Journal of Fluorine Chemistry 156 (2013) 230–235

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Synthesis and characterization of liquid crystalline azobenzene chromophores with fluorobenzene terminal

Md Lutfor Rahman [a,*], Gurumurthy Hegde [a], Mahrokh Azazpour [a], Mashitah Mohd Yusoff [a], Sandeep Kumar [b]

[a] *Faculty of Industrial Sciences & Technology, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Malaysia*
[b] *Raman Research Institute, C.V. Raman Avenue, Sadashivanagar, Bangalore 560080, India*

ARTICLE INFO

Article history:
Received 12 July 2013
Received in revised form 14 September 2013
Accepted 1 October 2013
Available online 11 October 2013

Keywords:
Azobenzene chromophores
Fluorine-substituted benzene
Nematic phase
Smectic phase
Photo-switching property

ABSTRACT

Two series of fluorine-substituted benzoate ester type rod-shaped liquid crystals incorporating the azobenzene as side arm linked with terminal double bonds as polymerizable functional groups were synthesized and characterized by polarized-light optical microscopy (POM), differential scanning calorimetry (DSC) and UV–visible spectroscopy investigations. Thus, rod-shaped monomers, namely **4a** and **4b** having odd and even number of carbon in the terminal group exhibited nematic phase and SmA type phase was found at lower temperature. Compound **5** showed nematic phase whereas compound **6** showed SmA phase. These rod-shaped molecules exhibit strong photoisomerization behaviour in solution. The photoswitching properties of the compounds showed *trans* to *cis* isomerization in about 10 s, whereas the reverse process takes place about 120 min in solutions. Proposed materials may have potential to use it in optical storage devices.

1. Introduction

Liquid crystals (LCs) are widely used as anisotropic materials having self-organizing properties. They offer great advantages over isotropic systems [1]. Due to their unique properties, liquid crystals found widespread applications in display technology and in other areas such as optical storage device [2], solar cells [3], ion conductors [4,5] and templates for nanoparticles [6,7]. The introduction of a fluorine atom or fluorinated group into liquid crystalline systems changes physical characters of the LC materials, which could be of intensive interest in display and non-display applications [8]. The liquid crystals with fluorinated substituents alter many physical parameters such as, broader nematic phase range, lower melting point, high dielectric anisotropy, and good voltage holding ratios [9].

Some fluorinated liquid crystals (FLCs) of fused ring systems for TFT-LCD are currently commercially available [10]. However, FLCs are less reported materials in spite of their potential applications [11,12]. Tao et al. [1] synthesized pyridinium-based liquid crystals with an extended fluorinated pyrrolidine unit and studied the structure–properties relationship. There are many reports where 4-fluorobenzene and 3,4-difluorobenzene derivatives are used as STN and TFT liquid crystalline materials [10,13,14].

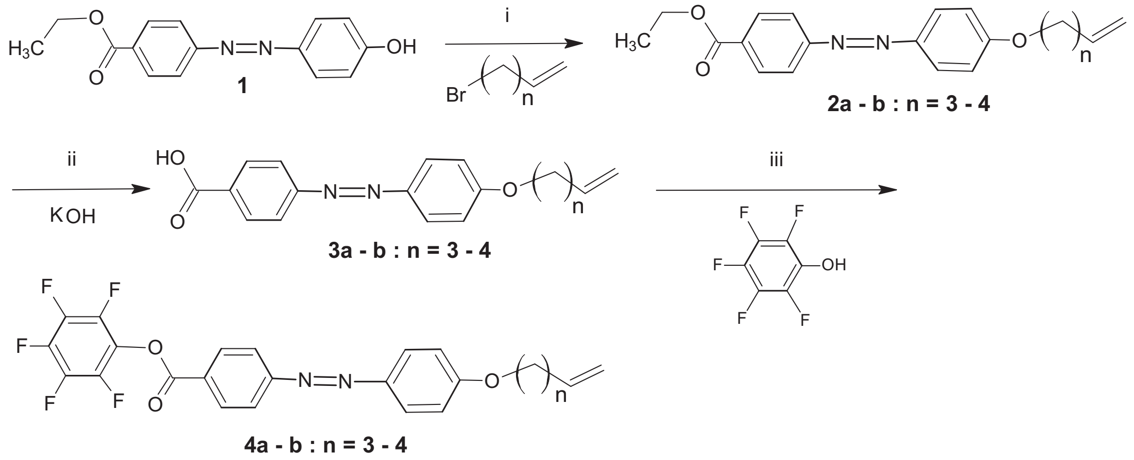
A field of research that is growing steadily is that of photoinduced phenomenon, in which incident light itself brings about molecular ordering/disordering of the liquid crystalline system [15]. The photoinduced dichroism and optical anisotropy is being proposed as future potential technology for optical storage devices [16,17]. The azobenzene moieties are well known molecules which exhibit reversible isomerization behaviour upon irradiations with UV and visible light [18]. The energetically more stable *trans* configuration convert into *cis* configuration upon absorption of UV light (~365 nm). Photoinduced effects are adopted by the liquid crystals in which the azobenzene group is either chemically attached to the molecule of interest or used as a dopant in a liquid crystal host material [19–22]. Liquid crystalline materials in which the phase transitions take place by the isomerization of the photoactive molecules are of significant interest. The time required for *trans* to *cis* isomerization is much lower compared to thermal back relaxation time. The UV irradiation is done in the nematic phase for the material exhibit a nematic–isotropic (N–I) transition and the lowering of the transition temperature, T_{NI}, could induce an isothermal N–I transition. Thus, the photochemically induced transition is promising for the optical image-storing systems.

In this work, we report the synthesis, characterization, and properties of liquid crystalline azobenzene chromophores with

---

* Corresponding author. Tel.: +60 169399011; fax: +60 95492766.
E-mail address: lutfor73@gmail.com (M.L. Rahman).

0022-1139/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jfluchem.2013.10.004



Scheme 1. Synthesis of compounds **4a**–**b**. Reagents and conditions: (i) K_2CO_3, KI; (ii) KOH, MeOH; (iii) DCC, DMAP.

terminal fluorobenzene moiety. It is been well known proven fact that, longer the thermal back relaxation, better is the device and with this aspect, presented compounds may be suitable for the creation of storage devices.

2. Results and discussion

2.1. Synthesis

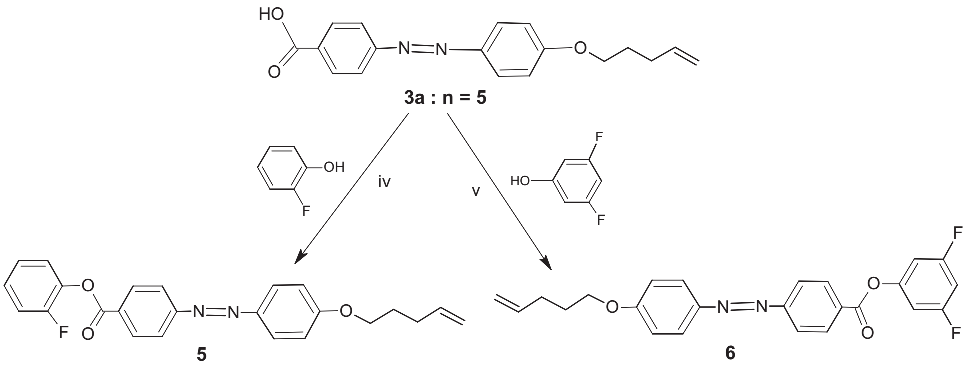
The synthesis and purification of compounds **4a** and **4b** were performed as depicted in Scheme 1. Compounds **1** was alkylated with 5-bromo-1-pentene in the presence of potassium carbonate as base to give ethyl 4-{2-[4-(pent-4-enyloxy)phenyl]diazenyl}-benzoate **2a**. Compound **2b** was prepared with the same method of compound **2a**. Then the ester compounds **2a**–**b** were hydrolyzed under basic conditions to yield the benzoic acid 4-{2-[4-(pent-4-enyloxy) phenyl]diazenyl}benzoic acid **3a**. Compound **3b** was prepared with the same method of compound **3a**. In the final step, two equivalents of the acids **3a**–**b** were esterified with one equivalent of pentafluorophenol by DCC and DMAP to achieve the target molecules **4a**–**b** (Scheme 1). The synthesis of compounds **5** and **6** were performed as depicted in Scheme 2. About one equivalent of the acids **3a** was esterified with one equivalent of 2-fluorophenol or 3,6-difluorophenol by DCC and DMAP to achieve the target molecules **5** and **6** (Scheme 2).

2.2. Mesomorphic properties

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** shows three transition peaks on heating which correspond to the Cr–SmA, SmA–N and N–I transitions. On cooling, the isotropic–nematic, nematic–smectic and smectic-crystal transition appears for compound **4a** (Table 1). Compound **4b** displayed also three peaks on heating and on cooling, again three transition peaks were observed, which shows nematic and smectic phase (Table 1). Both compounds showed stable enantiotropic mesophases. In compounds **5** and **6** only two transitions peaks were obtained which correspondence to nematic phase for **5** and SmA phase for **6**, respectively. Compound **4a** having odd numbered alkyl chain (C5 including vinyl group) shows nematic to isotropic transition is at 145.2 °C whereas compound **4b** having even number of alkyl chain (C6 including vinyl group) shows nematic to isotropic transition at 158.2 °C. On the other hand compound **5** and **6** also having odd numbered alkyl chain (C5 including vinyl group), but fluorine atom is different from compound **4a**. Compound **5** possesses only one fluorine atom whereas compound 6a contains two fluorine atoms. Compound **5** shows the nematic–isotropic transition at 158.9 °C while compound **6** exhibits the SmA–isotropic transition at 157.6 °C. Thus, as the number of fluorine atom increases, transition temperatures decreases [23].

2.2.1. Polarizing optical microscopy (POM) studies

Under the polarizing microscope, a schlieren texture as typical for nematic phase for compound **4a** was observed upon cooling from the isotropic phase. Optical texture was taken for compound **4a** at 124 °C (Fig. 1a) and on further cooling a broken fan shaped texture as typical for smectic A phase was found at lower



Scheme 2. Synthesis of compounds **5a** and **6a**. Reagents and conditions: (iv) DCC, DMAP; (v) DCC, DMAP.

Table 1
Phase transition temperature ($T/^{\circ}C$) and associated transition enthalpy values ($\Delta H/J\,g^{-1}$) in parentheses given for the second heat and cooling of DSC scans for compounds **4a**–**b**, **5** and **6**.

Compound	Scan	Phase transitions
4a	Heat	Cr 110.5 (69.4) SmA 117.7 (1.3) N 145.2 (1.1) I
	Cool	I 142.5 (0.91) N 110.1 (1.0) SmA 70.8 (52.0) Cr
4b	Heat	Cr 105.7 (59.2) SmA 116.8 (1.2) N 158.2 (1.4) I
	Cool	I 147.4 (0.9) N 113.7 (1.2) SmA 80.8 (50.0) Cr
5	Heat	Cr 111.1 (57.0) N 158.9 (1.0) I
	Cool	I 149.4 (1.5) N 83.5 (34.6) Cr
6	Heat	Cr 131.8 (62.8) SmA 157.6 (12.0) I
	Cool	I 148.0 (11.8) SmA 112.1 (58.4) Cr

Abbreviations: Cr = crystal, N = nematic, SmA = smectic A phase, I = isotropic phase.

temperature (Fig. 1b). For compound **4b**, a schlieren texture was also observed for nematic phase upon cooling from the isotropic phase. On further cooling a fan shaped texture which is smectic A phase was observed as shown in Fig. 1d. Compound **5** also exhibits schlieren texture (Fig. 1e) of typically nematic phase upon cooling from the isotropic phase, however, on further cooling no phase was observed. In the case of compound **6**, a broken fan shaped texture, typical for smectic A phase, was also observed as shown in Fig. 1f. On further cooling no other phase was observed except crystallization. All the transition temperatures observed under POM were matching with DSC data.

2.2.2. Photo-switching study

Our preliminary investigation showed that all rod-shaped molecules exhibit similar absorption spectra due to their similar molecular structure, the only minor difference is the alkyl chain ($n = 3–4$) and fluorine atom which does not alter the electronic transitions. Consequently, compounds **4a** and **4b** were considered for photoisomerization study. Photoswitching studies were performed on solutions with appropriate solvents give an idea of the materials behaviour with respect to UV light and also these results are indispensable for creating optical storage devices.

Figs. 2 and 3 depict the absorption spectra of **4a** and **4b**, respectively before and after UV illumination with 365 nm filter. Heat filter is used to prevent any heat effects arising to the sample. The absorption spectra of compound **4a** and **4b** show absorbance maxima at 364 nm. The absorption spectra of compound was carried out in dimethyl formamide (DMF) solution having concentration $C = 1.1 \times 10^{-5}$ mol L^{-1}. The strong absorbance in the UV region at 364 nm corresponds to $\pi–\pi^*$ transition of the E isomer (*trans isomer*) and a very weak absorbance in the visible region around 450 nm represents to $n–\pi^*$ transition of Z isomer (*cis isomer*). After ~10 s illumination, there is no change in

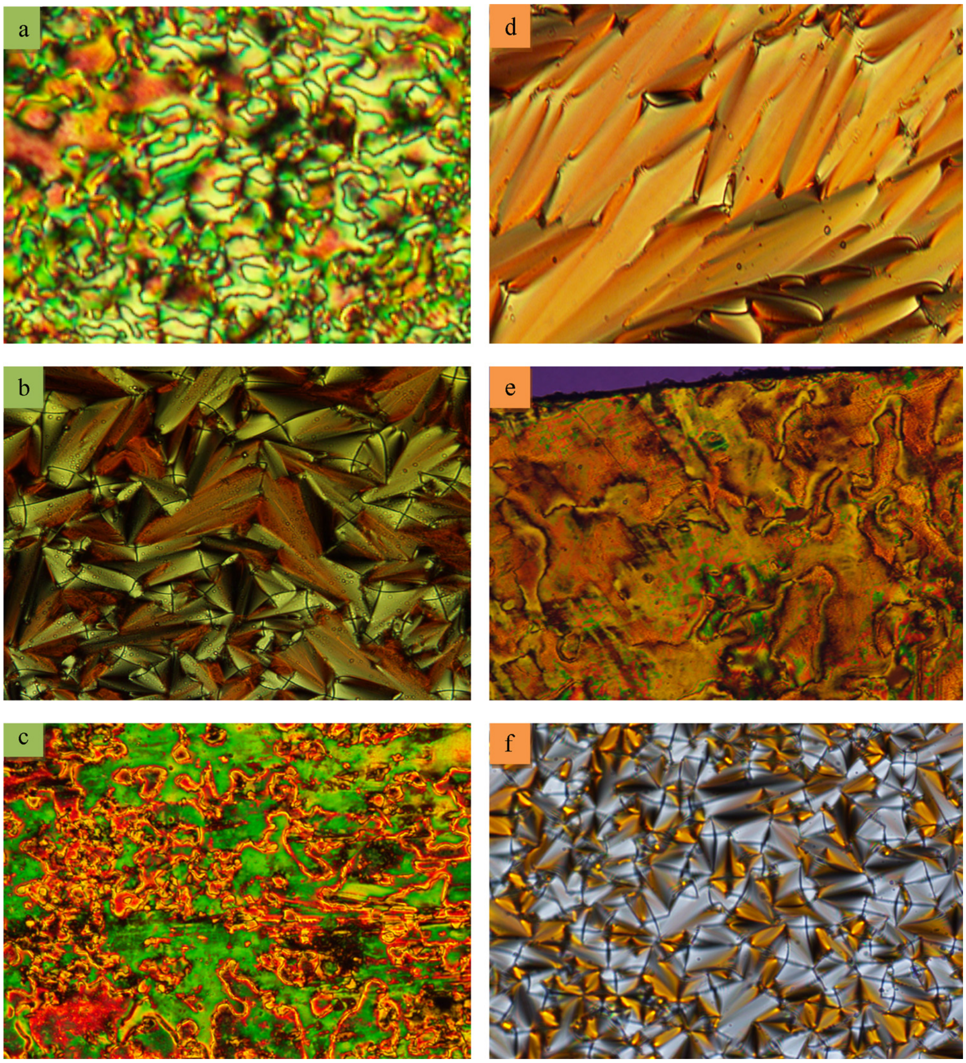


Fig. 1. Polarized optical micrographs obtained from cooling of isotropic phases of (a) nematic phase of **4a** at 124 °C, (b) SmA phase of **4a** at 105 °C, (c) nematic phase of **4b** at 142 °C, (d) SmA phase of **4b** at 110 °C, (e) nematic phase of **5a** at 125 °C, (f) SmA phase of **6a** at 130 °C.

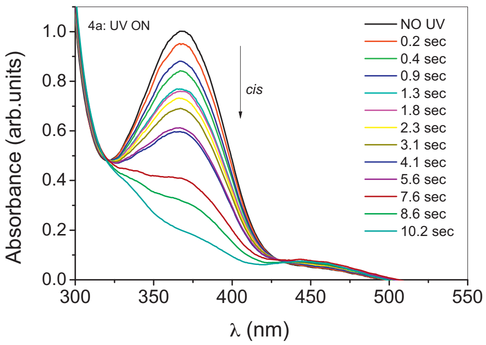


Fig. 2. Absorption spectra of **4a** with different exposure time of UV light with 365 nm filter. No UV corresponds to the 0 s of UV light illumination (absence of UV light).

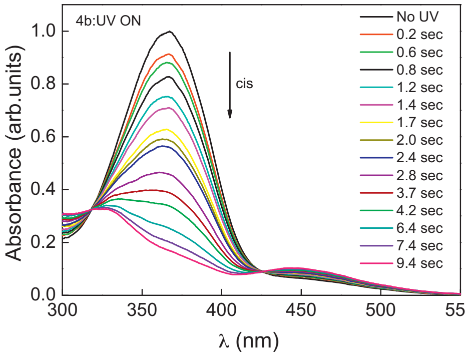


Fig. 3. Absorption spectra of **4b** with different exposure time of UV light. No UV corresponds to the 0 s of UV light illumination (absence of UV light).

absorption spectrum confirms the photo saturation of *E*–*Z* isomerization process.

The *E*–*Z* absorption of compound **4a** and **4b** as a function of exposure time is shown in Fig. 4. Data is extracted from Figs. 2 and 3 at fixed wavelength of 364 nm and absorption values at different exposure time were recorded. The time dependent curve shows that photosaturation occurs within 10 s of illumination which is very fast as compared with nematic to isotropic phase involved photoisomerization [24]. The reverse transformation from *Z* to *E* can be brought by two methods, one by keeping the solution in dark and other by shining white light of higher wavelength. The earlier process is well known as thermal back relaxation [2].

The thermal back relaxation process of compound **4a** and **4b** is shown in Figs. 5 and 6, respectively where the solution is shined continuously for 20 s (photo stationery state) and kept in the dark and then at subsequent time intervals, spectral data were recorded.

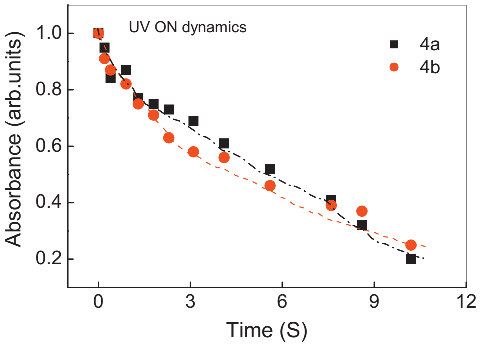


Fig. 4. Time dependence photoisomerization curve of *E* isomer (**4a**–**4b**) showing effect of UV illumination.

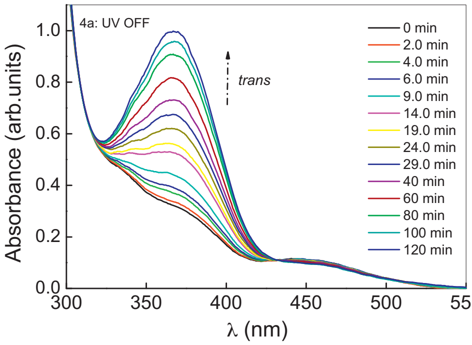


Fig. 5. Thermal back relaxation process for the compound **4a** shows that to relax from *cis* to *trans* takes around 120 min. 0 min corresponds to the UV off, after illuminating the material for 20 s (photo stationery state).

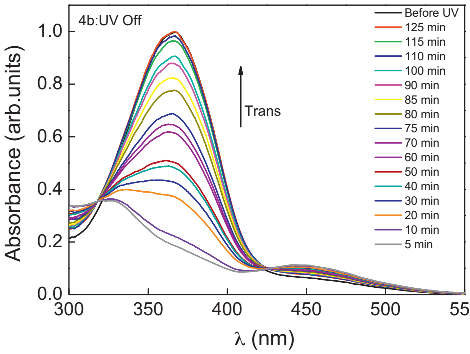


Fig. 6. Thermal back relaxation process for the compound **4b** after illuminating the material for 20 s (photo stationery state) shows that to relax from *cis* to *trans* takes around 125 min. Before UV corresponds to the state before illuminating the materials.

The time dependence of the *Z*–*E* absorption of compound **4a** and **4b** is shown in Fig. 7. Data were obtained from Figs. 5 and 6 at fixed wavelength of 364 nm as a function of recovery time. The curve shows that thermal back relaxation occurs within 125 min which is reasonably fast as compared with nematic to isotropic phase involved thermal back relaxation [24]. Presented studies may lead to the creation of optical storage devices due to their impressive thermal back relaxation time.

A possible reason for observing faster thermal back relaxation as well as UV ON process could be that the phases involved on both sides of transition possess a layer structure (Smectic phase) and that the change that occurs is confined to in-plane rotation of the molecules. The argument is supported by the fact that a similar feature was observed in another case wherein the two phases involved have a layer structure [24].

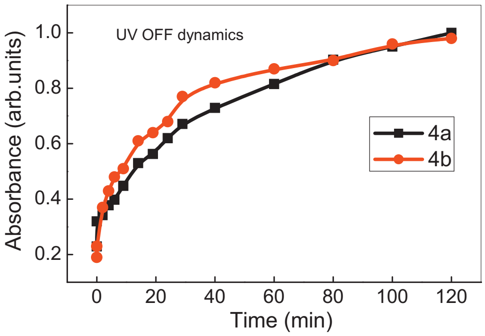


Fig. 7. Time dependence photoisomerization curve of *Z* isomer (**4a**–**b**) showing thermal back relaxation time.

3. Conclusion

The fluorine-substituted benzoate ester linked to rod-shaped azobenzene liquid crystals with terminal double bonds as polymerizable functional groups were synthesized and characterized. The double bonds can be used for preparation of polymers or silyl functionalized mesogens, whereas the presence of the azo linkage in these liquid crystals monomer is suitable for photochromism studies and *trans-cis-trans* isomerizations cycles under UV irradiation. Two compounds (**4a** and **4b**) exhibited nematic phase and on further cooing SmA phase, in addition another two compounds with less fluorine atoms show only one type mesophase with little higher temperature. These rod-shaped molecules exhibit strong photoisomerization behaviour in solutions. The photoswitching properties of compounds shows *trans* to *cis* isomerization ranging 10–11 s, whereas reverse process takes about 125 min in solutions. Presented studies may lead to the creation of optical storage devices due to their impressive thermal back relaxation time.

4. Experimental

4.1. Materials synthesis

Ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate (**1**) was synthesized according to our earlier paper [25]. Other intermediate compounds such as ethyl 4-{2-[4-(pent-4-enyloxy)phenyl]diazenyl}benzoate (**2a**), ethyl 4-{2-[4-(hex-5-enyloxy)phenyl]diazenyl} benzoate (**2b**), 4-{2-[4-(pent-4-enyloxy) phenyl]diazenyl}benzoic acid (**3a**) and 4-{2-[4-(hex-5-enyloxy)phenyl]diazenyl}benzoic acid (**3b)** were synthesized according to the earlier paper [2,26].

4.2. 2,3,4,5,6-Pentaflourophenyl 4-{[4-(pent-4-en-1-yloxy)phenyl]diazenyl}benzoate (*4a*)

Compound **3a** (0.311 g, 1.00 mmol), pentafluorophenol (0.184 g, 1.00 mmol), 85 ml of dry dichloromethane, DMAP (14.6 mg, 0.012 mmol) and DCC (0.2480 g, 1.20 mmol) were stirred for 48 h. The mixture was filtered and the filtrate was washed with acetic acid and water. The solvent was removed under reduced pressure and the product was purified by column chromatography over silica gel 60 eluted with dichloromethane and hexane (10:1). Finally product was recrystallized from ethanol/chloroform (2:1). Yield of **4a**: 35%. IR, ν_{max}/cm^{-1} 3124 (=CH_2), 2922 (CH_2), 2852 (CH_2), 1764 (C=O, ester), 1626 (C=C, vinyl), 1600, 1519, 1456 (C=C, aromatic), 1240, 1138, 1051 (C–O), 844 (C–H). ^1H NMR ($CDCl_3$) δ: 8.32 (d, 2H, J = 8.5 Hz), 8.00 (d, 2H, J = 7.0 Hz), 7.96 (d, 2H, J = 8.4 Hz), 7.04 (d, 2H, J = 8.8 Hz), 5.86 (m, 1H, CH=), 5.05 (dd, 1H, J = 17.6 Hz, =CH_2), 5.02 (dd, 1H, J = 8.8 Hz, =CH_2), 4.08 (t, 2H, J = 6.4 Hz, OCH_2–), 2.16 (m, 2H, –CH_2–), 1.88 (m, 2H, –CH_2). ^{13}C NMR ($CDCl_3$) δ: 26.39, 28.35, 69.39, 115.22, 118.77, 120.20, 121.90, 122.55, 125.47, 130.58, 131.73, 132.56, 138.56, 145.23, 147.46, 155.62, 161.68, 164.87.

4.3. 2,3,4,5,6-Pentaflourophenyl 4-{[4-(hex-5-en-1-yloxy)phenyl]diazenyl}benzoate (*4b*)

Compound **3b** (0.325 g, 1.00 mmol), pentafluorophenol (0.184 g, 1.00 mmol), 85 ml of dry dichloromethane, DMAP (14.6 mg, 0.012 mmol) and DCC (0.2480 g, 1.20 mmol) were stirred for 48 h. Esterification was carried out as synthesis of 4a. Yield of **4b**: 40%. IR, ν_{max}/cm^{-1} 3116 (=CH_2), 2924 (CH_2), 2852 (CH_2), 1755 (C=O, ester), 1622 (C=C, vinyl), 1600, 1518, 1456 (C=C, aromatic), 1261, 1057 (C–O), 858 (C–H). ^1H NMR ($CDCl_3$) δ: 8.33 (d, 2H, J = 8.6 Hz), 8.00 (d, 2H, J = 7.5 Hz), 7.95 (d, 2H, J = 8.5 Hz), 7.03 (d, 2H, J = 8.7 Hz), 5.82 (m, 1H, CH=), 5.09 (dd, 1H, J = 17.2 Hz, =CH_2), 5.01 (dd, 1H, J = 8.6 Hz, =CH_2), 4.08 (t, 2H, J = 6.5 Hz, OCH_2–), 2.27 (m, 2H, –CH_2–), 1.95 (m, 2H, –CH_2), 1.54 (m, 2H, –CH_2). ^{13}C NMR ($CDCl_3$) δ: 28.28, 30.04, 34.34, 67.61, 114.89, 115.48, 120.20, 122.79, 125.49, 127.61, 130.58, 131.73, 132.56, 137.56, 138.56, 146.89, 156.44, 161.02, 162.59, 164.98.

4.4. 2-Flourophenyl 4-{[4-(pent-4-en-1-yloxy)phenyl]diazenyl}benzoate (*5*)

Compound **3a** (0.075 g, 0.2419 mmol), 2-fluorophenol (0.027 g, 0.2419 mmol), 30 ml of dry dichloromethane, DMAP (3.6 mg, 0.030 mmol) and DCC (0.0610 g, 0.30 mmol) were stirred for 48 h. Esterification was carried out as synthesis of 4a. Yield of **5**: 36%. IR, ν_{max}/cm^{-1} 3122 (=CH_2), 2924 (CH_2), 2850 (CH_2), 1755 (C=O, ester), 1620 (C=C, vinyl), 1601, 1522, 1459 (C=C, aromatic), 1242, 1132, 1050 (C–O), 842 (C–H). ^1H NMR ($CDCl_3$) δ: 8.31 (d, 2H, J = 8.4 Hz), 8.00 (d, 2H, J = 7.1 Hz), 7.95 (d, 2H, J = 8.6 Hz), 7.76 (d, 2H, J = 8.7 Hz), 7.22 (s, 1H), 7.20 (s, 1H), 7.02 (d, 2H, J = 8.6 Hz), 5.83 (m, 1H, CH=), 5.06 (dd, 1H, J = 17.3 Hz, =CH_2), 5.04 (dd, 1H, J = 8.6 Hz, =CH_2), 4.05 (t, 2H, J = 6.4 Hz, OCH_2–), 2.16 (m, 2H, –CH_2–), 1.87 (m, 2H, –CH_2). ^{13}C NMR ($CDCl_3$) δ: 25.45, 27.95, 69.43, 115.28, 118.81, 120.14, 121.95, 122.47, 125.37, 130.66, 131.82, 132.46, 138.66, 145.67, 147.34, 155.55, 161.45, 164.65.

4.5. 3,5-Diflourophenyl 4-{[4-(pent-4-en-1-yloxy)phenyl]diazenyl}benzoate (6)

Compound **3a** (0.075 g, 0.2419 mmol), 2-fluorophenol (0.0314 g, 0.2419 mmol), 30 ml of dry dichloromethane, DMAP (3.6 mg, 0.030 mmol) and DCC (0.0610 g, 0.30 mmol) were stirred for 48 h. Esterification was carried out as synthesis of 4a. Yield of **6**: 39%. IR, ν_{max}/cm^{-1} 3127 (=CH_2), 2928 (CH_2), 2851 (CH_2), 1757 (C=O, ester), 1622 (C=C, vinyl), 1600, 1521, 1452 (C=C, aromatic), 1249, 1133, 1057 (C–O), 840 (C–H). ^1H NMR ($CDCl_3$) δ: 8.32 (d, 2H, J = 8.6 Hz), 8.00 (d, 2H, J = 7.2 Hz), 7.96 (d, 2H, J = 8.4 Hz), 7.76 (d, 2H, J = 8.6 Hz), 7.21 (s, 1H), 7.03 (d, 2H, J = 8.7 Hz), 5.84 (m, 1H, CH=), 5.08 (dd, 1H, J = 17.6 Hz, =CH_2), 5.06 (dd, 1H, J = 8.6 Hz, =CH_2), 4.04 (t, 2H, J = 6.4 Hz, OCH_2–), 2.18 (m, 2H,–CH_2–), 1.86 (m, 2H, –CH_2). ^{13}C NMR ($CDCl_3$) δ: 25.88, 27.87, 69.39, 115.29, 118.71, 120.27, 121.87, 122.42, 125.37, 130.46, 131.55, 132.33, 138.56, 145.72, 147.32, 155.54, 161.34, 164.67.

4.6. Instruments

The structures of the intermediates and product were confirmed by spectroscopic 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^{-1} and melting point of the intermediate compounds were determined by DSC. Optical textures were obtained by using Olympus BX51 polarizing optical microscope equipped with a MettlerToledo FP82HT hot stage and a FP90 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 with OMNICURE S2000 UV source equipped with 365 nm filter.

Acknowledgments

This research was supported by UMP Research Grant (Nos: RDU 100338 and RDU 130619). A special thank goes to Mrs. K.N. Vasudha for supporting many aspect regarding this work carry out.

References

[1] J. Tao, J. Zhong, P. Liu, S. Daniels, Z. Zeng, J. Fluorine Chem. 144 (2012) 73–78.

[2] M.R. Lutfor, G. Hegde, M.M. Yusoff, N.F.A. Malek, H.T. Srinivasa, S. Kumar, New J. Chem. 38 (2013), http://dx.doi.org/10.1039/c3nj00359k.

[3] N. Yamanaka, R. Kawano, W. Kubo, T. Kitamura, Y. Wada, M. Watanabe, S. Yanagida, Chem. Commun. (2005) 740–742.

[4] N. Yamanaka, R. Kawano, W. Kubo, N. Masaki, T. Kitamura, Y. Wada, M. Watanabe, S. Yanagida, J. Phys. Chem. B111 (2007) 4763–4769.

[5] S. Yazaki, M. Funahashi, J. Kagimoto, H. Ohno, T. Kato, J. Am. Chem. Soc. 132 (2010) 7702–7708.

[6] W. Dobbs, J.M. Suisse, L. Douce, R. Welter, Angew. Chem. Int. Ed. Engl. 45 (2006) 4179–4182.

[7] A. Taubert, Angew. Chem. Int. Ed. Engl. 43 (2004) 5380–5382.

[8] M. Hird, Chem. Soc. Rev. 36 (2007) 2070–2095.

[9] D. Pauluth, K. Tarumi, J. Mater. Chem. 14 (2004) 1219–1227.

[10] D. Ster, U. Baumeister, J.L. Chao, C. Tschierske, G. Israel, J. Mater. Chem. 17 (2007) 3393–3400.

[11] I. Pibiri, A. Pace, S. Buscemi, V. Causin, F. Rastrelli, G. Saielli, Phys. Chem. Chem. Phys. 14 (2012) 14306–14314.

[12] F. Lo Celso, I. Pibiri, A. Triolo, R. Triolo, A. Pace, S. Buscemi, N. Vivona, J. Mater. Chem. 17 (2007) 1201–1208.

[13] K. Lava, K. Binnemans, T. Cardinaels, J. Phys. Chem. B113 (2009) 9506–9511.

[14] D. Demus, Y. Goto, S. Sawada, E. Nakagawa, H. Saito, R. Tarao, Mol. Cryst. Liq. Cryst. 260 (1995) 1–21.

[15] S.K. Prasad, G. Nair, G. Hegde, Adv. Mater. 17 (2005) 2086–2091.

[16] L.M. Blinov, J. Nonlinear, Opt. Phys. Mater. 5 (1996) 165–187.

[17] H.S. Nalwa (Ed.), Handbook of Advanced Electronic and Photonic Materials and Devices, vol. 7, Academic, New York, 2001.

[18] T. Ikeda, I. Tsutsumi, Science 268 (1995) 1873–1875.

[19] G. Nair, S.K. Prasad, G. Hegde, Phys. Rev. E 69 (2004) 021708–21716.

[20] S.K. Prasad, G. Nair, G. Hegde, J. Phys. Chem. B 111 (2007) 345–350.

[21] L.M. Blinov, M.V. Kozlovsky, M. Ozaki, K. Skar, K. Yoshino, J. Appl. Phys. 84 (1998) 3860–3867.

[22] M.R. Lutfor, S. Kumar, C. Tschierske, G. Israel, D. Ster, G. Hegde, Liq. Cryst. 36 (2009) 397–407.

[23] M.R. Lutfor, G. Hegde, S. Kumar, C. Tschierke, V.G. Chigrinov, Opt. Mater. 32 (2009) 176–183.

[24] G.G. Nair, S.K. Prasad, C.V. Yelamaggad, J. Appl. Phys. 87 (2000) 2084–2089.

[25] M.R. Lutfor, J. Asik, S. Kumar, S. Silong, M.Z.Ab. Rahman, Phase Transit. 82 (2009) 228–239.

[26] M.R. Lutfor, J. Asik, S. Kumar, C. Tschierske, Liq. Cryst. 35 (2008) 1263–1270.