JOURNAL OF Materials CHEMISTRY

Design of photonic liquid crystal materials: synthesis and evaluation of new chiral thioindigo dopants designed to photomodulate the spontaneous polarization of ferroelectric liquid crystals†

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Received 16th April 1999, Accepted 8th June 1999

Irradiation of a ferroelectric S_C* liquid crystal phase induced by the photochromic dopants (*R,R*)-6,6′-bis(2-octyloxy)-5,5′-dinitrothioindigo and (*R,R*)-5,5′-dichloro-6,6′-bis(2-octyloxy)thioindigo at $\lambda = 514$ and 532 nm, respectively, causes an increase in spontaneous polarization (P_S) by a factor ranging from 1.4 to 4.0. This increase in P_S is achieved without concomitant destabilization of the S_C* phase, and is consistent with an increase in transverse dipole moment of the thioindigo core as a result of *trans–cis* photoisomerization. The contribution of the thioindigo core towards P_S is achieved through stereo-polar coupling with the chiral side-chains, which is enhanced by the presence of the nitro and chloro substituents.

Introduction

A ferroelectric smectic C* (S_C*) liquid crystal phase suitable for spatial light modulator (SLM) applications is generally obtained by doping a single chiral component (dopant) into an achiral smectic C (S_C) liquid crystal mixture formulated to optimize parameters such as azimuthal viscosity, tilt angle and temperature range.[1] On the time average, the symmetry elements of an achiral S_C phase include a C_2 axis normal to the tilt plane (defined by the director ***n*** and layer normal ***z***) and a reflection plane of symmetry σ congruent with the tilt plane, as shown in Fig. 1. The presence of a chiral dopant breaks the reflection symmetry of the S_C phase and results in a polar ordering of transverse dipoles along the C_2 axis, which is now a *polar* axis, thus resulting in a net spontaneous polarization (P_S).[2]

According to phenomenological theories, the spontaneous polarization and tilt angle (θ) of a chiral S_C* phase are related by eqn. (1) to the reduced polarization P_o, which is intrinsic to the chiral component of the S_C* phase at a fixed temperature difference below the S_C* phase transition temperature ($T - T_C$).[1] The propensity of a chiral dopant to induce a spontaneous polarization can be expressed as the polarization power δ_p according to eqn. (2), where x_d is the dopant mole fraction.[3] The magnitude of δ_p depends in large part on the degree of steric coupling between the chiral center and the polar functional group(s) contributing to a dipole moment transverse to the molecular long axis (stereo-polar coupling).[4]

$$P_o = P_S/\sin\theta \quad (1)$$

$$\delta_p = \left(\frac{dP_o(x_d)}{dx_d}\right)_{x_d \to 0} \quad (2)$$

By virtue of its spontaneous polarization, a surface-stabilized ferroelectric liquid crystal (SSFLC) can be switched between two degenerate states corresponding to opposite tilt orientations using an applied electric field, thus producing a change in birefringence when the SSFLC film is placed between crossed polarizers.[5] Considerable efforts have been made over the past decade to develop photonic analogues to the SSFLC-SLM, which can be triggered by the action of light, because of their potential use in optical computing, dynamic holography, telecommunications and optical data storage.[6] Most of the optical switching mechanisms developed for optically addressed SSFLC spatial light modulator (SSFLC-OASLM) devices have been extrinsic in nature, using a photoconductive or photodiode layer to trigger the switching of an underlying SSFLC film upon illumination. Other studies have focused on an alternative *intrinsic* approach to optical switching of SSFLC-OASLM devices which is based on the photomodulation of P_S using a photochromic dopant.[7–15]

Several groups have shown that the spontaneous polarization of a SSFLC can be photomodulated in the near-UV range *via* the reversible *trans–cis* photoisomerization of chiral azobenzene dopants and azobenzene-containing side-chain FLC copolymers.[7–10,12–15] The origin of this modulation is thought to be a disruption in the order of the S_C* phase caused by the photoinduced change in shape of the azobenzene dopant from rod-like (*trans*) to bent (*cis*). This so-called photomechanical effect causes a decrease in P_S and a downward shift of the S_C*–S_A* or S_C*–N* phase transition temperature, producing in some cases an isothermal phase transition to a non-ferroelectric mesophase.[9,10,12,14] In this paper, we describe a new approach to photomodulate P_S in the visible range, without concomitant destabilization of the S_C* phase. This approach is based on the *trans–cis* photoisomerization of chiral thioindigo dopants which can maintain a rod-like shape in both isomeric forms (Fig. 2).[16]

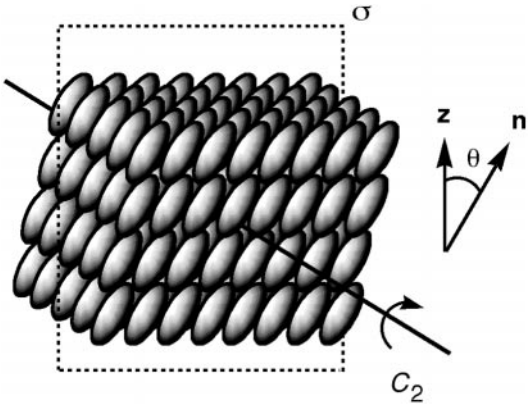


Fig. 1 Schematic representation of the achiral smectic C liquid crystal phase. The vectors ***z*** and ***n*** are in the plane of the page.

†IUPAC name for thioindigo: 2,2′,3,3′-tetrahydro[$\Delta^{2,2'}$-bi-1-benzothiophene]-3,3′-dione.

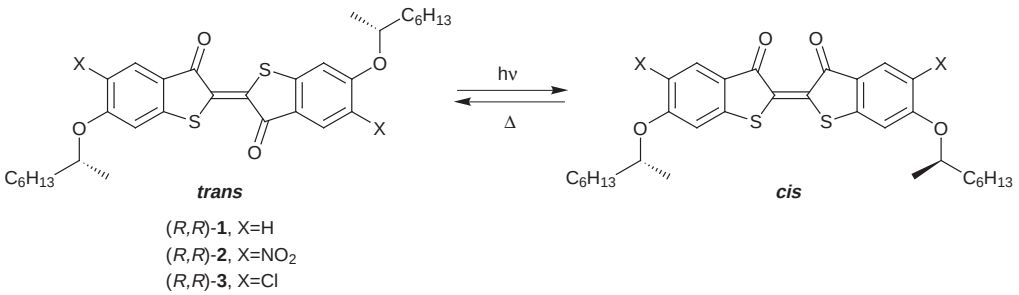


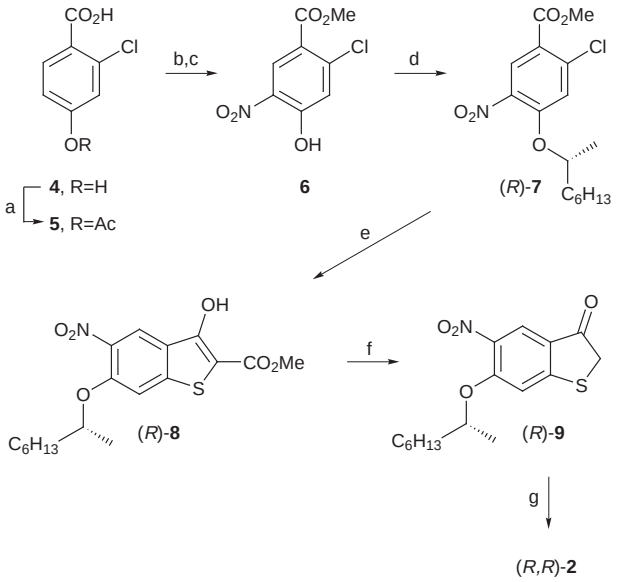
Fig. 2 Photoisomerization of chiral thioindigo dopants.

In the *trans*-form, the thioindigo chromophore is non-polar; in the *cis*-form, it possesses a transverse dipole moment which can contribute to P_S provided that some degree of stereo-polar coupling exists between the chromophore and a chiral structural unit. Previous work has shown that *trans–cis* photoisomerization of the thioindigo dopant (*R,R*)-**1** in an achiral S_C liquid crystal host has a negligible effect on the spontaneous polarization of the induced S_C* phase due to a lack of steric coupling between the chiral 2-octyloxy side-chains and the thioindigo core.[11] In order to address this problem and harness the photoinduced change in transverse dipole moment of the thioindigo core to produce a measurable change in P_S, we have synthesized and evaluated the dopants (*R,R*)-**2** and (*R,R*)-**3**, in which the chiral side-chains are strongly coupled to the thioindigo core *via* steric and dipole–dipole coupling with the adjacent nitro and chloro substituents.

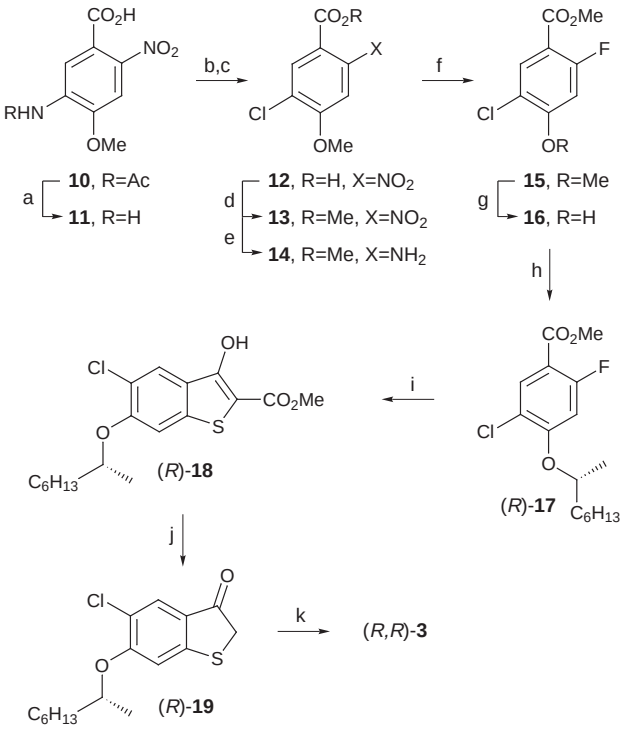
Results and discussion

Synthesis

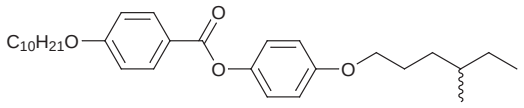
The thioindigo dopant **2** was synthesized in racemic and optically pure forms according to Scheme 1. Selective nitration of 2-chloro-4-hydroxybenzoic acid (**4**) was achieved *via* the acetoxy derivative **5** and followed by esterification to give **6**. The chiral (*R*)-2-octyloxy side-chain was introduced *via* a Mitsunobu reaction to give (*R*)-**7**, which was converted to the enol ester (*R*)-**8** by reaction with methyl thioglycolate under basic conditions.[17] Ester hydrolysis and decarboxylation to give the benzothiophenone (*R*)-**9** was followed by oxidation with potassium ferricyanide to give (*R,R*)-**2** in 6% overall yield. The synthesis of dopant **3** followed a similar approach, although a more reactive fluoro leaving group was required to selectively carry out the substitution reaction with methyl thioglycolate in the presence of a chloro group at the 5-position. As shown in Scheme 2, hydrolysis of 5-acetylamino-4-methoxy-2-nitrobenzoic acid (**10**) to give **11** followed by reaction of the corresponding diazonium salt with CuCl and subsequent esterification gave the 5-chloro-2-nitro derivative **13**. Reaction of **13** with one equivalent of methyl thioglycolate gave a mixture of products resulting from displacement of the nitro and/or chloro leaving groups. This selectivity problem was solved by converting the nitro group to a fluoro group *via* thermal decomposition of the corresponding diazonium tetrafluoroborate salt to give **15**. Following deprotection of the 4-hydroxy group with boron tribromide, the chiral (*R*)-2-octyloxy side-chain was introduced and subsequent reaction with methyl thioglycolate gave the desired enol ester (*R*)-**18** cleanly. Hydrolysis/decarboxylation



Scheme 1 *Reagents and conditions*: a, Ac_2O; b, fuming HNO_3, AcOH, 25 °C; c, MeOH, H_2SO_4, reflux; d, (*S*)-octan-2-ol, DIAD, Ph_3P, CH_2Cl_2, 25 °C; e, methyl thioglycolate, LiOH, DMF, 25 °C; f, 15% KOH in 1:1 EtOH–H_2O, reflux; g, $K_3Fe(CN)_6$, 25 °C.



Scheme 2 *Reagents and conditions*: a, 10% HCl, reflux; b, $NaNO_2$, H_2O, 5 °C; c, CuCl, conc HCl; d, MeOH, H_2SO_4, reflux; e, $SnCl_2 \cdot 2H_2O$, EtOH, reflux; f, $NaNO_2$, 48% HBF_4, 5 °C, then heat; g, 1 M BBr_3, CH_2Cl_2, 25 °C, then MeOH, H_2SO_4, reflux; h, (*S*)-octan-2-ol, DIAD, Ph_3P, CH_2Cl_2, 25 °C; i, methyl thioglycolate, LiOH, DMF, 25 °C; j, 15% KOH in 1:1 EtOH–H_2O, reflux; k, $K_3Fe(CN)_6$, 25 °C.



PhB; phase sequence: X 35 S_C 70.5 S_A 72 N 75 I

gave the corresponding benzothiophenone (*R*)-**19**, which was oxidized to give (*R,R*)-**3** in 7% overall yield.

Ferroelectric properties

Doping the S_C liquid crystal host **PhB** with either (*R,R*)-**2** or (*R,R*)-**3** induced a ferroelectric S_C* phase. The dinitro derivative **2** proved to be much less soluble than either **1** or **3**, reaching its solubility limit at *ca.* 3 mol% in **PhB**. By contrast, the dichloro derivative **3** dissolved readily in **PhB** at a concentration of 10 mol% without any appreciable disruption of the host mesogenic properties. Spontaneous polarization and tilt angle values were measured for (*R,R*)-**2**–**PhB** and (*R,R*)-**3**–**PhB** mixtures at 10 K below the S_C*–S_A* phase transition temperature ($T-T_C=-10$ K) while keeping the 4 μm thin films shielded from light at $\lambda<600$ nm, thus maintaining the thioindigo chromophores in the *trans*-form. The corresponding reduced polarization values (P_o) were plotted as a function of dopant mole fraction x_d and the resulting plots were fitted to second order polynomials ($R^2=0.989$ and 0.998, respectively), as shown in Fig. 3. Polarization power values (δ_p) were derived for each dopant using eqn. (2).[3] The apparent leveling of the induced polarization with increasing concentration of (*R,R*)-**2** suggests a saturation of the S_C* phase due to the low solubility of the dopant. In the case of (*R,R*)-**3**, the positive deviation

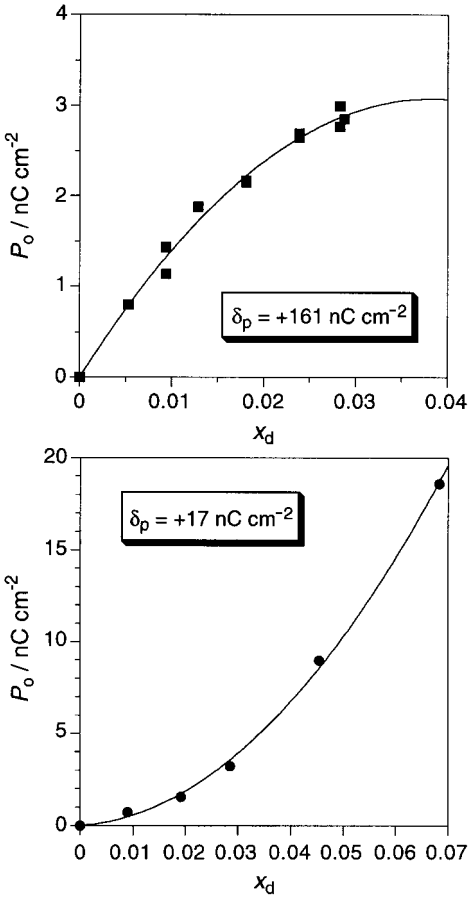
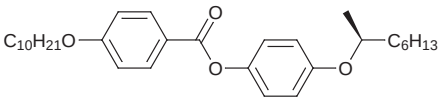


Fig. 3 Reduced polarization P_o measured as a function of dopant mole fraction x_d for the FLC mixtures (*R,R*)-**2**–**PhB** (top) and (*R,R*)-**3**–**PhB** (bottom).

from linearity of the P_o (x_d) function is consistent with that observed with some dopants with rigid chiral cores (Type II dopants), which is thought to arise from local field effects.[18] Such behavior, which is not observed with (*R,R*)-**1**,[11] is consistent with a strong coupling of the chiral side-chains with the thioindigo core (*vide infra*).

Under the same conditions, dopant (*R,R*)-**1** exhibits a polarization power of $+200$ nC cm^{-2}, which is roughly twice that



MDW222

exhibited by dopants bearing a single 2-octyloxy side chain, *e.g.*, **MDW222** ($\delta_p=-88$ nC cm^{-2} at $T-T_C=-30$ K).[19] This suggests that the two chiral side-chains in (*R,R*)-**1** are behaving independently from the thioindigo core due to a lack of steric coupling, which is consistent with the lack of P_S modulation observed upon *trans–cis* photoisomerization of the dopant.[11] As expected, dopants (*R,R*)-**2** and (*R,R*)-**3** gave lower δ_p values, even though the transverse dipole moment of each chiral structural unit is increased by coupling to the *ortho*-substituent. These results are consistent with steric coupling of the chiral 2-octyloxy side-chains with the thioindigo core, which forces the alkoxy groups in an anti/coplanar conformation with respect to the *ortho*-substituents,[20] and orients the corresponding transverse dipoles in opposite directions with respect to the polar axis when the thioindigo core is in the *trans*-configuration.

Photophysical properties

Solutions of (±)-**2** and (±)-**3** in air-saturated benzene (10^{-4} M) were irradiated at wavelengths corresponding to the visible absorption bands of the *trans*-isomers—514 nm (Ar laser) for **2** and 532 nm (Nd:YAG laser) for **3**—to give photostationary states enriched with the corresponding *cis*-isomers ($\lambda_{max}=455$ and 465 nm, respectively), as shown in Fig. 4. Upon standing in the dark for 24 h, the two dopants thermally isomerized back to the more stable *trans*-isomers. The photochromic behavior of **2** and **3** is consistent with that previously observed for **1**.[11]

Photomodulation of P_S

Irradiation of the (*R,R*)-**2**–**PhB** and (*R,R*)-**3**–**PhB** mixtures at $\lambda=514$ and 532 nm, respectively, caused an increase in spontaneous polarization that is consistent with an increase in transverse dipole moment of the chiral dopant *via trans–cis* photoisomerization. In the case of (*R,R*)-**2**–**PhB** mixtures, photomodulation experiments were carried out over the mole fraction range $0.005<x_d<0.031$ at $T-T_C=-10$ K. As shown in Fig. 5 and Table 1, irradiation of 4 μm thin films at 514 nm caused an increase in P_S by a relatively constant factor of 1.7–2.0, with the P_S values leveling off as x_d approaches the dopant solubility limit of 0.03. In the case of (*R,R*)-**3**–**PhB** mixtures, photomodulation experiments were carried out over a wider mole fraction range, $0.019<x_d<0.10$, at $T-T_C=-10$ K. Irradiation of 4 μm thin films at 532 nm caused increases in P_S by factors ranging from 4.0 ($x_d=0.019$) to 1.4 ($x_d=0.10$). The decrease in relative P_S photomodulation with increasing mole fraction of (*R,R*)-**3** is an interesting phenomenon that remains unexplained, although we suspect that it is related to the non-linear dependence of the induced polarization on x_d (*vide supra*). In both sets of experiments, the initial P_S value was restored within a period of one minute after shutting off the laser, which indicates that thermal relaxation to the *trans*-isomer is much faster in the S_C* phase than in

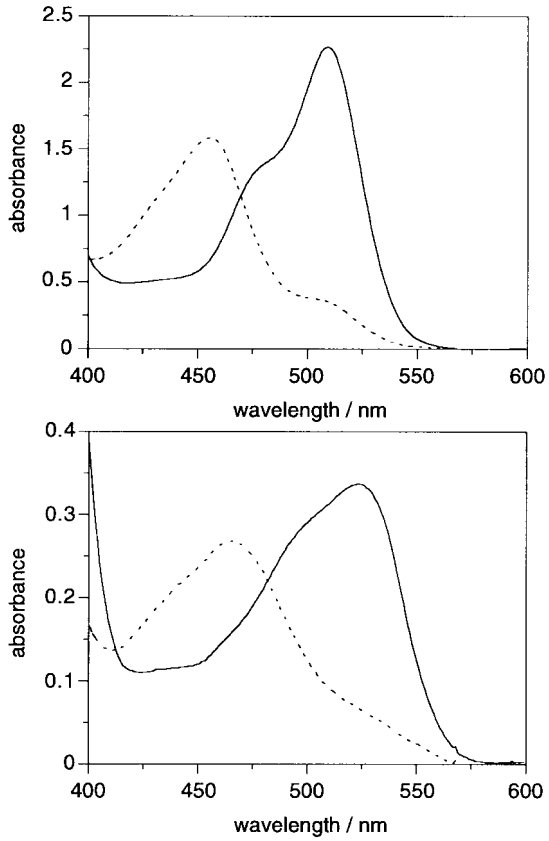


Fig. 4 UV–VIS absorption spectra of 10^{-4} M solutions of (±)-**2** (top) and (±)-**3** (bottom) in air-saturated benzene after irradiation at $\lambda =$ 514 and 532 nm (dashed lines), and after standing in the dark for 24 h (solid lines).

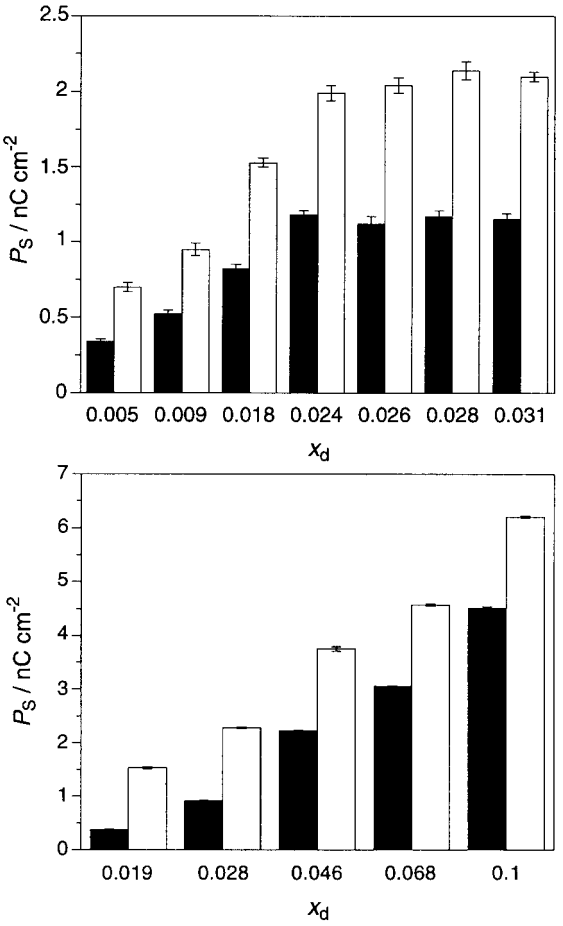


Fig. 5 Spontaneous polarization P_S measured as a function of dopant mole fraction x_d for the FLC mixtures (*R,R*)-**2**–**PhB** (top) and (*R,R*)-**3**–**PhB** (bottom) under constant irradiation at $\lambda = 514$ and 532 nm (white columns), and in the dark (black columns).

isotropic liquid solution. This irradiation/thermal relaxation cycle was repeated several times with both sets of samples without any decrease in spontaneous polarization and/or P_S photomodulation.

Control experiments

In order to determine the effect, if any, of *trans–cis* photoisomerization on the thermal stability of the S_C* phase in (*R,R*)-**2**–**PhB** and (*R,R*)-**3**–**PhB** mixtures, P_S was measured as a function of temperature with the 4 μm thin films kept in the dark, and under constant irradiation at 514 and 532 nm, respectively. As shown in Fig. 6 (top), extrapolation of the P_S *vs.* T plot to $P_S = 0$ for a 2.6 mol% (*R,R*)-**2**–**PhB** mixture shows that *trans–cis* photoisomerization does not cause an appreciable shift in the S_C*–S_A* phase transition temperature. At the same dopant mole fraction, an (*R,R*)-**3**–**PhB** mixture gave the same result. However, at higher dopant mole fractions, *e.g.* $x_d = 0.07$, *trans–cis* photoisomerization does cause a relatively small depression (by 1 K) of the S_C*–S_A* phase transition temperature, as shown in Fig. 6 (bottom). At a comparable dopant mole fraction, the *trans–cis* photoisomerization of an azobenzene-containing side-chain FLC copolymer caused a 15 K drop in the S_C*–S_A* phase transition temperature.[10]

In a second experiment aimed at ruling out photomechanical and/or local heating effects as the cause of P_S photomodulation, the racemic dopants (±)-**2** and (±)-**3** were each doped into a ferroelectric S_C* host consisting of a mixture of the chiral dopant (*S,S*)-4,4′-bis[(2-chloro-3-methylbutanoyl)oxy]biphenyl in **PhB** (*ca.* 2 mol%); the thioindigo dopant concentrations were 2.4 and 2.9 mol%, respectively. Irradiation of these two S_C* mixtures under the usual conditions caused no photomodulation of P_S, as shown in Table 1, which further

Table 1 Spontaneous polarization P_S of thioindigo-doped FLC mixtures measured in the dark and under constant irradiation at $T - T_C = -10$ K

		P_S/nC cm^{-2}[a]	
FLC mixture	x_d	Dark[b]	Irradiated[c]
(*R,R*)-**2**–**PhB**	0.005	+0.34±0.02	+0.70±0.03
	0.009	+0.52±0.03	+0.95±0.04
	0.018	+0.82±0.03	+1.53±0.03
	0.024	+1.18±0.03	+2.00±0.05
	0.026	+1.12±0.05	+2.04±0.05
	0.028	+1.17±0.04	+2.14±0.06
	0.031	+1.15±0.04	+2.10±0.03
(*R,R*)-**3**–**PhB**	0.019	+0.38±0.01	+1.54±0.02
	0.028	+0.92±0.01	+2.28±0.01
	0.046	+2.22±0.01	+3.75±0.04
	0.068	+3.06±0.01	+4.57±0.02
	0.10	+4.51±0.03	+6.21±0.02
(±)-**2**–**PhB***[d]	0.024	−2.51±0.02	−2.50±0.02
(±)-**3**–**PhB***[d]	0.029	−1.35±0.01	−1.36±0.01

[a]Each P_S value is the average of measurements taken over a minimum of 10 irradiation/thermal relaxation cycles; uncertainties are given as ± one standard deviation. [b]The samples were allowed to equilibrate in the dark for 2 min before each measurement. [c]Mixtures containing dopant **2** were irradiated at 514 nm; mixtures containing dopant **3** were irradiated at 532 nm. [d]The S_C* host **PhB*** consists of a mixture of the chiral dopant (*S,S*)-4,4′-bis[(2-chloro-3-methylbutanoyl)oxy]biphenyl in **PhB** (*ca.* 2 mol%).

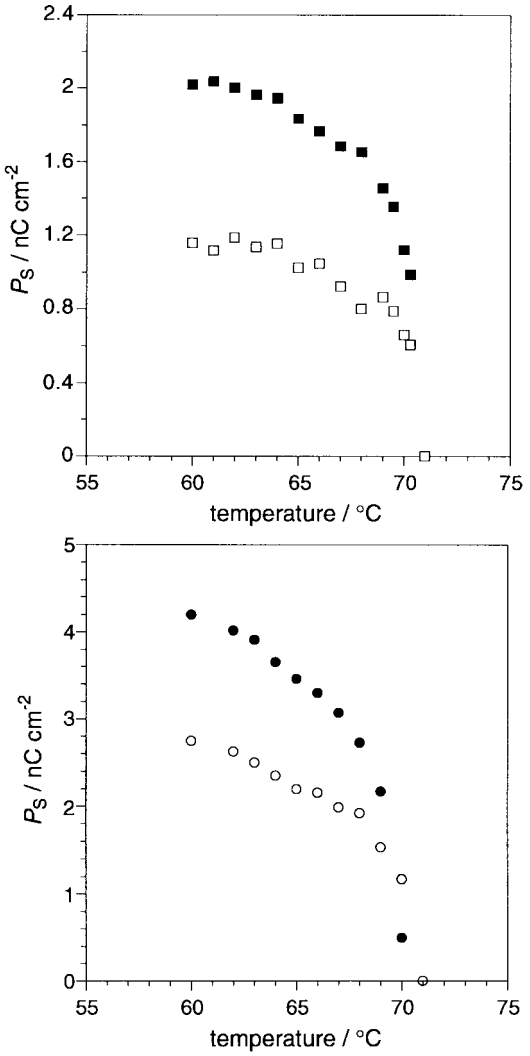


Fig. 6 Spontaneous polarization P_S as a function of temperature for the FLC mixtures (*R,R*)-**2**–**PhB** (top) and (*R,R*)-**3**–**PhB** (bottom) under constant irradiation at $\lambda = 514$ and 532 nm (filled symbols), and in the dark (open symbols). The dopant mole fractions are 0.026 and 0.07, respectively.

indicates that P_S photomodulation in (*R,R*)-**2**–**PhB** and (*R,R*)-**3**–**PhB** mixtures is caused almost exclusively by a photoinduced change in transverse dipole moment of the thioindigo core, which is sterically coupled to the chiral 2-octyloxy side-chains.

Summary

We have shown that the spontaneous polarization of a ferroelectric liquid crystal can be photomodulated using visible light, with no appreciable destabilization of the S_C* phase, *via trans–cis* photoisomerization of the chiral thioindigo dopants (*R,R*)-**2** and (*R,R*)-**3**. In a 1.9 mol% mixture of (*R,R*)-**3** in the S_C host **PhB**, irradiation at 532 nm using a Nd:YAG laser caused a 4-fold increase in P_S, from 0.38 to 1.54 nC cm^{-2}. This result is consistent with an increase in the transverse dipole moment of the thioindigo core, which is sterically coupled to two chiral 2-octyloxy side-chains through steric interactions with adjacent chloro substituents. In terms of device applications, the dichloro dopant (*R,R*)-**3** is more advantageous than the dinitro analogue (*R,R*)-**2** by virtue of its higher solubility and better photomodulation performance. Using (*R,R*)-**3** in combination with a photoinert chiral dopant inducing a negative spontaneous polarization, we have recently demonstrated the first optically addressed SSFLC spatial light modulator based on photoinduced P_S inversion.[21]

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200 and Avance 300 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 are 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. UV–visible spectra were recorded on a Varian Cary 3 spectrophotometer in benzene. Elemental analyses were performed by MHW Laboratories (Phoenix, AZ). Melting points were measured on a Mel-Temp II melting point apparatus and are uncorrected.

Materials

All reagents were obtained from commercial sources and used without further purification unless otherwise noted. Dimethylformamide (DMF) was distilled from BaO under reduced pressure and stored over molecular sieves. Methylene chloride (CH_2Cl_2) was distilled from P_2O_5 under N_2. Flash chromatography was performed with 40–63 μm/230–400 mesh silica gel (Rose Scientific). 2-Chloro-4-hydroxybenzoic acid (**4**), 5-acetylamino-4-methoxy-2-nitrobenzoic acid (**10**), (±)-4-(4-methylhexyloxy)phenyl 4-decyloxybenzoate (**PhB**) and (*S,S*)-4,4′-bis[(2-chloro-3-methylbutanoyl)oxy]biphenyl were prepared according to published procedures and shown to have the expected physical and spectral properties.[22–25]

Methyl 2-chloro-4-hydroxy-5-nitrobenzoate (6). A solution of **4** (1.55 g, 9.0 mmol) in acetic anhydride (5 ml) was heated on a steam bath for 30 min, then poured over ice and filtered in a Buchner funnel. The solid residue was washed with water and dried in air to give 1.76 g of the acetoxy derivative **5**. Without further purification, compound **5** was dissolved in a mixture of fuming HNO_3 (15 ml) and glacial AcOH (15 ml) and stirred at 25 °C for 24 h. The mixture was then concentrated, and the yellow residue was dissolved in a mixture of MeOH (20 ml) and conc. H_2SO_4 (0.5 ml) and refluxed overnight. After cooling, the mixture was poured into water and extracted with Et_2O (2×). The combined extracts were washed with water, brine, then dried ($MgSO_4$) and concentrated. Purification by flash chromatography on silica gel (30% EtOAc–toluene) gave 0.64 g (31%) of **6** as a yellow solid: mp 94–95 °C; ^{1}H NMR (200 MHz, acetone-d_6) δ 3.91 (s, 3H), 7.36 (s, 1H), 8.64 (s, 1H), 10.8 (s, OH); ^{13}C NMR (50 MHz, acetone-d_6) δ 52.9, 122.3, 122.9, 130.0, 134.0, 142.3, 157.0, 164.1; MS (EI) *m/z* 233 (M+2, 6), 231 (M^+, 18), 202 (35), 200 (100), 170 (5), 156 (15), 154 (38), 142 (8), 126 (13), 113 (6), 97 (12); HRMS (EI) Calcd. for $C_8H_6{}^{37}ClNO_5$: 232.9905. Found: 232.9888.

Methyl (*R*)-2-chloro-4-(2-octyloxy)-5-nitrobenzoate ((*R*)-7). Under an N_2 atmosphere, diisopropyl azodicarboxylate (DIAD, 202 mg, 0.99 mmol) was added dropwise to a stirred solution of **6** (153 mg, 0.66 mmol), Ph_3P (260 mg, 0.99 mmol) and (*S*)-octan-2-ol (90 mg, 0.69 mmol) in dry CH_2Cl_2 (10 ml). After stirring at 25 °C for 2 h, the solvent was removed *in vacuo*, and the oily residue was purified by flash chromatography on silica gel (30% EtOAc–toluene) to give 195 mg (86%) of (*R*)-**7** as a yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J=6.6 Hz, 3H), 1.20–1.80 (m, 10H), 1.38 (d, J=6.0 Hz, 3H), 3.92 (s, 3H), 4.56 (m, J=6.0 Hz, 1H), 7.10 (s, 1H), 8.45 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 19.3, 22.5, 25.0, 29.0, 31.6, 36.0, 52.6, 77.6, 117.6, 120.5, 129.5, 138.0, 140.3, 154.0, 163.6; MS (CI) *m/z* 346 (M+3, 32), 344 (M+1, 100), 316 (22), 314 (67), 301 (13), 299 (36), 279 (17),

262 (35), 260 (96), 234 (25), 232 (69), 201 (6), 149 (4), 91 (16); HRMS (EI) Calcd. for $C_{15}H_{19}{}^{35}ClNO_4$ ($M-OCH_3$): 312.1001. Found: 312.1004.

Methyl (*R*)-3-hydroxy-6-(2-octyloxy)-5-nitro-1-benzothiophene-2-carboxylate ((*R*)-8). Under an N_2 atmosphere, a mixture of (*R*)-**7** (197 mg, 0.57 mmol), anhydrous LiOH (48 mg, 2 mmol) and methyl thioglycolate (91 mg, 0.86 mmol) in dry DMF (10 ml) was stirred overnight at 25 °C. The mixture was poured into water (40 ml), acidified with 3 M HCl and extracted with EtOAc (3×). The combined extracts were washed with 1 M HCl, brine, dried ($MgSO_4$) and concentrated to a yellow oil. Purification by flash chromatography on silica gel (30% EtOAc–toluene) gave 135 mg (62%) of (*R*)-**8** as a yellow waxy solid: mp 54–55 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, $J=6.7$ Hz, 3H), 1.24–1.80 (m, 10H), 1.39 (d, $J=6.2$ Hz, 3H), 3.95 (s, 3H), 4.54 (m, $J=6.0$ Hz, 1H), 7.26 (s, 1H), 8.31 (s, 1H), 10.1 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 19.2, 22.6, 25.2, 29.1, 31.7, 36.1, 52.3, 77.0, 101.5, 107.8, 120.1, 122.3, 140.0, 143.5, 151.7, 159.2, 166.8; MS (CI) *m/z* 382 (M+1, 3), 270 (100), 232 (98), 212 (18), 202 (48), 149 (12), 113 (19); HRMS (EI) Calcd. for $C_{18}H_{23}NO_6S$: 381.1246. Found: 381.1252.

(*R,R*)-6,6′-Bis(2-octyloxy)-5,5′-dinitro-2,2′,3,3′-tetrahydro-[$\Delta^{2,2'}$-bi-1-benzothiophene]-3,3′-dione ((*R,R*)-2). A suspension of (*R*)-**8** (153 mg, 0.36 mmol) in a 15% solution of KOH in 1:1 EtOH–H_2O (15 ml) was heated to reflux for 5 h to give (*R*)-**9**. After cooling to room temperature, the solution was treated with 300 mg of $K_3[Fe(CN)_6]$ dissolved in H_2O (2 ml) and stirred for 1 h. After removing the alcohol *in vacuo*, the mixture was extracted with $CHCl_3$ (2×), and the combined extracts were washed with H_2O, dried ($MgSO_4$) and concentrated to a red solid. Purification by flash chromatography on silica gel (toluene) gave 40 mg (35%) of (*R,R*)-**2** as a red solid. The compound was further purified by recrystallization from 15% $CHCl_3$–hexanes: mp 189–190 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, $J=6.6$ Hz, 6H), 1.15–1.85 (m, 20H), 1.44 (d, $J=6.1$ Hz, 6H), 4.66 (m, $J=6.0$ Hz, 2H), 7.12 (s, 2H), 8.37 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 19.3, 22.5, 25.1, 29.0, 31.6, 36.0, 78.1, 109.0, 120.3, 124.4, 133.1, 139.6, 154.6, 157.6, 186.8; MS (EI) *m/z* 642 (M^+, 1), 418 (100), 388 (4), 372 (5), 359 (2), 326 (2), 253 (2), 208 (4), 165 (16), 111 (26), 83 (59); Anal. Calcd. for $C_{32}H_{38}N_2O_8S_2$: C, 59.79; H, 5.96; S, 9.98; N, 4.36. Found: C, 59.66; H, 6.02; S, 9.97; N, 4.36.

(±)-6,6′-Bis(2-octyloxy)-5,5′-dinitro-2,2′,3,3′-tetrahydro-[$\Delta^{2,2'}$-bi-1-benzothiophene]-3,3′-dione ((±)-2). The procedure described for the synthesis of (*R,R*)-**2** was repeated using (±)-octan-2-ol to give (±)-**2** as a red solid: mp 202–205 °C.

5-Chloro-4-methoxy-2-nitrobenzoic acid (12). A mixture of **10** (15 g, 59 mmol) and 10% aq HCl (200 ml) was heated to reflux for 4 h, then cooled and concentrated to give the crude amino acid **11**. Without further purification, the solid was dissolved in 6 M HCl (175 ml) and cooled in an ice bath. A solution of $NaNO_2$ (5.0 g, 72 mmol) in water (40 ml) was then added dropwise, and the mixture was stirred in the ice bath for 1.5 h. The brown solution was then slowly poured into a stirred mixture of CuCl (7.85 g) in conc. HCl (75 ml) to form a precipitate. After the foaming subsided, the precipitate was collected by filtration and dried in a vacuum oven to give 11.4 g (83%) of **12** as a tan powder: mp 196–199 °C; ^{1}H NMR (300 MHz, acetone-d_6) δ 4.14 (s, 3H), 7.65 (s, 1H), 7.99 (s, 1H); ^{13}C NMR (75 MHz, acetone-d_6) δ 57.4, 108.3, 118.2, 125.4, 132.0, 150.2, 158.5, 163.6; MS (EI) *m/z* 233 (M+2, 10), 231 (M^+, 29), 187 (14), 185 (22), 175 (4), 173 (12), 170 (10), 159 (4), 157 (13), 142 (25), 141 (40), 131 (21), 129 (63), 126 (23), 116 (15), 114 (53), 107 (100), 99 (54), 97 (82), 85 (43), 79 (96); HRMS (EI) Calcd. for $C_8H_6{}^{37}ClNO_5$: 232.9905. Found: 232.9893.

Methyl 5-chloro-4-methoxy-2-nitrobenzoate (13). A mixture of **12** (17.3 g, 74.7 mmol) and conc. H_2SO_4 (5 ml) in methanol (750 ml) was refluxed for 4 days. The reaction mixture was then concentrated to a solid residue which was dissolved in EtOAc, washed with water, brine, dried ($MgSO_4$) and concentrated to give 14.7 g (80%) of **13** as a brown solid: mp 89–94 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 3H), 4.00 (s, 3H), 7.33 (s, 1H), 7.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 53.7, 57.4, 107.5, 119.7, 127.7, 132.0, 148.6, 157.8, 164.6; MS (EI) *m/z* 247 (M+2, 11), 245 (M^+, 31), 216 (33), 214 (100), 201 (2), 199 (6), 156 (18), 142 (17), 140 (56), 125 (27), 113 (30), 99 (37), 97 (80), 77 (36); HRMS (EI) Calcd. for $C_9H_8{}^{35}ClNO_5$: 245.0091. Found: 245.0090.

Methyl 2-amino-5-chloro-4-methoxybenzoate (14). To a solution of **13** (14.3 g, 58.2 mmol) in absolute EtOH (670 ml) was added 60 g of $SnCl_2\cdot 2H_2O$ (265 mmol) and the reaction mixture was refluxed with stirring for 4 h. After cooling, the mixture was poured into ice–water and neutralized with aq $NaHCO_3$. The mixture was extracted with EtOAc (2×) and the combined extracts were washed with water, brine, dried ($MgSO_4$) and concentrated. The crude product was purified by flash chromatography on silica gel (50% EtOAc–hexanes) to give 10.1 g (80%) of **14** as a yellow solid: mp 105–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.84 (s, 3H), 6.10 (s, 1H), 7.81 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 51.9, 56.4, 99.1, 104.6, 110.8, 132.7, 151.6, 159.6, 167.9; MS (EI) *m/z* 217 (M+2, 29), 215 (M^+, 84), 185 (40), 183 (100), 158 (9), 156 (26), 140 (21), 129 (9), 113 (9); HRMS (EI) Calcd. for $C_9H_{10}{}^{35}ClNO_3$: 215.0349. Found: 215.0356.

Methyl 5-chloro-2-fluoro-4-methoxybenzoate (15). To a solution of **14** (30 g, 0.14 mol) in 48% aq HBF_4 (125 ml) and water (50 ml) cooled in ice was added dropwise a solution of $NaNO_2$ (15.2 g, 0.22 mol) in water (80 ml). After stirring for 10 min, the precipitated tetrafluoroborate salt was collected by filtration and washed successively with cold water, MeOH, and Et_2O. The salt was dried under vacuum for 2 days and then decomposed at atmospheric pressure by heating with a heat gun. The resulting black oil was dissolved in EtOAc, washed with water and 10% aq NaOH, dried ($MgSO_4$) and concentrated. Purification by Kugelrohr distillation (1 Torr, 100 °C) gave 11.4 g (37%) of **15** as a white solid: mp 89–91 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 3H), 3.92 (s, 3H), 6.67 (d, 1H, $J_{H\text{-}F}=12.3$ Hz), 7.95 (d, 1H, $J_{H\text{-}F}=7.8$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.3, 56.7, 101.0 ($J_{C\text{-}F}=28$ Hz), 111.1 ($J_{C\text{-}F}=11$ Hz), 117.8, 132.8, 159.4 ($J_{C\text{-}F}=11$ Hz), 160.1, 163.6; MS (EI) *m/z* 220 (M+2, 6), 218 (M^+, 19), 189 (34), 187 (100), 174 (2), 172 (6), 146 (3), 144 (8), 118 (3), 116 (12), 95 (26), 81 (33); HRMS (EI) Calcd. for $C_9H_8{}^{37}ClFO_3$: 220.0116. Found: 220.0117.

Methyl 5-chloro-2-fluoro-4-hydroxybenzoate (16). Under an Ar atmosphere, a 1.0 M solution of BBr_3 in CH_2Cl_2 (80 ml) was slowly added by syringe to a solution of **15** (5.1 g, 23.2 mmol) in dry CH_2Cl_2 (120 ml) cooled in ice. The reaction mixture was stirred for 4 days and then poured slowly into a cold 5% aq NaOH solution (200 ml). After stirring for a few minutes, the mixture was acidified with 2 M HCl and extracted with EtOAc (2×). The combined organic extracts were washed with 2 M HCl, water, brine, dried ($MgSO_4$) and concentrated. Without further purification, the crude product was dissolved in MeOH (350 ml) and conc. H_2SO_4 (5 ml) and heated to reflux for 2 days. After cooling, the reaction mixture was concentrated and the residue dissolved in EtOAc. The solution was washed with 5% aq $NaHCO_3$, water, brine, dried ($MgSO_4$) and concen-

trated to give 3.53 g (74%) of **16** as a white solid: mp 115–117 °C; ^{1}H NMR (200 MHz, acetone-d_6) δ 3.84 (s, 3H), 6.85 (d, $J_{H\text{-}F}$ = 12 Hz, 1H), 7.87 (d, $J_{H\text{-}F}$ = 8 Hz, 1H), 10.08 (s, 1H); ^{13}C NMR (50 MHz, acetone-d_6) δ 52.5, 105.7 (d, $J_{C\text{-}F}$ = 27 Hz), 111.8 (d, $J_{C\text{-}F}$ = 11 Hz), 117.0 (d, $J_{C\text{-}F}$ = 3 Hz), 133.7 (d, $J_{C\text{-}F}$ = 3 Hz), 159.0 (d, $J_{C\text{-}F}$ = 12 Hz), 162.5 (d, $J_{C\text{-}F}$ = 257 Hz), 163.9 (d, $J_{C\text{-}F}$ = 4 Hz); MS (EI) *m/z* 206 (M + 2, 10), 204 (M^+, 32), 175 (47), 173 (100), 117 (20); HRMS (EI) Calcd. for $C_8H_6{}^{35}ClFO_3$: 204.0003. Found: 204.0016.

Methyl (*R*)-5-chloro-2-fluoro-4-(2-octyloxy)benzoate ((*R*)-17). Under a N_2 atmosphere, diisopropyl azodicarboxylate (DIAD, 146 mg, 0.72 mmol) was added dropwise to a stirred solution of **16** (98 mg, 0.47 mmol), Ph_3P (189 mg, 0.72 mmol) and (*S*)-octan-2-ol (95 mg, 0.72 mmol) in dry CH_2Cl_2 (10 ml). After stirring at 25 °C for 2 h, the solvent was removed *in vacuo* and the oily residue was purified by flash chromatography on silica gel (30% EtOAc–toluene) to give 158 mg (95%) of (*R*)-**17** as an oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, 3H), 1.26–1.78 (m, 10H), 1.34 (d, J = 6.1 Hz, 3H), 3.88 (s, 3H), 4.34–4.43 (m, 1H), 6.62 (d, $J_{H\text{-}F}$ = 12.6 Hz, 1H), 7.94 (d, $J_{H\text{-}F}$ = 7.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3, 19.6, 22.8, 24.4, 29.3, 31.9, 36.3, 52.4, 76.7, 102.7 (d, $J_{C\text{-}F}$ = 28 Hz), 110.8 (d, $J_{C\text{-}F}$ = 11 Hz), 118.9 (d, $J_{C\text{-}F}$ = 3 Hz), 133.2 (d, $J_{C\text{-}F}$ = 3 Hz), 158.7 (d, $J_{C\text{-}F}$ = 11 Hz), 161.9 (d, $J_{C\text{-}F}$ = 258 Hz), 163.9 (d, $J_{C\text{-}F}$ = 5 Hz); MS (CI) *m/z* 319 (M + 3, 11), 317 (M + 1, 32), 207 (32), 205 (100); HRMS (EI) Calcd. for $C_{16}H_{22}{}^{35}ClFO_3$: 316.1251. Found: 316.1262.

Methyl (*R*)-5-chloro-3-hydroxy-6-(2-octyloxy)-1-benzothiophene-2-carboxylate ((*R*)-18). Under an Ar atmosphere, a mixture of (*R*)-**17** (212 mg, 0.67 mmol), anhydrous LiOH (101 mg, 4.2 mmol) and methyl thioglycolate (360 mg, 3.4 mmol) in dry DMF (10 ml) was stirred overnight at 25 °C. The mixture was poured into water (40 ml), acidified with 2 M HCl and extracted with EtOAc (2 ×). The combined extracts were washed with 1 M HCl, brine, dried ($MgSO_4$) and concentrated to an oil. Purification by flash chromatography on silica gel (20% EtOAc–toluene) gave 182 mg (73%) of (*R*)-**18** as a yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, 3H), 1.26–1.83 (m, 10H), 1.36 (d, 3H), 3.91 (s, 3H), 4.40–4.49 (m, 1H), 7.13 (s, 1H), 7.89 (s, 1H), 10.06 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3, 19.7, 22.8, 25.5, 29.4, 32.0, 36.5, 52.3, 76.5, 100.5, 107.2, 123.5, 124.2, 124.3, 139.0, 155.3, 159.1, 167.6; MS (EI) *m/z* 372 (M + 2, 1), 370 (M +, 3), 260 (10), 258 (27), 228 (38), 226 (100), 170 (14); HRMS (EI) Calcd. for $C_{18}H_{23}{}^{35}ClO_4S$: 370.0987. Found: 370.0980.

(*R,R*)-5,5′-Dichloro-6,6′-bis(2-octyloxy)-2,2′,3,3′-tetrahydro-[$\Delta^{2,2'}$-bi-1-benzothiophene]-3,3′-dione ((*R,R*)-3). A suspension of (*R*)-**18** (180 mg, 0.48 mmol) in a 15% solution of KOH in 1 : 1 EtOH–H_2O (30 ml) was heated to reflux for 6 h to give (*R,R*)-**19**. After cooling, the mixture was treated with a solution of $K_3[Fe(CN)_6]$ (413 mg, 1.25 mmol) in water (5 ml) and stirred for 3 h at 25 °C. After removing the ethanol *in vacuo*, the mixture was extracted with EtOAc (2 ×), and the combined extracts were washed with water, brine, dried ($MgSO_4$) and concentrated to a red solid. Purification by flash chromatography on silica gel (30% EtOAc–toluene) gave 101 mg (67%) of (*R,R*)-**3** as a red solid. The compound was further purified by recrystallization from 95% EtOH and then from hexanes: mp 144–146 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 6H), 1.23–1.83 (m, 20H), 1.40 (d, J = 6.1 Hz, 6H), 4.49–4.58 (m, 2H), 6.93 (s, 2H), 7.86 (s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3, 19.7, 22.8, 25.4, 29.3, 31.9, 36.3, 77.0, 108.1, 122.1, 123.3, 128.4, 133.3, 149.8, 160.4, 187.5; MS (EI) *m/z* 624 (M + 4, 1.4), 622 (M + 2, 4.8), 620 (M^+, 6.3), 400 (20), 398 (76), 396 (100), 258 (12), 226 (47), 213 (10), 171 (23), 149 (88). Anal. Calcd. for $C_{32}H_{38}Cl_2O_4S_2$: C, 61.82; H, 6.16; S, 10.32; Cl, 11.41. Found: C, 62.06; H, 6.17; S, 10.50; Cl, 11.26.

(±)-5,5′-Dichloro-6,6′-bis(2-octyloxy)-2,2′,3,3′-tetrahydro-[$\Delta^{2,2'}$-bi-1-benzothiophene]-3,3′-dione ((±)-3). The procedure described for the synthesis of (*R,R*)-**3** was repeated using (±)-octan-2-ol to give (±)-**3** as a red solid: mp 131–133 °C.

Ferroelectric measurements

Texture analyses and transition temperature measurements for the doped liquid crystal mixtures were carried out using a Nikon Labophot-2 polarizing microscope fitted with an Instec HS1-i hot stage. Spontaneous polarization (P_S) values were measured as a function of temperature by the triangular wave method (6 V μm^{-1}, 60–80 Hz) using a Displaytech APT III polarization testbed in conjunction with the Instec hot stage.[26] Polyimide-coated ITO glass cells (4 μm × 0.25 cm^2) supplied by Displaytech Inc. were used for all the measurements. Good alignment was obtained by slow cooling of the filled cells from the isotropic phase *via* the N* and S_A* phases. Tilt angles (θ) were measured as a function of temperature between crossed polarizers as half the rotation between two extinction positions corresponding to opposite polarization orientations. The sign of P_S along the polar axis was assigned from the relative configuration of the electric field and the switching position of the sample according to the established convention.[4]

Photoisomerization in solution

Thermally equilibrated solutions of (±)-**2** and (±)-**3** in air-saturated benzene (1×10^{-4} M) were irradiated in sealed 1 cm Pyrex cells at room temperature. Compound (±)-**2** was irradiated at 514 nm using a 20 mW Ar laser and (±)-**3** was irradiated at 532 nm using a 50 mW Nd : YAG laser to produce *cis*-enriched phtostationary states. The photoisomerization and *cis–trans* thermal relaxation were monitored by UV–VIS spectroscopy.

Photomodulation of P_S

Mixtures of (*R,R*)-**2** and (*R,R*)-**3** in the S_C liquid crystal host **PhB** were introduced in polyimide-coated ITO glass cells (4 μm × 0.25 cm^2) and fitted in the hot stage with the 0.25 cm^2 addressed area fully exposed through the stage aperture. The spontaneous polarization was measured as a function of temperature with the sample in the dark and under constant irradiation at either 514 nm or 532 nm using the APT-III polarization testbed (6 V μm^{-1}, 60–80 Hz). The laser output was circularly polarized using a Fresnel rhomb. These experiments were repeated using mixtures of (±)-**2** and (±)-**3** in an S_C* host consisting of a mixture of the chiral dopant (*S,S*)-4,4′-bis[(2-chloro-3-methylbutanoyl)oxy]biphenyl in **PhB** (*ca.* 2 mol%).

Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

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Paper 9/03052B