

Photomodulation of the Spontaneous Polarization of a Ferroelectric Liquid Crystal: Harnessing the Transverse Dipole Modulation of a Chiral Thioindigo Dopant

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Received May 15, 1997

The search for new chiral materials exhibiting or inducing a chiral smectic C (S_C^*) liquid crystal phase has been motivated by the potential applications of such materials in ferroelectric liquid crystal (FLC) light valves and displays.¹ An important area of interest in this field focuses on the optical switching of FLC light valves. In principle, a FLC light valve can be controlled by modulating the spontaneous polarization (P_S) of the S_C^* phase above and below a switching threshold defined by the applied voltage pulse.^{1b} Previous work has shown that P_S can be photomodulated in the near-UV range via the reversible *trans*–*cis* photoisomerization of chiral azobenzene dopants in S_C or S_C^* liquid crystal hosts² and of azobenzene-containing side-chain FLC copolymers.³ The origin of P_S modulation is thought to be a disruption of 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* generally results in a decrease of the S_C^* – S_A^* or S_C^* – N^* phase transition temperature, producing in some cases a total loss of polarization via an isothermal phase transition.^{2a,c,d} In this communication, we describe a new approach to photomodulate P_S in the visible range, without concomitant destabilization of the S_C^* phase, which is based on the transverse dipole modulation of a chiral photochromic dopant that can maintain a rod-like shape in both isomeric forms.⁴

Previous work has shown that *trans*–*cis* photoisomerization of the thioindigo dopant **1** in a S_C liquid crystal host produces a 10% decrease of P_S , which is opposite in trend to that expected from the change in transverse dipole moment of the thioindigo core.⁵ We ascribed this result to the lack of stereopolar coupling between the core and the chiral side chains and postulated that

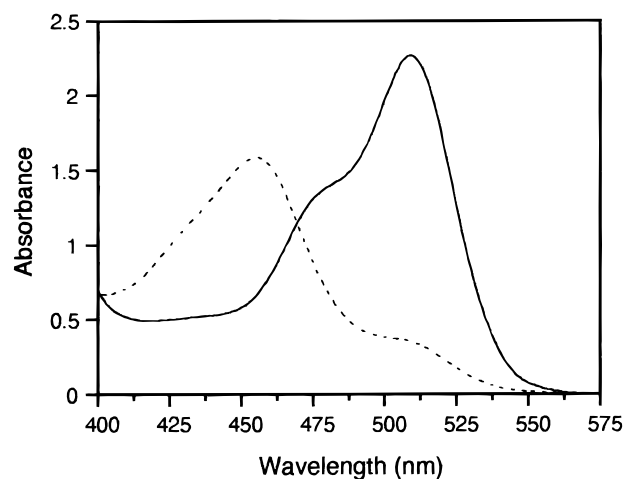
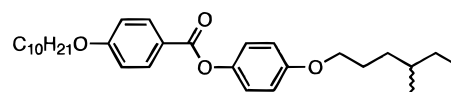
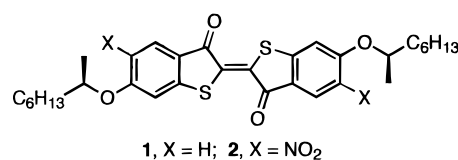


Figure 1. UV-vis absorption spectra of a 1.1×10^{-4} M solution of **2** in benzene after irradiation at $\lambda > 505$ nm (dashed line) and after standing in the dark for 20 h (solid line).

the modulation may be caused by a change in the conformational equilibrium of the chiral side chains imposed by the transoid S_C lattice upon photoisomerization to the *cis*-form. In order to reverse this trend, and further enhance P_S photomodulation by harnessing the large change in transverse dipole moment of the thioindigo core upon *trans*–*cis* photoisomerization, we have synthesized (*R,R*)-6,6'-bis(1-methylheptyloxy)-5,5'-dinitrothioindigo (**2**), in which the chiral side chains should be strongly coupled to the thioindigo core via both steric and dipole–dipole coupling with the adjacent nitro groups, as described by Walba and co-workers.⁶



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

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(4) For other recent examples of the use of photochromic molecules to control the properties of liquid crystal materials using light, see: (a) Huck, N. P. M.; Jager, W. F.; de Lange, B.; Feringa, B. L. *Science* **1996**, *273*, 1686. (b) Feringa, B. L.; Huck, N. P. M.; van Doren, H. A. *J. Am. Chem. Soc.* **1995**, *117*, 9929. (c) Janicki, S.; Schuster, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 8524. (d) Suarez, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1995**, *117*, 6732, and references cited therein. (e) Ikeda, T.; Tsutsumi, O. *Science* **1995**, *268*, 1873. (f) Natarajan, L. V.; Bunning, T. J.; Kim, S. Y. *Macromolecules* **1994**, *27*, 7248. (g) Kurihara, S.; Ikeda, T.; Tazuke, S.; Seto, J. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3251. (h) Ikeda, T.; Horiiuchi, S.; Karanjit, D. B.; Kurihara, S.; Tazuke, S. *Macromolecules* **1990**, *23*, 36, 42. (i) Yitzchaik, S.; Cabrera, I.; Buchholtz, F.; Krongauz, V. *Macromolecules* **1990**, *23*, 707. (j) Cabrera, I.; Krongauz, V.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1178.

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Compound **2** was synthesized by an adaptation of the approach reported for **1**.⁵ Irradiation of a 10^{-4} M solution of **2** in air-saturated benzene at $\lambda > 505$ nm using a 150 W high-pressure Xe arc lamp fitted with a cutoff filter gave rise to a photostationary state consisting primarily of the *cis*-isomer ($\lambda_{\max} = 457$ nm), as shown in Figure 1. Upon standing in the dark for several hours, the compound isomerized to the thermodynamically more stable *trans*-isomer ($\lambda_{\max} = 509$ nm, $\log \epsilon = 4.31$).⁷ Compound **2** was doped in the racemic S_C host **PhBz**⁸ over the mole fraction range $0.005 < x_d < 0.03$ to give an induced S_C^* liquid crystal phase. We could not exceed 3.0 mol % due to the poor solubility of **2** in liquid crystal hosts. P_S and tilt angle (θ) measurements at 5 °C below the S_C^* – S_A^* phase transition temperature ($T - T_{AC} = -5$ °C) gave a polarization power (δ_p) of +95 nC/cm² for *trans*-**2**, which is ca. one-half the δ_p value of *trans*-**1** in **PhBz**.^{5,9} This is consistent with the expected coupling of the chiral side-chains with the

(6) Walba, D. M.; Ros, M. B.; Clark, N. A.; Shao, R.; Robinson, M. G.; Liu, J.-Y.; Johnson, K. M.; Doroski, D. *J. Am. Chem. Soc.* **1991**, *113*, 5471.

(7) The *cis*-isomer of compound **2** was not isolated. The UV spectra shown in Figure 1 are fully consistent with those reported for the isolated *cis*-isomer ($\lambda_{\max} = 460$ nm, $\log \epsilon = 4.08$) and *trans*-isomer ($\lambda_{\max} = 516$ nm, $\log \epsilon = 4.17$) of 6,6'-diethoxythioindigo in benzene: Wyman, G. M.; Zarnegar, B. M. *J. Phys. Chem.* **1973**, *77*, 831.

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thioindigo core in **2**, which should orient the alkoxy dipoles in opposite directions with respect to the polar axis in the *trans*-form.

A 2.6 mol % mixture of **2** in **PhBz** was introduced in a 4 μm ITO glass cell and slowly cooled from the isotropic liquid phase to the S_C^* phase at $T - T_{AC} = -10$ °C, giving a well aligned sample of good optical quality. P_S was measured with the sample under constant irradiation at two different wavelengths producing the *cis*-enriched photostationary state ($\lambda > 505$ nm) and the thermally relaxed *trans*-isomer ($\lambda > 650$ nm, no absorption) using the 150W Xe arc lamp fitted with a water filter and the appropriate cutoff filter. An 82% increase in P_S was achieved upon irradiation of the thermally relaxed *trans*-isomer (1.12 ± 0.07 nC/cm²) to the *cis*-enriched photostationary state (2.04 ± 0.06 nC/cm²). Under these conditions, thermal relaxation to the *trans*-isomer occurred within 10 s in the S_C^* phase, a much faster rate than that observed in benzene solution at room temperature (*vide infra*).¹⁰ The irradiation cycle was repeated several times without any decrease in the degree of photomodulation.

The occurrence of a photomechanical effect can be ruled out based on the results of two control experiments. In the first one, the temperature dependence of P_S was examined under the two conditions of irradiation (Figure 2). Extrapolation of the two plots to $P_S = 0$ suggests that the photoisomerization of **2** in **PhBz** does not shift the $S_C^* - S_A^*$ phase transition temperature to any significant extent. In the second experiment, the racemic form of **2** was doped in a S_C^* host consisting of a 2.1 mol % mixture of (*S,S*)-4,4'-bis[(2-chloro-3-methylbutanoyl)oxy]biphenyl in **PhBz**.¹¹ In this case, a photomechanical effect would result in a decrease of P_S by virtue of a change in molecular shape of the photochromic dopant. However, irradiation of this mixture at $\lambda > 505$ nm under the same conditions caused no modulation of P_S , which further indicates

(9) P_S was measured by the triangular wave method using a Displaytech Automated Polarization Testbed III (6 V/ μm , 100 Hz) in conjunction with a Instec HS1-i hot stage. Polyimide-coated ITO glass cells (4 $\mu\text{m} \times 0.25$ cm²) supplied by Displaytech Inc. (Longmont, CO) were used for all measurements. Tilt angles (θ) were measured between crossed polarizers using a red cutoff filter ($\lambda > 650$ nm) as half the rotation between two extinction positions corresponding to opposite polarization orientations. The polarization power (δ_p) of dopant **2** was obtained as the slope of a plot of $P_S/\sin \theta$ vs x_d : Siemensmeyer, K.; Stegemeyer, H. *Chem. Phys. Lett.* **1988**, *148*, 409.

(10) Preliminary results suggest that the thermal *cis-trans* isomerization of **2** follows second-order kinetics, which may explain the rate acceleration in this case. The concentration of **2** in **PhBz** is approximately 10^{-1} M.

(11) In this case, the spontaneous polarization is induced by a nonphotoactive chiral dopant: Bommelburg, J.; Hansel, C.; Heppke, G.; Hollidi, J.; Lotzsch, D.; Scherf, K.-D.; Wuthe, K.; Zschke, H. *Mol. Cryst. Liq. Cryst.* **1990**, *192*, 335.

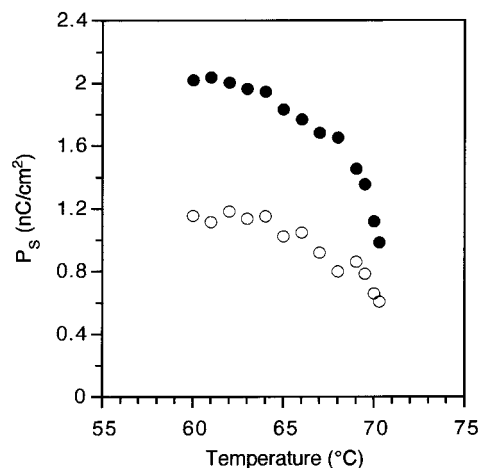


Figure 2. Spontaneous polarization P_S as a function of temperature for the S_C^* phase of a 2.6 mol % mixture of **2** in **PhBz** under constant irradiation at $\lambda > 505$ nm (filled circles) and at $\lambda > 650$ nm (open circles). A $S_C^* - S_A^*$ phase transition temperature of 71 °C was measured by polarized microscopy under illumination at $\lambda > 650$ nm.

that the *trans-cis* photoisomerization of **2** has no effect on the stability of the S_C^* phase. The experiment also rules out the possible contribution of a local heating effect to the photomodulation achieved with optically active **2**.

In summary, we have demonstrated that the spontaneous polarization of a FLC can be nearly doubled, without concomitant destabilization of the S_C^* phase, by photomodulating the transverse dipole moment of a chiral thioindigo dopant using visible light. The increase in P_S upon *trans-cis* photoisomerization of **2** is consistent with the stereopolar coupling of the chiral side chains with the thioindigo core. We plan to develop liquid crystalline analogues of dopant **2** that exhibit a greater compatibility with other liquid crystals in order to probe the influence of a variety of S_C hosts on the degree of photomodulation achieved by these compounds. This work is currently in progress.

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 financial support of this work.

Supporting Information Available: Synthetic procedures and analytical data for compound **2** (3 pages). See any current masthead page for ordering and Internet access instructions.

JA9715758