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Bistable Ferroelectric Liquid Crystal Photoswitch Triggered by a Dithienylethene Dopant

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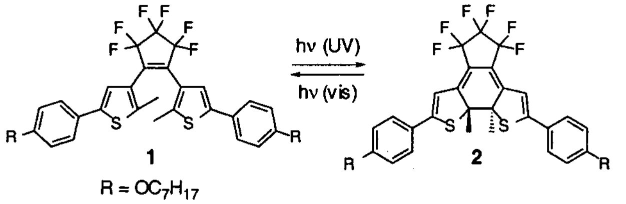
Ferroelectric SmC* liquid crystals are characterized by a spontaneous electric polarization (P_S) that can be coupled to an electric field to produce an ON−OFF spatial light modulator.[1] Over the past decade, considerable efforts have been made to develop light-driven FLC spatial light modulators (photoswitch) because of their potential use in optical computing, dynamic holography, telecommunications, and optical data storage.[2] While most FLC photoswitching mechanisms have been extrinsic in nature, using a photoconductive or photodiode layer to trigger the ON−OFF switching of an underlying FLC film, a number of studies have focused on intrinsic mechanisms based on the photomodulation of P_S. In most cases, the photomodulation of P_S is achieved via the trans−cis photoisomerization of a 4,4′-disubstituted azobenzene dopant, which causes a destabilization of the SmC* phase due to the change in shape of the azobenzene from rodlike (trans) to bent (cis).[3−9] At constant temperature, such destabilization results in a decrease of P_S. The photomodulation of P_S has also been achieved without destabilizing the SmC* phase via trans−cis photoisomerization of a chiral thioindigo dopant.[10,11]

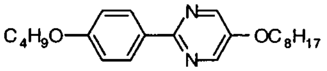
With azobenzene or thioindigo dopants, the principle of a FLC photoswitch has been demonstrated by modulating P_S above and below a switching threshold,[3] by causing an inversion in the sign of P_S,[9,11] and by causing an isothermal phase transition to a nonferroelectric SmA* phase.[4] However, none of the FLC photoswitches reported thus far are photochemically bistable due to thermal reversion of the cis isomers back to the thermodynamically more stable trans isomers. In this Communication, we report the first example of a photochemically bistable FLC photoswitch using a photochromic dithienylethene dopant.

Dithienylethenes are considered to be the most promising photochromic materials for optical memory and photoswitching applications because of their fatigue resistance and the thermal stability of both photoisomers.[12] They undergo a reversible photocyclization reaction between colorless ring-opened and colored ring-closed forms, as shown in Scheme 1. Recently, 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.[13] However, there are no published reports of doping experiments involving dithienylethenes in smectic liquid crystals. To investigate the effect of photoisomerization of a dithienylethene dopant on the spontaneous polarization of a FLC host, we chose derivative **1** as the prototype. In this system, the 4-heptyloxyphenyl substituents increase the aspect ratio of the dithienylethene chromophore to make it more compatible with the lamellar structure of the SmC* phase and shift the absorption maximum of the ring opened form to longer wavelengths to avoid overlap with the absorption spectrum of the FLC host.

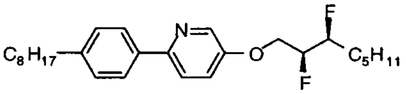
Scheme 1



Compound **1** was readily obtained by alkylation of the known 1,2-bis[5′-(4"-hydroxyphenyl)-2′-methylthien-3′-yl]perfluorocyclopentene[14] and recrystallized from ethanol.[15] The dithienylethene was doped in a FLC host consisting of a 10 mol % mixture of the Displaytech compound (*S*,*S*)-5-(2,3-difluorooctyl)-2-(4-octylphenyl)pyridine (**MDW950**) in the achiral SmC liquid crystal 2-(4-butyloxyphenyl)-5-octyloxypyrimidine (**PhP1**). Despite its increased aspect ratio, dopant **1** caused a significant lowering of the SmA*-SmC* phase transition temperature, from 84 °C in the absence of **1** to 67 °C in the presence of **1**, at a concentration of 3.0 mol %.



PhP1; phase sequence: Cr 58 SmC 85 SmA 95 N 98 I



MDW 950

FLC mixtures doped with the dithienylethene **1** at concentrations of 1.0 and 3.0 mol % were introduced in polyimide-coated ITO glass cells with a 4 μm spacing and aligned by slow cooling from the isotropic liquid phase to the SmC* phase. FLC mixtures with dopant concentrations greater than 3 mol % showed signs of phase separation by polarized microscopy and were discarded. P_S was measured as a function of temperature before and after irradiation of the FLC films with UV light for a period of 3 min with use of a 365 nm lamp (4 W, Spectroline).[16,17] As shown in Figure 1, photocyclization of the dithienylethene dopant causes the P_S vs T plots to shift to lower temperatures, which indicates a destabilization of the SmC* phase. Extrapolation of the plots to $P_S = 0$ shows that the SmC*-SmA* phase transition temperature decreases by 2 K upon irradiation of the 1 mol % mixture, and by 10 K upon irradiation of the 3 mol % mixture. At any given temperature in the SmC* phase, the result of this photomechanical effect is either a decrease of P_S or a complete disappearance of polarization due to a phase transition to the nonferroelectric SmA* phase. For

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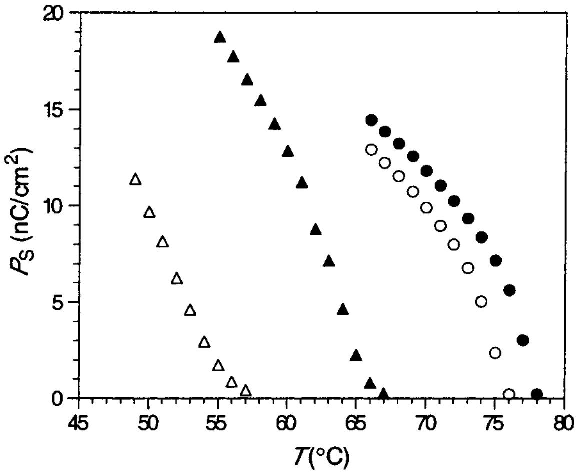

Figure 1. Spontaneous polarization P_S as a function of temperature T for FLC mixtures doped with **1** at 1.0 mol % (circles) and 3.0 mol % (triangles) before and after irradiation with UV light (filled and open symbols, respectively).

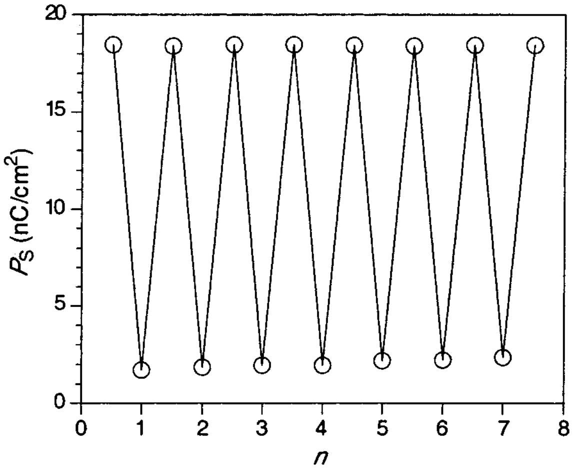

Figure 2. Modulation of P_S for the FLC mixture doped with **1** at 3 mol % during alternating irradiation with UV and visible light at 55 °C (n = number of cycles).

example, irradiation of the 3 mol % mixture held at 58 °C results in a modulation of P_S from 15.5 to 0 nC/cm^2. The spontaneous polarization can be fully restored by reversing the photocyclization by using visible light at $\lambda > 455$ nm (100 W Xe arc lamp). As shown in Figure 2, the P_S photomodulation cycle can be repeated many times without any sign of photochemical degradation. To test the bistability of the FLC photoswitch, the 3 mol % sample was kept in the dark at 55 °C for 4 days after irradiation with UV light. No increase in P_S indicative of a $\mathbf{2} \rightarrow \mathbf{1}$ thermal reversion was observed over that time period.

The P_S photomodulation achieved with dopant **1** is comparable to that usually achieved with azobenzene dopants.[3-9] The photomechanical effect observed with the dithienylethene dopant suggests that the open form **1** is more compatible with the SmC* phase than the closed form **2**, which may be explained by the difference in conformational degrees of freedom of the two photoisomers. According to molecular modeling (AM1), the structures of **1** and **2** have a bent shape that should disrupt the SmC* phase. However, the open form **1** should be more adaptable to the lamellar ordering imposed by the SmC* phase by virtue of its conformational flexibility. The closed form **2** is more rigid and should therefore be more disruptive.

In summary, we have shown that the spontaneous polarization of a ferroelectric liquid crystal can be modulated reversibly via photoisomerization of the dithienylethene dopant **1**. The magnitude of the photomodulation increases with dopant concentration up to 3 mol %, and the resulting photoswitch is fatigue resistant and bistable. To the best of our knowledge, this is the first example of a bistable FLC photoswitch to be reported in the literature. A more systematic structure–property investigation of this new class of photochromic FLC dopants is in progress and will be reported in due course.

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References

(1) (a) Clark, N. A.; Lagerwall, S. T. *Appl. Phys. Lett.* **1980**, *36*, 899. (b) Goodby, J. W.; Blinc, R.; Clark, N. A.; Lagerwall, S. T.; Osipov, M. A.; Pikin, S. A.; Sakurai, T.; Yoshino, K.; Zeks, B. *Ferroelectric Liquid Crystals: Principles, Properties and Applications*; Gordon & Breach: Philadelphia, PA, 1991. (c) Lagerwall, S. T. *Ferroelectric and Antiferroelectric Liquid Crystals*; Wiley-VCH: Weinheim, Germany, 1999.

(2) Moddel, G. In *Spatial Light Modulator Technology: Materials, Devices and Applications*; Efron, U., Ed.; Marcel Dekker: New York, 1995; pp 287–359.

(3) (a) Ikeda, T.; Sasaki, T.; Ichimura, K. *Nature* **1993**, *361*, 428. (b) Sasaki, T.; Ikeda, T.; Ichimura, K. *J. Am. Chem. Soc.* **1994**, *116*, 625.

(4) Walton, H. G.; Coles, H. J.; Guillon, D.; Poeti, G. *Liq. Cryst.* **1994**, *17*, 333.

(5) Negishi, M.; Tsutsumi, O.; Ikeda, T.; Hiyama, T.; Kawamura, J.; Aizawa, M.; Takehara, S. *Chem. Lett.* **1996**, 319.

(6) Blinov, L. M.; Kozlovsky, M. V.; Nakayama, K.; Ozaki, M.; Yoshino, K. *Jpn. J. Appl. Phys.* **1996**, *35*, 5405.

(7) Oge, T.; Zentel, R. *Macromol. Chem. Phys.* **1996**, *197*, 1805.

(8) Langhoff, A.; Giesselmann, F. *Ferroelectrics* **2000**, *244*, 283.

(9) Komitov, L.; Tsutsumi, O.; Ruslim, C.; Ikeda, T.; Ichimura, K.; Yoshino, K. *J. Appl. Phys.* **2001**, *89*, 7745.

(10) (a) Dinescu, L.; Lemieux, R. P. *J. Am. Chem. Soc.* **1997**, *119*, 8111. (b) Dinescu, L.; Maly, K. E.; Lemieux, R. P. *J. Mater. Chem.* **1999**, *9*, 1679.

(11) Dinescu, L.; Lemieux, R. P. *Adv. Mater.* **1999**, *11*, 42.

(12) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.

(13) (a) Denekamp, C.; Feringa, B. *Adv. Mater.* **1998**, *10*, 1080. (b) Uchida, K.; Kawai, Y.; Shimizu, Y.; Vill, V.; Irie, M. *Chem. Lett.* **2000**, 654. (c) Yamagushi, T.; Inagawa, T.; Nakazumi, H.; Irie, S.; Irie, M. *Chem. Mater.* **2000**, *12*, 869. (d) Yamaguchi, T.; Inagawa, T.; Nakazumi, H.; Irie, S.; Irie, M. *J. Mater. Chem.* **2001**, *11*, 2453.

(14) Kawai, S. H.; Gilat, S. L.; Ponsinet, R.; Lehn, J.-M. *Chem. Eur. J.* **1995**, *1*, 285.

(15) Under an Ar atmosphere, diisopropylazodicarboxylate (38 mg, 0.19 mmol) was added dropwise to a stirred solution of 1,2-bis[5′-(4″-hydroxyphenyl)-2′-methylthien-3′-yl]perfluorocyclopentene (50 mg, 0.09 mmol), 1-heptanol (37 mg, 0.32 mmol), and triphenylphosphine (52 mg, 0.2 mmol) in 5 mL of dry THF. After being stirred overnight at room temperature, the mixture was concentrated and the residue purified by flash chromatography on silica gel (9:1 hexanes/ethyl acetate). Recrystallization from EtOH gave 31 mg (46%) of **1** as a light blue solid: mp 90–92 °C; ^{1}H 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; ^{19}F NMR (376 MHz, CDCl$_3$) δ −111.0, −132.9; MS (EI) m/e 748 (M$^+$, 89), 733 (7), 537 (15), 522 (16), 277 (19), 167 (27), 149 (100); HRMS (EI) calcd for $C_{41}H_{46}F_6O_2S_2$ 748.2850, found 748.2843.

(16) P_S was measured as a function of temperature by the triangular wave method (6 V/μm, 100 Hz) with a Displaytech APT-III polarization testbed in conjunction with a Linkam LTS 350 hot stage: Miyasato, K.; Abe, S.; Takezoe, H.; Fukuda, A.; Kuze, E. *Jpn. J. Appl. Phys.* **1983**, *22*, L661.

(17) The decrease in P_S was measured as a function of irradiation time and found to level off after a period of 3 min. Under these conditions, a 75% conversion of **1** to **2** is achieved in the SmC* film according to UV–vis spectroscopy measurements.

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