Research Article

Journal of Physical Organic Chemistry

Received: 23 September 2008, Revised: 12 November 2008, Accepted: 13 November 2008, Published online in Wiley InterScience: 15 January 2009

(www.interscience.wiley.com) DOI 10.1002/poc.1506

Chiral tetraphenylethenes as novel dopants for calamitic and discotic liquid crystals

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Three series of novel chiral tetraphenylethenes have been prepared: citronellyl-derived ethers 1a, b, lactate-derived ethers 2d, g, h, i and lactate-derived esters 3a–c, e–h. Helical twisting powers (HTPs) were determined for those derivatives of 1–3, which were sufficiently miscible with the nematic host 5CB 13 or the discotic nematic host hexayne 14. For binary solutions HTP values of 5.7–10.4 μm^{-1} for 13/1, 12.8–16.5 μm^{-1} for 13/2, 8.0–28.7 μm^{-1} for 13/3 and 2.1–2.9 μm^{-1} for hexayne 14/3 were determined, indicating a much stronger interaction between the C_4-symmetrical propeller-shaped tetraphenylethenes 1–3 with the calamitc host 5CB 13 than with the discotic C_6-symmetrical propeller-shaped host hexayne 14. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: tetraphenylethenes; helical twisting power; chiral dopant; chiral nematic liquid crystals

INTRODUCTION

Tetraarylethenes are an attractive class of compounds because of their various interesting chemical and physical properties. For example, Kochi and others have shown that they can undergo reversible redox reactions[1–4] and X-ray crystal structure analyses of their dianions and dications[1,5–10] revealed that the twisted molecular structure of the tetraarylethene[11] is strongly affected by redox reactions. Tang recently reported that tetraphenylethenes tethered to ammonium salts are fluorescent 'light-up' bioprobes due to aggregation induced emission in the presence of biopolymers such as DNA or proteins.[12] We have shown that tetraarylethenes provide useful building blocks for discotic liquid crystals[13–21] which can be converted to the corresponding liquid crystalline phenanthrenes by oxidative photocyclization.[22–46] For switching devices, molecules are particularly attractive, which show significant spectral changes upon photo- and electrochemical transformations. A redox-driven chiroptical switch based on optically active tetrakis(*p*-alkoxyphenyl)ethenes has been reported by Mori and Inoue.[47]

In addition, enantiomerically pure tetraarylethenes should be able to transfer their chirality to an achiral liquid crystalline host phase, a unique phenomenon that is generally known for chiral compounds added to e.g. nematic liquid crystalline phases.

Uniaxial nematic liquid crystalline phases are characterized by long-range orientational order of the principal axes of the so-called mesogens. The average common orientation of the mesogens is represented by the director, which in optically uniaxial mesophases coincides with the optic axis of the medium. The presence of chiral molecules (dopants) in the phase results in the formation of a chiral nematic phase where the dopant induces a helical twisting of the director field.[48–58] This can be visualized under the polarizing optical microscope by a characteristic fingerprint texture of equidistant bright and dark stripes, which reveal different director orientations (see e.g. Fig. 1). The distance d between two equally bright lines are directly correlated with the helical periodicity (pitch) p via $d = p/2$. The efficiency of the dopant induced twisting depends on the temperature, the dopant concentration and, above all, on the dopant molecule itself. In order to compare the chiral induction of different dopants independent of their concentration and the temperature, the helical twisting power (HTP) has been introduced by Solladié[59] as

$$\mathrm{HTP} = \lim_{x \to 0} \frac{\partial(1/p)}{\partial x} \quad (1)$$

where x is the molar fraction of the chiral dopant and the pitch is measured at a certain relative temperature with respect to the nematic–isotropic transition temperature (clearing point).

For rod-like dopants numerous studies have been conducted towards structure–property relationships concerning the chiral induction,[48–57,60–79] however, surprisingly, much less is known about chiral discotic dopants in liquid crystals. In particular, studies on the relationship between chiral molecular structure and HTP in an achiral host phase are quite rare for discotic compounds,[21] although early investigations by Destrade and Malthete[80,81] on chiral alkyl carboxylates and *p*-alkoxy benzoates of triphenylenes, truxenes and benzenes revealed a striking dependence of mesomorphic properties and the chirality transfer to achiral host phases on the molecular structure of the chiral chain. Thus, we synthesized a series of chiral tetrakis

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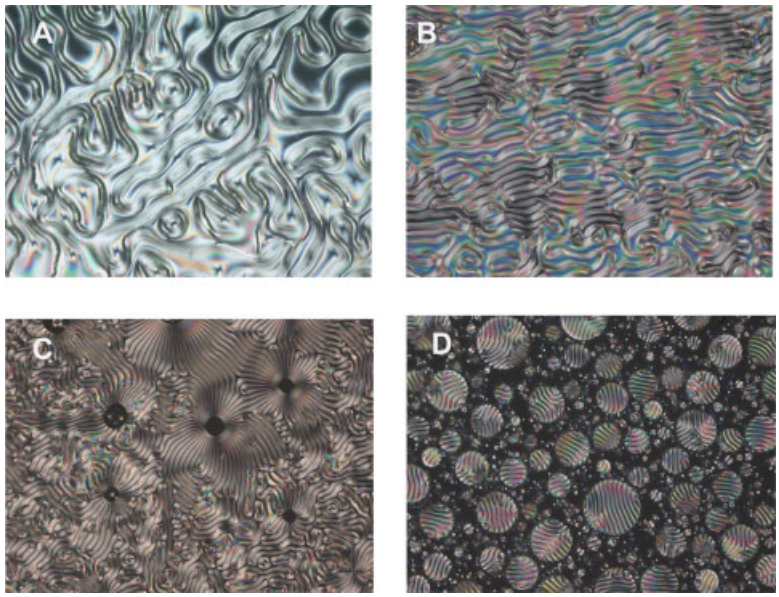


Figure 1. Fingerprint textures of solutions of 5CB **13** with various mole fractions x of **1a** at T_{IN}^{*}, 10 K (magnification 200×). A: $x = 0.5$ mol%. B: $x = 1.0$ mol%. C: $x = 1.5$ mol%. The dark circles originate from air bubbles. D: $x = 5.0$ mol%. Phase separation is found (formation of chiral nematic droplets within an isotropic phase)

(*p*-alkoxyphenyl)ethenes and studied their chirality transfer in doping experiments with achiral nematic host phases formed by calamitic and discotic molecules, respectively. The results are discussed below.

EXPERIMENTAL SECTION

General

^{1}H NMR spectra were recorded on a Bruker ASC 250, ARX 300 and ARX 500 with tetramethylsilane as internal standard. ^{13}C multiplicities were assigned by DEPT experiments. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer with ATR technique. Mass spectrometry was performed on a Varian MAT 711 mass spectrometer with EI ionization (70 eV), a Finnigan MAT 95 with CI ionization using methane as reactand gas and a Bruker micrOTOF_Q with electrospray ionization. UV/Vis spectra were recorded on a PerkinElmer Lambda7 spectrometer. Elemental analyses were performed on a Carlo Erba Strumentazione Elemental Analyzer Modell 1106. Column chromatography was performed using silica gel 60 (Fluka, mesh 40–63 μm) with hexanes (b.p. 30–75 °C). Optical rotations were performed on a PerkinElmer Polarimeter 241 at 589 nm (Na^{D}). Differential scanning calorimetry was performed using a Mettler Toledo DSC822 and optical polarizing microscopy using an Olympus BX 50 polarizing microscope combined with a Linkam LTS 350 hot stage. Reactions were performed using standard Schlenk type conditions under inert athmosphere. Compounds **9a**–**d** and **10a**–**c**, **e** were prepared according to the literature.[82–90]

Physicochemical properties of the chiral dopants in nematic hosts

The nematic liquid crystal 5CB **13** was purchased from AlfaAesar and used without further purification. Hexayne **14** was prepared following literature procedures.[91–93]

The chiral nematic solutions of the novel synthesized chiral dopants and the nematic liquid crystalline hosts **13** and **14** were prepared by weighing the components together into small glass vials. To homogenize the solution $CHCl_3$ was added (0.5–1 mL) and stirred. A drop of this solution was placed on a cleaned microscope slide and $CHCl_3$ allowed to evaporate. Several such drops were covered with a cover slip giving a liquid–crystal thickness of about 30 μm. The overall error of the dopant concentration is about ±5%. An optical polarizing microscope was used to determine the binary phase diagrams via the observed textures. The pitch of the chiral nematic phase at a certain temperature was measured directly from calibrated texture images using the image processing program Analysis® 3.0. The overall error of the pitch is about ±3%.

Tetrakis-{4-[(3′R)-3′,7′-dimethyloct-6′enyloxy]phenyl}ethene (1a)

A mixture of 2.07 g (15.0 mmol) K_2CO_3 and 0.5 g (1.3 mmol) tetrakis(4-hydroxyphenyl)ethene **7** in 20 mL DMF was treated with 1.21 g (5.5 mmol) (3*R*)-citronellylbromide **5** and stirred at 80 °C for 48 h. Then the mixture was poured onto 30 g ice, filtered via Celite and diluted with 30 mL CH_2Cl_2. The layers were separated and the aqueous layer was extracted with 3 × 30 mL CH_2Cl_2, the organic layers were dried over $MgSO_4$, evaporated and the residue was purified by flash chromatography (hexanes/ethyl acetate 40: 1) to yield 0.49 g (43%) of a highly viscous, green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.93 (d, $^{3}J = 6.6$ Hz, 12H, 3′-CH_3), 1.15-1.45 (m, 8H, 4′-H), 1.50-1.86 (m, 12H, 3′-H, 2′-H), 1.60 (d, $^{4}J = 0.8$ Hz, 12H, CCH_3), 1.68 (d, $^{4}J = 1.35$ Hz, 12H, CCH_3), 1.92–2.08 (m, 8H, 5′-H), 3.83–3.98 (m, 8H, 1′-H), 5.10 ("t", $^{3}J = 7.1$ Hz, 4H, 6′-H), 6.62 (d, $^{3}J = 8.9$ Hz, 8H, 6H, 2H), 6.91 (d, $^{3}J = 8.6$ Hz, 8H, 5H, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 17.7 (CCH_3), 19.6 ($CHCH_3$), 25.5 (C-5′), 25.7 (CCH_3), 29.5 (C-3′), 36.2 (C-2′), 37.2 (C-4′), 66.1 (C-1′), 113.5 (C-2, C-6), 124.7 (C-6′), 131.3 (C-7′), 132.5 (C-3, C-5), 138.3 (C=C), 136.8, 157.3 (C-1, C-6). MS (EI):

m/z (%) = 949 (100) $[M]^+$, 878 (3), 810 (5), 717 (1), 672 (1), 396 (8), 303 (5), 211 (3), 185 (8), 109 (5), 95 (8), 83 (15), 69 (65). CHN: $C_{66}H_{92}O_4$ (949.43) calcd. C 83.49%, H 9.77%, found C 83.28%, H 9.81%. FT-IR (ATR): ν = 3033 (w), 2958 (s), 2912, 2870 (s), 2037 (w), 1605 (m), 1506, 1474, 1453 (vs), 1377 (s), 1238 (vs) cm^{-1}. $[\alpha]_D^{20}$ = +3.1 (c = 3.5, $CHCl_3$).

Tetrakis-{4-[(3′R)-3′,7′-dimethyloctyloxy]phenyl}ethene (1b)

Following the procedure described for **1a** flash chromatography (hexanes/ethyl acetate 200:1) yielded 0.87 g (70%) of a highly viscous, green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.87 (d, ^3J = 6.6 Hz, 24H, CH_3), 0.92 (d, ^3J = 6.5 Hz, 12H, 3-CH_3), 1.06-1.39 (m, 24H), 1.45–1.88 (m, 16H), 3.64–4.01 (m, br, 8H, 1′-H), 6.62 (d, ^3J = 8.6 Hz, Hz, 8H, 2H, 6H), 6.91 (m, 8H, 3H, 5H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 19.7 ($CHCH_3$), 22.6, 22.7 ($CHCH_3CH_3$), 27.9, 29.9 (C-3′, C-7′), 24.7, 36.3, 37.3, 39.2 (C-2′, C-4′, C-5′, C-6′), 66.1 (C-1′), 113.5 (C-2, C-6), 132.5 (C-3, C-5), 138.3 (C=C), 136.8, 157.3 (C-1, C-4). MS (EI): m/z (%) = 956.8 (60) $[M]^+$, 830.6 (100), 816 (5), 690 (5), 69 (5), 57 (10), 44 (10). CHN: $C_{66}H_{100}O_4$ (957.50) calcd. C 82.79%, H 10.53%, found C 82.81%, H 10.43%. FT-IR (ATR): ν = 3035 (w), 2952 (s), 2924, 2868 (vs), 1884 (m), 1607, 1506, 1466, 1439 (vs), 1382, 1365 (s), 1237, 1172 (vs) cm^{-1}. $[\alpha]_D^{20}$ = +4.3 (c = 7.0, $CHCl_3$).

General procedure for the preparation of methyl (2S)-alkoxypropionates (9e–g)

To a solution of 14.4 mmol methyl (2*S*)-lactate **8** and 21.6 mmol alkyl bromide in 20 mL Et_2O was added 3.34 g (14.4 mmol) freshly prepared silver oxide in ten portions over 1 h and the mixture was heated at 40 °C for 18 h. After cooling to room temperature the mixture was filtered and evaporated and the crude product was purified by flash chromatography.

Methyl (2S)-pentyloxypropionate (9e)

According to the general procedure flash chromatography (hexanes/Et_2O 40:1) yielded 1.8 g (26%) of a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.90 (t, ^3J = 7.0 Hz, 3H, 5′-H), 1.30–1.37 (m, 4H, 3′-H, 4′-H), 1.40 (d, ^3J = 6.9 Hz, 3H, 3-H), 1.56–1.65 (m, 2H, 2′-H), 3.36 (dt, ^2J = 8.8 Hz, ^3J = 6.9 Hz, 1H, 1′-H_A), 3.55 (dt, ^2J = 8.8 Hz, ^3J = 6.9 Hz, 1H, 1′-H_B), 3.75 (s, 3H, OCH_3), 3.96 (q, ^3J = 6.9 Hz, 1H, 2-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 14.0 (C-5′), 18.7 (C-3), 22.5, 29.5 (C-3′, C-4′), 28.2 (C-2′), 51.9 ($COOCH_3$), 70.5 (C-1′), 74.9 (C-2), 174.0 ($COOCH_3$). MS (EI): m/z (%) = 174 (5) $[M]^+$, 144 (5), 131 (5), 115 (75), 97 (5), 88 (40), 84 (10), 71 (100), 59 (10), 55 (20), 45 (40), 43 (80), 41 (20), 39 (10), 28 (20). HRMS (EI): m/z (%) calcd. for $C_9H_{18}O_3$ 174.1256, found 174.1239. FT-IR (ATR): ν = 2955, 2932, 2860 (vs), 1753, 1737 (vs), 1448 (m), 1371 (w), 1270 (w), 1201 (s), 1152, 1125 (vs), 1048 (m) cm^{-1}. $[\alpha]_D^{20}$ = −40.0 (c = 1.0, $CHCl_3$).

Methyl (2S)-octyloxypropionate (9f)

According to the general procedure flash chromatography (hexanes/Et_2O 100:1) yielded 37.0 mg (16%) of a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.88 [t, ^3J = 7.0 Hz, 3H, $CH_2CH_2(CH_2)_5CH_3$], 1.19–1.38 [m, 10H, $CH_2CH_2(CH_2)_5CH_3$], 1.40 (d, ^3J = 6.9 Hz, 3H, 3H), 1.57–1.63 [m, 2H, $CH_2CH_2(CH_2)_5CH_3$], 3.35 [dt, ^2J = 9.0 Hz, ^3J = 6.8 Hz, 1H, $CH_{2A}CH_2(CH_2)_5CH_3$], 3.54 [dt, ^2J = 9.0 Hz, ^3J = 6.8 Hz, 1H, $CH_{2B}CH_2(CH_2)_5CH_3$], 3.75 (s, 3H, OCH_3), 3.96 (q, ^3J = 6.9 Hz, 1H, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 14.1 [$CH_2(CH_2)_6CH_3$], 18.7 (C-3), 22.7, 26.0, 29.2, 29.4, 29.7, 31.8 [$CH_2(CH_2)_6CH_3$], 51.9 ($COOCH_3$), 70.5 [$CH_2(CH_2)_6CH_3$], 74.9 (C-2), 174.0 ($COOCH_3$). MS (EI): m/z (%) = 216 (5) $[M]^+$, 173 (1), 157 (100), 113 (20), 105 (5), 88 (60), 71 (85), 57 (90), 45 (15), 43 (35). HRMS (EI): m/z (%) calcd. for $C_{12}H_{24}O_3$ 216.1725, found 216.1703. FT-IR (ATR): ν = 2925, 2855 (vs), 2559 (m), 2189 (m), 2004 (m), 1971 (m), 1720 (vs), 1458 (s), 1239 (s), 1126 (vs) cm^{-1}. $[\alpha]_D^{20}$ = −36.6 (c = 1.0, $CHCl_3$).

Methyl (2S)-2-decyloxypropionate (9g)

According to the general procedure flash chromatography (hexanes/Et_2O 100:1) yielded 2.35 g (20%) of a colourless oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.88 [t, ^3J = 6.9 Hz, 3H, $CH_2CH_2(CH_2)_7CH_3$], 1.19–1.32 [m, 16H, $CH_2CH_2(CH_2)_7CH_3$], 1.40 (d, ^3J = 6.8 Hz, 3H, 3-H), 1.56–1.64 [m, 2H, $CH_2CH_2(CH_2)_7CH_3$], 3.35 [dt, ^2J = 8.9 Hz, ^3J = 6.9 Hz, 1H, $CH_{2A}CH_2(CH_2)_7CH_3$], 3.54 [dt, ^2J = 8.9 Hz, ^3J = 6.7 Hz, 1H, $CH_{2B}CH_2(CH_2)_7CH_3$], 3.75 (s, 3H, OCH_3), 3.96 (q, ^3J = 6.9 Hz, 1H, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 14.1 [$CH_2(CH_2)_8CH_3$], 18.7 (C-3), 22.9, 26.0, 29.3, 29.4, 29.6, 29.7, 31.9 [$CH_2(CH_2)_8CH_3$], 51.9 ($COOCH_3$), 70.5 [$CH_2(CH_2)_8CH_3$], 74.9 (C-2), 174.0 ($COOCH_3$). MS (ESI): m/z (%) = 267.19 $[M + Na]^+$. HMRS (ESI): calcd. for $C_{14}H_{28}NaO_3$ $[M + Na]^+$ 267.1936, found 267.1931. FT-IR (ATR): ν = 2923, 2854 (vs), 1755, 1738 (vs), 1457 (m), 1371 (w), 1271 (w), 1201 (s), 1127 (vs), 1073 (m) cm^{-1}. $[\alpha]_D^{20}$ = −40.4 (c = 1.0, $CHCl_3$).

General procedure for the (2S)-alkoxypropionic acids (10f, g)

To a cooled solution of 11.5 mmol (2*S*)-alkoxypropionate **9** in 15 mL MeOH was slowly added LiOH 25.5 mmol in H_2O at 0 °C and then heated under reflux for 6 h. After cooling to room temperature the mixture was washed with 10 mL CH_2Cl_2, the aqueous layer was separated, the pH was adjusted to 1–2 with 3 N HCl. After extraction with 3 × 20 mL CH_2Cl_2, drying over $MgSO_4$ and evaporating the solvent, a colorless liquid was obtained.

(2S)-Octyloxypropionic acid (10f)

According to the general procedure 0.18 g (79%) of a colourless liquid was obtained.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.88 [t, ^3J = 6.9 Hz, 3H, $CH_2CH_2(CH_2)_5CH_3$], 1.21–1.38 [m, 10H, $CH_2CH_2(CH_2)_5CH_3$], 1.45 (d, ^3J = 6.9 Hz, 3H, 3-H), 1.56–1.66 [m, 2H, $CH_2CH_2(CH_2)_5CH_3$], 3.50 [dt, ^2J = 9.1 Hz, ^3J = 6.7 Hz, 1H, $CH_{2A}CH_2(CH_2)_5CH_3$], 3.56 [dt, ^2J = 9.1 Hz, ^3J = 6.7 Hz, 1H, $CH_{2B}CH_2(CH_2)_5CH_3$], 3.99 (q, ^3J = 6.9 Hz, 1H, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 14.1 [$CH_2CH_2(CH_2)_5CH_3$], 17.9 (C-3), 22.6, 25.9,29.2, 29.3, 29.7 [$CH_2CH_2(CH_2)_5CH_3$], 31.8 [$CH_2CH_2(CH_2)_5CH_3$], 70.6 [$CH_2CH_2(CH_2)_5CH_3$], 74.6 (C-2), 174.7 (C-1). MS (EI): m/z (%) = 203.2 (5) $[M + H]^+$, 185 (1), 157.2 (80), 127 (2), 113.1 (40), 91 (5), 74 (20), 71.1 (100), 69 (10), 57 (90), 45 (15), 43 (35). HMRS (ESI): calcd. for $C_{11}H_{22}NaO_3$ $[M + Na]^+$ 225.1467, found 225.1461. FT-IR (ATR): ν = 3101 (s), 2925, 2855 (vs), 2456 (m), 1738 (vs), 1399 (m), 1338 (w), 1121, 1099 (vs), 938 (m) cm^{-1}. $[\alpha]_D^{20}$ = −20.5 (c = 1.0, $CHCl_3$).

(2S)-Decyloxypropionic acid (10g)

According to the general procedure 0.54 g (83%) of a colourless liquid was obtained.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.88 [t, ^3J = 7.0 Hz, 3H, $CH_2CH_2(CH_2)_7CH_3$], 1.18–1.38 [m, 16H, $CH_2CH_2(CH_2)_7CH_3$], 1.45 (d,

$^3J = 7.0$ Hz, 3H, 3-H), 1.56–1.66 [m, 2H, $CH_2CH_2(CH_2)_7CH_3$], 3.49 [dt, $^2J = 8.9$ Hz, $^3J = 6.7$ Hz, 1H, $CH_{2A}CH_2(CH_2)_7CH_3$], 3.56 [dt, $^2J = 8.9$ Hz, $^3J = 6.7$ Hz, 1H, $CH_{2B}CH_2(CH_2)_7CH_3$], 3.99 (q, $^3J = 7.0$ Hz, 1H, 2-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 14.1 [$CH_2CH_2(CH_2)_7CH_3$], 18.0 (C-3), 20.7, 25.9, 29.3, 29.4, 29.5, 29.7, 31.9 [$CH_2(CH_2)_8CH_3$], 70.6 [$CH_2CH_2(CH_2)_7CH_3$], 74.5 (C-2), 176.8 (COOH). MS (ESI): m/z (%) = 253.18 $[M + Na]^+$. HMRS (ESI): calcd. for $C_{13}H_{26}NaO_3$ $[M + Na]^+$ 253.1780, found 253.1774. FT-IR (ATR): ν = 3075 (s), 2922, 2854 (vs), 1722 (vs), 1458 (m), 1372 (w), 1198 (w), 1126 (vs), 1072 (m) cm^{-1}. $[\alpha]_D^{20} = -19.9$ ($c = 1.0$, $CHCl_3$).

General procedure for the preparation of (2S)-2-alkoxypropan-1-ols (11d, g)

To a suspension of 40.6 mmol $LiAlH_4$ in 50 mL Et_2O was dropwise added a solution of 12.3 mmol methyl (2*S*)-2-alkyloxypropionate **9** in 20 mL Et_2O at 0 °C and the resulting mixture was heated under reflux for 18 h. After cooling to 0 °C, 7 mL H_2O, 10 mL NaOH (10 wt%) and 25 mL H_2O were added sequentially over 1 h, the precipitate was removed by filtration and the aqueous layer was extracted with 5 × 50 mL Et_2O, the organic layers were dried over $MgSO_4$, evaporated and the residue was purified by flash chromatography.

(2S)-2-Butyloxypropan-1-ol (11d)

According to the general procedure flash chromatography (hexanes/Et_2O 1:1) yielded 1.25 g (80%) of a pale yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.93 (t, $^3J = 7.6$ Hz, 3H, $CH_2CH_2CH_2CH_3$), 1.11 (d, $^3J = 6.0$ Hz, 3H, 3-H), 1.38 (qt, $^3J = 7.6$ Hz, $^3J = 7.5$ Hz, 2H, $CH_2CH_2CH_2CH_3$), 1.57–1.62 (m, 2H, $CH_2CH_2CH_2CH_3$), 2.11 (s, br, OH), 3.38 (dt, $^2J = 9.2$ Hz, $^3J = 6.7$ Hz, Hz, 1H, $CH_{2A}CH_2CH_2CH_3$), 3.43 (dd, $^2J = 10.9$ Hz, $^3J = 7.9$ Hz, 1H, 1-H_A), 3.52 (dqd, $^3J = 7.1$ Hz, $^3J = 6.0$ Hz, $^3J = 3.3$ Hz, 1H, 2-H), 3.54–3.60 (m, 1H, 1-H_B), 3.58 (dt, $^2J = 9.2$ Hz, $^3J = 6.7$ Hz, 1H, $CH_{2B}CH_2CH_2CH_3$). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 13.9 ($CH_2CH_2CH_2CH_3$), 15.9 (C-3), 19.4 ($CH_2CH_2CH_2CH_3$), 32.2 ($CH_2CH_2CH_2CH_3$), 66.4 (C-1), 69.6 ($CH_2CH_2CH_2CH_3$), 75.7 (C-2). MS (EI): m/z (%) = 132 (<1) $[M]^+$, 101 (80) $[M–HOCH_2]^+$, 83 (5), 59 (15), 57 (95), 55 (10), 45 (100) $[M–HOCH_2—C_4H_9]^+$, 41 (35), 39 (5). HRMS (CI): m/z (%) calcd for $C_7H_{17}O_2$ $[M + H]^+$ 133.1229, found 133.1214. FT-IR (ATR): ν = 3423 (vs), 2959, 2931, 2871 (vs), 2228, 2186 (w), 1713, 1667 (w), 1457 (m), 1376 (s), 1342 (w), 1231 (m), 1090 (vs), 986 (m) cm^{-1}. $[\alpha]_D^{20} = +34.3$ ($c = 1.0$, $CHCl_3$).

(2S)-2-Decyloxypropan-1-ol (11g)

According to the general procedure flash chromatography (hexanes/Et_2O 3:1) yielded 1.25 g (99%) of a pale yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.88 [t, $^3J = 7.1$ Hz, 3H, $CH_2CH_2(CH_2)_7CH_3$], 1.11 (d, $^3J = 6.2$ Hz, 3H, 3H), 1.20–1.38 [m, 16H, $CH_2CH_2(CH_2)_7CH_3$], 1.52–1.61 [m, 2H, $CH_2CH_2(CH_2)_7CH_3$], 2.09 (s, br, 1H, OH), 3.37 [dt, $^2J = 9.2$ Hz, $^3J = 6.7$ Hz, 1H, $CH_{2A}CH_2(CH_2)_7CH_3$], 3.41–3.46 (m, 1H, 2H), 3.57 [dt, $^2J = 9.2$ Hz, $^3J = 6.7$ Hz, 1H, $CH_{2B}CH_2(CH_2)_7CH_3$], 3.48–3.60 (m, 2H, 1-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 14.1 ($CH_2(CH_2)_8CH_3$), 15.9 (C-3), 22.7, 26.2, 29.4, 29.5, 29.6, 29.7, 30.1, 31.9 ($CH_2(CH_2)_8CH_3$), 66.4 (C-1), 68.9 ($CH_2(CH_2)_8CH_3$), 75.8 (C-2). MS (EI): m/z (%) = 217 (2) $[M + H]^+$, 185 (100), 168 (10), 141 (40), 112 (5), 99 (20), 97 (10), 85 (80), 83 (15), 71 (70), 69 (15), 57 (80), 55 (25), 45 (10), 43 (45). HMRS (ESI): calcd. for $C_{13}H_{28}NaO_2$ $[M + Na]^+$ 239.1987, found 239.1982. FT-IR (ATR): ν = 3392 (vs), 2922, 2853 (vs), 2359 (w), 1464 (m), 1375 (w), 1341 (w), 1094, 1046 (vs), 988 (m) cm^{-1}. $[\alpha]_D^{20} = +20.2$ (c = 1.0, $CHCl_3$).

(2S)-1-Brom-2-decyloxypropane (12g)

To a solution of 1.01 g (4.6 mmol) (2*S*)-2-decyloxypropanol **11g** in 40 mL CH_2Cl_2 were added 3.62 g (13.8 mmol) PPh_3, 1.81 g (6.9 mmol) CBr_4 and 4.5 mL (3.3 g, 32.0 mmol) triethylamine at 0 °C and the mixture was stirred at room temperature for 18 h. Then, 40 mL H_2O was added, the layers separated and the aqueous layer was extracted with 3 × 20 mL CH_2Cl_2, the organic layers were dried over $MgSO_4$, evaporated and the crude product purified by flash chromatography (hexanes/ethyl acetate) to yield 0.89 g (67%) of a pale yellow oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.88 [t, $^3J = 7.1$ Hz, 3H, $CH_2CH_2(CH_2)_7CH_3$], 1.27 (d, $^3J = 6.2$ Hz, 3H, 3H), 1.20-1.38 [m, 16H, $CH_2CH_2(CH_2)_7CH_3$], 1.52–1.62 [m, 2H, $CH_2CH_2(CH_2)_7CH_3$], 3.33 (dd, $^2J = 10.4$ Hz, $^3J = 5.9$ Hz, 1H, 1-H_{2A}), 3.41 (dd, $^2J = 10.4$ Hz, $^3J = 4.9$ Hz, 1H, 1-H_{2B}), 3.47 [td, $^3J = 6.7$ Hz, $^4J = 1.5$ Hz, 2H, $CH_2CH_2(CH_2)_7CH_3$], 3.60 (qdd, $^3J = 6.2$ Hz, $^3J = 5.9$ Hz, $^3J = 4.9$ Hz, 1H, 1*H*). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 14.1 ($CH_2(CH_2)_8CH_3$), 18.9 (C-3), 22.7, 26.1, 29.3, 29.4, 29.58, 29.61, 30.0, 31.9 ($CH_2(CH_2)_8CH_3$), 36.5 (C-1), 69.4 ($CH_2(CH_2)_8CH_3$), 74.8 (C-1). MS (EI): m/z (%) = 279 (1) $[M^+]$, 263 (1), 185 (100), 168 (5), 153 (5), 141 (30), 121 (10), 112 (5), 99 (15), 85 (50), 71 (45), 57 (50), 43 (30). HMRS (ESI): calcd. for $C_{13}H_{27}BrNaO$ $[M + Na]^+$ 301.1143, found 301.1137. FT-IR (ATR): ν = 2923, 2853 (vs), 2359 (s), 2341 (s), 1457 (m), 1375 (m), 1325 (m), 1228 (w), 1195 (w), 1140 (s), 1096 (vs), 669 (s) cm^{-1}. $[\alpha]_D^{20} = +5.8$ ($c = 1.0$, $CHCl_3$).

General procedure for the preparation of tetrakis{4-[(2S)-alkoxypropionate]-phenyl}ethenes (3a–c, e–h)

To a solution of 0.4 g (1.0 mmol) tetrakis(4-hydroxyphenyl)ethene 7 and 0.54 g (4.4 mmol) DMAP in 50 mL CH_2Cl_2 was dropwise added at 0 °C a solution of 0.79 g (4.4 mmol) methyl (2*S*)-benzyloxypropionic acid 10 h and 1.69 g (8.8 mmol) *N*-3-dimethylaminopropyl-*N*-ethylcarbodiimide (EDC) in 20 mL CH_2Cl_2. After stirring at room temperature for 18 h, the mixture was filtered via Celite, washed with 2 × 50 mL 1 N HCl, 50 mL H_2O, dried over $MgSO_4$ and evaporated. The crude product was purified by flash chromatography.

Tetrakis{4-[(2S)-methoxypropionate]phenyl}ethene (3a)

According to the general procedure flash chromatography (hexanes/ethyl acetate 10:1) yielded 0.33 g (89%) of a colourless solid.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.54 (d, $^3J = 6.9$ Hz, 12H, 3′-H), 3.48 (s, 12H, OCH_3), 4.07 (q, $^3J = 6.9$ Hz, 4H, 2′-H), 6.89 (d, $^3J = 8.9$ Hz, 8H, 2H, 6H), 7.03 (d, $^3J = 8.9$ Hz, 8H, 3H, 5H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 18.4 (C-3′), 57.9 (OCH_3), 76.4 (C-2′), 120.8 (C-2, C-6), 132.4 (C-3, C-5), 139.7 (C=C), 140.7 (C-1), 149.1 (C-4), 171.4 (C-1′). MS (EI): m/z (%) = 740 (100) $[M]^+$, 654 (60), 568 (50), 482 (40), 410 (5), 396 (75), 379 (5), 303 (5), 273 (5), 185 (5), 59 (80). CHN: $C_{42}H_{44}O_{12}$ calcd. C 68.10%, H 5.99%, found C 67.92%, H 6.01%. FT-IR (ATR): ν = 3040 (w), 2988, 2936, 2829 (m), 2323 (w), 1754 (vs), 1602 (m), 1502, 1445, 1354 (s), 1197, 1162, 1000 (vs) cm^{-1}. $[\alpha]_D^{20} = -92.0$ ($c = 1.0$, $CHCl_3$).

Tetrakis{4-[(2S)-ethoxypropionate]phenyl}ethene (3b)

According to the general procedure flash chromatography (hexanes/ethyl acetate 3:1) yielded 0.18 g (99%) of a highly viscous, pale green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.27 (t, ^3J = 7.0 Hz, 12H, CH_2CH_3), 1.54 (d, ^3J = 6.8 Hz, 12H, 3′-H), 3.54 (dq, ^2J = 8.9 Hz, ^3J = 7.0 Hz, 4H, $CH_{2A}CH_3$), 3.73 (dq, ^2J = 8.9 Hz, ^3J = 7.0 Hz, 4H, $CH_{2B}CH_3$), 4.16 (q, ^3J = 6.8 Hz, 4H, 2′-H), 6.89 (d, ^3J = 8.8 Hz, 8H, 2H, 6H), 7.03 (d, ^3J = 8.8 Hz, 8H, 3H, 5H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 14.2 (CH_2CH_3), 18.7 (C-3′), 65.9 (CH_2CH_3), 74.8 (C-2′), 120.8 (C-2, C-6), 132.4 (C-3, C-5), 139.7 (C═C), 140.7 (C-1), 149.1 (C-4), 171.8 (C-1′). MS (EI): m/z (%) = 796 (100) $[M]^+$, 696 (90), 596 (80), 496 (60), 452 (5), 424 (10), 396 (100), 379 (5), 273 (5), 185 (5), 73 (80), 45 (75). HMRS (ESI): calcd. for $C_{46}H_{52}NaO_{12}$ $[M + Na]^+$ 819.3356, found 819.3344. FT-IR (ATR): ν = 3038 (w), 2979, 2935, 2875 (s), 2572 (m), 2364 (m), 2183 (m), 1980 (m), 1765 (vs), 1600 (m), 1503, 1445 (vs), 1406, 1372 (m), 1239 (m), 1198, 1163, 1110 (vs) cm^{-1}. $[\alpha]_D^{20}$ = −65.8 (c = 1.0, $CHCl_3$).

Tetrakis{4-[(2S)-propyloxypropionate]phenyl}ethene (3c)

According to the general procedure flash chromatography (hexanes/ethyl acetate 5:1) yielded 0.13 g (82%) of a highly viscous, pale green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.95 (t, ^3J = 7.0 Hz, 12H, $CH_2CH_2CH_3$), 1.54 (d, ^3J = 6.9 Hz, 12H, 3′-H), 1.66 (qdd, ^3J = 7.4 Hz, ^3J = 6.7 Hz, ^3J = 6.7 Hz, 8H, $CH_2CH_2CH_3$), 3.42 (dt, ^2J = 8.9 Hz, ^3J = 6.7 Hz, 4H, $CH_{2A}CH_2CH_3$), 3.63 (dt, ^2J = 8.9 Hz, ^3J = 6.7 Hz, 4H, $CH_{2B}CH_2CH_3$), 4.15 (q, ^3J = 7.0 Hz, 4H, 2H),6.89 (d, ^3J = 8.8 Hz, 8H, 2H, 6H), 7.02 (d, ^3J = 8.8 Hz, 8H, 3H, 5H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 10.5 ($CH_2CH_2CH_3$), 18.7 (C-3′), 22.9 ($CH_2CH_2CH_3$), 72.2 ($CH_2CH_2CH_3$), 74.9 (C-2′), 120.8 (C-2, C-6), 132.4 (C-3, C-5), 139.7 (C═C), 140.7 (C-1), 149.2 (C-4), 171.8 (C-1′). MS (ESI): m/z (%) = 875.4 $[M + Na]^+$. HRMS (ESI): m/z (%) calcd. for $C_{50}H_{60}O_{12}Na$ $[M + Na]^+$ 875.3982, found 875.3971. FT-IR (ATR): ν = 2963, 2936, 2876 (m), 1768 (s), 1601, 1503, 1454 (s), 1372 (m), 1238 (m), 1198, 1163, 1111, 1015 (vs), 903 (s), 873 (s) cm^{-1}. $[\alpha]_D^{20}$ = −71.6 (c = 1.0, $CHCl_3$).

Tetrakis{4-[(2S)-pentyloxypropionate]phenyl}ethene (3e)

According to the general procedure flash chromatography (hexanes/ethyl acetate 10:1) yielded 32.0 mg (7%) of a highly viscous, pale green oil.

^{1}H-NMR (250 MHz, $CDCl_3$): δ (ppm) = 0.90 (t, ^3J = 6.9 Hz, 12H, 2″-H), 1.27–1.44 (m, 16H, 3″-H, 4″-H), 1.54 (d, ^3J = 7.0 Hz, 12H, 3′-H), 1.55–1.74 (m, 8H, 2″-H), 3.45 (dq, ^2J = 9.1 Hz, ^3J = 6.7 Hz, 4H, 1″-H_A), 3.66 (dq, ^2J = 9.1 Hz, ^3J = 6.7 Hz, 4H, 1″-H_B), 4.13 (q, ^3J = 7.0 Hz, 4H, 2′-H), 6.88 (d, ^3J = 8.6 Hz, 8H, 2-H, 6-H), 7.03 (d, ^3J = 8.6 Hz, 8H, 3H, 5H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 14.0 (C-5″), 18.7 (C-3′), 22.5, 29.5 (C-3″, C-4″), 28.2 (C-2″), 70.7 (C-1″), 74.9 (C-2′), 120.8 (C-2, C-6), 132.4 (C-3, C-5), 139.7 (C═C), 140.7 (C-1), 149.2 (C-4), 171.8 (C-1′). HRMS (ESI): m/z (%) calcd. for $C_{58}H_{76}O_{12}Na$ $[M + Na]^+$ 987.5234, found 987.5238. FT-IR (ATR): ν = 2955, 2932, 2870 (vs), 2365, 2184 (m), 1757 (vs), 1613, 1501, 1445 (s), 1196, 1165, 1114, 1017 (vs), 734 (s) cm^{-1}. $[\alpha]_D^{20}$ = −60.3 (c = 1.0, $CHCl_3$).

Tetrakis{4-[(2S)-octyloxypropionate]phenyl}ethene (3f)

According to the general procedure flash chromatography (hexanes/ethyl acetate 20:1) yielded 48.0 mg (47%) of a highly viscous, pale green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.87 [t, ^3J = 7.1 Hz, 12H, $CH_2CH_2CH_2(CH_2)_4CH_3$], 1.19–1.33 [m, 32H, $CH_2CH_2CH_2(CH_2)_4CH_3$], 1.33-1.42 [m, 8H, $CH_2CH_2CH_2(CH_2)_4CH_3$], 1.54 (d, ^3J = 6.9 Hz, 12H, 3′-H), 1.58–1.68 [m, 8H, $CH_2CH_2CH_2(CH_2)_4CH_3$], 3.45 [dt, ^2J = 9.0 Hz, ^3J = 6.6 Hz, 4H, $CH_{2A}CH_2CH_2(CH_2)_4CH_3$], 3.66 [dt, ^2J = 9.0 Hz, ^3J = 6.6 Hz, 4H, $CH_{2B}CH_2CH_2(CH_2)_4CH_3$], 4.14 (q, ^3J = 6.9 Hz, 4H, 2′-H), 6.88, 7.02 (d, ^3J = 8.7 Hz, 8H, ^3J = 8.7 Hz, 8H, 2H, 3H, 5H, 6H). ^{13}C-NMR (125 MHz, CDCl3): δ (ppm) = 14.1 [$CH_2(CH_2)_6CH_3$], 18.7 (C-3′), 22.7, 26.1, 29.2, 29.4, 29.8, 31.8 [$CH_2(CH_2)_6CH_3$], 70.7 [$CH_2(CH_2)_6CH_3$], 74.9 (C-2′), 120.8 (C-3, C-5), 132.4 (C-2, C-6), 139.7 (C═C), 140.7 (C-1), 149.2 (C-4), 171.8 (C═O). MS (ESI): m/z = 1155.7 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{70}H_{100}NaO_{12}$ $[M + Na]^+$ 1155.7112, found 1155.7096. FT-IR (ATR): ν = 2923, 2854 (vs), 1720 (vs), 1458 (s), 1371 (m), 1239 (m), 1127, 1071 (vs) cm^{-1}. $[\alpha]_D^{20}$ = −68.8 (c = 1.0, $CHCl_3$).

Tetrakis{4-[(2S)-decyloxypropionate]phenyl}ethene (3g)

According to the general procedure flash chromatography (hexanes/ethyl acetate 20:1) yielded 0.19 g (52%) of a highly viscous, pale green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.87 [t, ^3J = 6.9 Hz, 12H, $CH_2CH_2CH_2(CH_2)_6CH_3$], 1.19–1.32 [m, 48H, $CH_2CH_2CH_2(CH_2)_6CH_3$], 1.32–1.40 [m, 8H, $CH_2CH_2CH_2(CH_2)_6CH_3$], 1.53 (d, ^3J = 6.9 Hz, 12H, 3′-H), 1.59–1.66 [m, 8H, $CH_2CH_2CH_2(CH_2)_6CH_3$], 3.44 [dt, ^2J = 8.8 Hz, ^3J = 6.8 Hz, 4H, $CH_{2A}CH_2CH_2(CH_2)_6CH_3$], 3.66 [dt, ^2J = 8.8 Hz, ^3J = 6.8 Hz, 4H, $CH_{2B}CH_2CH_2(CH_2)_6CH_3$], 4.14 (q, ^3J = 6.8 Hz, 4H, 2′-H), 6.88, 7.02 (d, ^3J = 8.7 Hz, 8H, ^3J = 8.7 Hz, 8H, 2H, 3H, 5H, 6H). ^{13}C-NMR (125 MHz, CDCl3): δ (ppm) = 14.1 [$CH_2(CH_2)_8CH_3$], 18.7 (C-3′), 22.7, 26.1, 29.3, 29.5, 29.6, 29.8, 30.9 [$CH_2(CH_2)_8CH_3$], 70.7 [$CH_2(CH_2)_8CH_3$], 74.9 (C-2′), 120.8 (C-3, C-5), 132.4 (C-2, C-6), 139.7 (C═C), 140.7 (C-1), 149.2 (C-4), 171.8 (C═O). MS (ESI): m/z = 1267.8 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{78}H_{116}NaO_{12}$ $[M + Na]^+$ 1267.8364, found 1267.8345. FT-IR (ATR): ν = 2922, 2853 (vs), 1770 (vs), 1503, 1456 (s,), 1372 (m), 1237 (m), 1199, 1163, 1111, 1016 (vs) cm^{-1}. $[\alpha]_D^{20}$ = −62.0 (c = 1.0, $CHCl_3$).

Tetrakis{4-[(2S)-benzyloxypropionate]phenyl}ethene (3h)

According to the general procedure flash chromatography (hexanes/ethyl acetate 4:1) yielded 0.85 g (82%) of a highly viscous, pale green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.58 (d, ^3J = 6.8 Hz, 12H, 3′-H), 4.26 (q, ^3J = 6.8 Hz, 4H, 2′-H), 4.55 (d, ^2J = 11.6 Hz, 4H, CH_{2A}), 4.78 (d, ^2J = 11.6 Hz, 4H, CH_{2B}), 6.89 (d, ^3J = 8.8 Hz, 8H, 2H, 6H), 7.04 (d, ^3J = 8.8 Hz, 8H, 3H, 5H), 7.27-7.32 (m, 4H, 4″-H), 7.33-7.42 (m, 16 H, 2″-H, 3″-H, 5″-H, 6″-H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 18.7 (C-3′), 72.3 (CH_2), 74.0 (C-2′), 120.8 (C-2, C-6), 128.0 (C-4″), 128.1, 128.5 (C-2″, C-3″, C-5″, C-6″), 132.4 (C-3, C-5), 137.3 (C-1″), 139.7 (C═C), 140.8 (C-1), 149.1 (C-4), 171.5 (C-1′). MS (EI): m/z (%) = 1044 (15) $[M]^+$, 972 (15), 938 (40), 894 (10), 882 (80), 810 (20), 776 (40), 737 (10), 720 (50), 704 (10), 105 (20), 91 (100), 43 (20). CHN: $C_{66}H_{60}O_{12}$ (1045.18 g mol^{-1}) calcd. C 75.84%, H 5.79%, found C 75.75%, H 5.94%. FT-IR (ATR): ν = 3320 (w), 3031 (w), 2984, 2936, 2870 (m), 2356 (w), 1763 (s), 1599, 1502, 1453 (s), 1197, 1162, 1105, 1014 (s) cm^{-1}. $[\alpha]_D^{20}$ = −95.8 (c = 1.0, $CHCl_3$).

General procedure for the preparation of tetrakis{4-[(2S)-alkoxypropyl]phenyl}-ethenes (2d, g–i)

To a suspension of 4.2 g (30.0 to a solution of 0.4 g (1.0 mmol) tetrakis(4-hydroxyphenyl)ethene 7 and 0.54 g (4.4 mmol) DMAP in 50 mL CH_2Cl_2 was dropwise added at 0 °C a solution of 0.79 g (4.4 mmol) methyl (2*S*)-benzyloxypropionic acid 10 h und 1.69 g (8.8 mmol) EDC in 20 mL CH_2Cl_2. After stirring at room temperature for 18 h, the mixture was filtered via Celite, washed with 2 × 50 mL 1 N HCl, 50 mL H_2O, dried over $MgSO_4$ and

evaporated. (The crude product was purified by flash chromatography.) Cs_2CO_3 and 0.91 g (2.3To a solution of 0.4 g (1.0 mmol) tetrakis(4-hydroxyphenyl)ethene 7 and 0.54 g (4.4 mmol) DMAP in 50 mL CH_2Cl_2 was dropwise added at 0 °C a solution of 0.79 g (4.4 mmol) methyl (2*S*)-benzyloxypropionic acid 10 h und 1.69 g (8.8 mmol) EDC in 20 mL CH_2Cl_2. After stirring at room temperature for 18 h, the mixture was filtered via Celite, washed with 2×50 mL 1 N HCl, 50 mL H_2O, dried over $MgSO_4$ and evaporated. (The crude product was purified by flash chromatography.) Tetrakis(4-hydroxyphenyl)ethene **7** in 40 mL DMF were added 2.5 g (10.9To a solution of 0.4 g (1.0 mmol) tetrakis(4-hydroxyphenyl)ethene 7 and 0.54 g (4.4 mmol) DMAP in 50 mL CH_2Cl_2 was dropwise added at 0 °C a solution of 0.79 g (4.4 mmol) methyl (2*S*)-benzyloxypropionic acid 10 h und 1.69 g (8.8 mmol) EDC in 20 mL CH_2Cl_2. After stirring at room temperature for 18 h, the mixture was filtered via Celite, washed with 2×50 mL 1 N HCl, 50 mL H_2O, dried over $MgSO_4$ and evaporated. The crude product was purified by flash chromatography.) (2*S*)-Benzyloxypropylbromide **12c** and the mixture was heated at 80 °C for 72 h and then poured onto 50 g ice and diluted with 150 mL CH_2Cl_2. The layers were separated, the aequos layer was extracted with 150 mL CH_2Cl_2, the combined organic layers were dried over $MgSO_4$, evaporated and purified by flash chromatography.

Tetrakis{4-[(2S)-butyloxypropyl]phenyl}ethene (2d)

According to the general procedure flash chromatography (hexanes/ethyl acetate 20:1) yielded 0.29 g (72%) of a highly viscous, pale green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.91 (t, ^3J = 7.3 Hz, 12H, $CH_2CH_2CH_2CH_3$), 1.24 (d, ^3J = 6.1 Hz, 12H, 3′-H), 1.33–1.42 (m, 8H, $CH_2CH_2CH_2CH_3$), 1.52–1.59 (m, 8H, $CH_2CH_2CH_2CH_3$), 3.52 (dt, ^2J = 9.3 Hz, ^3J = 6.6 Hz, 4H, $CH_{2A}CH_2CH_2CH_3$), 3.55 (dt, ^2J = 9.3 Hz, ^3J = 6.6 Hz, 4H, $CH_{2B}CH_2CH_2CH_3$), 3.71–3.77 (m, 4H, 2′-H), 3.78 (dd, ^2J = 9.3 Hz, ^3J = 5.0 Hz, 4H, 1′-H_A), 3.91 (dd, ^2J = 9.3 Hz, ^3J = 5.5 Hz, 4H, 1′-H_B), 6.63, 6.90 (d, ^3J = 9.0 Hz, 8H, ^3J = 8.9 Hz, 8H, 2H, 3H, 5H, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 13.9 ($CH_2CH_2CH_2CH_3$), 17.5 (C-3′), 19.3 ($CH_2CH_2CH_2CH_3$), 32.2 ($CH_2CH_2CH_2CH_3$C-2), 69.3 ($CH_2CH_2CH_2CH_3$), 71.4 (C-1′), 73.8 (C-2′), 113.7, 132.5 (C-2, C-3, C-5, C-6), 136.9 (C-1), 138.4 (C═C), 157.1 (C-4). MS (ESI): m/z = 852.0 $[M]^+$. HRMS (ESI): calcd. for $C_{54}H_{80}NO_8$ $[M + NH_4]^+$ 870.5884, found 870.5866. FT-IR (ATR): ν = 3035 (w), 2957, 2930, 2869 (vs), 1604 (vs), 1506, 1455 (vs), 1374 (m), 1286 (m), 1237, 1149, 1104, 1038 (vs), 827 (vs) cm^{-1}. $[\alpha]_D^{20} = -35.2$ (c = 1.0, $CHCl_3$).

Tetrakis{4-[(2S)-decyloxypropyl]phenyl}ethene (2g)

According to the general procedure flash chromatography (hexanes/ethyl acetate 40:1) yielded 0.32 g (72%) of a highly viscous, pale green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.81 [t, ^3J = 6.8 Hz, 12H, $CH_2CH_2(CH_2)_7CH_3$], 1.17 (d, ^3J = 6.2 Hz, 12H, 3′-H), 1.14-1.31 [m, 56H, $CH_2CH_2(CH_2)_7CH_3$], 1.44–1.55 [m, 8H, $CH_2CH_2(CH_2)_7CH_3$], 3.46 [dt, ^2J = 6.8 Hz, ^4J = 2.2 Hz, 8H, $CH_2CH_2(CH_2)_7CH_3$], 3.63–3.73 (m, 8H, 2′-H, 1′-H_A), 3.48 (dd, ^2J = 9.2 Hz, ^3J = 5.4 Hz, 4H, 1′-H_B), 6.56, 6.83 (d, ^3J = 8.6 Hz, 8H, ^3J = 8.6 Hz, 8H, 2H, 3H, 5H, 6H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 13.1 [$CH_2(CH_2)_8CH_3$], 16.4 (C-3′), 21.7, 25.1, 28.3, 28.56, 28.60, 28.68, 29.1, 30.89 [$CH_2(CH_2)_8CH_3$], 68.6 [$CH_2(CH_2)_8CH_3$], 70.3 (C-1′), 72.7 (C-2′), 112.6 (C-3, C-5), 126.5 (C-1), 128.7 (C═C), 131.5 (C-2, C-6), 156.1 (C-4). MS (CI): m/z = 1189.9 (100) $[M + H]^+$, 1029.7 (30), 987.7 (5), 897.7 (30), 831.5 (2), 757.5 (5), 595.5 (5). HRMS (CI): calcd. for $C_{78}H_{125}O_8$ $[M + H]^+$ 1189.9374, found 1189.9369. FT-IR (ATR): ν = 2955, 2924, 2853 (vs), 1949 (m), 1733 (m), 1613 (s), 1507, 1455, 1439 (vs), 1375 (m), 1259, 1239 (vs), 1123, 1101, 1037 (vs), 840, 801 (vs) cm^{-1}. $[\alpha]_D^{20} = -28.1$ (c = 1.0, $CHCl_3$).

Tetrakis{4-[(2S)-benzyloxypropyl]phenyl}ethene (2h)

According to the general procedure flash chromatography (hexanes/ethyl acetate 10:1) yielded 0.82 g (36%) of a highly viscous, pale green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.28 (d, ^3J = 6.2 Hz, 12H, 3′-H), 3.76–3.82 (m, 4H, 2′-H), 4.17 (dd, ^2J = 11.4 Hz, ^3J = 6.2 Hz, 4H, 1′-H_A), 4.22 (dd, ^2J = 11.4 Hz, ^3J = 4.3 Hz, 4H, 1′-H_B), 4.55 (d, ^3J = 11.9 Hz, 4H, CH_{2A}), 4.61 (d, ^3J = 11.9 Hz, 4H, CH_{2B}), 6.5–6.7 (m, 8H, 3H, 5H), 6.8–6.9 (m, 8H, 2H, 6H), 7.26–7.38 (m, 20H, 2H″, 3H″, 4H″, 5H″, 6H″). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 17.8 (C-3′), 72.5 (C-1′), 73.2 (C-2′), 126.9, 127.5, 127.7, 128.36, 128.6 (C-2″, C-3″, C-4″, C-5″, C-6″), 127.6, 128.44 (C-2, C-3, C-5, C-6), 138.3 (C-4), 138.7 (C-1), 140.9 (C═C), 177.1 (C-1″). MS (ESI): m/z = 1011.5 $[M + Na]^+$. HRMS (ESI): calcd. for $C_{66}H_{68}NaO_8$ $[M + Na]^+$ 1011.4812, found 1011.4824. FT-IR (ATR): ν = 3063 (m), 2978, 2872 (m), 1958 (m), 1613 (s), 1453, 1376 (s), 1271, 1238 (vs), 1139, 1055 (vs), 735, 696 (vs) cm^{-1}. $[\alpha]_D^{20} = -32.4$ (c = 1.0, $CHCl_3$).

Tetrakis{4-[(2S)-methoxymethoxypropyl]phenyl}ethene (2i)

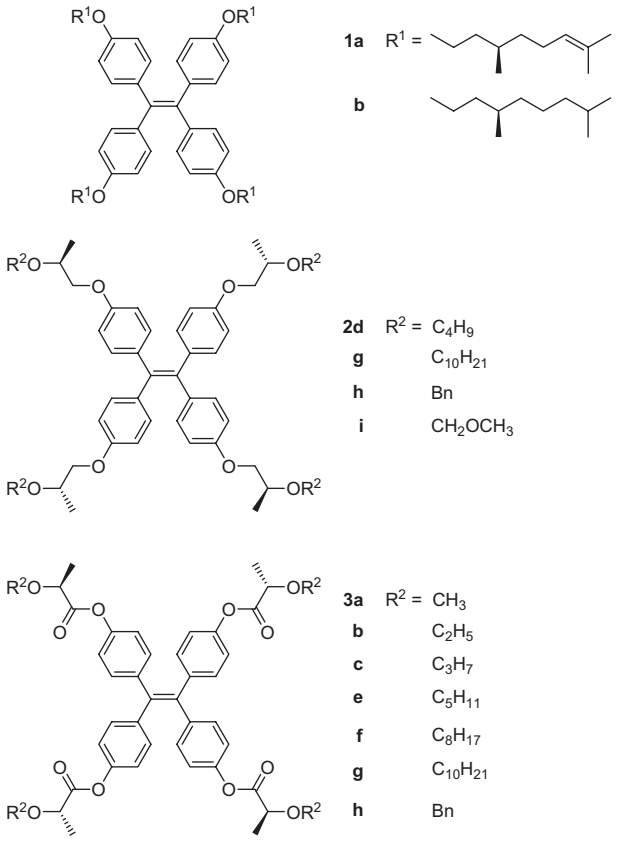
According to the general procedure flash chromatography (hexanes/ethyl acetate 5:1) yielded 0.15 g (63%) of a highly viscous, pale green oil.

^{1}H-NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.28 (d, ^3J = 6.4 Hz, 12H, 3′-H), 3.39 (s, 12H, OMe), 3.84 (dd, ^2J = 9.8 Hz, ^3J = 4.5 Hz, 4H, 1′-H_A), 3.91 (dd, ^2J = 9.8 Hz, ^3J = 6.2 Hz, 4H, 1′-H_B), 4.06 (qdd, ^3J = 6.4 Hz, ^3J = 6.2 Hz, ^3J = 4.5 Hz, 4H, 2′-H), 4.73 (d, ^2J = 6.8 Hz, 4H, OCH_2O-H_A), 4.75 (d, ^2J = 6.8 Hz, 4H, OCH_2O-H_B), 6.63 (d, ^3J = 8.9 Hz, 8H, 2H, 6H), 6.90 (d, ^3J = 8.9 Hz, 8H, 3H, 5H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 17.5 (C-3′), 55.3 (OCH_3), 71.3 (C-2′), 71.4 (C-1′), 95.4 (OCH_2O), 113.6, 132.5 (C-2, C-3, C-5, C-6), 136.9 (C-1), 138.4 (C═C), 156.9 (C-4). MS (ESI): m/z = 804 $[M]^+$. HRMS (ESI): calcd. for $C_{46}H_{60}NaO_{12}$ $[M + Na]^+$ 827.3982, found 827.3957. FT-IR (ATR): ν = 3032 (w), 2973 (s), 2930 (s), 2889 (s), 2537 (m), 2164 (m), 2009 (m), 1604 (vs), 1506 (vs), 1454 (vs), 1376 (m), 1238, 1143, 1103 (vs), 1027, 989 (vs), 915 (vs), 829 (vs) cm^{-1}. $[\alpha]_D^{20} = -38.0$ (c = 1.0, $CHCl_3$).

RESULTS AND DISCUSSION

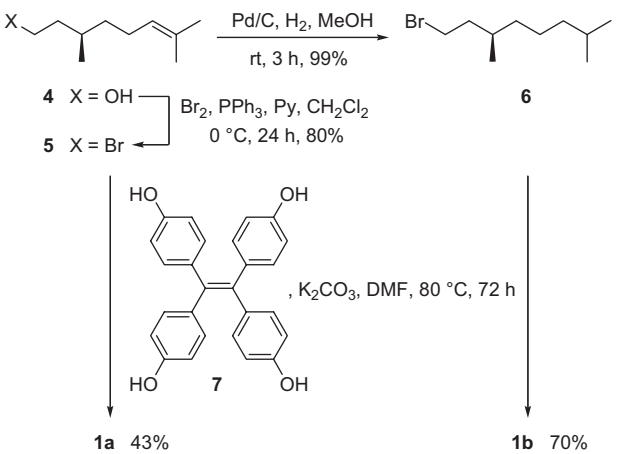
Synthesis

The following three series of compounds were prepared: citronellyl ethers **1a**, **b**, lactate-derived ethers **2d**, **g**–**i** and lactates **3a**–**c**, **e**–**h** (Scheme 1). These derivatives were chosen because they are readily available building blocks. In the case of lactates, a common precursor can be used for the synthesis of both esters and ethers. Thus, the influence of different parameters on the HTP could be studied very easily, i.e. dipole moment of ester *versus* ether moiety as well as chain lengths. Various chain lengths up to ten carbon atoms were chosen in order to obtain good miscibility between the nematic host phase and the dopant. Following the procedure by Chattopadhyay[94] (*R*)-citronellol **4** was treated with bromine and PPh_3 in the presence of pyridine in CH_2Cl_2 at 0 °C for 24 h and the

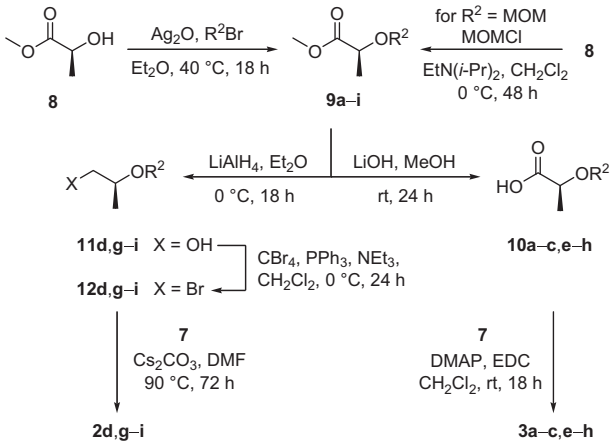


Scheme 1.

corresponding bromide **5** was isolated in 80% yield (Scheme 2). Subsequent catalytic hydrogenation under 1 atm of hydrogen in the presence of Pd/C in MeOH at room temperature yielded the saturated bromide **6**. Tetrakis(4-hydroxytetraphenyl)ethene **7** was then submitted to Williamson etherification with bromides **5** and **6**, respectively, in the presence of K_2CO_3 in DMF at 80 °C for 72 h to give the citronellyl ethers **1a**, **b** in 43 and 70% yield, respectively. Although, similar conversions of the four-fold etherification were obtained in both cases, the yield of compound **1a** was compromised by tedious chromatographic removal of partially alkylated byproducts.



Scheme 2.



Scheme 3.

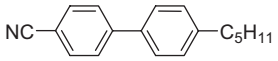
The synthesis of lactate ethers **2** and lactates **3** commenced with alkylation of methyl lactate **8** with alkyl bromides in the presence of Ag_2O in Et_2O at 40 °C for 18 h according to the procedure by Molteni[95] to give the corresponding ethers **9** in 10–99% yield (Scheme 3, Table 1). The yields of alkylation products **9** were extremely sensitive to the quality of Ag_2O. Thus, Ag_2O had to be freshly prepared. We observed decreased conversions with increasing chain lengths which is probably due to steric effects in this S_N2 type reaction. It should be noted that other conditions compromised the optical purity of the lactate and were therefore not considered. Subsequent saponification with LiOH in MeOH at room temperature produced the carboxylic acids **10** in 69–99% yield, which were esterified with tetrakis(4-hydroxyphenyl)ethene **7** in the presence of DMAP and EDC in CH_2Cl_2 at room temperature to give the lactates **3** in 7–99% yield. Treatment of methyl lactate **8** with methoxymethylchloride and Hünig's base at room temperature for 48 h yielded the O-MOM-protected lactate **9i** in 71%.[96,97] After reduction of methyl lactates **9** with $LiAlH_4$ in Et_2O at 0 °C, the alcohols **11** were isolated in 80–99% yield. Bromination of **11** with bromine and PPh_3 in the presence of NEt_3 in CH_2Cl_2 at 0 °C gave the bromides **12** in 42–98% yield. Upon final Williamson etherification with **7** under the usual conditions the lactate-derived ethers **2** were obtained in 36–72%.

Chiral properties of the dopants in nematic phases

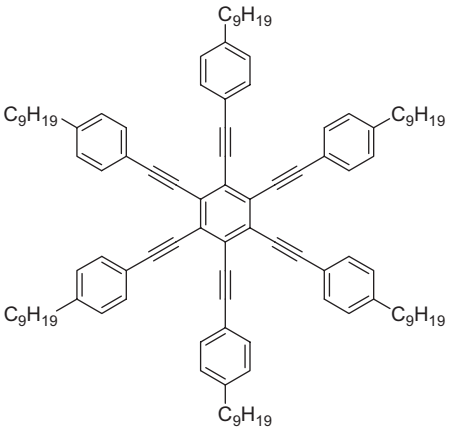
The chiral nematic liquid crystalline solutions were prepared by adding the chiral dopant, i.e. the tetraphenylethene derivatives **1**–**3** in various concentrations to the commercially available calamitic host liquid crystal 4-pentylcyanobiphenyl 5CB **13** (Scheme 4), which displays a nematic mesophase between 23 °C and 35 °C.[98] Alternatively, the discotic hexakis(4-nonylphenylethynyl)benzene **14**,[91–93] which displays a discotic nematic mesophase N_D between 67 and 83 °C, was used as host material. It should be noted that pure compounds **1**–**3** are non-mesogenic.

Citronellyl-derived tetraphenylethenes **1a**, **b** were miscible up to 5 mol% with 5CB **13** and thus characteristic fingerprint textures could be obtained, as shown in Fig. 1 for different solutions of **1a** with **13**.

For the binary solutions of 5CB **13** with the tetraphenylethenes **1**–**3** phase diagrams were determined. Depending on the molar



13
5CB (Cr 23 N 35 I)



14
hexayne (Cr 67 N_D 83 I)

Scheme 4.

fraction and the temperature an isotropic phase, a two-phase region with coexisting isotropic and chiral nematic phase and a chiral nematic phase were observed. The phase diagram for the solution of 5CB **13** and citronellyl-derivative **1a** is shown in Fig. 2. Helical pitches were determined after cooling the solution (cooling rate 1 K min^{-1}) from the isotropic phase to the specified temperature and subsequent annealing for 1 h in order to obtain stable textures. The reciprocal pitches were plotted *versus* the molar fractions of the dopant and the HTP values were obtained from the initial slopes at low dopant concentrations (Fig. 3).

A typical phase diagram for binary solutions of 5CB **13** and lactate-derived tetraphenylene ester **3b** is shown in Fig. 4. The reciprocal pitches were plotted *versus* the molar fraction for binary solutions of 5CB **13** and **3b**, **c**, **e**–**g** (Fig. 5) and HTP values were determined as described above.

In contrast, for most of the other tetraphenylethene derivatives **2**, **3** phase separation occurred at dopant concentrations higher than 3 mol% and therefore only solutions between 0.2 and 2.0 mol% were considered for the HTP measurements.

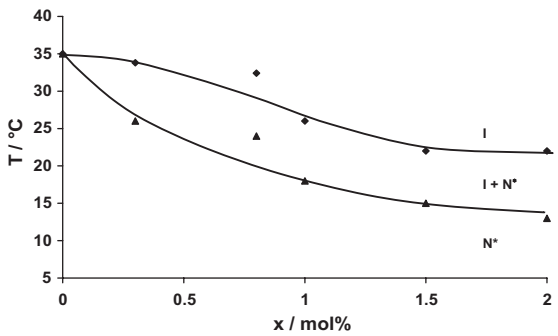


Figure 2. Partial phase diagram of binary solutions of 5CB **13** and dopant **1a**. N* denotes the chiral nematic phase, I + N* denotes the two-phase region, I denotes the isotropic phase

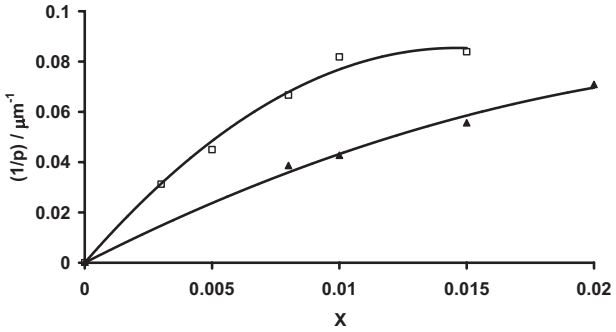


Figure 3. Reciprocal pitch 1/p as a function of the molar fraction *x* for binary solutions of 5CB **13**/**1a** (▲) and 5CB **13**/**1b** (□)

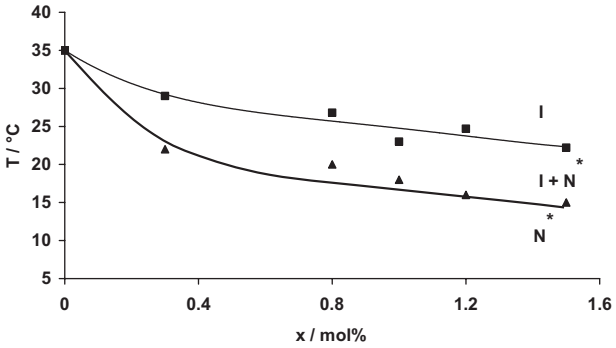


Figure 4. Partial phase diagram of binary solutions of 5CB **13** and dopant **3b**. N* denotes the chiral nematic phase, I + N* denotes the two-phase region, I denotes the isotropic phase

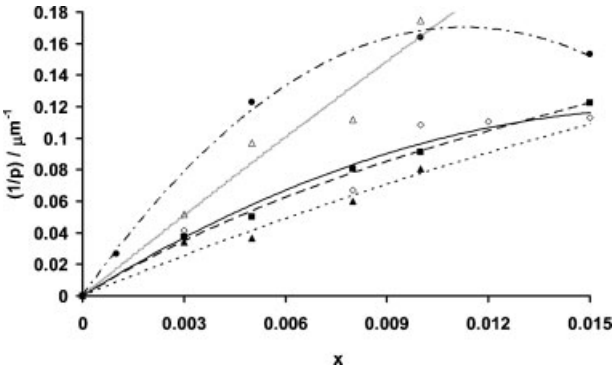


Figure 5. Reciprocal pitch 1/p as a function of the molar fraction *x* for binary solutions of 5CB **13** and **3b** (◇), **3c** (■), **3e** (▲), **3f** (●), **3g** (△)

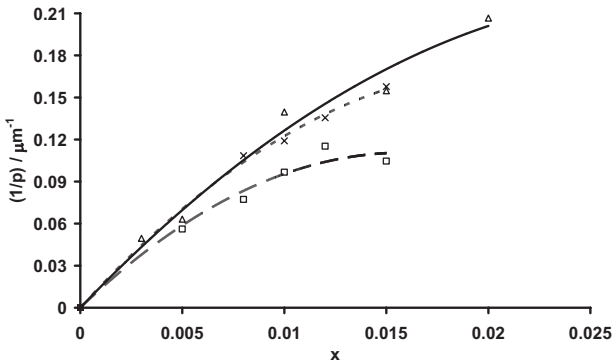


Figure 6. Reciprocal pitch 1/p as a function of the molar fraction *x* for binary solutions of 5CB **13** and **2g** (□), **2d** (x), **2i** (△)

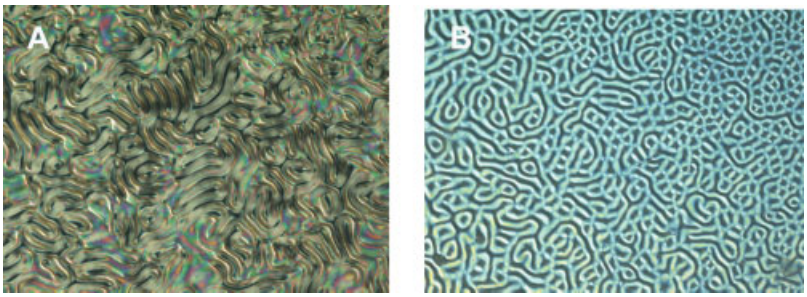


Figure 7. Fingerprint textures of solutions of hexayne **14** with 2 mol% **3b** (A) and 5 mol% **3b** (B) (magnification 200×)

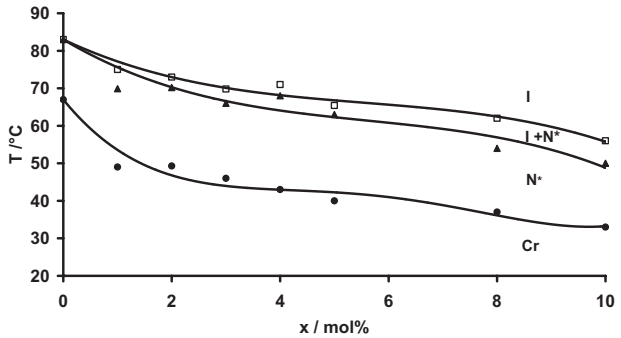


Figure 8. Partial phase diagram of binary solutions of hexayne **14** and dopant **3b**. N* denotes the chiral nematic phase, I + N* denotes the two-phase region, I denotes the isotropic phase, Cr denotes the crystalline phase

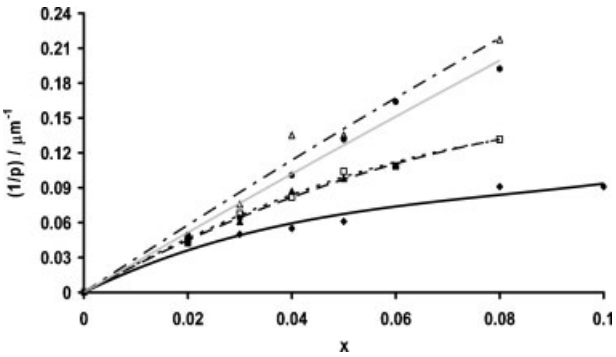


Figure 9. Reciprocal pitch 1/p as a function of the molar fraction × for binary solutions of hexayne **14** and **3b** (◆), **3c** (▲), **3e** (□), **3f** (●), **3g** (△)

Benzyloxy-substituted tetraphenylene ether **2h** and ester **3h** were not suitable as dopants because they were completely immiscible with 5CB **13** even at low concentrations. Also methoxy-substituted tetraphenylene ester **3a** could not be used, because even very dilute solutions which were spin-coated onto the glass slide immediately crystallized.

Next, reciprocal pitch *versus* molar fraction diagrams of binary solutions of 5CB **13** and **2** were prepared (Fig. 6) and the HTP values calculated.

Neither citronellyl-derived tetraphenylethene ethers **1a**, **b** nor lactate-derived ethers **2** did induce fingerprint textures in the nematic discotic host **14**. However, lactate-derived tetraphenylethene esters **3** were suitable as dopants (Fig. 7) and HTP values could be obtained by the above-described procedure. A typical phase diagram for binary solution of hexayne **14** and **3b** and the reciprocal pitch *versus* molar fraction diagram of binary solutions of **14** with **3b**, **c**, **e**–**g** are shown in Figs 8 and 9, respectively.

The results concerning HTPs are summarized in Table 2. HTP values are in the range between 2.1 and 28.7 μm^{-1} and molar HTP (MHTP) values in the range between 1.7 and 35.8 μm^{-1} mol^{-1} kg were observed. Dihydrocitronellyl-derivative **1b** displayed a higher HTP as compared to the corresponding citronellyl-derivative **1a** (entries 1, 2). It is known from the literature,[54,99] that even small variations at the lateral side chains can have a large influence on mesomorphic properties. In case of compound **1a** the less flexible olefinic moiety presumably interfers with tight packing of the side chains within the chiral nematic helix. Solutions of lactate-derived ethers **2d**, **g**, **i** in host 5CB **13** showed HTPs around 14–15 μm^{-1} irrespective of the substituent R^2 (entries 3–5). For solutions of lactate-derived esters **3** and 5CB **13** HTP values decrease with increase in side chain lengths from C_2 to C_5 (entries 6–8), whereas longer alkyl chains again resulted in increased HTP values as compared to C_5 derivative **3e** (entries 8–10). This observation is in good agreement with results by Tsukamoto, who studied chiral 4-alkyl-4′-alkyloxyazobenzenes systematically and found a decrease of the HTP in the series methoxy—hexyloxy and a slight increase for longer side chains.[100] Other authors reported even–odd effects and an overall increase of the HTP values with increasing chain lengths.[101,102] While the effect of the chain lengths on the HTP values were much more pronounced in solutions of 5CB **13** with **3**, a completely different picture emerged for solutions of hexayne **14** with **3**. Overall, HTP values

Table 1. Yields of compounds **9**–**12**, **2** and **3** according to Scheme 3

	R^2=	**9** (%)	**10** (%)	**3** (%)	**11** (%)	**12** (%)	**2** (%)
a	CH_3	70	80	89			
b	C_2H_5	88	69	99			
c	C_3H_7	34	95	82			
d	C_4H_9	10	—	—	80	62	72
e	C_5H_{11}	26	84	7[a]			
f	C_8H_{17}	16	79	47			
g	$C_{10}H_{21}$	14	99	52	99	67	72
h	Bn	99	95	82	92	98	36
i	MOM	71	—	—	80	42	63

[a] The poor yield is due to tedious chromatographic separation.

Table 2. HTPs of chiral tetraphenylethenes **1**–**3** in nematic host **13** or discotic host **14**[a]

Entry	Host	Dopant	HTP, μm^{-1}	MHTP, $\mu m^{-1} mol^{-1} kg$
1	**13**	**1a**	5.7	5.4
2	**13**	**1b**	10.4	10.0
3	**13**	**2d**	16.5	14.1
4	**13**	**2g**	12.6	15.0
5	**13**	**2i**	16.5	14.1
6	**13**	**3b**	12.8	10.2
7	**13**	**3c**	11.3	9.6
8	**13**	**3e**	8.0	7.7
9	**13**	**3f**	17.3	19.6
10	**13**	**3g**	28.7	35.8
11	**14**	**3b**	2.1	1.7
12	**14**	**3c**	2.2	1.9
13	**14**	**3e**	2.3	2.2
14	**14**	**3f**	2.9	3.3
15	**14**	**3g**	2.5	3.1

[a] HTP values were obtained from the fingerprint texture, temperature: T_{IN}^*, 10 K.

were much smaller as compared to solutions with host **13** (entries 11–15) and a slight increase was observed with increase in chain lengths (up to C_8), followed by a decrease for longer alkoxy chains (entry 15).

With respect to 5CB host **13** it should be noted that Lemieux found for axially chiral 1,11-dimethyl-5,7-dihydrodibenzo [c,e]thiepines that the helical topography of the dopant is important in promoting chirality in the N* phase.[66] Nevertheless, it is somewhat surprising that the C_4-symmetrical propeller-shaped tetraphenylethenes **1**–**3** interact much stronger with the rod-shaped 5CB host **13**, as compared to the C_6-symmetrical propeller-shaped hexayne host **14**.

Until now, we were not able to determine the handedness of the helices experimentally.[48–57] However, if one considers the empirical rule established by Gray,[103] the twist sense of the helix might be assigned as left-handed for all compounds **1**–**3** based on the absolute configuration of the chiral centre and the distance of the chiral centre from the core unit.[104,105] However, as was shown by Heppke,[92] such an assignment has to be handled with care.

CONCLUSIONS

The HTP of novel chiral tetraphenylethenes with citronellyl ethers (**1a**, **b**), with lactate-derived ethers (**2d**, **g**, **i**) and the corresponding esters (**3b**, **c**, **e**–**g**) in solution with achiral hosts 5CB **13** and hexayne **14** was studied. In solutions of citronellyl ethers **1** in nematic host **13** the side chain had a considerable effect on the HTP value. HTPs of lactate-derived ethers **2** in 5CB **13** were larger than those for **1** in **13**, but changed only slightly with the substituent in contrast to solutions of lactate-derived esters **3** in **13**, where a strong substituent effect was observed. In contrast, HTP values of **3** in discotic host **14** were one order of magnitude smaller than those in host **13** and did not show any pronounced substituent effect. Thus, the chirality transfer from a propeller-shaped dopant to a flat rod-shaped host seems to be more efficient as compared to a propeller-shaped host. One might expect that the difference in the twist elastic constants are the reason for the different behaviour of hosts 5CB **13** and hexayne **14** with regard to the same dopant **3**. However, as shown by Glushchenko[106] and Krüerke,[107] the twist elastic constants of **13** and **14** are in the same range. Further works to understand this disc to rod *versus* disc-to-disc interaction is currently in progress.

Acknowledgements

Generous financial support by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden-Württemberg and the Bundesministerium für Bildung und Forschung is gratefully acknowledged.

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