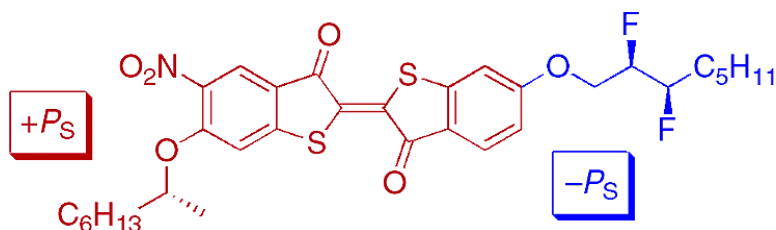


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J. Am. Chem. Soc., **2003**, 125 (23), 6862-6863 • DOI: 10.1021/ja0353309 • Publication Date (Web): 14 May 2003

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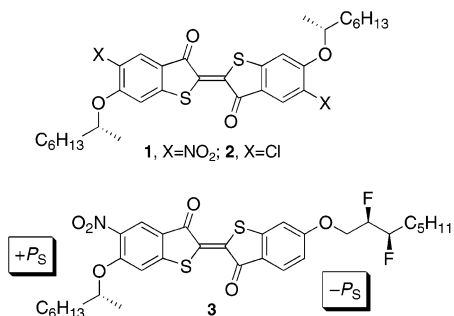
Photoinduced Polarization Inversion in a Ferroelectric Liquid Crystal Using an Ambidextrous Chiral Thioindigo Dopant

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Ferroelectric liquid crystals (FLC) have generated a considerable amount of research activity over the past 25 years, ranging from fundamental studies of the molecular origins of spontaneous polar ordering in the SmC* phase to the commercial development of high-resolution reflective FLC microdisplays.^{1,2} The ferroelectric SmC* phase is a chiral liquid crystal phase characterized by a spontaneous electric polarization (P_S) which can be coupled to an electric field to produce an electrooptical light shutter.³ In the past 10 years, a growing interest in photonic liquid crystal materials has led a number of research groups to investigate optical switching mechanisms for FLC light shutters (photoswitch) based on the photo-modulation of P_S .^{4–6} Such photoswitching mechanisms may allow one to record images and write diffraction gratings on bistable FLC films on the time scale of a few microseconds.



Let us consider two contrasting approaches to photomodulate the spontaneous polarization of a ferroelectric SmC* phase. One approach is based on the change in molecular shape of achiral photochromic dopants such as 4,4'-disubstituted azobenzenes, which do not contribute intrinsically to P_S .^{4d,e,h,i} In a ferroelectric SmC* host, the trans–cis photoisomerization of an achiral azobenzene dopant destabilizes the SmC* phase (photomechanical effect), which results in a decrease of P_S at constant temperature. Another approach is based on the photoinduced change in transverse dipole moment of a chiral photochromic dopant which maintains a rodlike shape in both photoisomeric forms.⁵ In an achiral, non-ferroelectric SmC host, the chiral photochromic dopant induces a spontaneous polarization, and its photoisomerization causes a change in P_S without concomitant destabilization of the induced SmC* phase. Examples of such dopants include the chiral thioindigos **1** and **2**, which undergo trans–cis photoisomerization in the visible range of the spectrum. The increase in P_S observed upon trans–cis photoisomerization of **1** and **2** is attributed to the increase in transverse dipole moment of the thioindigo core, which is strongly coupled to the chiral 2-octyloxy side chains via interactions with the adjacent nitro and chloro substituents.⁷ This so-called *stereo-*

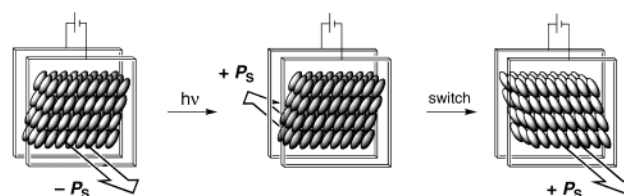


Figure 1. Photoswitching of a ferroelectric SmC* liquid crystal film via P_S sign inversion. The FLC is aligned between ITO-coated glass slides, and a dc electric field is maintained across the film. The P_S vector is perpendicular to the plane of the page.

polar coupling is essential to the photomodulation of P_S because it imparts conformational asymmetry to the thioindigo core. Without stereo-polar coupling, i.e., when X = H, the thioindigo core does not contribute to the spontaneous polarization and the effect of trans–cis photoisomerization on P_S is negligible.⁸

A potentially useful FLC photoswitching mechanism which has yet to be fully exploited is the photoinduced sign inversion of P_S (Figure 1). This concept was first demonstrated in a SmC host using the thioindigo dopant **2** in combination with a photoinert chiral dopant which induces a spontaneous polarization of opposite sign.^{5b} More recently, Komitov and co-workers reported a photoinversion of P_S via the trans–cis photoisomerization of an achiral azobenzene dopant in a chiral SmC* host which undergoes an inversion of P_S as a function of temperature.⁴ⁱ In this Communication, we report the first example of FLC photoswitching based on a photoinduced sign inversion of the polarization power of a single chiral dopant.⁹ This is achieved without concomitant destabilization of the SmC* phase using an “ambidextrous” thioindigo dopant (**3**) with competing chiral side chains that induce spontaneous polarizations of opposite signs.¹⁰ The (*R*)-2-octyloxy side chain is sterically coupled to the thioindigo core via the nitro substituent and induces a positive P_S ,¹¹ whereas the (*R,R*)-2,3-difluoroctyloxy side chain is decoupled from the core and induces a negative P_S .¹² With this new design, the increase in transverse dipole moment of the thioindigo core upon trans–cis photoisomerization raises the polarization power of the coupled 2-octyloxy/thioindigo unit above that of the 2,3-difluoroctyloxy unit and inverts the net sign of P_S .

The dopant **3** was obtained by alkylation of the known compound (*R*)-6'-hydroxy-5-nitro-6-(2-octyloxy)thioindigo¹³ with (*R,R*)-2,3-difluoroct-1-yl tosylate, which was supplied by Displaytech, Inc.¹⁴ A 1.0 mol % mixture of dopant **3** in the SmC host (\pm)-4-(4-methylhexyloxy)phenyl 4-decyloxybenzoate (**PhB**)¹⁵ was introduced in a polyimide-coated ITO glass cell with a 4- μ m spacing and aligned by slow cooling from the isotropic liquid phase to the SmC* phase. The spontaneous polarization of the FLC film was measured as a function of temperature with the film shielded with a red cutoff filter (i.e., in the dark), and under constant irradiation with visible light at $\lambda = 510$ and 450 nm using a 450-W high-pressure Xe arc lamp fitted with interference filters (Figure 2).¹⁶ The sign of P_S

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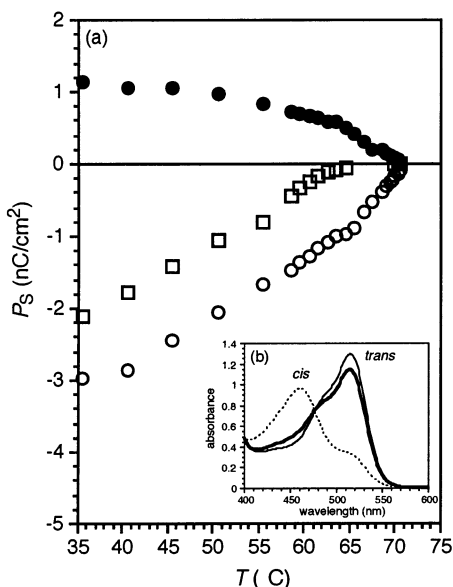


Figure 2. (a) Spontaneous polarization P_S as a function of temperature T for the 1 mol % mixture of **3** in PhB kept in the dark (○) and under constant irradiation at $\lambda = 510$ (●) and 450 nm (□). (b) UV-vis absorption spectra of a 10^{-4} M solution of **3** in benzene after irradiation at $\lambda = 510$ (dashed line) and 450 nm (heavy line) and after the solution was left to stand in the dark for 24 h (fine line).

induced by *trans*-**3** was determined to be negative on the basis of the relative configuration of the electric field and the switching position of the sample,¹¹ which indicates that the polarization power of the 2,3-difluorooctyloxy unit predominates in the *trans* form. *Trans*-*cis* photoisomerization of **3** by irradiation of the FLC film at 510 nm causes a sign inversion of P_S , from -1.3 to $+0.66$ nC/cm² at 10 K below the SmA*–SmC* transition temperature (T_C), which indicates that the polarization power of the coupled 2-octyloxy/thioindigo core unit predominates in the *cis* form.¹⁷ The increase in absorbance of the FLC film at 450 nm (*cis* isomer) upon irradiation at 510 nm is only 5% of that observed in dilute isotropic solution (inset, Figure 2), which is consistent with previous studies of 6,6'-dialkoxythioindigo photoisomerization in other organized multilayer assemblies.¹⁸ Irradiation of a 4.0 mol % mixture of **3** in PhB at 510 nm does not invert the sign of P_S and results in a smaller modulation of P_S in relative terms, from -6.8 to -2.6 nC/cm² at $T - T_C = -10$ K. These results are consistent with previous observations^{5a} which suggest that *trans*-*cis* photoisomerization is gradually suppressed with increasing concentration of dopant as a result of aggregate formation.¹⁹

The polarization inversion can be reversed by irradiation at 450 nm, which should give a *trans*-enriched photostationary state. Complete reversion to the original polarization state is achieved by thermal *cis*-*trans* isomerization after the solution is left to stand in the dark for ca. 60 s. The P_S vs T plots show that the SmC*–SmA* transition temperature at $P_S = 0$ does not change upon photoisomerization of **3**, which suggests that the polarization photoinversion is achieved without a photomechanical effect. To the best of our knowledge, this system represents the simplest approach yet to photoswitch a ferroelectric liquid crystal film without destabilizing the SmC* phase.

Acknowledgment. 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 support of this work.

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JA0353309