Combination of Chiral and Achiral Triphenylene Units in a Novel Unsymmetrical Columnar Twin

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The synthesis, characterization, and mesomorphic properties of a new type of liquid-crystalline twin bearing a pentadecyloxytriphenylene subunit tethered *via* a decyl spacer to a chiral pentakis(3,7-dimethyloctyloxy)-triphenylene are reported. The target compound displays a hexagonal columnar mesophase, which is metastable at room temperature.

Introduction. – Among the two major classes of thermotropic liquid crystals, *i.e.*, calamitic (rod-shaped) and discotic (disk-shaped) liquid crystals, the latter type, which forms columnar short-range-ordered assemblies in the mesophase, has attracted many researchers during the last decade [1][2]. The interest in discotic liquid crystals is mainly due to their promising physical properties, such as electrical and photoconductivity, and high charge-carrier mobility along the columns [3]. From this work, the so-called columnar twins or oligomers have emerged recently, constituting two or more discotic subunits connected to each other by a flexible spacer [4]. 2,3,6,7,10,11-Hexasubstituted triphenylenes are ideally suited building blocks for columar liquid crystals, and many examples of both symmetrical and unsymmetrical twins based on triphenylenes are known (for recent examples, see [5]). However, only few polymeric liquid crystals and columnar twins containing chiral triphenylenes have been published so far (for chiral polymeric triphenylenes, see [6]; for chiral monomeric triphenylenes, see [7]). Particularly attractive to us seemed unsymmetrical twins bearing chiral and achiral moieties of similar sizes, because these twins might be able to form different chiral and achiral microdomains within a columnar mesophase. The presence of chiral subunits might induce helical twisting of the columns, which is a prerequisite for ferroelectricity [8]. Those unsymmetrical dimers may either retain the mesomorphic properties of the subunits by columnar stacking of *like* subunits, or form supramolecular aggregates by columnar stacking of *unlike* subunits and thus display novel mesomorphic properties. As shown in *Fig. 1*, four different orientations are conceivable, *i.e.*, *a*) formation of two-dimensional domains within one lattice sheet, *b*) an intracolumnar regular ordered pattern, with the chiral and achiral subunits being segregated in different columns, *c*) an intracolumnar regular mixed pattern, with chiral and achiral subunits of neighboring twins stacked alternatively within the columns, and *d*) an intracolumnar randomly mixed pattern [9]. The micro-segregation in *a*–*c* should lead to different mesomorphic properties, *e.g.*, increased phase stability, as compared to

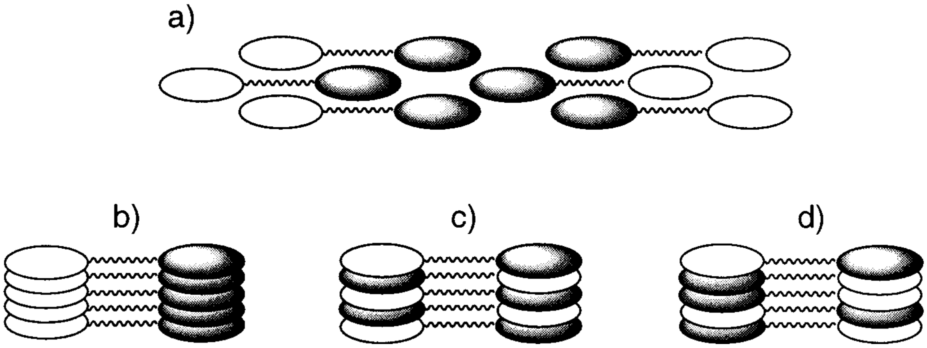


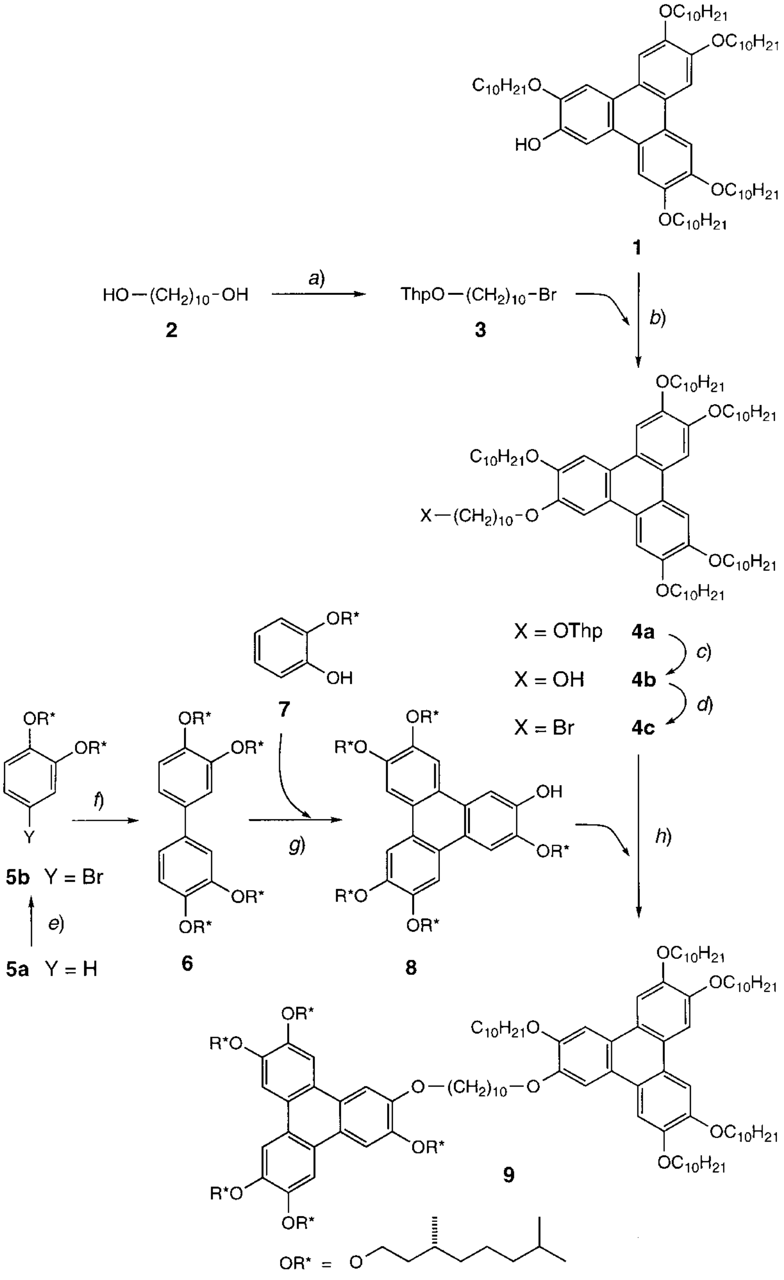
Fig. 1. *Possible arrangements of unsymmetrical twins in columnar mesophases. a*) Formation of two-dimensional domains within the hexagonal lattice; *b*) intracolumnar regularly ordered; *c*) intracolumnar regularly mixed; and *d*) intracolumnar randomly mixed.

the properties of monomeric subunits. As a model system for such unsymmetrical twins, compound **9**, bearing (3*R*)-dihydrocitronellyloxy moieties [9] on one triphenylene and decyloxy chains on the other achiral subunit, was chosen (*Scheme*).We report here the synthesis and mesomorphic properties of **9**.

Results and Discussion. – For the synthesis of **9**, a convergent strategy was used, in which the chiral triphenylene moiety **8** was attached to the tether carrying achiral triphenylene **4c** in the final step. Thus, decane-1,10-diol (**2**) was converted to the 3,4,5,6-tetrahydro-2*H*-pyran-2-yl(Thp)-protected bromo derivative **3**, which was further coupled with achiral hydroxytriphenylene **1** [10] to give **4a** in 90% yield. Deprotection and bromination of the primary OH group yielded **4c**. To obtain the required chiral hydroxy triphenylene **8**, a three-step sequence starting from 1,2-dialkyloxybenzene **5a** was elaborated. Compound **5a** was first brominated to give **5b**, which underwent subsequent BuLi-mediated aryl coupling [11] to the biphenyl **6**. $FeCl_3$-Mediated cyclization of 1,1′-biphenyl **6** and gujacol derivative **7** to **8** proceeded in 51% yield. With regard to the yield, this coupling was found advantageous compared to the direct coupling of 1,2-dialkyloxybenzene **5a** with **7** [10]. Final condensation of the achiral building block **4c** with the chiral subunit **8** in the presence of K_2CO_3 provided the desired twin **9** in 64% yield.

The mesomorphic behavior of compound **9** was studied by differential scanning calorimetry (DSC). During the first heating cycle, two phase transitions, a melting process at 34° ($\Delta H = 21.4$ kJ mol^{-1}), and a clearing process at 45° ($\Delta H = 3.9$ kJ mol^{-1}) were observed. However, during cooling (and subsequent heating) only the clearing transition was detected ($T_{\text{M-I}} = 41°$, $\Delta H = 8.5$ kJ mol^{-1} and $T_{\text{I-M}} = 42°$, $\Delta H = 9.5$ kJ mol^{-1}). Even after prolonged cooling to 0°, the mesophase did not crystallize. Under the optical polarizing microscope, twin **9** displayed a fan-shaped texture at 44° (upon cooling) typical for columnar mesophases. Supercooling of the mesophase below room temperature was observed (*Fig. 2*) and crystallization could be induced only by scratching or shaking the supercooled sample, indicating that the columnar mesophase of **9** is metastable. In comparison with the monomeric subunits hexadecyloxytriphenylene (C 58° Col$_h$ 69° I) [12] and hexakis[(3′*R*)-3,7-dimethyloctyloxy]tri-

Scheme. *Synthesis of Columnar Twin* **9**.



a) Dihydropyran, TsOH · H_2O, THF, –5°, 2 d; 41%; Br_4C, Ph_3P, THF, r.t., 20 h; 32%. *b*) K_2CO_3; DMF, 80°, 20 h; 90%. *c*) TsOH · H_2O, MeOH, CH_2Cl_2, r.t., 18 h; 93%. *d*) Br_4C, Ph_3P, THF, r.t., 18 h; 24%. *e*) Br_2, $CHCl_3$, 0°, 2 h; r.t., 18 h; 65%. *f*) BuLi (0.5 equiv.), THF, –11°, 0.5 h; r.t., 20 h; 43%. *g*) $FeCl_3$ (10 equiv.), H_2SO_4, CH_2Cl_2, r.t., 2 h; 51%. *h*) K_2CO_3, DMF, 80°, 24 h; 64%.

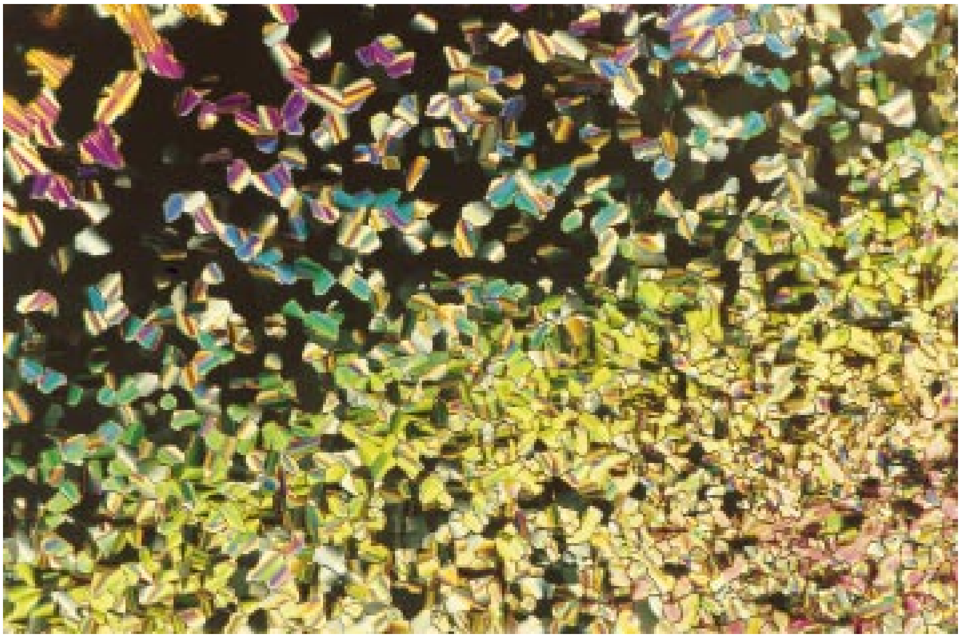


Fig. 2. *Fan-shaped texture of the twin* **9**. The photomicroscopic image of the mesophase was obtained with a polarizing microscope (*Olympus BX 50* equipped with a *Linkam LTS 50* hot stage) at 13° on cooling (0.2° min^{-1}) from the isotropic liquid (crossed polarizers, magnification ×200).

phenylene (C 19° Col_{hd} 36° I) [7k], twin **9** displays intermediate transition temperatures.

The X-ray-diffraction data were obtained after heating the sample to 55° and subsequent cooling to room temperature. As shown in *Fig. 3*, a distinct 10 reflection ($\Theta = 2.1°$, intensity 1100 cps) together with 11 reflection ($\sqrt{3}$ reflection) indicates a hexagonal columnar lattice ($a = 2.4$ nm). In the wide-angle region (inset of *Fig. 3*), three diffuse scatterings can be seen. The diffuse halo at *ca.* 10° corresponds to the distance of the flexible alkyl side chains. The second scattering maximum at 13° can be assigned to the columnar stacking of the aromatic cores. The third, very broad and weak scattering maximum at *ca.* 7° hints at a sandwich-like packing of the two different species (chiral and achiral) in the columns in a short-range order. Overall, the X-ray data are consistent with a supramolecular array in which the different subunits of the twin are positioned in neighboring columns. This observation is in good agreement with ^{2}H-NMR experiments on symmetrical hexapentyloxytriphenylene-containing dimers by *Luz* and co-workers, which also proved restricted planar reorientation in such twin systems [5e]. To achieve optimum space-filling of the side chains in **9**, a regularly alternate stacking of chiral and achiral triphenylenes (*Fig. 1,c*) is conceivable.

In conclusion, a non-symmetrical columnar twin bearing chiral and achiral triphenylene units of similar size has been prepared *via* a convergent route. No evidence for a chiral mesophase has been found. However, the twin displays a metastable hexagonal columnar mesophase at ambient temperature.

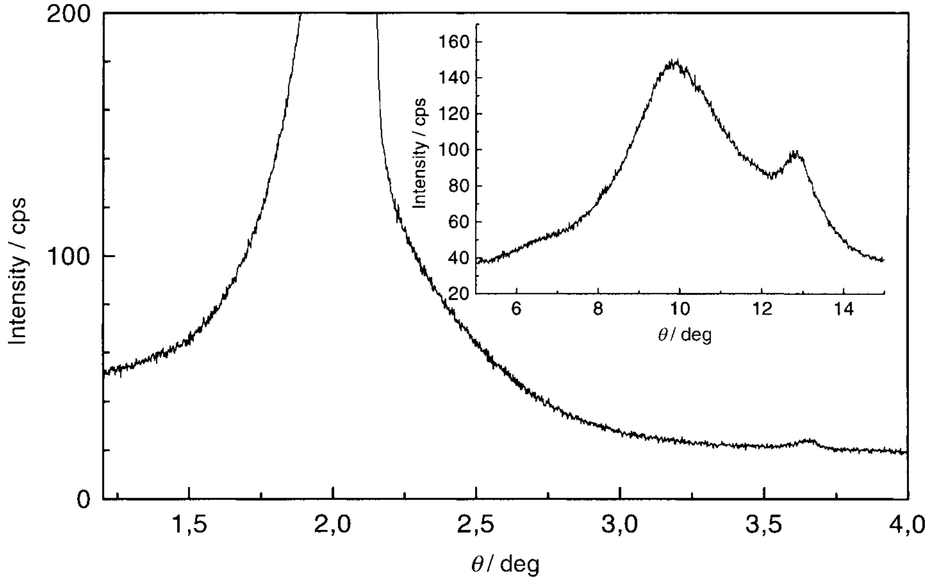


Fig. 3. *X-Ray diffractogram of the twin* **9**. The small-angle region is given in the inset.

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Experimental Part

General. NMR Spectra: *Bruker AM-400* and *AC-200 P*; δ in ppm and J in Hz. Differential scanning calorimetry (DSC): *Rheometric Scientific DSC SP*, heating and cooling rate: 10 K min^{-1}. Polarizing microscopy: *Olympus BX50* polarizing microscope combined with a *Linkam LTS350* hot stage and *Linkam TP 93* central processor. *(3R)-1,2-Bis(3,7-dimethyloctyloxy)benzene* (**5a**) was prepared according to [13], *(3R)-1-bromo-3,7-dimethyloctane* was prepared according to [14], and *2-hydroxy-3,6,7,10,11-pentakis(decyloxy)triphenylene* (**1**) was prepared according to [10].

1-Bromo-10-[(3,4,5,6-tetrahydro-2H-pyran-2-yl)oxy]decane (**3**). To a cooled soln. of *decane-1,10-diol* (**2**; 17.4 g, 0.10 mol) and 3,4-dihydro-2*H*-pyran (5.05 g, 0.06mol) in THF (500 ml) was added TsOH · H_2O (0.95 g, 5.00 mmol) at $-5°$. After stirring for 24 h at $-5°$, the mixture was poured onto sat. $NaHCO_3$ (500 ml), and the aq. layer was extracted with Et_2O (4 × 100 ml). The combined org. layers were dried ($MgSO_4$), evaporated, and purified by flash chromatography (FC) (hexanes/AcOEt 10:1) to yield 10-[(3,4,5,6-tetrahydropyran-2*H*-yl)oxy]decan-1-ol as a white solid (6.40 g, 41%). To a vigorously stirred soln. of 10-[(3,4,5,6-tetrahydro-2*H*-pyran(-2-yl)oxy]decan-1-ol (2.60 g, 10.0 mmol) in THF (150 ml) were added Ph_3P (2.26 g, 10.0 mmol) and Br_4C (3.32 g, 10.0 mmol), and stirring was continued for 12 h at r.t. The precipitate was removed by filtration over *Celite*, and the filtrate was concentrated. Purification by FC (hexanes/AcOEt 50:1): **3** (1.02 g, 32%). Colorless liquid. ^1H-NMR (200 MHz, $CDCl_3$): 1.30–1.43, 1.50–1.59, 1.71–1.78, 1.82–1.89 (*m*, 22 H); 3.32–3.39 (*m*, 1 H); 3.41 (*t*, $J = 6.9$, 2 H); 3.67 (*m*, 1 H); 3.71–3.79 (*m*, 1 H); 3.82–3.88 (*m*, 1 H); 4.58 (*t*, $J = 3.7$, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 19.7; 25.5; 26.2; 26.9; 28.2; 28.7; 29.3; 29.4; 29.7; 32.8; 34.0; 62.3; 67.7; 98.8. EI-MS: 321 (4, M^+), 319 (3), 247 (2), 164 (2), 162 (2), 150 (5), 148 (5), 115 (3), 101 (6), 97 (7), 85 (100).

3,6,7,10,11-Pentakis(decyloxy)-2-{10-[(3,4,5,6-tetrahydro-2H-pyran-2-yl)oxy]decyloxy}triphenylene (**4a**). A mixture of **1** (150 mg, 0.15 mmol), **3** (48 mg, 0.15 mmol), and K_2CO_3 (100 mg, 0.73 mmol) in DMF (2 ml) was heated at 80° for 20 h. Then, the mixture was poured onto ice, and the resulting precipitate was filtered over *Celite*, redissolved in CH_2Cl_2 (10 ml), dried ($MgSO_4$), and evaporated. Purification by FC (hexanes/CH_2Cl_2 10:3) yielded 0.17 g (0.134 mmol, 89.5%) of **4a** (170 mg, 90%). Purple amorphous solid. ^1H-NMR (200 MHz, $CDCl_3$): 0.85–0.91 (*t*, $J = 6.5$, 15 H); 1.28–1.70 (*m*, 90 H); 1.87–1.97 (*m*, 14 H); 3.22–3.40 (*m*, 1 H); 3.44–3.52

(*m*, 1 H); 3.68 – 3.76 (*m*, 1 H); 3.79 – 3.87 (*m*, 1 H); 4.23 (*t*, $J = 6.5$, 12 H); 4.58 (*t*, $J = 4.4$, 1 H); 7.83 (*s*, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 14.1; 19.7; 22.7; 25.5; 26.2; 29.4; 29.5; 29.5; 29.6; 29.7; 30.8; 31.9; 62.3; 67.6; 69.9; 107.4; 123.6; 149.0. EI-MS: 1265 (65, M^+), 1182 (4), 312 (9), 186 (10), 95 (10), 85 (100). Anal. calc. for $C_{83}H_{140}O_8$: C 78.74, H 11.15; found: C 78.81, H 11.10.

10-[3,6,7,10,11-Pentakis(decyloxy)triphenylen-2-yl]decan-1-ol (**4b**). To a soln. of **4a** (130 mg, 0.10 mmol) in MeOH (5 ml) and CH_2Cl_2 (0.5 ml) was added $TsOH \cdot H_2O$ (2 mg, 0.01 mmol), and the mixture was stirred for 18 h at r.t. Then, the mixture was poured onto sat. $NaHCO_3$ (10 ml). The aq. layer was extracted with CH_2Cl_2 (3 × 10 ml) and the combined org. extracts were dried ($MgSO_4$), evaporated, and purified by FC (hexanes/AcOEt 10 : 1) to give **4b** (110 mg, 93%). Amorphous purple solid. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.20 – 1.70 (*m*, 84 H); 1.80 – 2.10 (*m*, 12 H); 3.63 (*t*, $J = 6.7$, 2 H); 4.21 (*t*, $J = 6.5$, 12 H); 7.83 (*s*, 6 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 14.1; 22.7; 26.0; 29.2; 29.3; 29.4; 29.5; 31.9; 62.0; 67.0; 107.0; 123.2; 149.0. EI-MS: 1181 (100, M^+), 1154 (5), 1041 (5), 1025 (3), 900 (4), 744 (2), 603 (5), 463 (4), 390 (14), 323 (8), 295 (6), 148 (3), 83 (6). Anal. calc. for $C_{78}H_{132}O_7$: C 79.27, H 11.26; found: C 79.26, H 11.31.

2-(10-Bromodecyloxy)-3,6,7,10,11-pentakis(decyloxy)triphenylene (**4c**). To a soln. of **4b** (118 mg, 0.10 mmol) in THF (5 ml) were sequentially added Ph_3P (26 mg, 0.10 mmol) and Br_4C (33 mg, 0.10 mmol), and the resulting mixture was stirred overnight. The precipitate was removed by filtration, and the filtrate was dissolved in CH_2Cl_2 (25 ml), washed with H_2O (2 × 20 ml), dried ($MgSO_4$), and evaporated. Purification by FC (hexanes/AcOEt 20 : 1) yielded **4c** (30 mg, 24%). Purple amorphous solid. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (*t*, $J = 7.0$, 15 H); 1.28 – 1.48, 150 – 1.62 (*m*, 82 H); 1.83 – 1.93, 1.93 – 2.03 (*m*, 14 H); 3.40 (*t*, $J = 7.0$, 2 H); 4.23 (*t*, $J = 6.6$, 12 H); 7.84 (*s*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.1; 22.6; 26.2; 28.1; 29.3; 29.4; 29.5; 29.6; 29.7; 31.9; 32.8; 33.9; 69.7; 107.4; 123.6; 149.0. EI-MS: 1244 (100, M^+), 1164 (16), 1105 (18), 1025 (14), 964 (14), 885 (13), 744 (10), 603 (33), 463 (22), 323 (37), 296 (13), 97 (5).

(3R)-1-Bromo-3,4-bis[(3R)-3,7-dimethyloctyloxy]benzene (**5b**). To a cooled soln. of *(1,2-bis[(3R)-3,7-dimethyloctyl)oxy]benzene* (**5a**; 3.90 g, 0.01 mol) in $CHCl_3$ (25 ml) was added dropwise over 2 h at 0° a soln. of Br_2 (0.51 ml, 0.01 mmol) in $CHCl_3$ (15 ml). The cooling bath was removed, and the soln. was stirred at r.t. overnight and then poured into 10% aq. $NaHSO_3$ (20 ml). The org. layer was washed with 2N NaOH (10 ml), H_2O (10 ml), dried ($MgSO_4$), and evaporated. Purification by FC (hexanes/AcOEt 80 : 1) yielded **5b** (3.03 g, 65%). Yellow oil. $[\alpha]_D^{20} = +2.4$ ($c = 1.00$; $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.87 (*d*, $J = 6.6$, 12 H); 0.94 (*d*, $J = 6.4$, 6 H); 1.10 – 1.23, 1.24 – 1.37, 1.40 – 1.45, 1.45 – 1.72, 1.82 – 1.92 (*m*, 20 H); 3.98 (*m*, 4 H); 6.74 (*d*, $J = 9.1$, 1 H); 6.90 (*m*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.7; 22.7; 22.8; 24.8; 28.0; 29.9; 36.2; 37.4; 39.3; 67.8; 112.8; 115.1; 116.9; 123.4; 148.4; 150.0. EI-MS: 470 (12, M^+), 328 (10), 188 (88), 99 (11), 85 (68),71 (79), 57 (100).

(3,3′,4,4′)-Tetrakis[(3R)-3,7-dimethyloctyloxy-1,1′-biphenyl (**6**). Treatment of **5b** according to the procedure described [11] and subsequent purification by FC (hexanes/CH_2Cl_2 5 : 1) gave **6** (0.71 g, 0.91 mmol, 43%). Yellow amorphous solid. $[\alpha]_D^{20} = +3.7$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.86 (*d*, $J = 6.6$, 12 H); 0.87 (*d*, $J = 6.6$, 12 H); 0.95 (*d*, $J = 6.6$, 12 H); 1.11 – 1.22, 1.23 – 1.38, 1.46 – 1.57, 1.58 – 1.76, 1.83 – 1.95 (*m*, 20 H); 4.07 (*m*, 8 H); 6.93 (*d*, $J = 8.3$, 2 H); 7.51 (*m*, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.8; 22.7; 22.8; 24.8; 28.0; 30.0; 36.4; 37.4; 39.3; 67.8; 113.1; 114.1; 119.3; 134.3; 148.5; 149.3. EI-MS: 779 (100, M^+), 639 (4), 497 (2), 357 (5), 218 (6). Anal. calc. for $C_{52}H_{90}O_4$: C 80.15, H 11.64; found: C 80.12, H 11.69.

2-[(3R)-3,7-Dimethyloctyloxy]phenol (**7**). A mixture of benzene-1,2-diol (1.10 g, 10.0 mmol), (3*R*)-1-bromo-3,7-dimethyloctane (1.11 g, 5.00 mmol) and K_2CO_3 (3.01 g, 21.5 mmol) in EtOH (25 ml) was refluxed for 48 h. After evaporation of the solvent, the residue was redissolved in MeOH (4.5 ml) and H_2O (6.0 ml), and the aq. layer was washed with brine (20 ml) and H_2O (20 ml), dried ($MgSO_4$), and evaporated. Purification by FC (hexanes/AcOEt 50 : 1) yielded **7** (0.54 g, 43%). White amorphous solid. $[\alpha]_D^{20} = +1.6$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.87 (*d*, $J = 6.8$, 6 H); 0.95 (*d*, $J = 6.6$, 3 H); 1.15 – 1.24, 1.25 – 1.42, 1.50 – 1.59, 1.60 – 1.75, 1.83 – 1.93 (*m*, 10 H); 4.07 (*m*, 2 H); 5.63 (*s*, 1 H); 6.84 (*m*, 3 H); 6.93 (*dd*, $J = 7.7$, 1.9, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.7; 22.6; 22.7; 24.7; 28.0; 30.0; 36.3; 37.3; 39.3; 67.2; 111.6; 114.4; 120.1; 121.3; 145.8; 146.0. EI-MS: 250 (27, M^+), 198 (4), 183 (10), 121 (4), 110 (100), 95 (6), 85 (16), 71 (19). Anal. calc. for $C_{16}H_{26}O_2$: C 76.75, H 10.47; found: C 76.83, H 10.71.

3,6,7,10,11-Pentakis[(3R)-3,7-dimethyloctyloxy]triphenylen-2-ol (**8**). To a soln. of **6** (0.77 g, 0.99 mmol) and **7** (0.74 g, 2.96 mmol) in CH_2Cl_2 (15 ml) were carefully added conc. H_2SO_4 (0.15 ml) and anh. $FeCl_3$ (2.24 g, 14.0 mmol), and the mixture was stirred for 2 h at r.t. The mixture was poured into MeOH (40 ml), the resulting soln. was washed with hexanes (4 × 40 ml). The combined hexane layers were dried ($MgSO_4$), evaporated, and purified by FC (hexanes/AcOEt 80 : 1) to yield **8** (0.52 g, 51%). Yellow oil. $[\alpha]_D^{20} = +3.4$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.85 – 0.91 (*m*, 30 H); 1.00 – 1.06 (*m*, 15 H); 1.10 – 1.27, 1.28 – 1.44, 1.47 – 1.62, 1.67 – 1.86, 1.93 – 2.05 (*m*, 50 H); 4.19 – 4.39 (*m*, 10 H, 5 CH_2O); 5.89 (*s*, 1 H); 7.79, 7.83, 7.84 (*s*, 5 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 19.6; 22.4; 22.5; 24.5; 24.6; 26.7; 27.8; 29.8; 36.1; 36.2; 37.1; 37.2; 37.3; 39.0; 39.1; 67.4; 67.8;

68.2; 103.4; 104.3; 106.4; 107.1; 107.3; 107.5; 122.9; 123.2; 123.5; 123.6; 123.7; 123.9; 145.2; 145.8; 148.7; 148.9; 149.2. EI-MS: 1025 (100, M^+), 885 (8), 745 (4), 603 (12), 463 (7), 324 (6), 295 (4). Anal. calc. for $C_{68}H_{112}O_6$: C 79.63, H 11.01; found: C 79.48, H 11.05.

*2-(10-{[3,6,7,10,11-Pentakis(decyloxy)triphenylen-2-yl]oxy}decyloxy)-3,6,7,10,11-pentakis{[(3*R*)-3,7-dimethyloctyl]oxy}triphenylene* (**9**). A mixture of **4c** (70 mg, 0.056 mmol), **8** (58 mg, 0.056 mmol), and K_2CO_3 (34.5 mg, 0.23 mmol) in DMF (2 ml) was heated at 80° for 24 h. Then, the mixture was poured onto ice and the aq. layer was washed with CH_2Cl_2 (3×10 ml). The combined org. extracts were dried ($MgSO_4$), filtered and evaporated. Purification by FC (hexanes/Et_2O 30:1) yielded **9** (78 mg, 64%). Purple solid product. $[\alpha]^{20}_{D} = +1.4$ ($c = 1.00$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.86 (d, $J = 6.7$, 15 H); 0.87 (d, $J = 6.7$, 30 H); 1.02 (d, $J = 6.7$, 15 H); 1.10 – 1.47, 1.48 – 1.64, 1.68 – 1.85, 1.87 – 2.05 (m, 146 H); 4.22 (t, $J = 6.7$, 12 H); 4.23 – 4.31 (m, 12 H); 7.83 (s, 6 H); 7.84 (s, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.9; 19.6; 22.4; 22.5; 22.7; 24.8; 26.2; 26.3; 27.8; 29.4; 29.5; 29.6; 29.6; 29.7; 29.7; 29.8; 31.9; 36.4; 37.5; 39.3; 68.0; 69.7; 107.4; 123.5; 123.6; 149.0. MALDI-TOF-MS: 2188.6 (M^+). Anal. calc. for $C_{146}H_{242}O_{12}$: C 80.09, H 11.14; found: C 79.96, H 11.16.

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