

Convergent Synthesis of Columnar Twins and Tetramers from Triphenylene Building Blocks – The First Example of a Columnar Spiro-Twin[☆]

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The novel spiro-twins **3a–f** were prepared in three steps by one-pot oxidative coupling of guaiacol (**9**) and 1,2-dialkoxybenzenes **10a–f**, followed by demethylation of the triphenylene **11** and subsequent etherification with the tetrabromide **6**. A related strategy gave the tetramers **7a–f** in two steps. Whereas derivatives **3a,b** and **7a,b** with pentyloxy and hexyloxy chains showed isotropic melting behavior,

compounds **3c–f** and **7c–f** with longer alkyl chains displayed columnar mesophases. DSC, polarizing microscopy, X-ray diffraction and molecular modeling studies were used to further characterize the type of mesophase. For the spiro-twin **3** either a rectangular or a hexagonal columnar phase were conceivable. In case of **7f** a hexagonal columnar mesophase was assigned.

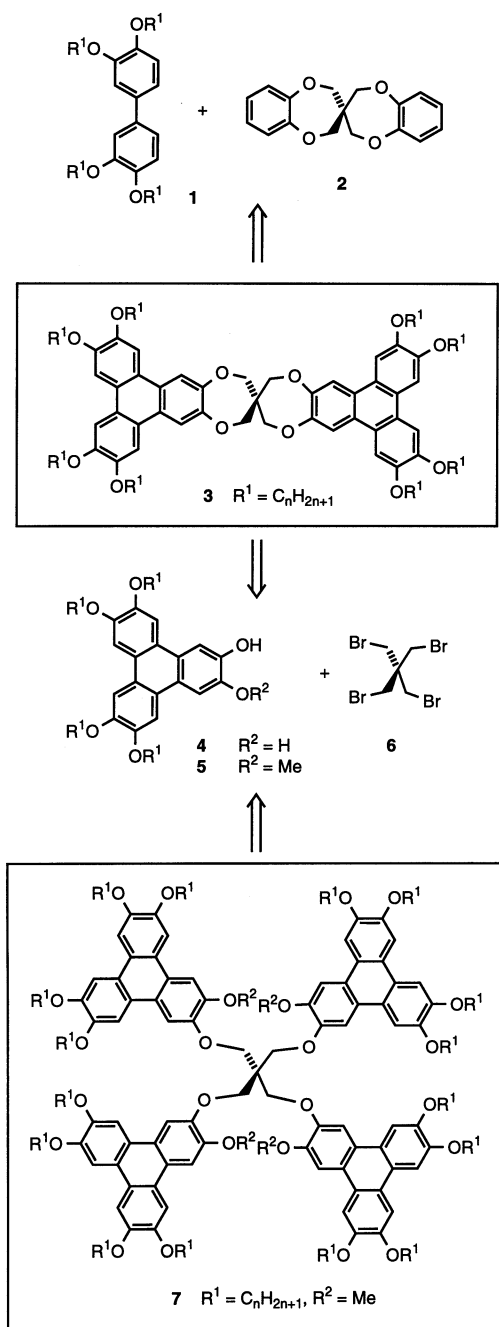
Besides the monomeric discotic (disc-shaped) liquid crystals^[1] the class of discotic oligomers recently has gained increased interest among material scientists. In these compounds several discotic monomeric subunits are connected by spacers. The first discotic twin containing two hexa-alkanoyloxybenzene subunits which are connected by a dicarboxylic acid spacer was described in 1985 by Lillya and Murthy^[2]. The authors observed hexagonal columnar (Col_h) phases for these novel liquid crystals. Triphenylenes were used first by Luz et al. in 1994 for the synthesis of bis[pentakis(pentyloxy)triphenylenoxy]decane^[3]. These twins showed high photo conductivities comparable to those found for inorganic semiconductors^{[4][5][6]}. If twins were prepared from different subunits, i.e. donor and acceptor monomers, charge-transfer interactions in Langmuir–Blodgett films could be observed^{[7][8][9]}. Similar properties were found for discotic oligomers^[10]. Ringsdorf et al. reported photoconductivity for a cyclosiloxane, whose silicon atoms are bound to four triphenylenes^[5]. However, the above-mentioned discotic twins and oligomers do not necessarily form columnar mesophases. In some cases nematic phases were also detected^[11]. In addition, it was found that the disc-like structure of a molecule is not a strict requirement for the formation of columnar mesophases. Thus, columnar oligomers were prepared by attaching disc-shaped lateral 3,4,5-trialkoxybenzoates fixed to

a tetrahedral central unit^[12]. With regard to the relationship between the type of mesophase and the structure of the mesogenic unit we were interested in the preparation of the unknown spiro-twin **3** based on triphenylene building blocks (Scheme 1)^{[13][14]}. In addition, the triphenylene tetramer **7** should be accessible from the same starting material **5**, **6** by using a similar convergent synthetic strategy. We wanted to investigate whether the twisting of compound **3** resulting from the spiro-annellation might prohibit a columnar orientation and induce a “quasi-cholesteric”, screw-like, or a nematic or smectic orientation in the liquid crystalline phase. By comparison of **3** and **7** we hoped to elucidate their structure, because we anticipated columnar mesogenic properties for the tetramer **7**. The results towards this end are described in this manuscript.

As outlined in the retrosynthetic analysis (Scheme 1) spiro compound **3** might be prepared either by coupling of two biphenyl units **1** with the known 3,3'-(4*H*,4'*H*)-spiro-bi[2*H*-1,5-benzodioxepin] (**2**)^[15] (method A) or by coupling of the tetrabromide **6** with two preformed triphenylene derivatives **4** (method B). Whereas all attempts for an oxidative coupling of **1** and **2** failed^{[16][17]}, the synthesis of **3** according to method B could be successfully realized (Scheme 2).

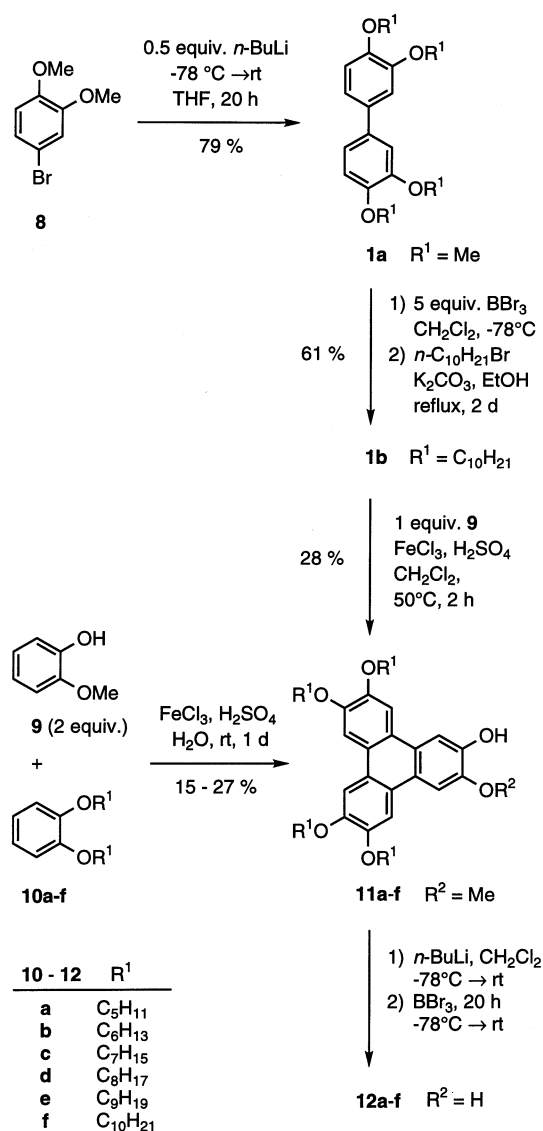
Following a procedure by Lau et al.^{[18][19]} 4-bromo-1,2-dimethoxybenzene (**8**) was treated with 0.5 equivalents of

Scheme 1



*n*BuLi in THF at -78°C to give the biphenyl **1a** after aqueous work-up and recrystallization in 79% yield. The reaction proceeded very cleanly without the use of expensive or toxic coupling agents^[20]. Biphenyl **1a** was then demethylated in the presence of BBr_3 followed by alkylation with *n*-decyl bromide to yield **1b**^{[17][21]}. Subsequent oxidative coupling with guaiacol (**9**) in the presence of FeCl_3 gave the tetrakisdecyl-substituted triphenylene **11f** ($R = C_{10}H_{21}$). Compound **11f** is thus available in 4 steps in 14% overall yield. However, the synthetic effort can be drastically reduced, if 1,2-dialkoxybenzene (**10**) is directly coupled with guaiacol (**9**) in aqueous H_2SO_4 in the presence of FeCl_3 . In

Scheme 2



order to improve the yield it was found advantageous to use 2 equivalents of **9**. If equimolar amounts of **9** and **10** were used instead, formation of the symmetrically substituted hexaalkoxytriphenylene was strongly favored. By using the one-pot methodology compound **11f** could be obtained in 2 steps in 15% yield. Derivatives **11a–e** with shorter alkyl chains were isolated in 20–27% overall yield. In addition, it should be mentioned that the one-pot coupling requires only one chromatographic purification step (of **11**) as compared to three chromatographic purifications for the biphenyl route. BBr_3 -induced demethylation of **11** gave the dihydroxytriphenylene **12**. Compound **12** was then treated with tetrakis(bromomethyl)methane (**6**) in the presence of K_2CO_3 in DMF to give the spiro compound **3** (Scheme 3, Table 1). Reaction of triphenylene **11** with tetrabromide **6** under similar conditions gave the tetramer **7** in good yields (Table 2).

Table 1. Yields of compounds **11** ($R^2 = \text{Me}$), **12** ($R^2 = \text{H}$), and **3**, and phase transitions of the spiro twins **3**^{[a][b][c]}

R^1		yields [%]		transition temperatures [°C] (and enthalpies [kJ mol ⁻¹]) of 3 ^[d]					I
		11	12	3	K		Col		
C ₅ H ₁₁	a	27	59	79	•	222 (16.3)	—	•	•
C ₆ H ₁₃	b	22	61	82	•	155 (8.1)	—	•	•
C ₇ H ₁₅	c	24	71	84	•	70 (16.6)	•	103 (1.7)	•
C ₈ H ₁₇	d	23	54	66	•	65 (21.6)	•	109 (2.0)	•
C ₉ H ₁₉	e	20	65	84	•	60 (19.1)	•	121 (5.2)	•
C ₁₀ H ₂₁	f	15	64	84	•	56 (30.0)	•	106 (2.3)	•

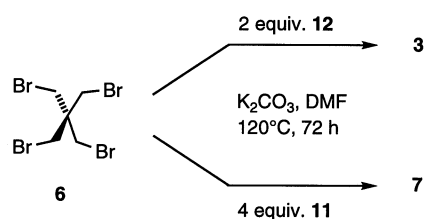
^[a] Transition temperatures were determined by differential scanning calorimetry. — ^[b] Preparation of **11** by one-pot coupling from **10**. — ^[c] Reaction conditions: see Schemes 2, 3. — ^[d] The following phases were observed: K (crystalline), Col (columnar), I (isotropic).

Table 2. Yields and phase transitions of the tetramers **7** ($R^2 = \text{Me}$)^{[a][b]}

R^1		yield of 7		transition temperatures [°C] (and enthalpies [kJ mol ⁻¹]) of 7 ^[b]					I
		[%]	g		K		Col _h		
C ₅ H ₁₁	a	71	—	•	142 (22.4)	—	—	•	•
C ₆ H ₁₃	b	69	—	•	116 (24.3)	—	—	•	•
C ₇ H ₁₅	c	74	•	—40	—	•	80 (23.5)	•	•
C ₈ H ₁₇	d	74	•	—59	—	•	79 (26.9)	•	•
C ₉ H ₁₉	e	73	•	—69	—	•	59 (16.1)	•	•
C ₁₀ H ₂₁	f	79	•	—61	—	•	58 (35.4)	•	•

^[a] See footnotes^{[a][b]} in Table 1. — ^[b] The following phases were observed: g (glass transition), K (crystalline), Col_h (hexagonal columnar), I (isotropic).

Scheme 3



The mesomorphic properties of **3** and **7** were determined by differential scanning calorimetry (DSC) and polarizing microscopy (Tables 1, 2). For pentyl- and hexyl-substituted spiro compounds **3a,b** isotropic melting behavior was observed. However, spiro-twins **3c–f** with longer alkyl chains displayed a mesophase with a width of 30–60°C. Polarizing microscopy revealed a fan-shaped texture (Figure 1). Therefore, we assume a columnar mesophase (Col)^{[22][23]}.

Figure 1. Fan-shaped texture of the spiro compound **3f** as seen between crossed polarizers at 100°C upon cooling ($\times 250$)

Isotropic melting was found for the pentyl- and hexyl-substituted tetramers **7a,b** similar to the corresponding spiro compounds **3a,b**. In contrast to the spiro-twins **3c–f** the tetramers **7c–f** with longer alkyl chains show properties typical for oligomeric compounds due to their molecular weight of 3000–4000 as determined by MALDI/TOF mass spectrometry. Compounds **7c–f** are highly viscous even upon heating. When DSC experiments were carried out at subambient temperatures (until -150°C) glass transitions between -40 and -69°C were detected. Polarizing microscopy of **7c–f** revealed no characteristic textures. However, the anisotropy of the mesophase could be demonstrated by observing a spreaded sample on a slide between crossed polarizers (Figure 2). The double refraction of compounds **7c–f** disappeared at the clearing temperatures.

An X-ray diffraction experiment of the mesophase of **3f** at 85°C produced a sharp reflection in the small-angle re-

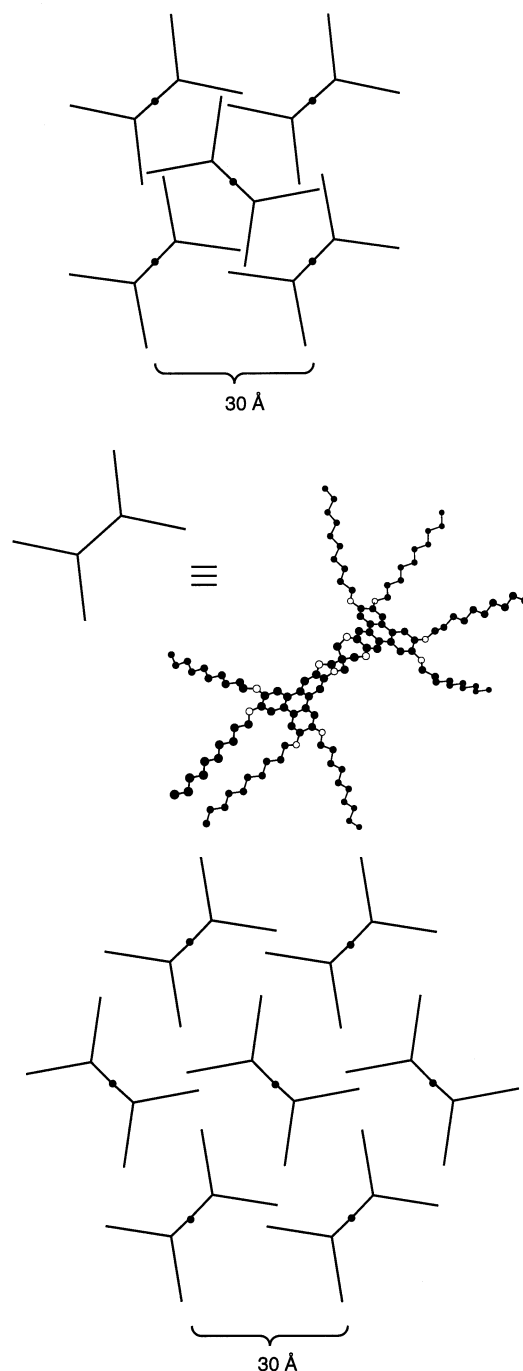
Figure 2. Spread sample of the tetramer **7f** as seen between crossed polarizers at 22°C ($\times 250$)

gion at $2\theta = 2.92^\circ$ and a broad halo at $2\theta = 19.4^\circ$. In a columnar mesophase these reflections can be correlated with the distance between two columns ($a = 30.0 \text{ \AA}$) and the intracolumnar distance ($d = 4.6 \text{ \AA}$), respectively^[24]. However, no higher order small-angle reflections typical for a hexagonal columnar mesophase (Col_h) could be detected. This might be due to the weakness of these reflections. Alternatively, a rectangular columnar mesophase (Col_r) with two almost equal lattice constants $a \approx b$ might explain the observed X-ray results^[25]. According to molecular modeling studies of the spiro twin **3f** an intramolecular distance of 13 \AA between the two triphenylene centres and a radius of 17 \AA for one triphenylene "hemisphere" was calculated^[26]. This should result in a total intercolumnar distance of 47 \AA . However, if one assumes that the spiro compounds **3** do not rotate freely within a layer of several columns, but align themselves parallel to each other as shown in Figure 3, the intercolumnar distance decreases to the experimental value^[25]. This alignment is conceivable both for a rectangular and a hexagonal lattice. The analogous formation of "correlated columnar" mesophases was observed by Swager for non-symmetrical copper bis(β -diketonate) complexes^[27].

Despite the absence of optical textures in the case of tetramers **7**, X-ray diffraction experiments of an unoriented sample of **7f** clearly indicated the presence of a columnar mesophase. A sharp reflection in the small-angle region at $2\theta = 3.19^\circ$ and several weaker reflections at $2\theta = 5.41$, 6.20 , and 8.15° with a ratio of positions of $1:(3)^{1/2}:2:(7)^{1/2}$ were observed. In addition a broad halo in the wide-angle region at $2\theta = 20.8^\circ$ was detected. These data support a hexagonal columnar mesophase with an intercolumnar distance $a = 28.0 \text{ \AA}$ and an intracolumnar distance $d = 4.3 \text{ \AA}$ ^[24]. Again molecular modeling studies were performed in order to estimate the volume requirements of the tetramer **7f**^[26]. In order to fit into a hexagonal lattice with the experimental lattice constants the tetramers should be oriented as shown in Figure 4. If the molecules are able to rotate freely around the axis pointing through the tetrahedral central unit, the calculated intercolumnar distance is 45 \AA . According to recent X-ray results by Luz et al. on alkanoyloxybenzene dimers the broad reflection at $\text{\AA} 4.5 \text{ \AA}$ is caused by the alkyl chains instead of the intracolumnar stacking^[24]. However, due to the steric requirement of the pentaerythritol unit the modeling studies of **3f** and **7f** revealed intracolumnar distances of 4.4 and 4.2 \AA respectively, which may be taken as further evidence for the proposed structures. In addition, the high values of the clearing transition enthalpies of **7c–f** as compared to the melting transition enthalpies of **7a,b** indicate a relatively high degree of order of the liquid-crystalline phase. A similar behavior was found by Luz et al. for the alkanoyloxybenzene dimers^[24].

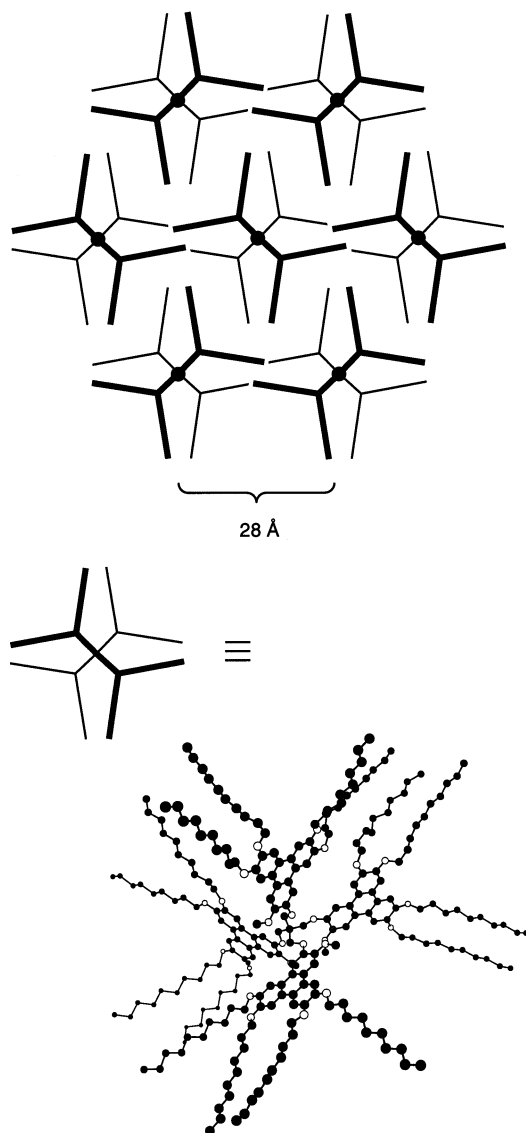
In conclusion, novel liquid-crystalline spiro-twins **3** and tetramers **7** can be prepared conveniently from triphenylenes in three and two steps, respectively. The results from DSC, X-ray diffraction, polarizing microscopy, and molecular modeling show that the triphenylene unit dominates the mesomorphic properties of **3c–f**. Despite the twisting due

Figure 3. Possible arrangements of spiro compound **3f** in (a) a rectangular columnar mesophase and (b) a hexagonal columnar mesophase; in each case one layer of the lattice is shown; the molecular model of **3f** was obtained by molecular mechanics calculations; for details see ref.^[26]



to the spiro annelation a columnar mesophase was observed. However, it was not possible to determine, whether **3** displays a hexagonal or a rectangular columnar mesophase. As expected a hexagonal columnar phase was found for tetramers **7c–f**. In both cases the central pentaerythritol unit seem to restrict the rotational freedom of the molecules **3**, **7**, leading to a two-dimensional order within a layer of several columns. Potential applications of these novel com-

Figure 4. Possible arrangement of tetramer **7f** in a hexagonal columnar mesophase; one layer of the lattice is shown; the molecular model of **7f** was obtained by molecular mechanics calculations; for details see ref. [26]



pounds concerning photo conductivity are currently under investigation.

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Experimental Section

General: All reactions were carried out under nitrogen using standard Schlenk techniques. Solvents were dried and deoxygenated by standard procedures. Analytical TLC was performed on precoated Merck Si 254 F plates (0.25 mm thickness) and the products were visualized by spraying with a solution of phosphomolybdic acid in EtOH (5%, v/v). Flash chromatography^[28] was carried out with Merck silica gel 60 (230–400 mesh). – NMR spectra: Bruker AC 200 P (¹H: 200 MHz, ¹³C: 50 MHz), Bruker AM 400 (¹H: 400 MHz, ¹³C: 100 MHz). Multiplets in ¹³C-NMR spectra

were assigned with the aid of DEPT and APT experiments. – Differential scanning calorimetry: Rheometric Scientific DSC SP, heating and cooling rate: 10 K min^{−1}. – IR: Nicolet 5DXC FT-IR spectrometer. – MS: Finnigan Model MAT 8430 (EI). – GC MS: Varian GC 3400 coupled with a Finnigan MAT 8230 (EI). – GC: Hewlett-Packard HP6890, HP5-fused silica capillary column (ID 0.32 mm, length 30 m). Temperature program: 220 °C with 1 °C min^{−1} up to 280 °C, then isothermal for 20 min. – Polarizing microscopy: Leitz Ortholux II-Pol-BK microscope combined with a Mettler FP 82 hot stage and Mettler FP 80 central processor. – X-ray diffraction experiments were performed with monochromatic Cu-K_α radiation (λ = 1.54 Å) using a two-dimensional image plate system (700 × 700 pixels). – Tetrakis(bromomethyl)methane (**6**) and 4-bromo-1,2-dimethoxybenzene (**8**) were purchased from Aldrich. The following compounds were prepared according to literature procedures: 3,3',4,4'-tetradecyloxybiphenyl (**1b**)^{[29][30]} and 1,2-dialkoxybenzenes (**10**)^[21a].

3,3',4,4'-Tetramethoxybiphenyl (1a): To a solution of 4-bromo-1,2-dimethoxybenzene (**8**, 69.5 g, 0.32 mol) in abs. THF (700 ml) was added *n*-butyllithium (100 ml, 0.16 mol, 1.6 M solution in hexane) by syringe at −78 °C over 30 min. The reaction mixture was allowed to warm to room temp. for about 12 h. After careful addition of 2 N aqueous HCl (100 ml), the layers were separated and the aqueous layer was extracted with diethyl ether (100 ml) and CH₂Cl₂ (2 × 100 ml). The combined organic layers were dried with MgSO₄ and concentrated in vacuo. Recrystallization from EtOH yielded 34.8 g (79%) of colorless crystals; mp. 134 °C. The analytic and spectroscopic data were in accord with ref. [20b][20d].

2-Hydroxy-3-methoxy-6,7,10,11-tetradecyloxytriphenylene (11f) by the Biphenyl Method: To a vigorously stirred solution of 3,3',4,4'-tetradecyloxybiphenyl (**1b**, 5.00 g, 6.40 mmol) and guaiacol (**9**, 2.38 g, 19.2 mmol) in CH₂Cl₂ were added carefully anhydrous FeCl₃ (10.4 g, 64.0 mmol) and conc. H₂SO₄ (1 ml). After stirring the mixture for 2 h at 50 °C, MeOH (10 ml) was added. The resulting suspension was filtered through a short column of SiO₂ (CH₂Cl₂/hexanes, 4:1). The solvent was removed in vacuo and the crude product was recrystallized from MeOH (250 ml) and further purified by flash chromatography on SiO₂ (hexanes/ethyl acetate, 20:1, then ethyl acetate) to give 1.63 g (1.81 mmol, 28%) of a colorless solid. The spectroscopic data of **11f** were in accord with ref. [29][30].

General One-Pot Procedure for the Synthesis of 6,7,10,11-Tetraalkoxy-2-hydroxy-3-methoxytriphenylenes 11: To a vigorously stirred suspension of 1,2-dialkoxybenzene **10** (0.10 mol) and guaiacol (**9**, 24.8 g, 0.20 mol) in H₂SO₄ (250 ml, 70% aqueous solution) was added carefully anhydrous FeCl₃ (64.9 g, 0.40 mol) in small portions over 1 h at −13 °C. The cooling bath was removed and stirring was continued for 1 d. The suspension was poured onto ice (500 g) and stirred for 1 h. The resulting dark precipitate was filtered through a fritted funnel, washed with water (500 ml) and EtOH (100 ml) and dissolved in CH₂Cl₂ (100 ml). After addition of EtOH (400 ml) a violet precipitate was obtained, which was filtered and dried over P₂O₅ at 50 °C for 12 h in vacuo. The crude product was further purified by flash chromatography on SiO₂ (hexanes/CH₂Cl₂, 1:1). The spectroscopic data of **11** were in accord with ref. [29][30].

General Procedure for the Synthesis of 6,7,10,11-Tetraalkoxy-2,3-dihydroxytriphenylenes 12: To a solution of 6,7,10,11-tetraalkoxy-2-hydroxy-3-methoxytriphenylene (**11**, 5.00 mmol) in CH₂Cl₂ (250 ml) was added dropwise over 15 min *n*-butyllithium (2.50 ml, 5.00 mmol, 2.0 M solution in pentane) at −78 °C. The resulting mixture was stirred for additional 15 min at −78 °C and 15 min at

room temp. Then the mixture was cooled again to -78°C and BBr_3 (5.00 ml, 5.00 mmol, 1.0 M solution in CH_2Cl_2) was added dropwise over 15 min. After warming to room temp., the mixture was stirred for 20 h and then hydrolyzed by addition of degassed water (100 ml) followed by stirring for 30 min. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (4×200 ml). The combined organic layers were dried with MgSO_4 and concentrated in vacuo. The crude products were purified by flash chromatography on SiO_2 (CH_2Cl_2 /ethyl acetate, 20:1) to give the triphenylenes **12** as colorless solids. The spectroscopic data of **12** were in accord with those in ref. [21a].

General Procedure for the Synthesis of Spiro-Twins 3: To a suspension of K_2CO_3 (1.66 g, 12.0 mmol) in DMF (40 ml) were added sequentially **12** (3.00 mmol) and tetrakis(bromomethyl)methane (**6**, 582 mg, 1.50 mmol) and the mixture was heated at 120°C for 72 h. After cooling to room temp., the suspension was poured on ice (100 g) and then it was stirred for 15 min. The precipitate was filtered using Celite and the resulting mixture of Celite and product **3** was suspended in CH_2Cl_2 (100 ml) and dried with MgSO_4 . The solvent was removed in vacuo and the crude product was purified by flash chromatography on SiO_2 (hexanes/ethyl acetate, 20:1), followed by recrystallization from CH_2Cl_2 /EtOH (1:5) to give a colorless solid.

3,3' (4H,4'H)-Spirobi[(8,9,12,13-tetrapentyloxy)-2H-triphenylene[2,3-f]-1,5-dioxepin] (3a). 1.66 g (1.30 mmol, 79%) of a colorless solid. DSC: K 222°C [16.3 kJ mol^{-1}] I. – IR (KBr): $\tilde{\nu} = 2956 \text{ cm}^{-1}$, 2933, 2870, 2862, 1616, 1506, 1467, 1460, 1427, 1382, 1316, 1294, 1188, 1168, 1146, 1075, 1035, 977, 867, 836, 815, 755. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.35$ (s, 4 H, 6-H, 15-H), 7.99, 7.98 ($2 \times$ s, 8 H, 7-H, 10-H, 11-H, 14-H), 4.12 (s, 8 H, 2-H, 4-H), 4.01 (t, $J = 6.4 \text{ Hz}$, 8 H, OCH_2CH_2), 3.93 (t, $J = 6.2 \text{ Hz}$, 8 H, OCH_2CH_2), 1.83–1.76, 1.54–1.42, 1.40–1.30 ($3 \times$ m, 48 H, CH_2), 0.98–0.89 (m, 24 H, CH_2CH_3). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.1$, 150.0, 149.6 (C-5a, C-8, C-9, C-12, C-13, C-15a), 126.1, 124.5, 123.8 (C-6a, C-6b, C-10a, C-10b, C-14a, C-14b), 114.4 (C-6, C-15), 107.6, 106.9 (C-7, C-10, C-11, C-14), 71.6 (C-2, C-4), 69.5, 68.8 (OCH_2CH_2), 48.2 (C-3), 29.6, 28.8, 28.7, 22.9, 22.8 (CH_2), 14.3 (CH_2CH_3). – MS (DEI); m/z (%): 1273 (100) [M^+], 1202 (18) [$\text{M}^+ - \text{C}_5\text{H}_{11}$], 656 (7), 639 (14), 636 (6), 569 (2), 429 (1), 359 (1), 356 (2), 43 (2). – $\text{C}_{81}\text{H}_{108}\text{O}_{12}$ (1273.7): calcd. C 76.38, H 8.55; found C 75.85, H 8.49.

3,3' (4H,4'H)-Spirobi[(8,9,12,13-tetrahexyloxy)-2H-triphenylene[2,3-f]-1,5-dioxepin] (3b): 1.71 g (1.23 mmol, 82%) of a colorless solid. DSC: K 155°C [8.1 kJ mol^{-1}] I. – IR (KBr): $\tilde{\nu} = 2955 \text{ cm}^{-1}$, 2931, 2870, 2859, 1616, 1506, 1467, 1460, 1427, 1382, 1340, 1316, 1293, 1262, 1188, 1169, 1145, 1034, 990, 986, 979, 929, 867, 838, 756. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.33$ (s, 4 H, 6-H, 15-H), 7.99, 7.97 ($2 \times$ s, 8 H, 7-H, 10-H, 11-H, 14-H), 4.13 (s, 8 H, 2-H, 4-H), 4.03 (t, $J = 6.4 \text{ Hz}$, 8 H, OCH_2CH_2), 3.95 (t, $J = 6.2 \text{ Hz}$, 8 H, OCH_2CH_2), 1.85–1.77, 1.56–1.48, 1.36–1.28 ($3 \times$ m, 64 H, CH_2), 0.98–0.90 (m, 24 H, CH_2CH_3). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.1$, 150.0, 149.5 (C-5a, C-8, C-9, C-12, C-13, C-15a), 126.1, 124.4, 123.8 (C-6a, C-6b, C-10a, C-10b, C-14a, C-14b), 114.4 (C-6, C-15), 107.6, 106.9 (C-7, C-10, C-11, C-14), 71.5 (C-2, C-4), 69.5, 68.9 (OCH_2CH_2), 48.2 (C-3), 32.1, 32.0, 29.9, 26.3, 23.1, 23.0 (CH_2), 14.3, 14.2 (CH_2CH_3). – MS (DEI); m/z (%): 1388 (10), 1386 (100) [M^+], 1385 (90), 1301 (20) [$\text{M}^+ - \text{C}_6\text{H}_{13}$], 696 (20), 660 (37), 491 (8), 407 (13), 335 (8), 295 (16), 266 (7), 149 (9), 93 (14), 55 (50), 43 (60). – $\text{C}_{89}\text{H}_{124}\text{O}_{12}$ (1386.0): calcd. C 77.13, H 9.02; found C 76.97, H 9.02.

3,3' (4H,4'H)-Spirobi[(8,9,12,13-tetraheptyloxy)-2H-triphenylene[2,3-f]-1,5-dioxepin] (3c): 1.76 g (1.18 mmol, 84%) of a color-

less solid. DSC: K 70°C [16.6 kJ mol^{-1}] Col 103°C [1.7 kJ mol^{-1}] I. – IR (KBr): $\tilde{\nu} = 2955 \text{ cm}^{-1}$, 2927, 2857, 1617, 1506, 1467, 1459, 1427, 1382, 1340, 1316, 1292, 1262, 1214, 1188, 1169, 1146, 1034, 981, 867, 837, 757, 722. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.33$ (s, 4 H, 6-H, 15-H), 7.99, 7.97 ($2 \times$ s, 8 H, 7-H, 10-H, 11-H, 14-H), 4.12 (s, 8 H, 2-H, 4-H), 4.02 (t, $J = 6.4 \text{ Hz}$, 8 H, OCH_2CH_2), 3.94 (t, $J = 6.2 \text{ Hz}$, 8 H, OCH_2CH_2), 1.84–1.77, 1.53–1.47, 1.32–1.27 ($3 \times$ m, 80 H, CH_2), 0.96–0.88 (m, 24 H, CH_2CH_3). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.1$, 150.0, 149.6 (C-5a, C-8, C-9, C-12, C-13, C-15a), 126.1, 124.5, 123.8 (C-6a, C-6b, C-10a, C-10b, C-14a, C-14b), 114.4 (C-6, C-15), 107.6, 106.9 (C-7, C-10, C-11, C-14), 71.6 (C-2, C-4), 69.5, 68.9 (OCH_2CH_2), 48.2 (C-3), 32.3, 32.2, 30.0, 29.9, 29.6, 26.6, 23.1, 23.0 (CH_2), 14.3 (CH_2CH_3). – MS (DEI); m/z (%): 1500 (14), 1497 (100) [M^+], 1399 (38) [$\text{M}^+ - \text{C}_7\text{H}_{15}$], 1397 (12), 769 (8), 753 (18), 752 (18), 653 (12), 555 (6), 457 (6), 323 (5), 295 (8), 279 (4), 70 (9), 57 (30), 43 (33). – $\text{C}_{97}\text{H}_{140}\text{O}_{12}$ (1498.2): calcd. C 77.77, H 9.42; found C 77.62, H 9.35.

3,3' (4H,4'H)-Spirobi[(8,9,12,13-tetraoctyloxy)-2H-triphenylene[2,3-f]-1,5-dioxepin] (3d): 1.37 g (0.85 mmol, 66%) of a colorless solid. DSC: K 65°C [21.6 kJ mol^{-1}] Col 109°C [2.0 kJ mol^{-1}] I. – IR (KBr): $\tilde{\nu} = 2955 \text{ cm}^{-1}$, 2925, 2855, 1617, 1506, 1467, 1427, 1383, 1316, 1291, 1263, 1189, 1170, 1145, 1034, 982, 959, 866, 838, 755, 721. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.36$ (s, 4 H, 6-H, 15-H), 8.04, 8.01 ($2 \times$ s, 8 H, 7-H, 10-H, 11-H, 14-H), 4.14 (s, 8 H, 2-H, 4-H), 4.06 (t, $J = 6.4 \text{ Hz}$, 8 H, OCH_2CH_2), 3.98 (t, $J = 6.2 \text{ Hz}$, 8 H, OCH_2CH_2), 1.88–1.82, 1.58–1.44, 1.39–1.23 ($3 \times$ m, 96 H, CH_2), 0.98–0.91 (m, 24 H, CH_2CH_3). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.1$, 150.0, 149.6 (C-5a, C-8, C-9, C-12, C-13, C-15a), 126.1, 124.5, 123.8 (C-6a, C-6b, C-10a, C-10b, C-14a, C-14b), 114.4 (C-6, C-15), 107.7, 107.0 (C-7, C-10, C-11, C-14), 71.6 (C-2, C-4), 69.6, 68.9 (OCH_2CH_2), 48.2 (C-3), 32.3, 32.2, 30.0, 29.9, 29.8, 26.7, 26.6, 23.1 (CH_2), 14.4, 14.3 (CH_2CH_3). – MS (DEI); m/z (%): 1612 (6), 1610 (100) [M^+], 1497 (8) [$\text{M}^+ - \text{C}_8\text{H}_{17}$], 824 (2), 808 (12), 805 (4), 471 (3), 359 (3), 93 (3), 55 (14), 43 (11). – $\text{C}_{105}\text{H}_{156}\text{O}_{12}$ (1610.4): calcd. C 78.31, H 9.76; found C 77.94, H 9.85.

3,3' (4H,4'H)-Spirobi[(8,9,12,13-tetranonyloxy)-2H-triphenylene[2,3-f]-1,5-dioxepin] (3e): 1.75 g (1.02 mmol, 84%) of a colorless solid. DSC: K 60°C [19.1 kJ mol^{-1}] Col 121°C [5.2 kJ mol^{-1}] I. – IR (KBr): $\tilde{\nu} = 2956 \text{ cm}^{-1}$, 2925, 2854, 1617, 1506, 1467, 1427, 1388, 1316, 1293, 1262, 1189, 1170, 1145, 1035, 993, 989, 971, 866, 837, 757, 721. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.35$ (s, 4 H, 6-H, 15-H), 8.01, 8.00 ($2 \times$ s, 8 H, 7-H, 10-H, 11-H, 14-H), 4.14 (s, 8 H, 2-H, 4-H), 4.06 (t, $J = 6.4 \text{ Hz}$, 8 H, OCH_2CH_2), 3.99 (t, $J = 6.2 \text{ Hz}$, 8 H, OCH_2CH_2), 1.89–1.81, 1.61–1.48, 1.42–1.23 ($3 \times$ m, 112 H, CH_2), 0.99–0.93 (m, 24 H, CH_2CH_3). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.1$, 150.0, 149.5 (C-5a, C-8, C-9, C-12, C-13, C-15a), 126.1, 124.5, 123.8 (C-6a, C-6b, C-10a, C-10b, C-14a, C-14b), 114.4 (C-6, C-15), 107.7, 107.0 (C-7, C-10, C-11, C-14), 71.5 (C-2, C-4), 69.6, 68.9 (OCH_2CH_2), 48.2 (C-3), 32.4, 32.3, 30.1, 30.0, 29.8, 26.7, 23.9, 23.1 (CH_2), 14.4, 14.3 (CH_2CH_3). – MS (DEI); m/z (%): 1721 (34) [M^+], 1595 (13) [$\text{M}^+ - \text{C}_9\text{H}_{19}$], 1553 (6), 884 (8), 841 (18), 828 (19), 359 (9), 307 (12), 97 (14), 85 (24), 70 (43), 57 (60), 55 (68), 43 (100). – $\text{C}_{113}\text{H}_{172}\text{O}_{12}$ (1772.6): calcd. C 78.79, H 10.06; found C 78.68, H 9.98.

3,3' (4H,4'H)-Spirobi[(8,9,12,13-tetradecyloxy)-2H-triphenylene[2,3-f]-1,5-dioxepin] (3f): 1.75 g (0.95 mmol, 84%) of colorless crystals. DSC: K 56°C [30.0 kJ mol^{-1}] Col 106°C [2.3 kJ mol^{-1}] I. – IR (KBr): $\tilde{\nu} = 2956 \text{ cm}^{-1}$, 2924, 2854, 1617, 1507, 1467, 1427, 1385, 1315, 1292, 1263, 1189, 1172, 1068, 1033, 994, 990, 978, 866, 838, 757, 721. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.34$ (s, 4 H, 6-H, 15-H), 8.02, 8.00 ($2 \times$ s, 8 H, 7-H, 10-H, 11-H, 14-H), 4.15 (s,

8 H, 2-H, 4-H), 4.07 (t, $J = 6.4$ Hz, 8 H, OCH_2CH_2), 4.00 (t, $J = 6.2$ Hz, 8 H, OCH_2CH_2), 1.90–1.82, 1.63–1.48, 1.42–1.23 (3 \times m, 128 H, CH_2), 0.98–0.92 (m, 24 H, CH_2CH_3). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.1, 150.0, 149.6$ (C-5a, C-8, C-9, C-12, C-13, C-15a), 126.1, 124.5, 123.8 (C-6a, C-6b, C-10a, C-10b, C-14a, C-14b), 114.4 (C-6, C-15), 107.7, 107.0 (C-7, C-10, C-11, C-14), 71.6 (C-2, C-4), 69.6, 68.9 (OCH_2CH_2), 48.2 (C-3), 32.4, 32.3, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 26.7, 23.1 (CH_2), 14.4, 14.3 (CH_2CH_3). – MS (DEI); m/z (%): 1833 (15) [M^+], 1705 (4), 1694 (7), 1496 (8), 1384 (16), 1300 (4), 1024 (4), 921 (9), 920 (4), 751 (3), 695 (9), 359 (16), 356 (13), 295 (7), 111 (11), 97 (19), 91 (27), 85 (47), 70 (48), 57 (100), 43 (99). – $\text{C}_{121}\text{H}_{188}\text{O}_{12}$ (1834.8): calcd. C 79.21, H 10.33; found C 78.91, H 10.50.

General Procedure for the Synthesis of Tetramers 7: To a suspension of K_2CO_3 (553 mg, 4.00 mmol) in DMF (40 ml) were added sequentially triphenylene **11** (2.00 mmol) and tetrakis(bromomethyl)methane (**6**, 194 mg, 0.50 mmol) and the mixture was heated at 120°C for 72 h. After cooling to room temp., the suspension was poured on ice (50 g) and then it was stirred for 15 min. The precipitate was filtered using Celite and the resulting mixture of Celite and product **7** was suspended in CH_2Cl_2 (100 ml) and dried with MgSO_4 . The solvent was removed in vacuo and the crude product was purified by flash chromatography on SiO_2 (hexanes/ethyl acetate, 20:1), followed by recrystallization from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ (1:4) to give either a colorless solid (**7a,b**) or a highly viscous oil (**7c–f**).

Tetrakis[(3-methoxy-6,7,10,11-tetrapentyloxytriphenylen-2-yl)-oxymethyl]methane (7a): 1.10 g (0.43 mmol, 71%) of a colorless solid. DSC: K 142°C [22.4 kJ mol $^{-1}$] I. – IR (KBr) $\tilde{\nu} = 3105$ cm $^{-1}$, 3099, 2956, 2933, 2870, 2860, 1617, 1515, 1467, 1448, 1430, 1387, 1263, 1189, 1165, 1075, 1047, 870, 836, 806, 773. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.41, 7.95, 7.84, 7.68, 7.55, 5.56$ (6 \times s, 24 H, 1-H, 4-H, 5-H, 8-H, 9-H, 12-H), 4.20–4.08 (m, 32 H, OCH_2CH_2), 4.01 [s, 8 H, $(\text{ArOCH}_2)_4\text{C}$], 3.70 [s, 12 H, OCH_3], 1.94–0.70 (m, 144 H, CH_2). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.1, 150.0, 149.8, 149.4, 149.2$ (C-2, C-3, C-6, C-7, C-10, C-11), 124.6, 124.2, 124.0, 123.8, 123.7 (C-4a, C-4b, C-8a, C-8b, C-12a, C-12b), 107.6, 107.3, 107.2, 105.2 (C-1, C-4, C-5, C-8, C-9, C-12), 69.5, 69.4, 69.3, 69.0 [$(\text{ArOCH}_2)_4\text{C}$, OCH_2CH_2], 55.5 (OCH_3), 48.3 [$(\text{ArOCH}_2)_4\text{C}$], 30.0, 29.8, 28.9, 28.8, 23.0, 22.9 (CH_2), 14.5, 14.4, 14.3, 14.2, 14.1 (CH_2CH_3). – MS (MALDI-TOF); m/z : 2540 [M^+]. – $\text{C}_{161}\text{H}_{220}\text{O}_{24}$ (2539.5): calcd. C 76.15, H 8.73; found C 75.99, H 8.75.

Tetrakis[(6,7,10,11-tetrahexyloxy-3-methoxytriphenylen-2-yl)-oxymethyl]methane (7b): 1.07 g (0.38 mmol, 69%) of a colorless solid. DSC: K 116°C [24.3 kJ mol $^{-1}$] I. – IR (KBr) $\tilde{\nu} = 3104$ cm $^{-1}$, 2955, 2931, 2870, 2858, 1617, 1517, 1509, 1467, 1448, 1430, 1386, 1263, 1187, 1164, 1046, 868, 838, 797. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.43, 7.94, 7.85, 7.69, 7.55, 5.59$ (6 \times s, 24 H, 1-H, 4-H, 5-H, 8-H, 9-H, 12-H), 4.20–4.13 (m, 32 H, OCH_2CH_2), 4.02 [s, 8 H, $(\text{ArOCH}_2)_4\text{C}$], 3.71 [s, 12 H, OCH_3], 1.94–0.71 (m, 176 H, CH_2 , CH_3). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 149.8, 149.4, 149.2$ (C-2, C-3, C-6, C-7, C-10, C-11), 124.2, 124.0, 123.8 (C-4a, C-4b, C-8a, C-8b, C-12a, C-12b), 107.6, 107.2, 107.1 (C-1, C-4, C-5, C-8, C-9, C-12), 70.0, 69.6, 9.4, 69.3, 69.1, 69.0 [$(\text{ArOCH}_2)_4\text{C}$, OCH_2CH_2], 55.4 (OCH_3), 48.3 [$(\text{ArOCH}_2)_4\text{C}$], 32.3, 32.2, 32.1, 32.0, 30.2, 30.1, 26.5, 26.4, 26.3, 23.1, 23.0, 22.9, 22.9, 22.8, 22.2 (CH_2), 14.2, 14.1, 14.0 (CH_2CH_3). – MS (MALDI-TOF); m/z : 2764 [M^+]. – $\text{C}_{177}\text{H}_{252}\text{O}_{24}$ (2763.9): calcd. C 76.92, H 9.19; found C 76.74, H 9.13.

Tetrakis[(6,7,10,11-tetraheptyloxy-3-methoxytriphenylen-2-yl)-oxymethyl]methane (7c): 1.12 g (0.38 mmol, 74%) of a colorless, highly viscous oil. DSC: g –40°C Col $_h$, 80°C [23.5 kJ mol $^{-1}$] I. –

IR (KBr): $\tilde{\nu} = 3104$ cm $^{-1}$, 2956, 2928, 2870, 2856, 1618, 1517, 1510, 1467, 1448, 1431, 1387, 1263, 1190, 1164, 1045, 868, 837, 782. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.45–7.48, 5.61$ (br., 24 H, 1-H, 4-H, 5-H, 8-H, 9-H, 12-H), 4.23–4.05 [s, 40 H, $(\text{ArOCH}_2)_4\text{C}$, OCH_2CH_2], 3.75 [s, 12 H, OCH_3], 1.96–0.75 (m, 208 H, CH_2 , CH_3). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.0, 149.8, 149.4, 149.1$ (C-2, C-3, C-6, C-7, C-10, C-11), 124.5, 124.2, 123.7 (C-4a, C-4b, C-8a, C-8b, C-12a, C-12b), 108.0, 107.6, 107.1 (C-1, C-4, C-5, C-8, C-9, C-12), 69.6, 69.4 [$(\text{ArOCH}_2)_4\text{C}$, OCH_2CH_2], 55.3 (OCH_3), 48.4 [$(\text{ArOCH}_2)_4\text{C}$], 32.3, 32.2, 32.1, 30.3, 30.2, 30.0, 29.7, 29.6, 29.5, 26.9, 26.7, 26.6, 23.0, 22.9 (CH_2), 14.3, 14.2 (CH_2CH_3). – MS (MALDI-TOF); m/z : 2989 [M^+]. – $\text{C}_{193}\text{H}_{284}\text{O}_{24}$ (2988.4): calcd. C 77.57, H 9.58; found C 77.34, H 9.68.

Tetrakis[(3-methoxy-6,7,10,11-tetraoctyloxytriphenylen-2-yl)-oxymethyl]methane (7d): 1.12 g (0.35 mmol, 74%) of a colorless, highly viscous oil. DSC: g –59°C Col $_h$, 79°C [26.9 kJ mol $^{-1}$] I. – IR (KBr): $\tilde{\nu} = 3105$ cm $^{-1}$, 2956, 2927, 2854, 1618, 1518, 1510, 1467, 1448, 1431, 1387, 1264, 1190, 1164, 1045, 868, 837, 798. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.60–7.40, 5.58$ (br., 24 H, 1-H, 4-H, 5-H, 8-H, 9-H, 12-H), 4.30–4.05 [m, br., 40 H, $(\text{ArOCH}_2)_4\text{C}$, OCH_2CH_2], 3.75 [s, br., 12 H, OCH_3], 2.05–0.75 (m, br., 240 H, CH_2 , CH_3). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.0, 149.8, 149.1$ (C-2, C-3, C-6, C-7, C-10, C-11), 124.6, 124.2, 123.7 (C-4a, C-4b, C-8a, C-8b, C-12a, C-12b), 108.0 (C-1, C-4, C-5, C-8, C-9, C-12), 69.6, 69.4 [$(\text{ArOCH}_2)_4\text{C}$, OCH_2CH_2], 55.3 (OCH_3), 32.8, 32.3, 32.2, 30.3, 30.1, 30.0, 29.9, 29.8, 29.7, 26.8, 26.7, 26.0, 23.1, 23.0 (CH_2), 14.3 (CH_2CH_3). – MS (MALDI-TOF); m/z : 3214 [M^+]. – $\text{C}_{209}\text{H}_{316}\text{O}_{24}$ (3212.8): calcd. C 78.13, H 9.91; found C 78.29, H 10.07.

Tetrakis[(3-methoxy-6,7,10,11-tetranonyloxytriphenylen-2-yl)-oxymethyl]methane (7e): 1.10 g (0.32 mmol, 73%) of a colorless, highly viscous oil. DSC: g –69°C Col $_h$, 59°C [16.1 kJ mol $^{-1}$] I. – IR (KBr): $\tilde{\nu} = 3105$ cm $^{-1}$, 2956, 2925, 2854, 1618, 1517, 1509, 1467, 1448, 1431, 1387, 1263, 1189, 1164, 1045, 868, 837. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.60–7.40, 5.56$ (br., 24 H, 1-H, 4-H, 5-H, 8-H, 9-H, 12-H), 4.30–4.05 [m, br., 40 H, $(\text{ArOCH}_2)_4\text{C}$, OCH_2CH_2], 3.77 [s, br., 12 H, OCH_3], 2.05–0.75 (m, br., 272 H, CH_2 , CH_3). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.0, 149.8, 149.2, 149.0$ (C-2, C-3, C-6, C-7, C-10, C-11), 124.6, 124.2, 123.7 (C-4a, C-4b, C-8a, C-8b, C-12a, C-12b), 108.0, 107.0 (C-1, C-4, C-5, C-8, C-9, C-12), 69.7, 69.6, 69.5, 69.4, 69.3 [$(\text{ArOCH}_2)_4\text{C}$, OCH_2CH_2], 55.3 (OCH_3), 32.4, 32.3, 30.3, 30.2, 30.1, 29.9, 29.8, 29.7, 29.1, 26.9, 26.8, 26.7, 23.1 (CH_2), 14.4, 14.3 (CH_2CH_3). – MS (MALDI-TOF); m/z : 3439 [M^+]. – $\text{C}_{225}\text{H}_{348}\text{O}_{24}$ (3437.2): calcd. C 78.62, H 10.20; found C 78.50, H 10.26.

Tetrakis[(6,7,10,11-tetradecyloxy-3-methoxytriphenylen-2-yl)-oxymethyl]methane (7f): 0.81 g (0.22 mmol, 79%) of a colorless, highly viscous oil. DSC: g –61°C Col $_h$, 58°C [35.4 kJ mol $^{-1}$] I. – IR (KBr) $\tilde{\nu} = 3105$ cm $^{-1}$, 2956, 2924, 2854, 1618, 1517, 1510, 1467, 1448, 1431, 1387, 1263, 1189, 1164, 1046, 869, 837, 799. – ^1H NMR (400 MHz, C_6D_6): $\delta = 8.50–7.40, 5.50$ (br., 24 H, 1-H, 4-H, 5-H, 8-H, 9-H, 12-H), 4.30–4.06 [m, br., 40 H, $(\text{ArOCH}_2)_4\text{C}$, OCH_2CH_2], 3.75 [s, br., 12 H, OCH_3], 2.05–0.85 (m, br., 304 H, CH_2). – ^{13}C NMR (100 MHz, C_6D_6): $\delta = 150.0$ (C-2, C-3, C-6, C-7, C-10, C-11), 124.0 (C-4a, C-4b, C-8a, C-8b, C-12a, C-12b), 108.0 (C-1, C-4, C-5, C-8, C-9, C-12), 69.6, 69.5, 69.4, 69.3 [$(\text{ArOCH}_2)_4\text{C}$, OCH_2CH_2], 55.3 (OCH_3), 32.4, 32.3, 30.7, 30.6, 30.5, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.7, 27.0, 26.9, 26.8, 26.7, 23.1 (CH_2), 14.4, 14.3 (CH_2CH_3). – MS (MALDI-TOF); m/z : 3664 [M^+]. – $\text{C}_{241}\text{H}_{380}\text{O}_{24}$ (3661.6): calcd. 79.05, H 10.46; found C 79.25, H 10.57.

- ☆ Dedicated to Professor *Gernot Boche* on the occasion of his 60th birthday.
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