5 (MeO); 104.5 (C(1), C(8)); 110.9 (C(3′)); 120.7 (C(5′)); 123.8, 123.9, 125.4, 126.4, 128.4 (C(4), C(5), C(4′), C(6′), olefin. C); 124.1, 126.6, 127.1, 134.7 (C(2), C(7), C(4a), C(8a), C(1′)); 156.1, 156.8 (C(2), C(7), C(2′)). FD-MS: 452 (100, M^+). Anal. calc. for $C_{30}H_{28}O_4$ (452.6): C 79.62, H 6.24; found: C 79.57, H 6.07.

*2,7-Bis(dodecyloxy)-3,6-bis{(*E*)-2-[2-(dodecyloxy)phenyl]ethenyl}naphthalene* (**1b**). Prepared as described for **1a**. Yield: 78%. Yellow solid. M.p. 64°. ^{1}H-NMR ($CDCl_3$): 0.80–1.12 (*m*, 4 Me); 1.15–1.47 (*m*, 32 CH_2); 1.47–1.59 (*m*, 4 CH_2); 1.80–2.00 (*m*, 4 CH_2); 3.98–4.15 (*m*, 4 CH_2O); 6.88–6.99 (*m*, 2 H–C(3′), 2 H–C(5′)); 6.99 (*s*, H–C(1), H–C(8)); 7.17–7.27 (*m*, 2 H–C(4′)); 7.55, 7.65 (*AB*, ^3J = 16.6, 4 olefin. H); 7.62–7.68 (*m*, 2 H–C(6′)); 7.96 (*s*, H–C(4), H–C(5)). ^{13}C-NMR ($CDCl_3$): 14.1 (Me); 22.7, 26.2, 29.3, 29.4, 29.5, 29.7, 31.9 (CH_2, partly superimposed); 68.3, 68.5 (CH_2O); 105.0 (C(1), C(8)); 112.1 (C(3′)); 120.6 (C(5′)); 124.1, 124.4, 125.7, 126.6, 128.2 (C(4), C(5), C(4′), C(6′), olefin. C); 124.0, 126.7, 127.5, 134.7 (C(3), C(6), C(1′), C(4a), C(8a)); 155.7, 156.5 (C(2), C(7), C(2′)). FD-MS: 1069 (100, M^+). Anal. calc. for $C_{74}H_{116}O_4$ (1069.7): C 83.09, H 10.93; found: C 83.38, H 10.82.

2,7-Bis[(2-ethylhexyl)oxy]-3,6-bis(2-{2-[(2-ethylhexyl)oxy]phenyl}ethenyl)naphthalene (**1c**). Prepared as described for **1a**. Yield: 74%. Yellow oil. Mixture of stereoisomers. ^{1}H-NMR ($CDCl_3$): 0.90–1.10 (*m*, 8 Me); 1.33–1.67 (*m*, 16 CH_2); 1.70–2.00 (*m*, 4 CH); 3.88–4.10 (*m*, 4 CH_2O); 6.60–8.03 (*m*, 16 arom. and olefin. H). ^{13}C-NMR ($CDCl_3$): 11.2, 14.1 (Me); 23.1, 24.0, 24.1, 24.2, 24.3, 29.1, 29.2, 30.6, 30.7, 30.8, 30.9 (CH_2); 39.3, 39.4, 39.5 (CH); 70.5, 70.6, 70.9, 71.2 (CH_2O); 104.5, 104.7, 111.6, 112.0, 119.8, 119.9, 120.5, 123.3, 123.6, 125.1, 125.4, 126.0, 128.0, 128.1, 128.7, 128.8, 129.5, 129.7 (arom. and olefin. CH); 123.0, 123.5, 125.5, 126.5, 126.6, 126.6, 126.7, 127.5, 134.5, 134.7 (arom. C_q); 155.7, 156.2, 156.5, 156.8, 157.0 (arom. C_qO). FD-MS: 845 (100, M^+). Anal. calc. for $C_{58}H_{84}O_4$ (845.3): C 82.41, H 10.02; found: C 82.24, H 10.13.

2,7-Bis[(2-butylhexyl)oxy]-3,6-bis(2-{2-[(2-butylhexyl)oxy]phenyl}ethenyl)naphthalene (**1d**). Prepared as described for **1a**. Mixture of stereoisomers. Yield: 89%. Yellow oil. ^{1}H-NMR ($CDCl_3$): 0.90–1.08 (*m*, 8 Me); 1.30–1.65 (*m*, 24 CH_2); 1.73–2.01 (*m*, 4 CH); 3.85–4.10 (*m*, 4 CH_2O); 6.60–8.03 (*m*, 16 arom. and olefin. H). ^{13}C-NMR ($CDCl_3$): 14.1 (Me); 21.4, 22.6, 23.1, 26.9, 29.1, 31.2, 31.3, 31.4, 31.6 (CH_2); 37.8, 37.9 (CH); 104.5, 104.6, 111.6, 111.8, 119.7, 120.4, 123.0, 123.5, 125.1, 125.2, 125.4, 125.9, 126.5, 127.6, 128.0, 128.2, 128.7, 129.0, 129.5, 129.6, 134.5, 134.6 (arom. CH and C_q); 155.8, 156.1, 156.3, 156.8, 157.0 (arom. C_qO). FD-MS: 957 (100, M^+). Anal. calc. for $C_{66}H_{100}O_4$ (957.5): C 82.79, H 10.53; found: C 82.60, H 10.42.

*2,7-Bis{(*E*)-2-[2,3-bis(hexyloxy)phenyl]ethenyl}-3,6-bis(hexyloxy)naphthalene* (**1e**). Prepared as described for **1a**. Yield: 40%. Yellow solid. M.p. 35–37°. ^{1}H-NMR ($CDCl_3$): 0.85–1.00 (*m*, 6 Me); 1.30–1.45 (*m*, 12 CH_2); 1.45–1.63 (*m*, 6 CH_2); 1.80–2.00 (*m*, 6 CH_2); 3.98–4.15 (*m*, 6 CH_2O); 6.80–6.87 (*m*, 2 H–C(4′)); 7.00 (*s*, H–C(1), H–C(8)); 7.00–7.09 (*m*, 2 H–C(5′)); 7.27–7.33 (*m*, 2 H–C(6′)); 7.57, 7.65 (*AB*, ^3J = 16.7, 4 olefin. H); 7.99 (*s*, H–C(4), H–C(5)). ^{13}C-NMR ($CDCl_3$): 14.2 (Me); 22.6, 22.6, 22.7, 25.9, 25.9, 26.0, 29.2, 29.4, 30.4, 31.6, 31.6, 31.8 (CH_2); 68.3, 68.7, 73.7 (CH_2O); 105.1 (C(1), C(8)); 112.2 (C(4′)); 117.9 (C(5′)); 123.6, 123.8, 124.7 (C(4), C(5), olefin. C); 123.8, 126.5, 132.7, 134.9 (C(3), C(6), C(4a), C(8a), C(1′)); 146.4, 152.7, 155.7 (C(2), C(7), C(2′), C(3′)). FD-MS: 933 (100, M^+). Anal. calc. for $C_{62}H_{92}O_6$ (933.4): C 79.78, H 9.93; found: C 79.73, H 10.03.

*2,7-Bis{(*E*)-2-[2,3-bis(dodecyloxy)phenyl]ethenyl}-3,6-bis(dodecyloxy)naphthalene* (**1f**). Prepared as described for **1a**. Yield: 92%. Yellow solid. M.p. 32–35°. ^{1}H-NMR ($CDCl_3$): 0.82–0.95 (*m*, 6 Me); 1.16–1.45 (*m*, 48 CH_2); 1.45–1.62 (*m*, 6 CH_2); 1.78–1.98 (*m*, 6 CH_2); 3.96–4.18 (*m*, 6 CH_2O); 6.78–6.85 (*m*, 2 H–C(4′)); 6.99 (*s*, H–C(1), H–C(8)); 6.99–7.07 (*m*, 2 H–C(5′)); 7.25–7.32 (*m*, 2 H–C(6′)); 7.55, 7.64 (*AB*, ^3J = 16.6, 4 olefin. H); 7.97 (*s*, H–C(4), H–C(5)). ^{13}C-NMR ($CDCl_3$): 14.1 (Me); 22.7, 26.3, 26.4, 29.4, 29.5, 29.7, 29.8, 31.9 (CH_2, partly superimposed); 68.4, 68.8, 73.7 (CH_2O); 105.2 (C(1), C(8)); 112.4

(C(4′)); 118.0 (C(5′)); 123.6, 123.8, 124.8, 125.8 (C(4), C(5), C(6′), olefin. C); 124.1 (C(4a)); 132.7 (C(3), C(6), 134.9 (C(8a)); 146.6, 152.7, 155.8 (C(2), C(7), C(2′), C(3′)). FD-MS: 1438 (100, M^+). Anal. calc. for $C_{98}H_{164}O_6$ (1438.4): C 81.83, H 11.49; found: C 81.65, H 11.71.

*2,7-Bis{(*E*)-2-[2,3-bis(hexyloxy)phenyl]ethenyl}-3,6-bis[(2-butylhexyl)oxy]naphthalene* (**1g**). Prepared as described for **1a**. Yield: 77%. Yellow oil. ^{1}H-NMR ($CDCl_3$): 0.81–0.96 (*m*, 8 Me); 1.20–1.44 (*m*, 16 CH_2); 1.44–1.61 (*m*, 8 CH_2); 1.75–2.00 (*m*, 4 CH_2, 2 CH); 3.95–4.10 (*m*, 6 CH_2O); 6.78–6.85 (*m*, 2 H–C(4′)); 6.99–7.09 (*m*, H–C(1), H–C(8), 2 H–C(5′)); 7.20–7.31 (*m*, 2 H–C(6′)); 7.60 ('*s*', 4 olefin. H); 8.01 (*s*, H–C(4), H–C(5)). ^{13}C-NMR ($CDCl_3$): 14.1 (Me); 22.6, 22.7, 23.1, 25.9, 26.0, 29.1, 29.4, 29.7, 30.4, 31.4, 31.6, 31.8 (CH_2, partly superimposed); 37.9 (CH); 68.6, 71.1, 73.7 (CH_2O); 104.9 (C(1), C(8)); 112.2 (C(4′)); 117.7 (C(5′)); 123.3, 123.6, 124.3, 125.1 (C(4), C(5), C(6′), olefin. C); 123.8, 126.5, 132.6, 135.0 (C(3), C(6), C(1′), C(4a), C(8a)); 146.3, 152.6, 155.8 (C(2), C(7), C(2′), C(3′)). FD-MS: 1045 (100, M^+). Anal. calc. for $C_{70}H_{108}O_6$ (1045.6): C 80.41, H 10.41; found: C 80.60, H 10.51.

General Procedure for the Preparation of the Hexahelicenes **3a**–**3g**. Depending on the solubility, 0.1–1.0 g of **1a**–**1g** and the twofold molar amount of I_2 were dissolved in 2,000 ml of dry benzene. The soln. was purged with O_2-free N_2 for 30 min, and a 5–10-fold molar excess of methyloxirane was added before the irradiation was started with a *Hanovia-450-W* medium-pressure lamp, equipped with a *Pyrex* filter. When the red color fades after some hours, the irradiation was stopped, and the concentrated soln. was treated with aq. $NaHSO_3$, to remove some still present I_2, and washed with H_2O. The purification of the formed hexahelicene was performed by CC (SiO_2) or, in the case of the hardly soluble **3a**, by treatment with boiling acetone.

4,7,10,13-Tetramethoxyhexahelicene (**3a**). Compound **1a** (1.00 g, 2.2 mmol) and 1.12 g (4.4 mmol) I_2 yielded 605 mg (61%) of **3a**. M.p. 218°. FD-MS: 448 (100, M^+). Anal. calc. for $C_{30}H_{24}O_4$ (448.5): C 80.34, H 5.39; found: C 80.55, H 5.56.

4,7,10,13-Tetrakis(dodecyloxy)hexahelicene (**3b**). Compound **1b** (710 mg, 0.66 mmol) and I_2 (355 mg, 1.40 mmol) gave after 5 h irradiation a yellow product, which was purified by CC (SiO_2 (3 × 50 cm); PE (b.p. 40–70°)/toluene 2:1) and recrystallization from EtOH. Yield: 580 mg (82%). M.p. 94°. FD-MS: 1065 (100, M^+). Anal. calc. for $C_{74}H_{112}O_4$ (1065.7): C 83.40, H 10.59; found: C 83.04, H 10.65.

4,7,10,13-Tetrakis[(2-ethylhexyl)oxy]hexahelicene (**3c**). Compound **1c** (680 mg, 0.80 mmol) and I_2 (408 mg, 1.61 mmol) gave after 22 h irradiation a yellow product, which was purified by CC (SiO_2 (3 × 50 cm); CH_2Cl_2) and recrystallization from MeOH. Yield: 305 mg (45%). M.p. 143–144°. FD-MS: 841 (100, M^+). Anal. calc. for $C_{58}H_{80}O_4$ (841.3): C 82.81, H 9.58; found: C 82.93, H 9.64.

4,7,10,13-Tetrakis[(2-butylhexyl)oxy]hexahelicene (**3d**). Compound **1d** (850 mg, 0.89 mmol) and I_2 (430 mg, 1.7 mmol) gave after 12 h irradiation a yellow product, which was purified by CC (SiO_2 (3 × 50 cm); PE (b.p. 40–70°)/CH_2Cl_2 3:1) and recrystallization from MeOH. Yield: 310 mg (37%). M.p. 106°. FD-MS: 953 (100, M^+). Anal. calc. for $C_{66}H_{96}O_4$ (953.5): C 83.14, H 10.15; found: C 83.29, H 10.19.

3,4,7,10,13,14-Hexakis(hexyloxy)hexahelicene (**3e**). Compound **1e** (1.01 g, 1.08 mmol) and I_2 (548 mg, 2.16 mmol) gave after 6 h irradiation a yellow product, which was purified by CC (SiO_2 (3 × 50 cm); PE (b.p. 40–70°)/toluene 1:3). Yield: 600 mg (60%). M.p. 69°. FD-MS: 929 (100, M^+). Anal. calc. for $C_{62}H_{88}O_6$ (929.4): C 80.13, H 9.54; found: C 80.24, H 9.47.

3,4,7,10,13,14-Hexakis(dodecyloxy)hexahelicene (**3f**). Compound **1f** (720 mg, 0.50 mmol) and I_2 (254 mg, 1.0 mmol) gave after 12 h irradiation a yellow product, which was purified by CC (SiO_2 (3 × 50 cm); PE (b.p. 40–70°)/toluene 5:2). Yield: 396 mg (55%). M.p. −8°. FD-MS: 1434 (100, M^+). Anal. calc. for $C_{98}H_{160}O_6$ (1434.4): C 82.06, H 11.24; found: C 81.91, H 11.41.

7,10-Bis[(2-butylhexyl)oxy]-3,4,13,14-tetrakis(hexyloxy)hexahelicene (**3g**). Compound **1g** (1.05 g, 1.00 mmol) and I_2 (508 mg, 2.00 mmol) gave after 20 h irradiation a yellow product, which was purified by CC (SiO_2 (3 × 50 cm); CH_2Cl_2). Yield: 200 mg (19%). Light yellow oil, which forms a glassy state at −50°. FD-MS: 1041 (100, M^+). Anal. calc. for $C_{70}H_{104}O_6$ (1041.6): C 80.72, H 10.06; found: C 80.54, H 9.89.

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