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Thioindigo-containing organosiloxane liquid crystals with electroclinic properties

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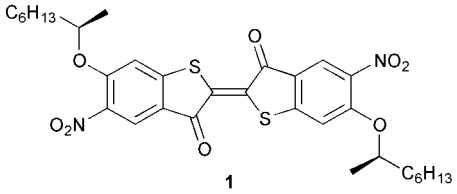
Two mesogenic thioindigo derivatives containing oligomeric di- and trisiloxane end-groups were synthesized in optically pure form. These materials form enantiotropic SmA* liquid crystal phases over temperature ranges of 120–143 °C and 110–146 °C, respectively, and exhibit electroclinic switching. The electroclinic coefficient for the trisiloxane derivative at $T - T_C = 8$ K is $0.4^\circ\ V^{-1}\ \mu m^{-1}$. The formation of a SmA* phase by these thioindigo derivatives is due primarily to the tendency of siloxane and paraffinic moieties to micro-segregate into distinct sublayers within a lamellar structure. To the best of our knowledge, these are the first two examples of thioindigo-containing liquid crystals to be reported in the literature.

Introduction

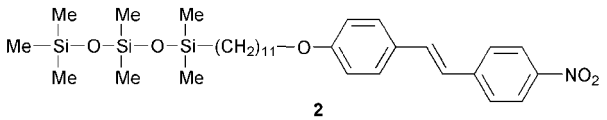
Over the last decade, a number of studies have shown that photochromic compounds can effectively photomodulate the chiral bulk properties of a liquid crystal phase.[1] For example, the *trans–cis* photoisomerization of an azobenzene dopant can modulate the spontaneous polarization (P_S) of a ferroelectric SmC* liquid crystal by destabilizing the SmC* phase, and trigger the switching of a ferroelectric liquid crystal spatial light modulator (FLC-SLM).[2–5] Chiral thioindigo dopants have also been shown to modulate P_S reversibly by *trans–cis* photoisomerization—without concomitant destabilization of the SmC* phase—as a result of the corresponding change in transverse dipole moment of the thioindigo core.[6] This transverse dipole photomodulation effect was used to trigger the electro-optical switching of a multi-component FLC-SLM prototype *via* a sign inversion of P_S.[7] However, a severe limitation of thioindigo dopant photoisomerization as a general approach to trigger the switching of FLC-SLM devices is the low solubility of thioindigo dopants in organic liquid crystal hosts.[8] For example, the symmetrical thioindigo dopant **1** has a solubility limit of only 3 mol% in a conventional phenyl benzoate SmC host.



1

In principle, the compatibilization of an insoluble dye such as thioindigo with a liquid crystal host can be achieved by introducing the dye molecule as a side-chain in a liquid crystalline copolymer.[9] In such cases, compatibility is attained at the expense of electrooptic switching performance since polymeric LC materials tend to have higher viscosities and are more difficult to align than low molecular weight LC materials. A compromise solution to this problem was proposed by Coles and co-workers using low molecular weight LC materials terminated with short siloxane oligomers.[10–12] The addition of oligomeric siloxane end-groups to mesomorphic materials has been shown to promote lamellar organization and the formation of smectic phases due to the tendency of siloxane and paraffinic moieties to micro-segregate into distinct sublayers within a lamellar structure.[13–21] The formation of this so-called *virtual siloxane backbone*[20] confers to low molecular weight organosiloxane LC materials some of the mechanical stability of side-chain polysiloxane materials without significantly compromising the electro-optical switching performance and ease of alignment of low molecular weight liquid crystals.

Hence, dye molecules bearing a siloxane end-group can be doped into an organosiloxane liquid crystal host in high concentrations by behaving like a pendant group on a side-chain polysiloxane liquid crystal. One advantage of this approach over conventional side-chain polysiloxanes is that the dye molecule is "grafted" on the virtual backbone simply by mixing the organosiloxane materials. For example, Coles showed that addition of a siloxane-terminated side-chain to a non-mesogenic dichroic dye such as 4-hydroxy-4′-nitrostilbene produces a liquid crystalline material (**2**) with SmA and SmC phases which forms homogeneous mixtures with organosiloxane LC hosts over a wide range of concentrations.[10,11] In order to improve the solubility of our thioindigo dopants in SmC liquid crystal hosts, we followed a similar approach and designed a new series of siloxane-terminated chiral thioindigo dopants **3** and **4**. Remarkably, these materials form enantiotropic SmA* phases and exhibit electroclinic switching. To the best of our knowledge, these are the first thioindigo-containing liquid crystals to be reported in the literature.



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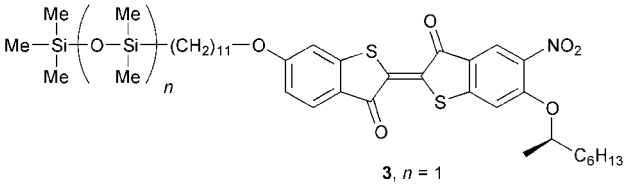
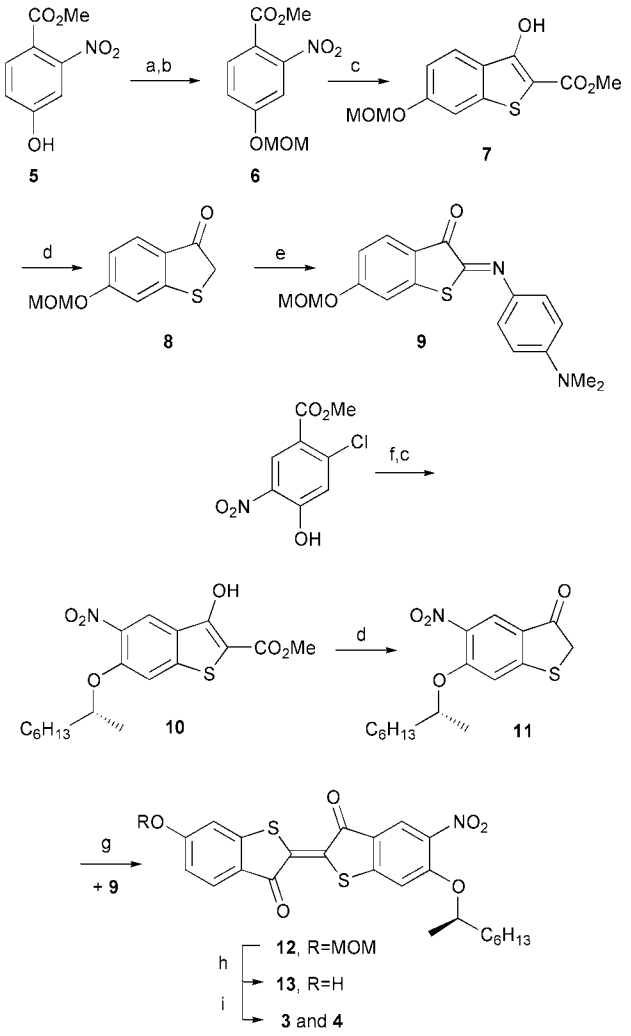


3, $n = 1$
4, $n = 2$



Scheme 1 *Reagents and conditions*: a, NaH, THF, 25 °C; b, MOMCl, THF, 25 °C; c, methyl thioglycolate, LiOH, DMF, 25 °C; d, 15% KOH in 1 : 1 EtOH–H_2O, reflux; e, *N*,*N*-dimethyl-4-nitrosoaniline, Na_2CO_3, H_2O, 75 °C; f, (*S*)-octan-2-ol, DIAD, Ph_3P, CH_2Cl_2, 25 °C; g, piperidine, chlorobenzene, 85 °C; h, HCl, AcOH, 85 °C; i, di- or trisiloxanylundecanol, DIAD, Ph_3P, THF, 25 °C.

Results and discussion

Synthesis

The synthesis of symmetrical thioindigo dopants such as **1** is normally achieved by oxidative dimerization of a benzothiophenone precursor. However, to obtain unsymmetrical thioindigo derivatives such as **3** and **4**, a different approach was required (Scheme 1). The synthesis developed for these systems begins with protection of the known methyl 4-hydroxy-2-nitrobenzoate (**5**)[22] as a methoxymethyl (MOM) ether (**6**), which makes possible the solubilization and purification of the subsequent intermediates. Reaction of **6** with methyl thioglycolate under basic conditions gives the enol ester **7**,[23] which is then hydrolyzed and decarboxylated to the benzothiophenone **8**. This intermediate, which oxidatively dimerizes upon prolonged exposure to air, is then rapidly converted to the stable Schiff base **9** (34% overall yield from **5**) by treatment with *N*,*N*-dimethyl-4-nitrosoaniline under basic conditions.[24] The other half of the thioindigo core bearing the chiral oct-2-yloxy side chain is obtained by a similar route from the known enol ester **10**,[6] which is hydrolyzed and decarboxylated to the chiral benzothiophenone **11** in 97% yield. Reaction of **11** with the Schiff base **9** in chlorobenzene in the presence of piperidine gives the unsymmetrical thioindigo **12** in 44% yield.[25] Final deprotection and alkylation with either 11-(1,1,1,3,3-pentamethyldisiloxanyl)undecanol or 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecanol *via* a Mitsunobu reaction gives the desired organosiloxane thioindigo derivatives **3** and **4** in 74% and 30% yields, respectively. This approach is different from that used in the synthesis of other organosiloxane mesogens, which normally consists of adding the siloxane end-group to the mesogen in the last step *via* Cp_2PtCl_2-catalyzed hydrosilation of a terminally unsaturated side-chain.[16–19] We first tested this approach with a symmetrical thioindigo bearing terminal undecenyloxy side-chains, but the hydrosilation reaction produced a complex mixture of products.

Mesophase characterization

Both disiloxane and trisiloxane thioindigo derivatives **3** and **4** form enantiotropic SmA* phases (Table 1). The mesophases were characterized by polarized microscopy, DSC and X-ray powder diffraction. On cooling from the isotropic liquid phase, the mesophase grows from the typical "batonnêt" structures into focal conic domains, as shown in Fig. 1. Both focal conic and homeotropic domains, which are characteristic of the SmA* phase, were observed by polarized microscopy.[26] The racemic form of the trisiloxane derivative also shows the same homeotropic domains, which rules out the possibility of a SmC* phase (the pseudo-homeotropic domain of a SmC* phase would appear as a Schlieren texture in the racemic form). The enthalpies of transition measured by DSC on heating and cooling are also consistent with SmA*–I and crystal–SmA* phase transitions (Table 1). The temperature range of the SmA* phase increases with the number of siloxanyl units, with a corresponding decrease in the Cr–SmA* phase transition temperature, which is consistent with previous observations made for other organosiloxane SmA* materials.[16] Analysis by variable temperature X-ray powder diffraction confirmed the smectic phase assignments. In each case, a single sharp Bragg peak was observed at small angles, with a broad diffuse band at wide angles. The Bragg angle remained constant over the temperature range of each SmA* phase, and the values ($2\theta = 2.5°$ for **3** and 2.4° for **4**) correspond to smectic layer spacings d of 35.3 Å and 36.8 Å, respectively. These values are shorter than the corresponding molecular lengths of **3** (41.7 Å) and **4** (44.1 Å) according to molecular mechanics calculations (MM2 force field), which suggests that the siloxane sublayers formed in the SmA* lamellar structures of **3** and **4** are interdigitated.[27,28]

Electrooptical properties

The coupling of an applied electric field to the transverse dipole moments of chiral mesogens in the SmA* phase causes an induced tilt of the director known as the electroclinic effect.[29,30] For small induced tilt angles θ, the relationship between θ and the applied field strength E is predicted to be linear according

Table 1 Transition temperatures and enthalpies of transitions for compounds **3** and **4**[a]

Compound	n	Cr–SmA*/°C	ΔH/J g^{-1}	SmA*–I/°C	ΔH/J g^{-1}	I–SmA*/°C	ΔH/J g^{-1}	SmA*–Cr/°C	ΔH/J g^{-1}
3	1	120	24.5	143	3.1	141	−18.0	91	−3.1
4	2	110	21.3	146	3.2	143	−15.9	84	−3.1

[a]Measured by differential scanning calorimetry from second heating and cooling cycles.

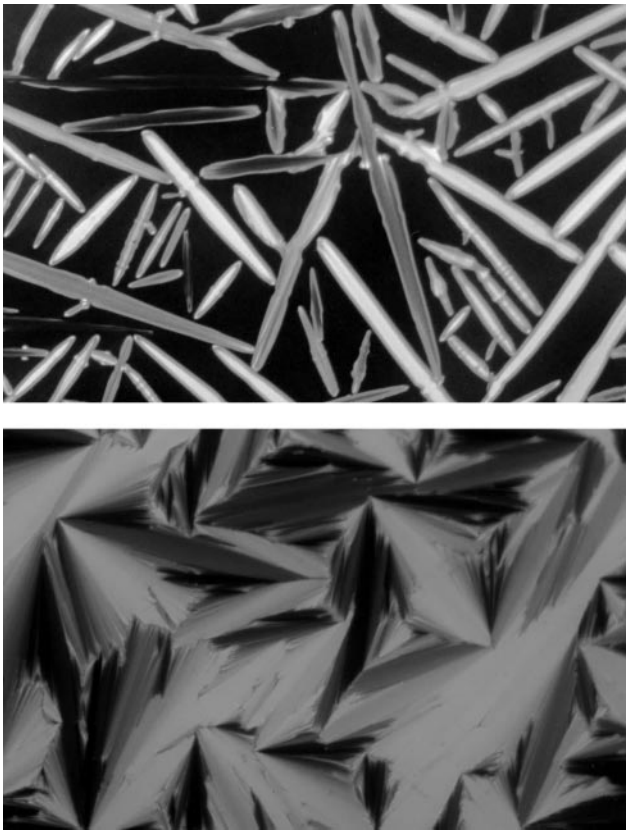


Fig. 1 Textures of compound **4** observed by polarized microscopy on cooling from isotropic liquid: 139 °C, batonnêt texture, I–SmA* phase transition (top); 120 °C, focal-conic texture, SmA* phase (bottom).

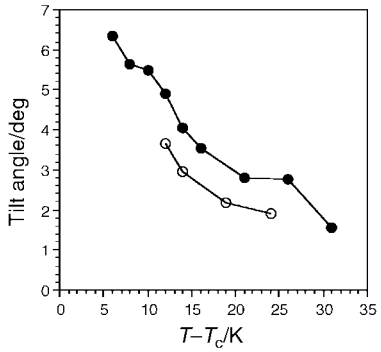


Fig. 2 Electroclinic tilt angle θ as a function of reduced temperature $T - T_C$ on cooling from isotropic liquid for compounds **3** (open circles) and **4** (filled circles) in the SmA* phase under an applied field strength E of 10 V μm^{-1}.

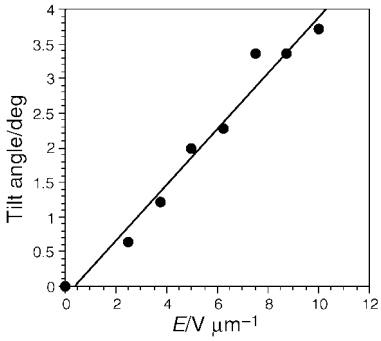


Fig. 3 Electroclinic tilt angle θ as a function of applied field strength E for compound **4** in the SmA* phase at $T - T_C = 8$ K.

to eqn. (1), where c is the electroclinic coupling constant, α_o is the first constant in the Landau free-energy expansion and T_C is the SmA*–crystal (or SmA*–SmC*) phase transition temperature.[31] Some organosiloxane SmA* liquid crystals have been reported to exhibit pronounced electroclinic effects, with electroclinic coefficients $d\theta/dE$ in the range of 2–2.5° V^{-1} μm^{-1} at a reduced temperature $T - T_C = 5$ K.[16,32]

$$\theta = \frac{cE}{\alpha_o(T - T_C)} \quad (1)$$

We were unable to obtain thin films (4 μm) with uniform alignment in the SmA* phase for compounds **3** and **4**, although slow cooling of the films while applying an ac field (10 Hz, 5 V μm^{-1}) across the film produced focal conic domains large enough to measure the electroclinic tilt angle by polarized microscopy. In the case of compound **4**, the induced tilt angle θ increases with decreasing reduced temperature at a constant field strength E of 10 V μm^{-1} (Fig. 2), which is characteristic of electroclinic SmA* materials. We were unable to measure θ below $T - T_C = 6$ K due to crystallization of the material promoted by the applied ac field upon further cooling. In the case of compound **3**, this tendency to crystallize upon application of the ac field was more pronounced and limited the measurement of θ to a narrow temperature range of 12 K. The induced tilt angle θ was measured as a function of E for compound **4** at a constant reduced temperature $T - T_C = 8$ K. As shown in Fig. 3, the electroclinic tilt increases linearly with E up to $E = 10$ V μm^{-1}. Above this field strength, electrohydrodynamic distortions of the focal conic domains made tilt measurements by polarized microscopy impossible to achieve. A least-squares fit of the θ *vs.* E plot ($R^2 = 0.972$) gives an electroclinic coefficient $d\theta/dE$ of 0.4 for compound **4**.

Conclusions

Thioindigo and simple derivatives of thioindigo are notorious for their high melting points and lack of solubility in organic solvents.[33] Previous work has shown that thioindigo derivatives with branched alkoxy side-chains (*e.g.*, **1**) have significantly lower melting points and higher solubilities in organic solvents and liquid crystal hosts.[6,34] However, despite possessing all the structural attributes of mesogens, none of these materials form liquid crystal phases. In this study, we have shown for the first time that similar chiral thioindigo derivatives bearing short di- or trisiloxane end-groups form stable enantiotropic SmA* phases, thus clearly demonstrating the unique ability of oligomeric siloxanes to promote the formation of smectic phases *via* the virtual backbone effect. Furthermore, these photochromic materials exhibit electroclinic properties which may be useful in the design of optical switching mechanisms based on photomodulation of the electroclinic tilt. This potential application of organosiloxane thioindigo materials is currently under investigation in our laboratory.

Experimental

General

^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on Bruker AC 200 and Avance 300, 400 and 500 spectrometers in deuterated chloroform or deuterated acetone. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane as internal standard. Low resolution EI and CI mass spectra were recorded on a Fisons VG Quattro triple quadrupole mass spectrometer; peaks being reported as *m*/*z* (% intensity relative to the base peak). High resolution EI mass spectra were

performed by the University of Ottawa Regional Mass Spectrometry Center. Differential scanning calorimetry analyses were performed on a Perkin-Elmer DSC-7 instrument with a scanning rate of 5 K min^{-1}. Texture analyses were performed using a Nikon Eclipse E600 POL polarized microscope fitted with a Linkam LTS 350 hot stage and TMS 93 temperature controller. Measurements of electroclinic tilt were performed as a function of applied voltage in polyimide-coated ITO glass cells with a 4 μm spacing (0.25 cm^2 addressed area) supplied by Displaytech Inc. (Longmont, CO). A partial alignment was achieved by slow cooling (0.1 K min^{-1}) of the organosiloxane materials while applying a 10 Hz, 5 V μm^{-1} ac field across the film fitted on the rotating hot stage of the polarized microscope. The electroclinic tilt was measured by polarized microscopy while applying a 0.1 Hz ac field as half the rotation between two extinction positions corresponding to opposite signs of the applied field. Variable temperature powder X-ray diffraction analyses were performed at the Centre de Recherche en Sciences et Ingénierie des Macromolécules (CERSIM) of Université Laval using a Siemens/Bruker Kristalloflex 760 diffractometer fitted with a Hi-Star bidimensional detector (Cu Kα radiation, $\lambda = 1.5418$ Å). Molecular mechanics calculations were performed using the MM2 force field implemented in Chem 3D Pro, version 4.0. Elemental analyses were performed by MHW Laboratories (Phoenix, AZ). Melting points were determined on a Mel-Temp II melting point apparatus and are uncorrected.

Materials

All reagents and chemicals were obtained from commercial sources and used without further purification unless otherwise noted. *N*,*N*-Dimethylformamide (DMF) was distilled from BaO under reduced pressure and stored over molecular sieves. Methylene chloride (CH_2Cl_2) was freshly distilled from P_2O_5. Tetrahydrofuran (THF) was freshly distilled from Na–benzophenone under nitrogen. Flash chromatography was performed with 40–63 μm (230–400 mesh) silica gel (Silicycle). Thin layer chromatography was performed on silica gel 60 F_{254} plates (EM Science). Methyl 4-hydroxy-2-nitrobenzoate (**5**)[22] and methyl (*R*)-3-hydroxy-5-nitro-6-(oct-2-yloxy)-1-benzothiophene-2-carboxylate (**10**)[6] were prepared according to published procedures and shown to have the expected physical and spectral properties.

11-(1,1,1,3,3-Pentamethyldisiloxanyl)undecanol

Under an Ar atmosphere, a solution of ω-undecenyl alcohol (1.53 g, 8.95 mmol), 1,1,1,3,3-pentamethyldisiloxane (1.63 g, 11 mmol), and dicyclopentadienylplatinum(II) chloride (0.55 mg, 1.4×10^{-3} mmol) in dry THF (20 mL) was stirred in an oil bath at 60 °C for 48 h. The mixture was concentrated to an oil, which was purified by flash chromatography on silica gel (90% hexanes–EtOAc) to give 2.5 g (87%) of 11-(1,1,1,3,3-pentamethyldisiloxanyl)undecanol as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 6 H), 0.06 (s, 9 H), 0.50 (t, $J = 7.6$ Hz, 2 H), 1.20–1.40 (m, 16 H), 1.55 (m, 2 H), 3.62 (t, $J = 6.8$ Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.6, 2.2, 18.7, 23.5, 26.0, 29.67, 29.74, 29.87, 29.90, 29.91, 33.1, 33.7, 63.2; ^{29}Si NMR (79 MHz, $CDCl_3$) δ 6.9, 7.6; MS (CI) *m*/*z* 319 (M + 1, 0.4), 230 (15), 229 (100), 166 (11), 164 (17); Anal. Calcd. for $C_{16}H_{38}O_2Si_2$: C, 60.31; H, 12.02. Found: C, 60.50; H, 11.86%.

11-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)undecanol

Under an Ar atmosphere, a solution of ω-undecenyl alcohol (0.525 g, 3.1 mmol), 1,1,1,3,3,5,5-heptamethyltrisiloxane (1.48 g, 6.74 mmol), and dicyclopentadienylplatinum(II) chloride (13 mg, 3.3×10^{-2} mmol) in dry THF (82 mL) was stirred in an oil bath at 60 °C for 24 h. The mixture was concentrated to an oil, which was purified by flash chromatography on silica gel to give 1.16 g (97%) of 11-(1,1,1,3,3,5,5-heptamethyldisiloxanyl)undecanol as a clear liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 6 H), 0.04 (s, 6 H), 0.07 (s, 9 H), 0.51 (t, $J = 7.6$ Hz, 2 H), 1.20–1.40 (m, 16 H), 1.52 (m, 2 H), 3.62 (t, $J = 6.8$ Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 1.5, 2.1, 18.6, 23.5, 26.1, 29.67, 29.74, 29.86, 29.90, 29.91, 33.1, 33.7, 63.2; ^{29}Si NMR (79 MHz, $CDCl_3$) δ −21.1, 6.9, 7.4; MS (CI) *m*/*z* 393 (M + 1, 29), 303 (35), 257 (11), 243 (23), 230 (13), 229 (71), 227 (11), 223 (33), 222 (22), 221 (100), 207 (20), 205 (10), 193 (10), 177 (11), 165 (26), 163 (12); Anal. Calcd. for $C_{18}H_{44}O_3Si_3$: C, 55.04; H, 11.29. Found: C, 55.16; H, 11.15%.

Methyl 4-(methoxymethyloxy)-2-nitrobenzoate (6)

Under an Ar atmosphere, 1.65 g of 60% NaH dispersed in oil (41.2 mmol) was washed twice with hexanes and suspended in dry THF (15 mL). A solution of **5** (1.54 g, 7.81 mmol) in dry THF (15 mL) was added to the NaH suspension and the mixture was stirred at room temperature for 30 min. A solution of chloromethyl methyl ether (1.8 g, 22.4 mmol) in dry THF (6 mL) was added dropwise and the mixture was stirred at room temperature for 24 h, then quenched by careful addition of sat. aq. NH_4Cl while cooling with an ice bath. The mixture was poured into brine (150 mL) and extracted with ether (2 × 75 mL). The combined extracts were washed with brine (2 × 40 mL), dried ($MgSO_4$) and concentrated to give a brown oil. Purification by flash chromatography on silica gel (70% toluene–EtOAc) gave 1.25 g (66%) of **6** as a brown oil: $R_f = 0.63$ (70% toluene–EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.46 (s, 3 H), 3.86 (s, 3 H), 5.23 (s, 2 H), 7.23 (dd, $J = 2.4$, 8.7 Hz, 1 H), 7.40 (d, $J = 2.4$ Hz, 1 H), 7.75 (d, $J = 8.7$ Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.1, 56.7, 94.8, 111.7, 119.1, 119.5, 132.1, 150.8, 160.2, 165.1; MS (EI) *m*/*z* 241 (M^+, 26), 211 (15), 210 (22), 209 (82), 180 (80), 179 (27), 166 (15), 165 (18), 151 (11), 150 (19), 149 (15), 148 (17), 135 (18), 134 (18), 133 (11), 122 (56), 121 (54), 120 (30), 119 (46), 118 (28), 117 (15), 115 (14), 109 (12), 108 (18), 107 (100), 106 (76), 105 (60), 104 (29), 103 (28); HRMS (EI) Calcd. for $C_{10}H_{11}NO_6$: 241.0586. Found: 241.0586.

Methyl 3-hydroxy-6-(methoxymethyloxy)-1-benzothiophene-2-carboxylate (7)

Under an Ar atmosphere, a mixture of **6** (1.09 g, 4.52 mmol), anhydrous LiOH (450 mg, 18.8 mmol) and methyl thioglycolate (854 mg, 8.04 mmol) in dry DMF (40 mL) was stirred at room temperature for 23 h. The mixture was poured into water (100 mL), acidified to pH = 4 with cold aq. HCl, and cooled with an ice bath. The resulting yellow precipitate was filtered, washed with cold dilute aq. HCl and water, and dried under high vacuum to give 850 mg (70%) of **7** as a tan solid: mp 82–83 °C; $R_f = 0.71$ (70% toluene–EtOAc); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.49 (s, 3 H), 3.92 (s, 3 H), 5.23 (s, 2 H), 7.08 (dd, $J = 2.2$, 9.0 Hz, 1 H), 7.36 (d, $J = 2.0$ Hz, 1 H), 7.81 (d, $J = 8.6$ Hz, 1 H), 10.13 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.3, 56.5, 94.9, 100.2, 108.7, 116.3, 124.2, 125.3, 141.0, 158.8, 159.9, 167.9; MS (EI) *m*/*z* 268 (M^+, 23), 236 (73), 205 (29), 175 (22), 163 (31), 150 (33), 137 (12), 136 (19), 135 (100), 121 (12), 120 (23), 119 (65), 109 (12), 108 (21), 107 (44), 106 (40), 103 (20); HRMS (EI) Calcd. for $C_{12}H_{12}O_5S$: 268.0406. Found: 268.0426.

6-(Methoxymethyloxy)-1-benzothiophen-3(2*H*)-one (8)

A suspension of **7** (862 mg, 3.21 mmol) in a 15% solution of KOH in 1 : 1 EtOH–H_2O (130 mL) was heated to reflux with stirring for 6 h. After cooling in an ice bath, cold 8% aq. HCl (100 mL) was added and the mixture was extracted with EtOAc (2 × 100 mL). The combined extracts were washed with brine, dried ($MgSO_4$) and concentrated to give 660 mg (98%) of **8** as a

thick orange oil which was used in the next step without further purification: $R_f = 0.64$ (70% toluene–EtOAc); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.47 (s, 3 H), 3.77 (s, 2 H), 5.22 (s, 2 H), 6.83 (dd, $J = 2.2$, 8.6 Hz, 1 H), 7.03 (d, $J = 2.0$ Hz, 1 H), 7.69 (d, $J = 8.6$ Hz, 1 H); MS (EI) *m*/*z* 210 (M^+, 44), 196 (60), 165 (13), 152 (22), 149 (10), 137 (22), 135 (12), 123 (14), 121 (15), 107 (11), 95 (27), 92 (16), 81 (10), 77 (22), 75 (69), 71 (12), 69 (59), 65 (18), 63 (100).

6-(Methoxymethyloxy)-2-[4-(*N*,*N*-dimethylamino)phenylimino]-1-benzothiophen-3(2*H*)-one (9)

A solution of Na_2CO_3 (666 mg, 6.29 mmol) in water (20 mL) was combined with **8** (660 mg, 3.14 mmol) and the mixture was stirred in an oil bath at 70–75 °C. A solution of *N*,*N*-dimethyl-4-nitrosoaniline (546 mg, 3.64 mmol) in water (30 mL) was then added and the heating continued for 3 h. The mixture was filtered hot and the residue was washed thoroughly with water and dissolved in EtOAc–acetone. The organic solution was dried ($MgSO_4$) and concentrated to give 820 mg (76%) of **9** as a dark purple solid: mp 139–141 °C; $R_f = 0.47$ (70% toluene–EtOAc); ^{1}H NMR (300 MHz, acetone-d_6) δ 3.07 (s, 6 H), 3.49 (s, 3 H), 5.38 (s, 2 H), 6.88 (m, 2 H), 7.04 (dd, $J = 2.1$, 8.4 Hz, 1 H), 7.27 (d, $J = 2.1$ Hz, 1 H), 7.41 (m, 2 H), 7.82 (d, $J = 8.7$ Hz, 1 H); ^{13}C NMR (100 MHz, acetone-d_6) δ 40.3, 56.6, 95.1, 112.1, 113.0, 116.0, 123.2, 126.7, 129.4, 136.7, 147.4, 151.7, 164.6, 184.1; MS (EI) *m*/*z* 342 (M^+, 9), 178 (11), 177 (22), 146 (34), 145 (100), 130 (11), 129 (31), 119 (15), 107 (22), 103 (22), 102 (23), 95 (16), 78 (72), 75 (53), 69 (24), 63 (99). HRMS (EI) Calcd. for $C_{18}H_{18}N_2O_3S$: 342.1038. Found: 342.1045.

(*R*)-5-Nitro-6-(oct-2-yloxy)-1-benzothiophen-3(2*H*)-one (11)

A suspension of **10** (470 mg, 1.23 mmol) in a 15% solution of KOH in 1 : 1 EtOH–H_2O (50 mL) was heated to reflux with stirring for 11 h. After cooling in an ice bath, the solution was poured into dilute aq. HCl (100 mL) and extracted with EtOAc. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated to give 388 mg (97%) of **11** as a thick purple oil which was used in the next reaction without further purification: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.85 (t, $J = 6.3$ Hz, 3 H), 1.10–1.90 (m, 10 H), 1.38 (d, $J = 6.0$ Hz, 3 H), 3.85 (s, 2 H), 4.56 (m, 1 H), 6.95 (s, 1 H), 8.18 (s, 1 H).

(*R*)-6-(Methoxymethyloxy)-5′-nitro-6′-(oct-2-yloxy)[$\Delta^{2,2'}$-bi-1-benzothiophene]-3(2*H*),3′(2′*H*)-dione (12)

Under an Ar atmosphere, a solution of **11** (388 mg, 1.20 mmol) in chlorobenzene (15 mL) was added dropwise over 45 min to a stirred solution of **9** (180 mg, 0.53 mmol) in chlorobenzene (10 mL) kept at 85 °C. The mixture was stirred at 85 °C for 80 min, then piperidine (1 mL) was added and the heating was continued for 1 h. After cooling, the mixture was concentrated to a dark purple residue which was purified by flash chromatography on silica gel (90% toluene–EtOAc) to give 122 mg (44% from **9**) of **12** as a dark purple solid: mp = 155–157 °C; $R_f = 0.71$ (70% toluene–EtOAc); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, $J = 6.8$ Hz, 3 H), 1.20–1.90 (m, 10 H), 1.42 (d, $J = 6.2$ Hz, 3 H), 3.50 (s, 3 H), 4.65 (m, 1 H), 5.27 (s, 2 H), 6.95 (dd, $J = 2.2$, 8.8 Hz, 1 H), 7.10 (s, 1 H), 7.15 (d, $J = 2.2$ Hz, 1 H), 7.85 (d, $J = 8.8$ Hz, 1 H), 8.35 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 19.7, 22.9, 25.4, 29.4, 32.0, 36.3, 57.0, 78.1, 94.7, 109.2, 111.1, 115.6, 121.0, 123.2, 124.6, 128.9, 131.4, 135.2, 139.6, 151.4, 155.3, 157.5, 164.4, 187.3, 188.4; MS (CI) *m*/*z* 530 (M + 1, 12), 500 (21), 418 (14), 294 (24), 225 (19), 223 (10), 212 (15), 211 (100), 182 (21), 181 (39), 179 (11), 167 (74), 165 (13), 130 (14), 129 (40), 122 (11), 113 (11), 112 (16), 111 (16), 110 (23). HRMS (EI) Calcd. for $C_{26}H_{27}NO_7S_2$: 529.1229. Found: 529.1223.

(*R*)-6-Hydroxy-5′-nitro-6′-(oct-2-yloxy)[$\Delta^{2,2'}$-bi-1-benzothiophene]-3(2*H*),3′(2′*H*)-dione (13)

To a solution of **12** (122 mg, 0.23 mmol) in AcOH (20 mL) were added 3 drops of conc. HCl. The solution was heated at 85 °C with stirring for 15 min, and then poured into water (200 mL) and extracted with EtOAc (2 × 75 mL). The combined extracts were washed with brine (2 ×), dried ($MgSO_4$) and concentrated to a red solid. Purification by flash chromatography on silica gel (70% toluene–EtOAc) gave 93 mg (84%) of **13** as a dark red solid: mp 250–252 °C; $R_f = 0.52$ (70% toluene–EtOAc); ^{1}H NMR (200 MHz, acetone-d_6) δ 0.88 (t, $J = 6.4$ Hz, 3 H), 1.20–1.90 (m, 10 H), 1.45 (d, $J = 6.2$ Hz, 3 H), 2.98 (s, 1 H), 4.94 (m, 1 H), 6.85 (dd, $J = 2.1$, 8.5 Hz, 1 H), 7.09 (d, $J = 2.2$ Hz, 1 H), 7.72 (s, 1 H), 7.74 (d, $J = 8.4$ Hz, 1 H), 8.23 (s, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ 13.7, 19.0, 22.6, 25.1, 29.2, 31.9, 36.1, 77.8, 110.3, 110.8, 115.2, 120.9, 121.4, 123.3, 128.9, 130.9, 134.8, 139.8, 151.3, 155.1, 157.1, 165.6, 186.9, 187.4; MS (CI) *m*/*z* 486 (M + 1, 29), 456 (36), 374 (60), 344 (11), 294 (13), 183 (14), 181 (18), 180 (15), 167 (100), 130 (28), 129 (58), 127 (13), 117 (27), 115 (13), 113 (15), 112 (24), 111 (30), 109 (11); HRMS (EI) Calcd. for $C_{24}H_{23}NO_6S_2$: 485.0967. Found: 485.0944.

(*R*)-6-[11-(1,1,1,3,3-Pentamethyldisiloxanyl)undecyloxy]-5′-nitro-6′-(oct-2-yloxy)[$\Delta^{2,2'}$-bi-1-benzothiophene]-3(2*H*),3′(2′*H*)-dione (3)

Under an Ar atmosphere, diisopropyl azodicarboxylate (141 mg, 0.69 mmol) was added dropwise to a stirred solution of **13** (79 mg, 0.16 mmol), triphenylphosphine (131 mg, 0.50 mmol), and 11-(1,1,1,3,3-pentamethyldisiloxanyl)undecanol (78 mg, 0.24 mmol) in dry THF (20 mL). The mixture was stirred at room temperature for 1 h, and then concentrated to a red solid. Purification by flash chromatography on silica gel (toluene) gave 111 mg (88%) of **3** as a red solid, which was further purified by recrystallization from EtOH after filtration through a 0.45 μm PTFE filter: $R_f = 0.63$ (toluene); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.01 (s, 6 H), 0.03 (s, 9 H), 0.48 (t, $J = 7.1$ Hz, 2 H), 0.86 (t, $J = 6.8$ Hz, 3 H), 1.20–1.90 (m, 28 H), 1.41 (d, $J = 6.3$ Hz, 3 H), 3.99 (t, $J = 6.5$ Hz, 2 H), 4.61 (m, 1 H), 6.71 (dd, $J = 2.0$, 8.6 Hz, 1 H), 6.83 (d, $J = 1.8$ Hz, 1 H), 7.03 (s, 1 H), 7.69 (d, $J = 8.7$ Hz, 1 H), 8.22 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.7, 2.3, 14.4, 18.7, 19.6, 22.9, 23.6, 25.4, 26.2, 29.3, 29.4, 29.66, 29.69, 29.87, 29.89, 29.94, 32.0, 33.7, 36.3, 69.4, 78.1, 109.0, 109.1, 114.6, 121.0, 122.1, 124.4, 128.7, 131.0, 135.3, 139.5, 151.5, 155.3, 157.4, 166.4, 187.0, 187.9; Anal. Calcd. for $C_{40}H_{59}NO_7S_2Si_2$: C, 61.11; H, 7.56; N, 1.78; S, 8.16. Found: C, 61.37; H, 7.35; N, 1.79; S, 7.99.

(*R*)-6-[11-(1,1,1,3,3,5,5-Heptamethyltrisiloxanyl)undecyloxy]-5′-nitro-6′-(oct-2-yloxy)[$\Delta^{2,2'}$-bi-1-benzothiophene]-3(2*H*),3′(2′*H*)-dione (4)

Under an Ar atmosphere, diisopropyl azodicarboxylate (70 mg, 0.35 mmol) was added dropwise to a stirred solution of **13** (65 mg, 0.13 mmol), triphenylphosphine (77 mg, 0.29 mmol), and 11-(1,1,1,3,3,5,5-heptamethyltrisiloxanyl)undecanol (98 mg, 0.25 mmol) in dry THF (22 mL). The mixture was stirred at room temperature for 1.25 h, and then concentrated to a red solid. Purification by flash chromatography on silica gel (toluene) gave 39 mg (34%) of **4** as a red solid, which was further purified by recrystallization from EtOH after filtration through a 0.45 μm PTFE filter: $R_f = 0.63$ (toluene); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.00 (s, 6 H), 0.04 (s, 6 H), 0.06 (s, 9 H), 0.51 (t, $J = 7.4$ Hz, 2 H), 0.87 (t, $J = 6.8$ Hz, 3 H), 1.10–1.90 (m, 28 H), 1.42 (d, $J = 6.0$ Hz, 3 H), 4.04 (t, $J = 6.3$ Hz, 2 H), 4.64 (m, 1 H), 6.78 (dd, $J = 1.8$, 8.6 Hz, 1 H), 6.91 (d, $J = 2.0$ Hz, 1 H), 7.08 (s, 1 H), 7.79 (d, $J = 8.4$ Hz, 1 H), 8.31 (s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 1.6, 2.1, 14.4, 18.6, 19.7, 22.9, 23.0, 23.5, 25.4, 26.2, 29.2, 29.4, 29.6, 29.8, 29.9, 32.0, 32.2, 33.8, 36.3, 69.4, 78.1, 109.11, 109.14, 114.7, 121.0,

122.2, 124.5, 128.9, 131.1, 135.5, 139.6, 151.6, 155.4, 157.5, 166.5, 187.3, 188.1; Anal. Calcd. for $C_{42}H_{65}NO_8S_2Si_3$: C, 58.63; H, 7.61; N, 1.63; S, 7.45. Found: C, 58.69; H, 7.46; N, 1.68; S, 7.31.

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References

1 For a recent review, see: B. L. Feringa, R. A. van Delden, N. Koumura and E. M. Geerstsema, *Chem. Rev.*, 2000, **100**, 1789.
2 T. Ikeda and A. Kanazawa, *Bull. Chem. Soc. Jpn.*, 2000, **73**, 1715.
3 L. M. Blinov, M. V. Kozlovsky, K. Nakayama, M. Ozaki and K. Yoshino, *Jpn. J. Appl. Phys.*, 1996, **35**, 5405.
4 T. Oge and R. Zentel, *Macromol. Chem. Phys.*, 1996, **197**, 1805.
5 H. G. Walton, H. J. Coles, D. Guillon and G. Poeti, *Liq. Cryst.*, 1994, **17**, 333.
6 L. Dinescu, K. E. Maly and R. P. Lemieux, *J. Mater. Chem.*, 1999, **9**, 1679.
7 L. Dinescu and R. P. Lemieux, *Adv. Mater.*, 1999, **11**, 42.
8 K. E. Maly, G. Wu and R. P. Lemieux, *Liq. Cryst.*, 2001, **28**, 457.
9 J.-C. Dubois, P. Le Barny, M. Mauzac and C. Noel, in *Handbook of Liquid Crystals*, ed. J. G. D. Demus, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, Vol. 3, pp. 207–275.
10 D. E. Shoosmith, A. Remnant, S. P. Perkins and H. J. Coles, *Ferroelectrics*, 2000, **243**, 75.
11 D. Shoosmith, C. Carboni, S. Perkins, S. Meyer and H. J. Coles, *Mol. Cryst. Liq. Cryst.*, 1999, **331**, 181.
12 J. Newton, H. Walton, H. Coles and P. Hodge, *Mol. Cryst. Liq. Cryst.*, 1995, **260**, 107.
13 H. J. Coles, S. Meyer, P. Lehmann, R. Deschenaux and I. Jauslin, *J. Mater. Chem.*, 1999, **9**, 1085.
14 W. K. Robinson, C. Carboni, P. Kloess, S. P. Perkins and H. J. Coles, *Liq. Cryst.*, 1998, **25**, 301.
15 E. Corsellis, D. Guillon, P. Kloess and H. Coles, *Liq. Cryst.*, 1997, **23**, 235.
16 J. Naciri, J. Ruth, G. Crawford, R. Shashidhar and B. R. Ratna, *Chem. Mater.*, 1995, **7**, 1397.
17 H. Poths, E. Wischerhoff, R. Zentel, A. Schönfeld, G. Henn and F. Kremer, *Liq. Cryst.*, 1995, **18**, 811.
18 J. Newton, H. Coles, P. Hodge and J. Hannington, *J. Mater. Chem.*, 1994, **4**, 869.
19 K. Sunohara, K. Takatoh and M. Sakamoto, *Liq. Cryst.*, 1993, **13**, 283.
20 H. J. Coles, H. Owen, J. Newton and P. Hodge, *Liq. Cryst.*, 1993, **15**, 739.
21 For a review of micro-segregation in liquid crystals, see: C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485.
22 J. M. L. Stephen, I. M. Tonkin and J. Walker, *J. Chem. Soc.*, 1947, 1035.
23 J. R. Beck, *J. Org. Chem.*, 1973, **38**, 4086.
24 N. S. Dokunikhin and Y. E. Gerasimenko, *J. Gen. Chem. USSR (Engl. Transl.)*, 1960, **30**, 1253.
25 H. Wakemoto and S. Ishihara, *Eur. Pat. Appl.* EP 199,111,29, 1986.
26 G. W. Gray and J. W. G. Goodby, *Smectic Liquid Crystals*, Leonard Hill, London, 1984.
27 G. H. Mehl and J. W. Goodby, *Chem. Ber.*, 1996, **129**, 521.
28 D. R. Medeiros, M. A. Hale, R. J. P. Hung, J. K. Leitko and C. G. Willson, *J. Mater. Chem.*, 1999, **9**, 1453.
29 S. Garoff and R. B. Meyer, *Phys. Rev. Lett.*, 1977, **38**, 848.
30 S. Garoff and R. B. Meyer, *Phys. Rev. A*, 1979, **19**, 338.
31 I. Abdulhalim and G. Moddel, *Liq. Cryst.*, 1991, **9**, 493.
32 M. Redmond, H. Coles, E. Wischerhoff and R. Zentel, *Ferroelectrics*, 1993, **148**, 323.
33 G. M. Wyman and W. R. Brode, *J. Am. Chem. Soc.*, 1951, **73**, 1487.
34 L. Dinescu and R. P. Lemieux, *Liq. Cryst.*, 1996, **20**, 741.