Synthesis and Photochemical Switching of the Antiferroelectric Liquid Crystals Containing a Diazenediyl Group

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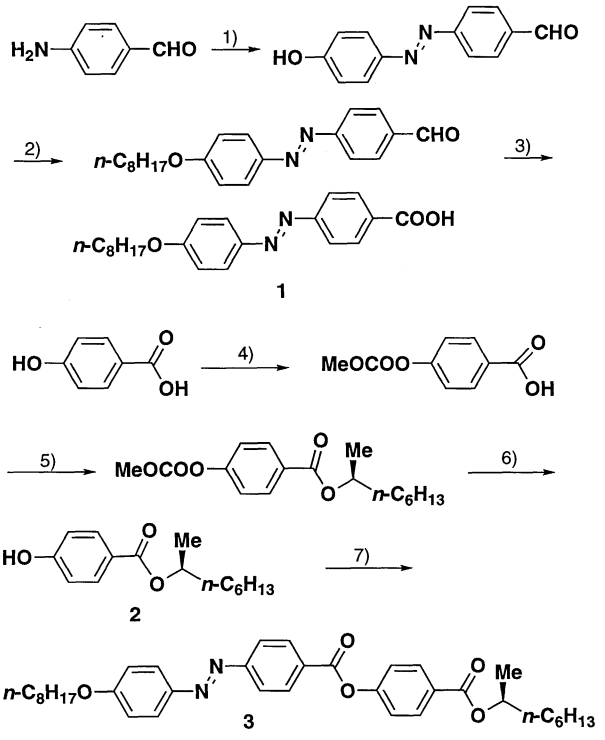
Photochromic antiferroelectric liquid crystals containing a diazene moiety were synthesized for the first time, and their photochemical switching behaviors were studied.

Liquid crystal displays on the market today are mainly based on the switching controlled by applied voltage.[1] In contrast, photochemical switching has been studied very recently to explore photonics materials for the future.[2] We report here that photochromic antiferroelectric liquid crystals (AFLCs) may be used for the logic devices of photonics.

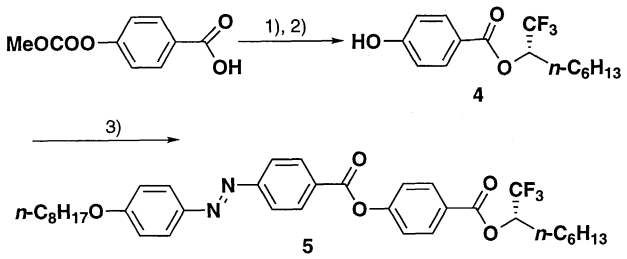
Since Fukuda, Takezoe and their coworkers discovered AFLCs in 1989,[3] many AFLCs have been synthesized.[4] However, the structures that exhibit AFLC have been limited to those akin to 4-(1-methylheptyloxycarbonyl)phenyl 4'-octyloxybiphenyl-4-carboxylate (MHPOBC). Consequently, studies on photonics device with photochromic AFLCs have been restricted. We designed and synthesized photoresponsive AFLC compounds **3** and **5** both having an azobenzene moiety and evaluated their photochemical behaviors.



1) (i) $NaNO_3$, aq HCl, Me_2CO, -15 °C
(ii) C_6H_5OH, NaOH, Me_2CO, -15 °C, 47% yield
2) K_2CO_3, n-$C_8H_{17}I$, DMF, r.t., 54% yield
3) $NaClO_2$, NaH_2PO_4, t-BuOH, H_2O, 45 °C, 89% yield
4) MeOCOCl, NaOH, H_2O, 4 °C, 30 min, 49%
5) diethyl azodicarboxylate, PPh_3, (*R*)-2-octanol, Et_2O, r.t., 50 h, 73% yield
6) NH_3 aq, MeOH, r.t., 2 h, 83% yield
7) **1**, 1,3-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, CH_2Cl_2, r.t., 68% yield

Scheme 1.

Synthetic procedures of **3** are shown in Scheme 1. Oxidation of 4-formyl-4'-octyloxydiazene[2d] with sodium chlorite afforded its acid **1** without any damage of the diazene moiety. Meanwhile, the hydroxyl group of 4-hydroxybenzoic acid was protected with a carbonate group, and the resulting acid was condensed with (*R*)-2-octanol under the Mitsunobu conditions to give, after deprotection, (*S*)-1-methylheptyl 4-hydroxybenzoate (**2**). Esterification of **1** with **2** afforded **3**. Similarly, the trifluoro derivative **5** was prepared in a manner shown in Scheme 2. Both **3** and **5** were recrystallized repeatedly to show finally >99% ee. The 2-octanol ester **3**, injected into a 2 μm gap glass cell equipped with ITO electrodes and coated by polyimide, showed phase transition temperatures of Cr 76 SmC_A* 102 SmC* 118 SmA 158 Iso. The trifluoro analog **5** also exhibited SmC_A* phase: Cr 93 SmC_A* 120 SmC* 122 SmA 133 Iso.



1) diethyl azodicarboxylate, PPh_3, (*R*)-1,1,1-trifluoro-2-octanol, Et_2O, r.t., 50 h, 25% yield
2) NH_3 aq, MeOH, r.t., 2 h, 89% yield
3) **1**, 1,3-dicyclohexylcarbodiimide, 4-dimethylaminopyridine, CH_2Cl_2, r.t., 63% yield

Scheme 2.

Optical behaviors of the compounds were measured as before.[2d] The sample was placed between two crossed polarizers, and the temperature was controlled by a thermostat. The phase transition caused by the photoisomerization of **3** and **5** was observed by measuring the transmittance of He-Ne laser (633 nm) through the crossed polarizers. In the steady-state measurement, the sample was photoirradiated with Hg lamp (366 nm) upon applying alternating voltage. For the time-resolved measurement, the sample was photoirradiated with YAG laser (the third harmonic, 355 nm; pulse width, 10 ns FWHM) with direct voltage being applied.

The optical hysteresis of **3** is shown in Figure 1. Before irradiation, namely when –N=N– moiety of **3** was *trans*, **3** exhibited two hysteresis loops (solid line), characteristic of AFLC. Upon irradiation (366 nm) at 90 °C, the two hysteresis loops changed into single hysteresis (dotted line). Thus, the *trans*→*cis* photoisomerization[5] of the -N=N- moiety induced the

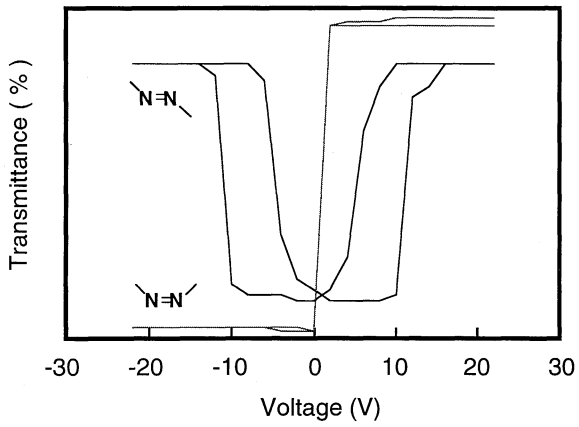


Figure 1. Optical hysteresis of **3** at 90 °C.

phase transition from SmC_A* to SmC* phase at 90 ℃.

Figure 2 shows the photochemical switching of **3** by the steady-state measurement. Before irradiation, the transmittance had three minimum and two maximum signals in one cycle. This behavior is clearly attributed to antiferroelectric character. During the irradiation, the transmittance followed the change of the applied voltage, because some parts of the -N=N- moiety isomerized to *cis* form and the sample changed into SmC* phase. After the irradiation was ceased, the sample restored SmC_A* phase in the dark according to *cis*→*trans* back isomerization.

Time-resolved measurement of optical switching at 90 ℃ is demonstrated in Figure 3. The curve reveals that *trans*→*cis* photoisomerization of the -N=N- moiety caused disappearance of the SmC_A* phase effectively, and the phase transition took place with the response time ($\tau_{0\text{-}90}$) of 340 μs.

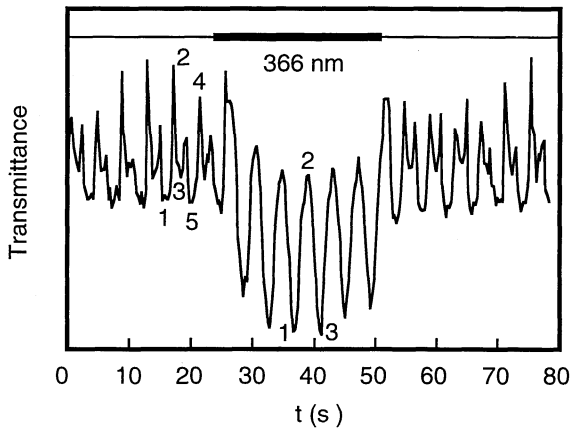


Figure 2. Change in transmittance on photoirradiation of **3** at 90 °C.

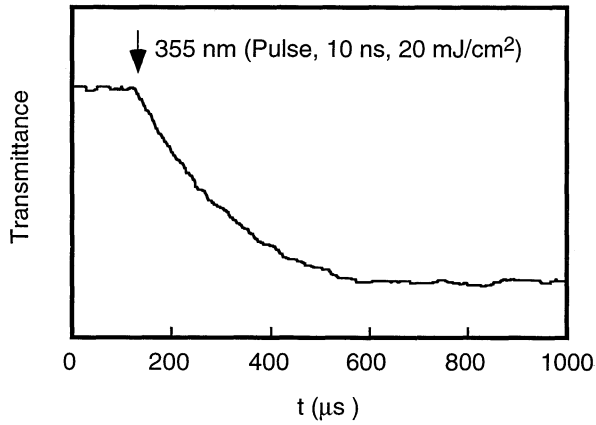


Figure 3. Time-resolved measurement of optical switching of **3** at 90 °C.

Photochemical behaviors of **5** were found to be similar to those of **3**. The *trans*→*cis* photoisomerization of **5** at 100 ℃ induced the phase transition from SmC_A* to SmC* phase in 360 μs, and SmC^*_A phase was recovered in the dark.

In conclusion, AFLCs with a diazenediyl group were prepared for the first time and shown to isomerize reversibly: photochemically from SmC_A* to SmC* and thermally from SmC* to SmC_A*. These observations should find applications in the photonic control of light in the near future.[6]

References and Notes

1 For typical examples, see: a) M. Schadt and W. Helfrich, *Appl. Phys. Lett.*, **18**, 127 (1971). b) T. J. Scheffer and J. Nehring, *Appl. Phys. Lett.*, **45**, 1021 (1987). c) N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).

2 a) T. Ikeda, T. Sasaki, and K. Ichimura, *Nature,* **361**, 428 (1993). b) T. Sasaki, T. Ikeda, and K. Ichimura, *J. Am. Chem. Soc.*, **116**, 625 (1994). c) T. Moriyama, J. Kajita, Y. Takanishi, K. Ishikawa, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.* **32**, L589 (1993). d) M. Negishi, O. Tsutsumi, T. Ikeda, T. Hiyama, J. Kawamura, M. Aizawa, and S. Takehara, *Chem. Lett.*, **1996**, 319.

3 A. D. Chandani, E, Gorecke, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.* **28**, L1265 (1989).

4 A. Fukuda, Y. Takanishi, T. Isozaki, K. Ishikawa, and H. Takezoe, *J. Mater. Chem.*, **4**, 997 (1994).

5 Although the photochemical equilibrium favors the cis-isomer, we consider that small portion of **3** probably near the cell surface isomerized to cause, as a result, the phase transition from SmC_A* to SmC*.

6 Thanks are due to Showa Shell Sekiyu K. K. for providing us with (*R*)-1,1,1-trifluoro-2-octanol.