Original article

Synthesis and photoswitching properties of azobenzene liquid crystals with a pentafluorobenzene terminal

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ABSTRACT

The fluorine-substituted benzoate ester rod-shaped liquid crystals containing an azobenzene side chain linked with terminal double bonds were synthesized and characterized. The mesophase and photoswitching properties were determined by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and UV–visible spectrometry. The rod-shaped compound **4a** having an odd number of carbon atoms in the alkyl chains exhibits nematic phase and SmA type phase whereas compound **4b** having an even number of carbon atoms showed only nematic phase. Both fluorine-containing compounds **4c** and **4d** showed only SmA type phases. The photoswitching properties of these compounds showed a rate of *trans* to *cis* isomerization ranging 19–20 s, whereas reverse process took around 230 min in solution. These materials may be ideal in the field of optically rewritable applications where both on and off rates should be crucial.

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1. Introduction

The unique properties of liquid crystals (LCs) have been utilized in the area of display technologies, optical storage devices, solar cells, ion conductors and templates for nanoparticles [1,2]. The insertion of a fluorine atom or fluorinated group into the liquid crystals molecules changes the physical characters, which may influence the display and non-display properties [3]. Literature survey reveals that few fluorinated liquid crystals (FLCs) are reported in spite of their potential unique applications. Replacing the fluorobenzene in the ionic LCs by the fluorinated heterocycles and the FLCs bearing fluorinated heterocycles were highly valuable because these materials may have some advantage in applications [1]. The 4-fluorobenzene and 3,4-difluorobenzene derivatives have been used as STN and TFT liquid crystal materials [4].

The field of photoinduced phenomena is growing fast using the molecular ordering/disordering of the liquid crystalline systems [5]. In photonic, the light controlled by stimulus is being proposed as a future potential technology for optical storage devices [6]. The molecules having azobenzene units exhibit reversible isomerization behaviour upon irradiations with UV and visible light [7]. The more stable *trans* configuration converts into their *cis*

configuration upon absorption of UV light [8]. In this case, time required for *trans* to *cis* isomerization is faster whereas the thermal back relaxation takes much longer. The UV irradiation is imposed to the nematic phase for the materials exhibit a nematic–isotropic (N–I) transition and the lowering of the transition temperature, T_{NI}, could induce an isothermal N–I transition. The photochemically induced transition is promising to develop an optical image-storing system and their optical rewritable ability.

In this paper, we report the synthesis, characterization and properties of some rod-shaped molecules containing fluorine substituted phenylenes as the terminal and the azobenzene units with terminal chains having double bonds, and also report the photoswitching properties of compounds in the field of optically rewritable applications.

2. Experimental

The structures of the compounds were confirmed by spectro-scopic methods: IR spectra were recorded with a Perkin Elmer (670) FTIR spectrometer. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded with a Bruker (DMX500) spectrometer. The transition temperatures and their enthalpies were measured by differential scanning calorimetry (Perkin DSC 7) with heating and cooling rates were 10 °C/min. Optical textures were obtained by using Olympus BX51 polarizing optical micro-scope equipped with a MettlerToledo FP82HT hot stage and a FP90

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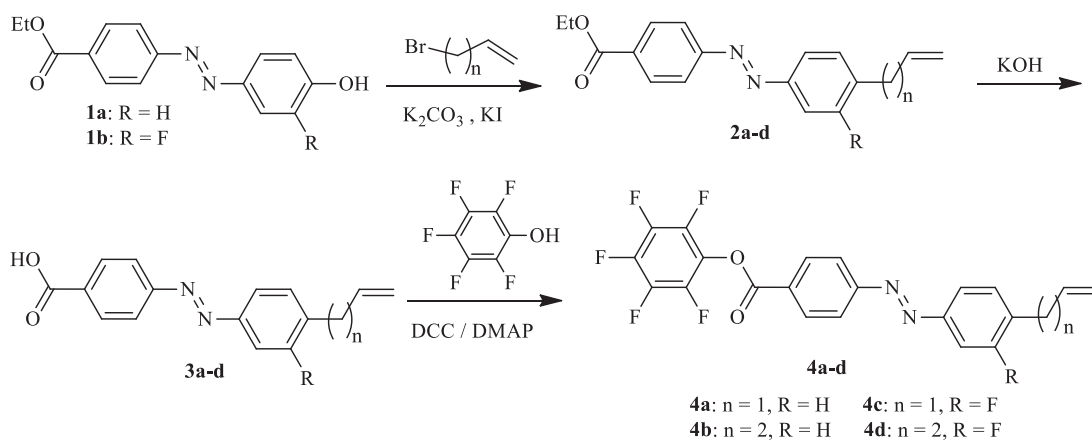
Scheme 1. Synthesis of liquid crystals compounds **4a–d**.
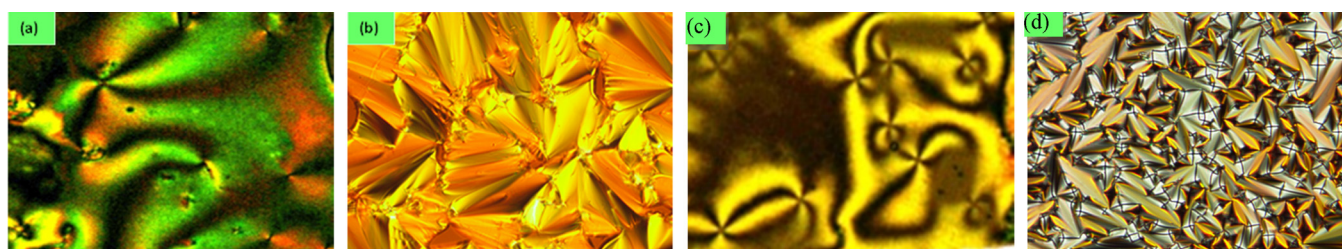
Fig. 1. Polarized micrographs obtained from isotropic phases of (a) nematic phase of **4a** at 154 °C, (b) smectic A phase of **4a** at 128 °C, (c) nematic phase of **4b** at 142 °C, (d) smectic A phase of **4c** at 120 °C. All textures were captured with 10× objective in Olympus BX51 at horizontal picture width 200 μm by Olympus DP26 camera.

central processor unit. UV/vis absorption spectra were recorded using UV-visible spectrophotometer obtained from Ocean Optics (HR2000+). For photo-switching studies in solutions, fluorine azobenzene liquid crystalline monomers were dissolved in dimethylformamide at suitable concentrations. Photo-switching behaviour of the azobenzene containing fluorine compounds investigated by illuminating quartz cuvette containing sample with OMNICURE S2000 UV source equipped with 365 nm filter along with heat filter inserted just before the sample to avoid any heat effects arising from the sample.

Compounds **4a–d** were synthesized as depicted in Scheme 1. Compound **1a** was alkylated with allyl bromide or 4-bromo-1-butene in the presence of K_2CO_3 and catalytic amount of KI to give ethyl 4-{2-(4-allylphenyl)diazenyl}benzoate **2a** or ethyl 4-{2-(4-(but-3-enyl)phenyl)diazenyl}benzoate **2b**. Similarly, fluorine-containing **1b** was alkylated with allyl bromide or 4-bromo-1-butene to give ethyl 4-{2-(4-allyl-3-fluorophenyl)diazenyl}benzoate **2c** or ethyl 4-{2-(4-(but-3-enyl)-3-fluorophenyl)diazenyl}benzoate **2d**. Therein the ester compounds **2a–d** were hydrolyzed under basic conditions to yield 4-{2-(4-allylphenyl)diazenyl}benzoic acid **3a** (other **3b–d** in Supporting information). Finally, acids **3a–d** were esterified with pentafluorophenol in the presence of DCC and DMAP to produce the desired compounds **4a–d** (pentaflourophenyl 4-{2-(4-allylphenyl)diazenyl}benzoate is **4a** and detail experimental procedures of **4b–d** are described in Supporting information).

3. Results and discussion

3.1. Mesomorphic properties

Polarizing optical microscopy (POM) studies: Under the optical polarizing microscope, compound **4a** showed a typical schlieren texture for nematic phase upon cooling from the isotropic phase.

Optical texture was taken at 154 °C for compound **4a** and on further cooling a typical fan shaped texture for smectic A phase was observed before crystallization (Fig. 1b). For compound **4b**, a schlieren texture was also observed for nematic phase upon cooling from the isotropic phase (Fig. S1 in Supporting information), on further cooling no mesophase was observed before crystallization. Both fluorine-containing compounds **4c** and **4d** showed a typical fan shaped texture for smectic A phase at lower temperature than non-fluorine compounds (Fig. S1). All the transition temperatures observed under POM matched with DSC data.

Differential scanning calorimetry (DSC) studies confirmed the phase transition temperatures (T/°C) observed by polarizing microscopy and gave the enthalpy changes (ΔH/J g^{-1}) associated with these phase transitions. Compound **4a** exhibits three transition peaks on heating, which correspond to the Cr–SmA, SmA–N and N–I transitions, respectively. On cooling, compound **4a** also showed the isotropic–nematic, nematic–smectic and smectic–crystal transitions (Table 1). Compound **4b** displayed two peaks on heating and on cooling and two transition peaks were observed for

Table 1

Phase transition temperature (T/°C) and associated transition enthalpy values (ΔH/J g^{-1}) in parentheses given for the second heating and cooling of DSC scans for compounds **4a** and **4b**.

Compd.	Scan	Phase transitions
4a	Heat	Cr 120.5 (65.5) SmA 141.2 (2.4) N 169.2 (1.6) I
	Cool	I 165.8 (1.7) N 136.4 (2.1) SmA 90.1 (62.9) Cr
4b	Heat	Cr 129.7 (55.3) N 161.6 (1.4) I
	Cool	I 155.0 (1.6) N 99.6 (50.2) Cr
4c	Heat	Cr 99.1 (27.3) SmA 148.5 (3.8) I
	Cool	I 145.2 (3.7) SmA 80.7 (25.5) Cr
4d	Heat	Cr 102.7 (32.5) SmA 141.9 (2.9) I
	Cool	I 135.4 (2.6) SmA 85.0 (30.6) Cr

Abbreviation: Cr, crystal; N, nematic; SmA, smectic A phase; I, isotropic phase.

only nematic phase (Table 1). Compounds **4c** and **4d** showed two peaks on heating and on cooling, which can be attributed to the Cr–SmA and SmA–I transitions at about 30 °C lower transition temperatures compared to **4a** and **4b** due to fluorine effects (Table 1). The DSC curves representing enthalpy changes are given in Supporting information.

3.2. Photoswitching study

The rod-shaped molecules **4a**–**d** were considered for a photoisomerization study in DMF solution with a concentration of $C = 1.1 \times 10^{-5}$ mol/L [9,10]. The absorption spectra of compound **4a**–**d** showed an absorbance maximum at 364 nm as shown in Fig. S2 (in Supporting information). The strong absorbance in the UV region at 364 nm corresponds to the π–π^* transition of the E isomer (*trans* isomer) and a very weak absorbance in the visible region around 450 nm represents the n–π^* transition of Z isomer (*cis* isomer). The photoswitching property study was performed using UV/visible spectroscopy in the absence and presence of UV light illumination. Compounds **4a**–**d** were illuminated with 365 nm UV light at different time intervals and immediately the absorption spectra were recorded. Heat filter is used just before sampling to avoid any heat radiation arising from the samples. The absorption maximum at 364 nm decreases due to the E/Z photoisomerization. After ~20 s of illumination, lack of change in the absorption spectrum confirms the saturation of E/Z isomerization process (Fig. S2).

Fig. 2 shows the E–Z absorption of compounds **4a**–**d** as a function of exposure time. Data were extracted from Fig. S2 at 364 nm, where peak wavelength was fixed and absorption values at 364 nm at different exposure time were recorded. The curve shows that photosaturation occurs within 19 s, which is faster than the photoisomerization from nematic to isotropic phase [11].

The thermal back relaxation process is shown Fig. S3 (in Supporting information) for compounds **4a**–**d** whose solution was shined continuously for 20 s (photo stationery state) and kept in the dark and then at subsequent time intervals, spectral data were recorded. Fig. 3 shows the time dependence of the Z–E absorption of compounds **4a**–**d**. Peak wavelength at 364 nm as obtained from Fig. S3 is plotted as a function of recovery time. The curve shows that thermal back relaxation occurs within 230 min, which is reasonably fast as compared with the thermal back relaxation from nematic to isotropic phase [11]. A possible reason for the observed relatively fast thermal back relaxation and the UV ON process could be that the phases involved on both sides of transition possess a layered structure and the changes that occurred were confined to the in-plane rotation of the molecules [12].
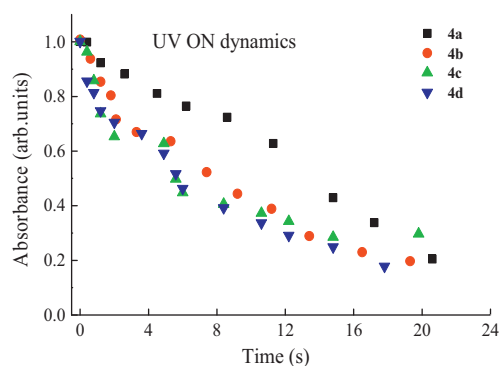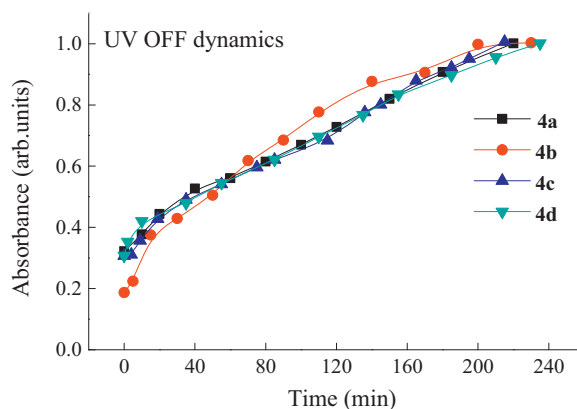

Fig. 3. Time dependence photoisomerization curve of Z isomer (**4a**–**d**) showing thermal back relaxation time.
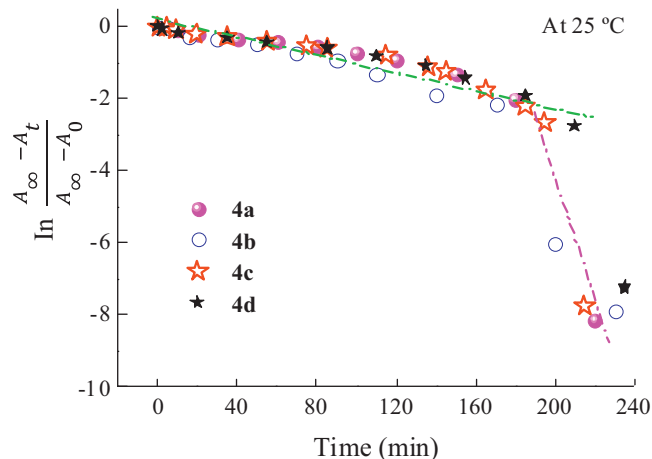

Fig. 4. First order plots for the compounds **4a**–**d** for *cis–trans* thermal isomerization at 25 °C.

We also calculated the rate constant for the *cis–trans* isomerization at room temperature for all four compounds using the following equation [13]:

$$K_{c-t} = \ln \frac{A_\infty - A_t}{A_\infty - A_0} \tag{1}$$

where A_t, A_0, A_∞ are the absorbance at 364 nm at time t, time zero and infinite time, respectively. Fig. 4 shows a typical first order plot using the above equation at room temperature for all four compounds. It is evident that throughout the relaxation curve a typical first order kinetic was observed except at the last point, which may be due to the small change in thermal variation that changed absorbance values. All four compounds, irrespective of their terminal substitutions, behaved in the similar way at room temperature.

4. Conclusion

We have successfully synthesized and characterized the fluorine-substituted benzoate ester linked to rod-shaped azobenzene liquid crystals with terminal double bonds as polymerizable functional groups. The alkyl side chain double bonds in the presence of an *azo* moiety are suitable for photochromism and *trans–cis–trans* isomerization cycles under UV irradiation. Compound **4a** showed both nematic phase and SmA phase whereas **4b** exhibited nematic phase only and both fluorine-containing compound **4c** and **4d** showed only SmA phase. The photoswitching properties of these compounds showed a *trans* to *cis* isomerization

Fig. 2. Time dependence photoisomerization curve of E isomer (**4a**–**d**) showing effect of UV illumination (364 nm wavelength).

rate ranging 19–20 s, whereas the reverse process took around 230 min in solution. The compounds showed first order exponential decay in solutions. The photoswitching behaviours of these materials may be useful in the field of optically rewritable display applications.

Acknowledgments

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cclet.2014.06.025.

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