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Reversible photocyclization of achiral dithienylperfluorocyclopentene dopants in a ferroelectric liquid crystal: bistable SSFLC photoswitching

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The spontaneous polarization (P_S) of a ferroelectric liquid crystal is modulated reversibly by photocyclization (λ = 313 nm) of dithienyl- and dibenzothienylperfluorocyclopentene dopants with relatively high aspect ratios. Photocyclization of these dopants causes a decrease of P_S due to a photomechanical effect which may originate from a loss of conformational flexibility of the dopant upon photocyclization. The degree of P_S photomodulation increases with dopant concentration up to the solubility limit of 3 mol%. The maximum polarization photomodulation, ΔP_S = 16.2 nC cm^{-2}, is achieved at 6 K below the Curie point with the dopant 1,2-bis(5-(4-heptyloxyphenyl)-2-methylthien-3-yl)perfluorocyclopentene (**3c**, 3 mol%). The resulting P_S photoswitch is fatigue resistant and photochemically bistable. Polarized spectroscopy experiments suggest that the dopants form homogeneous solutions with the FLC host and are integrated within the layer structure of the SmC* phase, with their molecular long axes approximately coincident with the director. To the best of our knowledge, this is the first example of a bistable ferroelectric liquid crystal photoswitch to be reported in the literature.

Introduction

The vast majority of liquid crystal display (LCD) devices currently on the market use nematic liquid crystals as electro-optical material.[1] However, smectic C liquid crystals formed by chiral molecules (SmC*) have received considerable attention as light shutters for the next generation of LCD devices because they can be switched ON and OFF about 10^3 times faster than nematic liquid crystals.[2] The chiral SmC* phase is a liquid crystal phase with diffuse layer ordering and a uniform tilt orientation within each layer. In a surface-stabilized planar alignment, the SmC* phase is ferroelectric, *i.e.*, it is possesses a spontaneous electric polarization (P_S) that can be coupled to an electric field E to produce a light shutter with ON and OFF states corresponding to opposite tilt orientations.[3] Surface-stabilized ferroelectric liquid crystal (SSFLC) light shutters are characterized by electro-optical switching times on the order of microseconds, which makes them attractive for some photonic and telecommunication applications.[4] In the past ten years, a growing interest in photonic liquid crystal materials has led a number of research groups to investigate optical switching mechanisms for SSFLC light shutters (photoswitch) based on the photomodulation of P_S.[5–13] Devices using photoswitchable SSFLC materials would enable the reversible inscription of images, diffraction gratings and waveguides, and could be useful in dynamic holography and optical data storage applications.

One approach to photomodulate P_S is based on the change in molecular shape of chiral and achiral photochromic dopants such as 4, 4′-disubstituted azobenzenes.[5–10] In a ferroelectric SmC* host, the *trans–cis* photoisomerization of an azobenzene dopant destabilizes the SmC* phase due to the change in shape of the azobenzene chromophore from rod-like (*trans*) to bent (*cis*). This so-called *photomechanical effect* causes a shift of the P_S vs. temperature profile by lowering the transition temperature to a non-ferroelectric SmA* or N* phase (Curie point). At constant temperature, the net result is a decrease of P_S or, in some cases, a complete loss of polarization due to a phase transition. Another approach is to combine a photochromic chiral dopant with an achiral SmC liquid crystal host and modulate P_S *via* a photoinduced change in the polarization power of the chiral dopant. For example, we have shown that P_S can be increased *via* the *trans–cis* photoisomerization of chiral thioindigo dopants that maintain a rod-like shape in both isomeric forms.[11] In this case, P_S photomodulation is attributed to the increase in transverse dipole moment of the thioindigo core, which is sterically coupled to chiral side-chains, and is achieved without concomitant destabilization of the SmC* phase.

Ikeda *et al.* showed that the photomechanical effect causes a lowering of the coercive force E_c required to switch the SSFLC, and that photoswitching of an azobenzene-doped SSFLC can be achieved *via* P_S photomodulation by setting the applied electric field E between E_c thresholds corresponding to the *trans*-state and photostationary *cis*-state (Fig. 1a).[5] Komitov *et al.* reported that SSFLC photoswitching can also be achieved *via trans–cis* photoisomerization of an achiral azobenzene dopant in a SmC* liquid crystal host which undergoes an inversion in the sign of P_S as a function of temperature.[10] In this case, SSFLC photoswitching results from a shift in the P_S vs. T curve characteristic of the photomechanical effect. By setting the temperature of the doped SSFLC film between the inversion temperatures T_{inv} corresponding to the *trans*- and *cis*-states, the photomechanical effect produces an isothermal inversion of the sign of P_S and switching of the SSFLC (Fig. 1b). A photoinduced inversion of the sign of P_S has also been achieved *via* transverse dipole modulation using a combination of chiral dopants which induce polarizations of opposite signs: a chiral thioindigo dopant with a positive polarization power (+δ_p) and a photoinert chiral dopant with a negative polarization power (−δ_p).[12] More recently, we achieved P_S sign reversal using a single "ambidextrous"

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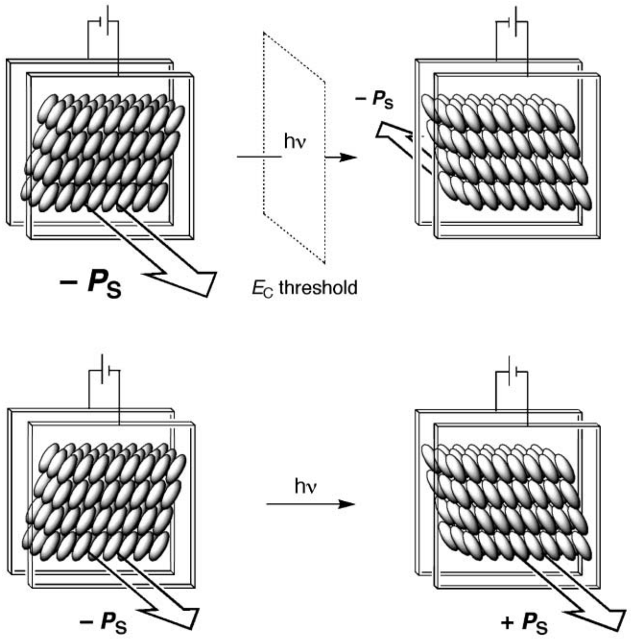
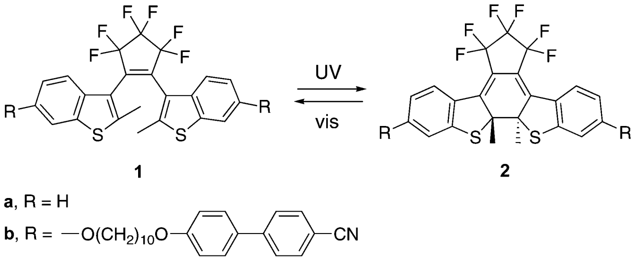


Fig. 1 Switching of a SSFLC film by (a) photomodulation of P_S below a coercive force threshold E_C (top) and (b) photoinduced inversion of P_S (bottom). In both cases, a dc electric field is maintained across the film and the P_S vector is perpendicular to the plane of the page.

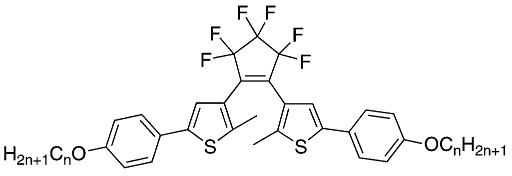
thioindigo dopant containing a chiral side-chain with $+\delta_p$ that is sterically coupled to the thioindigo core, and a chiral side-chain with $-\delta_p$ that is decoupled from the core.[13] In both cases, the photoinduced increase in transverse dipole moment of the thioindigo core raises the polarization induced by the $+\delta_p$ unit above that of the $-\delta_p$ unit, thereby inverting the sign of P_S.

Interestingly, none of the FLC photoswitches reported thus far is *photochemically* bistable (*i.e.*, a system in which each photostate is stable indefinitely in the dark) due to the thermal reversion of *cis*-isomers to the thermodynamically more stable *trans*-isomers, which limits their usefulness in optical data storage applications. To address this problem, we have recently undertaken a study of photochromic dithienylethene dopants in SmC* liquid crystal hosts.[14] The discovery of dithienylethenes as photochromic compounds is relatively new,[15] and they are considered to be among the most promising photochromic materials for optical data storage and other photoswitching applications because of their fatigue resistance and the thermal stability of both photoisomers.[16] These compounds undergo a reversible conrotatory photocyclization reaction, as shown in Scheme 1. Dithienylethenes bearing chiral substituents have been doped in nematic liquid crystals to induce chiral nematic (N*) phases and shown to cause a reversible modulation of the N* helical pitch upon photocyclization.[17] Despite their proven usefulness in modulating the bulk properties of nematic phases, simple dithienylethenes such as **1a** have inherent limitations as photochromic dopants in more ordered smectic phases, including a low aspect ratio and overlap of the UV spectrum of the uncyclized form with that of conventional smectic liquid crystals. Recently, Frigoli and Mehl reported that the dithienylethene **1a** can be integrated in a mesogenic structure by linking it to cyanobiphenyl mesogens *via* flexible spacers, and that mesogenic properties are modulated by photocyclization. For example, **1b** forms a broad SmC phase and a narrow nematic phase, whereas the photocyclized isomer **2b** forms an unidentified highly ordered SmX phase and a broad nematic phase.[18]

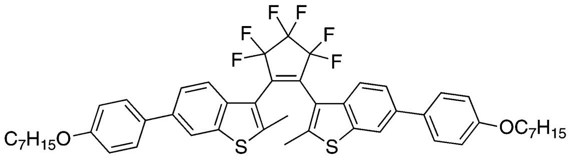


Scheme 1

In this paper, we extend the use of dithienylethene dopants to ferroelectric SmC* liquid crystals. Our approach to the design of dithienylethene dopants for SmC* photoswitches is to extend the conjugation of two well-known dithienylperfluorocyclopentene chromophores with 4-alkoxyphenyl side-chains. This modification afforded dopants with higher aspect ratios and shifted the absorption maxima of the uncyclized forms to longer wavelengths to avoid spectral overlap with the SmC* host. We report on the effect of photocyclization of the dithienyl dopants **3a–d** and the dibenzothienyl dopant **4** on the spontaneous polarization of a ferroelectric SmC* host and describe the first examples of a photochemically bistable FLC photoswitch based on these materials.



3a, n=1; **b**, n=4; **c**, n=7; **d**, n=9



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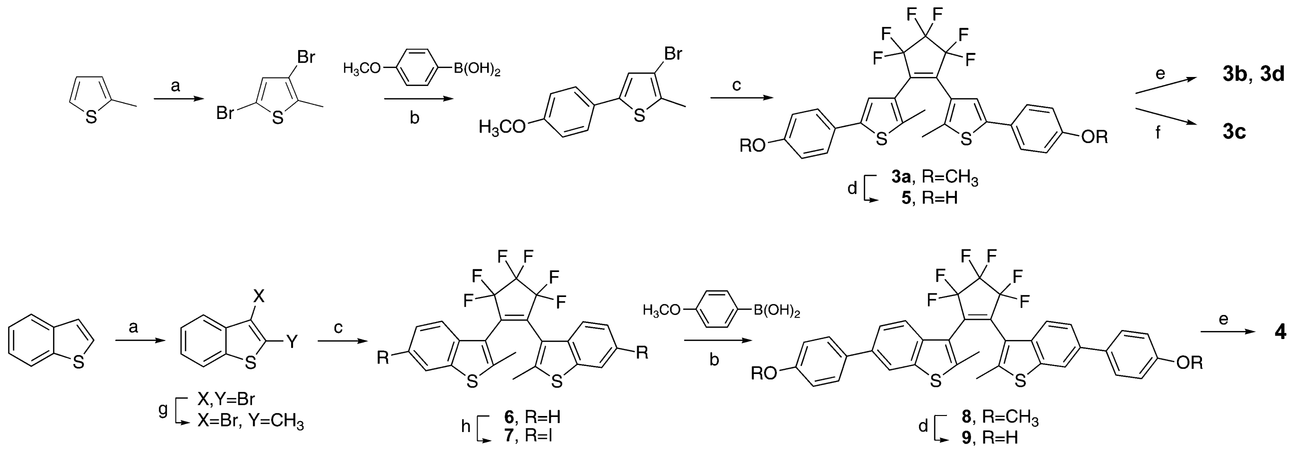
Results

Synthesis

The known dithienylperfluorocyclopentene **3a** was prepared according to Lehn *et al.*, as shown in Scheme 2.[19] Demethylation of **3a** with BBr_3 gave the diol **5**, which was alkylated to give the derivatives **3b–d**. The known dibenzothienylperfluorocyclopentene **6** was prepared according to Matsuda and Irie and iodinated to give **7**.[20] Extension of the conjugated backbone was achieved by Suzuki–Miyaura cross-couplings to give **8**, which was demethylated with BBr_3 and alkylated with bromoheptane to give **4**. Dithienylethenes are in dynamic equilibria between parallel and antiparallel conformations in solution, and the conrotatory photocyclization can proceed only from the latter. These two conformations can be distinguished by ^{1}H NMR spectroscopy in the case of **4** (*vide infra*) because of steric crowding about the two thienylethene bonds, which raises the activation barrier to *ca.* 70 kJ mol^{-1}.[21] The 35:65 parallel:antiparallel ratio measured by NMR spectroscopy is consistent with that reported in the literature for the parent compound.[22]

Photochromism

Extending the conjugation of the dithienylperfluorocyclopentene and dibenzothienylperfluorocyclopentene chromophores to give **3** and **4** resulted in bathochromic shifts of λ_{max} of 65 and 34 nm, respectively.[20,23] As shown in Fig. 2, irradiation of 2×10^{-5} M solutions of the dopants **3c** and **4** in benzene at λ = 313 nm resulted in photocyclization, and the appearance of colors characteristic of the cyclized products: blue and purple,



Scheme 2 *Reagents and conditions*: (a) 2 eq Br_2, $CHCl_3$, 90–100%. (b) $Pd(Ph_3P)_4$, Na_2CO_3, H_2O, THF, reflux, 45–52%. (c) (i) *s*-BuLi, THF, −78 °C; (ii) perfluorocyclopentene, THF, −78 °C, 75–80 %. (d) BBr_3, CH_2Cl_2,−78 °C, 82–84%. (e) $C_nH_{2n+1}Br$, K_2CO_3, 2-butanone, reflux, 40–65%. (f) 1-heptanol, DIAD, Ph_3P, THF, 25 °C, 46%. (g) *n*-BuLi, THF, −78 °C; (ii) CH_3I, 74–84%. (h) I_2, H_5IO_6, H_2SO_4, AcOH, 72%.

respectively. The degree of photocyclization of **3c** and **4** in dilute benzene solutions was determined by ^1H NMR spectroscopy in conjunction with UV–vis spectroscopy. Irradiation of more concentrated solutions of **3c** and **4** in deuterated benzene at 313 nm resulted in partial cyclization, as shown by the appearance of new signals corresponding to the methyl protons of the cyclized products (Fig. 3). Absorbances of the NMR solutions at λ_{max} of the cyclized products were measured by UV–vis spectroscopy, and the extinction coefficients of the cyclized products were then calculated by factoring in the cyclized:uncyclized ratios obtained by integration of the corresponding NMR signals. Using these extinction coefficients and the spectral data from Fig. 2, photoconversions of 90% (**3c**) and 100% (**4**) were derived, which are consistent with literature data for similar compounds in dilute solutions. For instance, Irie reported that compounds like **3** and **4** without alkoxy groups undergo photocyclization at 313 nm with photoconversions of 80% and 74%, respectively,[20,24] and showed that the addition of electron-donating substituents at the *para*-position of the phenyl groups can increase the photoconversion by 10–20%.[23]

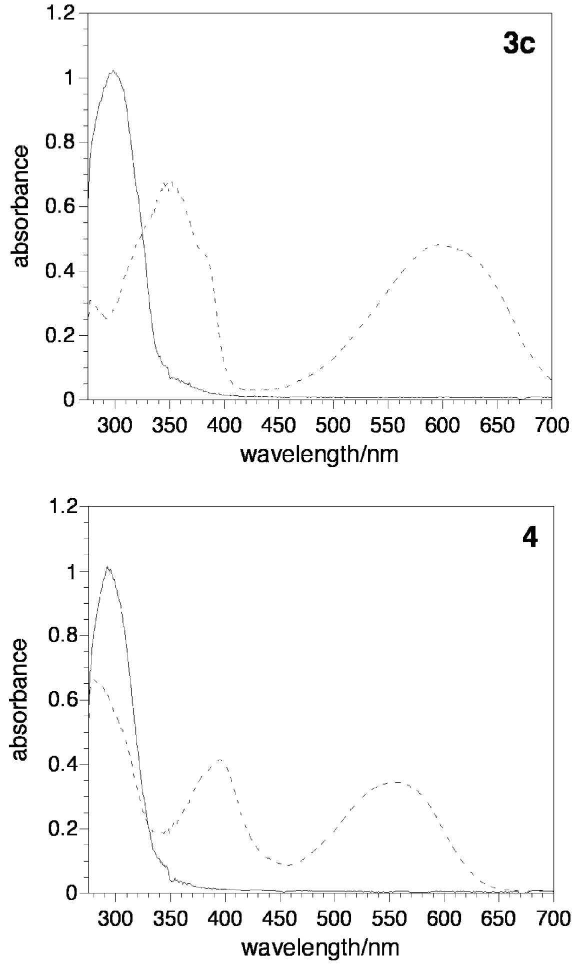


Fig. 2 UV–vis absorption spectra of **3c** (2.1×10^{-5} M) and **4** (2.3×10^{-5} M) in benzene before (—) and after irradiation (—) at $\lambda = 313$ nm.

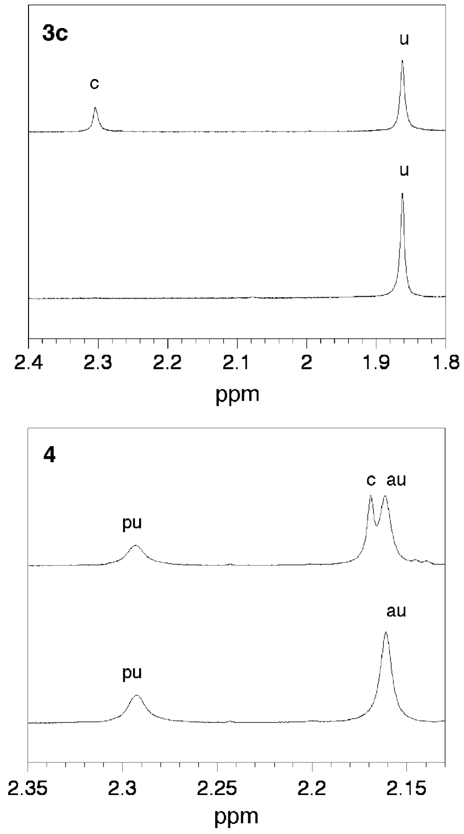
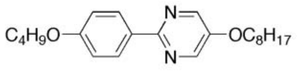


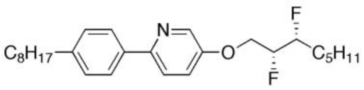
Fig. 3 Methyl ^1H NMR signals of compounds **3c** (7.2×10^{-3} M) and **4** (7.2×10^{-3} M) in deuterated benzene before (bottom) and after irradiation (top) at $\lambda = 313$ nm. The labels indicate the signals corresponding to the methyl protons of the uncyclized (u) and cyclized (c) forms, including the parallel (pu) and antiparallel (au) conformers of uncyclized **4**.

Polarization photomodulation

The compounds **3a–d** and **4** were doped in a ferroelectric liquid crystal host consisting of a 10 mol% mixture of the Displaytech compound **MDW950** in the achiral liquid crystal **PhP**.[25] In all cases, mixtures with dopant mole fractions greater than 3 mol% showed signs of phase separation by polarized microscopy and were discarded. Each doped FLC mixture was introduced in a rubbed polyimide-coated ITO glass cell with a 4 µm spacing and aligned by slow cooling from the isotropic liquid phase to the SmC* phase in a hot stage. The spontaneous polarization P_S was measured as a function of temperature T before and after irradiation of the SSFLC films at 313 nm for 3 min using a 450 W Xe arc lamp fitted with an interference filter. In a first experiment, P_S *vs.* T plots for 1 and 3 mol% mixtures of **3c** in the SmC* host were obtained (Fig. 4a). Extrapolation of the plots to $P_S = 0$ prior to photocyclization reveals that **3c** causes a substantial decrease of the SmC*–SmA* phase transition temperature (Curie point, T_C), from 84 °C without dopant to 65 °C for the 3 mol% mixture. Photocyclization of **3c** causes the P_S *vs.* T plots to shift to lower temperatures, the effect being more pronounced at the higher dopant mole fraction, which is consistent with a photomechanical destabilization of the SmC* phase. As shown in Fig. 4b, the photomechanical effect achieved with **3** increases with the length of the alkoxy side-chains, but appears to level off at C_7. Photocyclization of the dibenzothienyl dopant **4** also causes a shift in the P_S vs T plot, but to a lesser extent than the dithienyl analogue **3c** (Fig. 4c).



PhP: Cr 58 SmC 85 SmA 95 N 98 I



MDW950

At any given temperature in the SmC* phase, the result of this photomechanical effect is either a decrease in absolute value of P_S or a complete loss of polarization due to an isothermal transition to the non-ferroelectric SmA* phase. The maximum polarization photomodulation ΔP_S achieved with **3c** (3 mol%) is 16.2 nC cm^{-2} at 6 K below the Curie point ($T - T_C = -6$ K), which is double the photomodulation achieved with **4** (3 mol%), 7.7 nC cm^{-2} at $T - T_C = -4$ K. In all cases, the high polarization state was fully restored by reversing the photocyclization using visible light at $\lambda > 455$ nm. The P_S photomodulation cycle could be repeated a number of times without any sign of photochemical degradation, as shown in Fig. 5, for example. To test the bistability of this photoswitch, a SSFLC film containing 3 mol% of **3c** was kept in the dark at 55 °C for 4 days after irradiation at 313 nm. No increase of P_S indicative of a thermal reversion of the photocyclization was observed over that period of time.

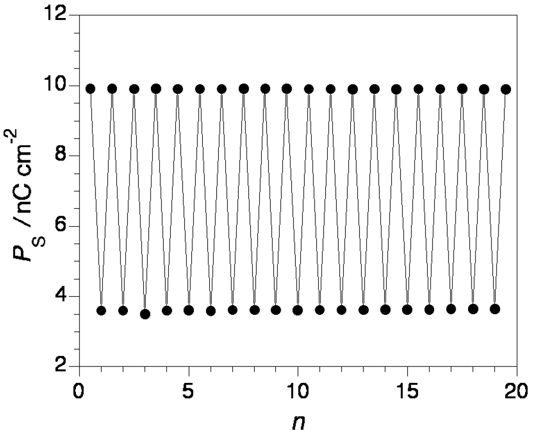


Fig. 5 Modulation of P_S for a FLC mixture doped with **4** at 3 mol% during alternating irradiation with UV ($\lambda = 313$ nm) and visible ($\lambda > 455$ nm) light at 64 °C (n = number of cycles).

Polarized spectroscopy

The cyclized photoproducts from **3** and **4** are characterized by a broad visible absorption band around 560–600 nm (Fig. 2) with a transition dipole moment oriented parallel to the long axis of the chromophores.[26] These compounds should therefore exhibit linear dichroism in the SmC* host if they are uniformly integrated within the lamellar structure of the SmC* phase. To assess the orientational order of the cyclized photoproducts from **3** and **4** in the SmC* host, polarized UV–vis spectroscopy measurements were performed on SSFLC films containing 3 mol% of **3a–d** and **4**. The doped FLC mixtures were carefully aligned in 4 µm ITO glass cells by slow cooling from the isotropic liquid phase to the SmC* phase and then irradiated at 313 nm. Absorption spectra were acquired as a function of the angle formed by the polarizer and the smectic layer normal while applying a positive or negative 10 V dc field across the SSFLC films. As shown in Fig. 6, the absorbance of the cyclized photoproducts from **3c** and **4** in the SmC* phase at $T - T_C = -10$ K is characterized by a relatively strong linear dichroism corresponding to order parameters of 0.70 and 0.82, respectively.[27] The order parameter increases with the alkoxy chain length in **3a–d**, from 0.58 to 0.78. The dichroic tilt angle, *i.e.*, the angle formed by the polarizer and the layer normal at maximum absorbance, is approximately the same (±2°) as the SmC* tilt angle measured by polarized microscopy, and decreases with increasing temperature, which is consistent with the temperature dependence of molecular tilt in the SmC*

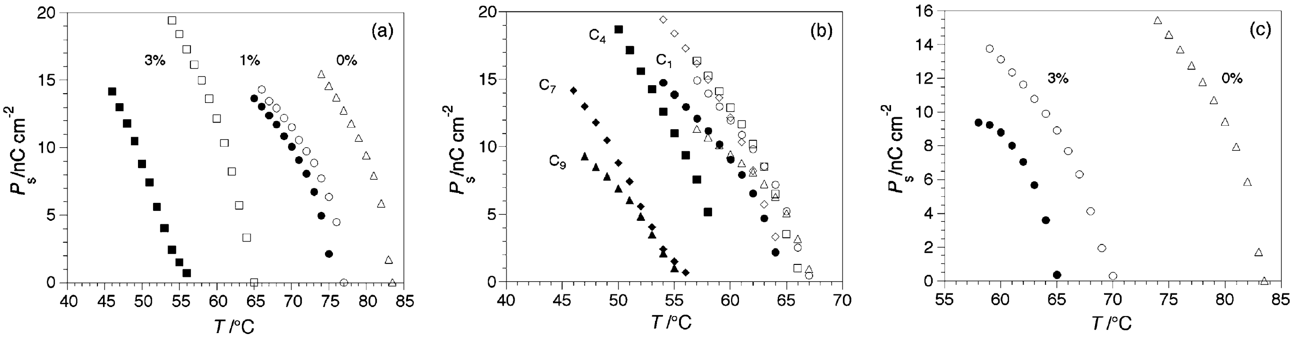


Fig. 4 Spontaneous polarization P_S as a function of temperature T. (a) FLC mixtures with no dopant (triangles), doped with **3c** at 1 mol% (circles) and 3 mol% (squares) before and after irradiation at $\lambda = 313$ nm (open and filled symbols, respectively). (b) FLC mixtures doped with **3a** (circles), **3b** (squares), **3c** (diamonds) and **3d** (triangles) at 3 mol% before and after irradiation at $\lambda = 313$ nm. (c) FLC mixtures with no dopant (triangles) and doped with **4** at 3 mol% (circles) before and after irradiation at $\lambda = 313$ nm.

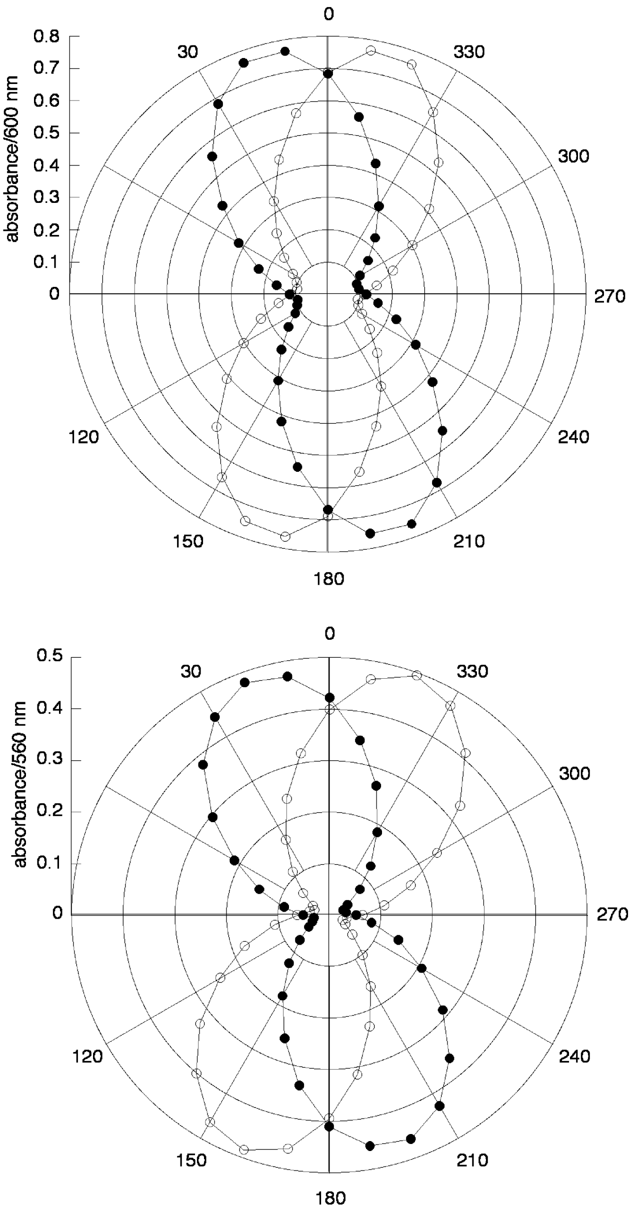


Fig. 6 Polar plots of linearly polarized light absorbance *vs.* angle formed by the polarizer and the layer normal for 4 μm SSFLC films of 3 mol% mixtures of **3c** (top) and **4** (bottom) in the SmC* host after irradiation at $\lambda = 313$ nm. The measurements were taken at $T - T_C = -10$ K while applying a dc field of +10 V (open circles) and −10 V (filled circles) across the films.

phase. These results strongly suggest that **3** and **4** form homogeneous solutions with the SmC* host and are integrated within the layer structure of the SmC* phase, with their molecular long axes approximately coincident with the director.

Discussion

The polarization photomodulation achieved with dopants **3c** and **4** is comparable to that generally achieved with azobenzene dopants.[5–10] The decrease in T_C caused by doping these compounds in the SmC* host is consistent with a destabilization of the SmC* phase, which is further enhanced by the photocyclization of the dopants. However, molecular modeling at the semiempirical AM1 level suggests that, unlike azobenzene dopants, the photocyclization of dithienylperfluorocyclopentenes results in relatively modest changes in molecular shape. As shown in Fig. 7, the AM1 model of **3c** in its most extended form has a bent shape that should indeed disrupt the lamellar ordering of the SmC* phase, and which remains more or less the same upon photocyclization. It is possible that the photomechanical effect achieved with these dopants is due to a difference in the conformational degrees of freedom of the uncyclized and cyclized chromophores. The uncyclized chromophores are conformationally more flexible by virtue of rotation about the thienylethene single bonds, and should therefore be more adaptable to the lamellar ordering imposed by the SmC* phase. However, the dopant loses its conformational flexibility upon photocyclization, effectively locking in the unfavorable bent shape of the chromophore, which should cause a greater destabilization of the SmC* phase. The AM1 model of **4** has approximately the same bent shape as **3c**, but the photocyclized form has a higher, more favorable aspect ratio, which is consistent with the higher order parameter measured by polarized spectroscopy and may explain why the photomechanical effect achieved with **4** is significantly less than with **3c**. The increase in photomechanical destabilization with increasing length of the alkoxy side-chains in the series **3a–d** is also consistent with this mechanism.

Summary

The spontaneous polarization of a ferroelectric liquid crystal can be modulated by the reversible photocyclization of dithienyl- and dibenzothienylperfluorocyclopentene dopants. The photomodulation of P_S is due to a photomechanical effect which may originate from a loss of conformational flexibility of the dopant upon photocyclization. The degree of photomodulation increases with dopant concentration up to 3 mol%, and the resulting P_S photoswitch is fatigue resistant and photochemically bistable. To the best of our knowledge, this is the first example of a bistable SSFLC photoswitch to be reported in the literature.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 and 400 spectrometers in deuterated chloroform and deuterated benzene. The chemical shifts are reported in δ (ppm) relative to tetramethylsilane. Low resolution electron impact

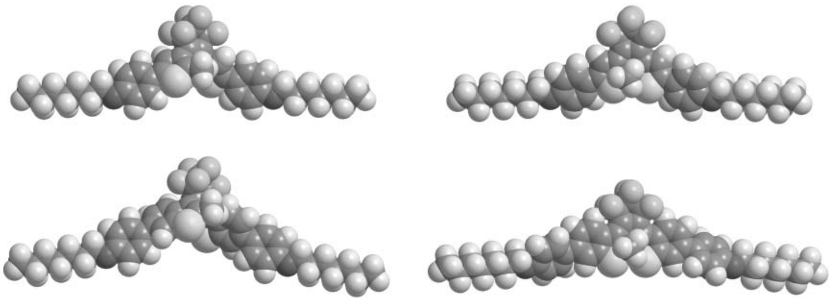


Fig. 7 Space-filling models of **3c** (top, left) and **4** (bottom, left) and their photoproducts.

(EI) 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 or the University of Toronto Mass Spectrometry Center. Elemental analyses were performed by MHW Laboratory (Phoenix, AZ). Melting points were determined on a Mel-Temp II melting point apparatus and are uncorrected. Polarized microscopy analyses were performed using a Nikon Eclipse E600 POL polarized light microscope fitted with a Linkam LTS 350 hot stage. Solution visible spectra were recorded on a Varian Cary-3 UV–visible spectrometer in spectrophotometric grade benzene or deuterated benzene. Flash chromatography was performed using 40–63 µm (230–400 mesh) silica gel (Silicycle) and thin layer chromatography was performed using silica gel 60 F_{254} plates (EM Science). Molecular modeling was performed at the AM1 level using MOPAC as implemented on Chem3D Pro, version 4.0.

Materials

All reagents, solvents and chemicals were obtained from commercial sources and used without further purification, unless otherwise noted. Methylene chloride was freshly distilled from P_2O_5 under nitrogen. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone under nitrogen. (*R*,*R*)-5-(2,3-difluorooctyl)-2-(4-octylphenyl)pyridine (**MDW950**) was supplied by Displaytech, Inc. 1,2-Bis(5-(4-methoxyphenyl)-2-methylthien-3-yl)perfluorocyclopentene (**3a**),[19] 1,2-bis(5-(4-hydroxyphenyl)-2-methylthien-3-yl)perfluorocyclopentene (**5**),[19] and 1,2-bis(6-iodo-2-methylbenzothiophen-3-yl)perfluorocyclopentene (**7**)[20] were prepared according to published procedures and shown to have the expected physical and spectral properties.

1,2-Bis(5-(4-butyloxyphenyl)-2-methylthien-3-yl)perfluorocyclopentene (3b)

Under an Ar atmosphere, a mixture of **5** (71 mg, 0.13 mmol), 1-bromobutane (59 mg, 0.43 mmol), and K_2CO_3 (117 mg, 0.85 mmol) in 2-butanone (10 mL) was refluxed for 24 h. After cooling, the mixture was poured into water and extracted twice with ether. The combined extracts were dried ($MgSO_4$), concentrated and the residue purified by flash chromatography on silica gel (9:1 hexanes/ethyl acetate). Recrystallization from ethanol gave 25 mg (30%) of **3b** as a light blue solid: mp 131–133 °C; ^1H NMR (400 MHz) δ 0.98 (t, 3H, *J* = 8 Hz), 1.50 (m, 2H), 1.77 (m, 2H), 1.94 (s, 3H), 3.98 (t, 2H, *J* = 8 Hz), 6.89 (d, 2H, *J* = 8 Hz), 7.15 (s, 1H), 7.44 (d, 2H, J = 8 Hz); ^{13}C NMR (100 MHz) δ 13.8, 14.5, 19.2, 31.2, 67.8, 114.9, 121.2, 125.7, 126.0, 126.9, 140.2, 142.2, 159.0; MS (EI) *m*/*z*: 666 (M + 2, 4), 665 (M + 1, 9), 664 (M^+, 23), 271 (16), 226 (12), 215 (13), 212 (11), 198 (21), 197 (19), 169 (73), 167 (30), 156 (21), 152 (13), 149 (100), 137 (42), 136 (24), 129 (21), 107 (34), 105 (30); HRMS (EI) calcd for $C_{35}H_{34}F_6O_2S_2$: 664.1904, Found: 664.1905.

1,2-Bis(5-(4-heptyloxyphenyl)-2-methylthien-3-yl)perfluorocyclopentene (3c)

Under an Ar atmosphere, diisopropylazodicarboxylate (38 mg, 0.19 mmol) was added dropwise to a stirred solution of **5** (50 mg, 0.09 mmol), 1-heptanol (37 mg, 0.32 mmol), and triphenylphosphine (52 mg, 0.2 mmol) in dry THF (5 mL). After stirring overnight at room temperature, the mixture was concentrated and the residue purified by flash chromatography on silica gel (9:1 hexane/ethyl acetate). Recrystallization from EtOH gave 31 mg (46%) of **3c** as a light blue solid: mp 90–92 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 6H), 1.32–1.47 (m, 16H), 1.79 (m, 4H), 1.94 (s, 6H), 3.98 (t, J = 6.5 Hz, 4H), 6.90 (d, J = 9.0 Hz, 4H), 7.14 (s, 2H), 7.44 (d, J = 9.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 14.8, 22.9, 26.3, 29.4, 29.5, 30.1, 68.5, 115.2, 121.5, 126.1, 126.3, 127.2, 140.5, 142.5, 159.4; MS (EI) m/e 748 (M^+, 89), 733 (7), 537 (15), 522 (16), 277 (19), 167 (27), 149 (100); UV (C_6H_6, open) λ_{max} 298 (log ε 4.70); HRMS (EI) calcd for $C_{41}H_{46}F_6O_2S_2$ 748.2850, found 748.2843.

1,2-Bis(5-(4-nonyloxyphenyl)-2-methylthien-3-yl)perfluorocyclopentene (3d)

The procedure used for the synthesis of **3b** was repeated with **5** (246 mg, 0.44 mmol), 1-bromononane (201 mg, 0.97 mmol) and K_2CO_3 (250 mg, 1.81 mmol) in 2-butanone (15 mL) to give 163 mg (46%) of **3d** as white needles: mp 82–83 °C; ^1H NMR (300 MHz) δ 0.89 (t, 3H, *J* = 7 Hz), 1.29–1.50 (m, 12H), 1.79 (m, 2H), 1.94 (s, 3H), 3.97 (t, 2H, *J* = 7 Hz), 6.90 (d, 2H, *J* = 9 Hz), 7.15 (s, 2H), 7.45 (d, 2H, *J* = 9 Hz); ^{13}C NMR (75 MHz) 14.5, 14.9, 23.1, 26.4, 29.7, 29.9, 32.2, 68.6, 115.3, 121.6, 126.1, 126.4, 127.3, 140.6, 142.6, 159.5; MS (EI) *m*/*z*: 807 (M + 3, 3), 806 (M + 2, 9), 805 (M + 1, 22), 804 (M^+, 42), 537 (24), 522 (22), 401 (13), 207 (15), 149 (100), 137 (55), 129 (14), 126 (25), 121 (20). Anal. calcd for $C_{45}H_{54}F_6O_2S_2$: C, 67.14; H, 6.76; F, 14.16; S, 7.97. Found: C, 67.36; H, 6.87; F, 14.43; S, 7.84.

1,2-Bis(6-(4-methoxyphenyl)-2-methylbenzothiophen-3-yl)perfluorocyclopentene (8)

Under an Ar atmosphere, $Pd(PPh_3)_4$ (83 mg, 0.072 mmol), Na_2CO_3 (1.3 g), water (5 mL) and 4-methoxyphenylboronic acid (0.45 g, 2.9 mmol) were added to a solution of **7** (0.52 g, 0.72 mmol) in THF (5 mL). The mixture was stirred under reflux for 24 h, then poured into water and extracted twice with ether. The combined extracts were washed with water, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography on silica gel (9:1 hexanes/ethyl acetate) to give **8** (0.22 g, 45%) as a pale yellow solid: mp 128–130 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 6H, antiparallel conformer), 2.54 (s, 6H, parallel conformer), 3.83 (s, 6H, parallel), 3.86 (s, 6H, antiparallel), 6.94–7.02 (m, 4H), 7.46–7.98 (m, 10H), parallel/antiparallel = 35:65; MS (EI) *m*/*e* 680 (M^+, 100), 650 (14), 340 (27); HRMS (EI) calcd for $C_{37}H_{26}F_6O_2S_2$ 680.1278, found 680.1274.

1,2-Bis(6-(4-hydroxyphenyl)-2-methylbenzothiophen-3-yl)perfluorocyclopentene (9)

Under an Ar atmosphere, a 1.0 M solution of BBr_3 in heptanes (1.2 mL) was added dropwise to a solution of **8** (120 mg, 0.17 mmol) in CH_2Cl_2 (3.5 mL) cooled to −78 °C. The mixture was stirred at −78 °C for 6 h, then allowed to warm to room temperature. Water was slowly added and the mixture was stirred for 1.5 h., then extracted twice with ether. The combined extracts were dried ($MgSO_4$) and concentrated to give **9** (97 mg, 84%) which was used in the next step without further purification. ^1H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 6H, antiparallel conformer), 2.52 (s, 6H, parallel conformer), 6.90–6.98 (m, 4H), 7.44–7.90 (m, 10H), parallel/antiparallel = 35:65.

1,2-Bis(6-(4-heptyloxyphenyl)-2-methylbenzothiophen-3-yl)perfluorocyclopentene (4)

A solution of **9** (80 mg, 0.12 mmol), 1-bromoheptane (72 mg, 0.40 mmol) and K_2CO_3 (110 mg, 0.80 mmol) in 2-butanone (8 mL) was refluxed for 48 h. After cooling to room temperature, the mixture was poured into water and extracted twice with ether. The combined extracts were washed with water, dried ($MgSO_4$) and concentrated. The residue was purified by flash chromatography on silica gel (15:1 hexanes/ethyl acetate) and recrystallization from ether-hexanes to give **4** (67 mg, 65%) as a white solid: mp 57–58 °C; ^1H NMR

(300 MHz, $CDCl_3$) δ 0.91 (t, J = 6.0 Hz, 6H), 1.34–1.49 (m, 16H), 1.83 (m, 4H), 2.26 (s, 6H, antiparallel conformer), 2.54 (s, 6H, parallel conformer), 3.99 (t, 4H, parallel), 4.03 (t, 4H, antiparallel), 6.96–7.02 (m, 4H), 7.46–7.87 (m, 10H), parallel/antiparallel = 35:65; UV (C_6H_6, open) λ_{max} 292 (log ε 4.64); MS (EI) *m/e* 848 (M^+, 8), 750 (3), 652 (6), 326 (6), 149 (10). Anal. calcd for $C_{49}H_{50}F_6O_2S_2$: C, 69.32; H, 5.94. Found: C, 69.25; H, 5.99.

P_S photomodulation experiments

Surface-stabilized FLC films were prepared using rubbed polyimide-coated ITO glass cells (4 μm spacing, 0.25 cm^2 addressed area) supplied by Displaytech Inc. The filled cells were fitted in a Linkam LTS 350 hot stage with the addressed area fully exposed through the hot stage aperture and slowly cooled (0.2 K min^{-1}) from the isotropic phase to the SmC* phase while applying a 10 Hz, 6 V μm^{-1} triangular ac field across the film. The SSFLC/hot stage assembly was positioned vertically in front of a PTI 450 W high-pressure Xe arc lamp fitted with an IR water filter and either an interference filter (λ = 313 nm) or a UV cutoff filter (λ > 455 nm). The spontaneous polarization (P_S) was measured as a function of temperature by the triangular wave method (6 V μm^{-1}, 80–100 Hz)[28] using a Displaytech APT III polarization testbed before and after irradiation of the SSFLC films for 3 min at λ = 313 nm. Irradiation of the SSFLC films at λ > 455 nm restored the original polarization state. Tilt angles were measured by polarized microscopy as half the rotation between two extinction positions corresponding to opposite polarization orientations.

Linear dichroism experiments

Surface-stabilized FLC films were prepared and mounted in a hot stage as described above and irradiated at λ = 313 nm prior to spectral acquisition. The SSFLC/hot stage assembly was positioned vertically between an Ocean Optics UV–vis light source and photodetector coupled to an Ocean Optics USB 2000 Miniature Fiber Optic Spectrometer interfaced to a PC. A linear polarizer on a radial mount was positioned between the light source and the sample and oriented so that the plane of polarization was coincident with the rubbing direction of the SSFLC cell at the start of each experiment. A baseline spectra of a dopant-free sample of the SmC* host was first acquired and subtracted from spectra of the doped FLC mixtures. Absorption spectra were acquired as a function of the angle formed by the polarizer and the smectic layer normal while applying a positive or negative 10 V dc field across the SSFLC films.

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