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Synthesis, liquid crystal characterization and photo-switching studies on fluorine substituted azobenzene based esters†

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A series of fluorinated azobenzene esters have been synthesized and studied by polarized optical microscopy (POM) and UV-Vis spectrophotometry. The $-CO_2C_2H_5$ group with monofluoro-substituted azobenzene exhibited nematic and smectic phases whereas difluoro-substituted azobenzene showed only the nematic phase. The addition of the electronegative fluorine atom plays an important role in photoisomerization of the azobenzene molecules. The monofluoro-substituted azobenzene gave strong photoisomerization in solution as compared with its diflouro counterparts. In these systems, *trans*–*cis* isomerization occurred after 4 minutes and *cis*–*trans* isomerization occurred after 22 hours which is much longer than expected for fluorine-substituted azobenzene systems. The presented results might have an influence on creating optical data storage devices.

1. Introduction

Photonics in which the molecular switching can be controlled by light as a stimulus has attracted a lot of attention due to its wide variety of applications ranging from display-electronics to bio photonics.[1,2] Azobenzene molecules have been highly discussed light sensitive chromophoric groups reported in the literature, especially for storage devices and molecular switches because they exhibit very interesting photoisomerization properties.[3,4] Energetically more stable *trans* configuration converts into less stable *cis* configuration with the illumination of light. Then, come back to original *trans* configuration form *cis* configuration, without any external aid.[4] This process is called Thermal back relaxation. It is basic concept for optical storage of information.[3]

Azobenzene is considered as a versatile compound due to their photo isomerization triggered by the π–π* excitation and result in inter-conversion between *cis* (*Z*) isomer and *trans* (*E*) isomers.[4–10] *E*–*Z* conversion occurs with UV light (around 365 nm), which corresponds to the π–π* transition while *Z*–*E* conversion occurs with irradiation of visible light (in the range 400–500 nm), which is equivalent to that of the n–π* transition. Alternatively, the latter change can also occur spontaneously in the dark by a process known as thermal back relaxation, where the metastable *Z* isomer relaxes to the thermodynamically more stable *E* form.[11] This azobenzene based systems allows light-induced inter-conversion to be used as photo switches for information processing as well as optical data storage devices and switches.[12,13]

One of the most important requirements for azobenzene to be used for optical data storage devices is long thermal back relaxation. The macroscopic properties can readily be fine-tuned with appropriate substitution and molecular geometry.[14] Until today, the molecular structure behaviour and also their light-induced orientations are determined by azobenzene with variety of substitutions.[15] Particularly, fluorine has a unique effect on molecular properties, attributed to its high electronegativity and lone pair electrons.[16] Moreover, fluorinated azo compounds exhibit greater stability to light than their non-fluorinated homologs.[17]

On the other hand, the rapid development in the area of optical storage devices leads to significant interest in liquid crystalline materials from fluorobenzene derivatives.[18–20] It has been reported recently by M. R. Lutfor *et al.*, on pentafluoro-substituted azobenzene moiety and their liquid crystalline behaviour along with photoswitching property. They showed that addition of fluorine substituents influences the thermal back relaxation.[21] Still there is no report on very long thermal back relaxation on adding fluorine substituents to azobenzene esters. Thus, the photo chemically induced transition is always a promising approach for the optical data storage device.

With this in mind, we report the synthesis, liquid crystalline property and photoswitching study of novel azobenzene based esters with terminal fluorobenzene moiety. The addition of fluorine will be expected to increase the thermal back

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† Electronic supplementary information (ESI) available: (i) The similar type of compounds which do not containing ester linkage and fluorine substitution were studied to justify the effects discussed in the manuscript. (ii) ^{1}H-NMR, ^{13}C-NMR raw data is given to support the synthetic chemistry description. See DOI: 10.1039/c4ra13700k

relaxation. Longer the thermal back relaxation, applicability also more for data storage. With this aspect, presented compounds may be suitable for the creation of optical data storage devices.

2. Experimental

2.1 Starting materials

Ethyl 4-amino benzoate (Fluka), aniline (Merck), sodium nitrite (Fluka), phenol (Merck), 1,3-dicyclohexylcarbodiimide (DCC) (Fluka), 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (Fluka), 4-fluoro benzoic acid (Merck), 3,5-difluoro benzoic acid (Merck), and silica gel-60 (Merck) were used. Acetone was dried over phosphorus pentaoxide (Merck) and dichloromethane was dried over calcium hydride (Fluka) and distilled out before use. Other solvents and chemicals were used as such.

2.2 General procedure for the preparation of *para* substituted azobenzene

Compound **A** (46.00 mmol, 1 equiv.) was dissolved in methanol (40 ml) cooled the solution to 2 °C. The 25% HCl was added dropwise (8.672 ml) to the reaction mixture, still maintained the temperature at 2 °C. $NaNO_2$ was dissolved with water (44.6 mmol, 1 equiv.) and added dropwise at 2 °C. The reaction mixture was stirred for 15 minutes to get compound **B**. Phenol solution was prepared with methanol (44.6 mmol, 1 equiv.) and added slowly at 2 °C. The pH was elevated to 8.5–9.0 by using 1 N NaOH solution. The reaction mixture was agitated for 4 hours. Diluted the reaction mixture with methanol (250 ml) and ice. Reduced the pH up to 4. The reddish yellow precipitate was filtered and dried. The crude product was recrystallized twice from methanol[26] and compound **C** was obtained.

A red coloured solid; $R_f = 0.42$ (40% CH_2Cl_2–EtOH); yield: 62%; melting point: 158.5 °C; IR (KBr pellet) γ_{max} in cm^{-1}: 1728, 1602, 1484, 1248, 1140, 829; ^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (t, $J = 7.68$ MHz, 1H, Ar), δ 7.50 (t, $J = 7.52$ MHz, 2H, Ar), δ 7.88 (t, $J = 8.11$ MHz, 2H, Ar), δ 7.44 (d, $J = 8.36$ MHz, 2H, Ar), δ 6.95 (d, $J = 8.32$ MHz, 2H, Ar), δ 7.88 (s, 1H, OH).

A red coloured solid; $R_f = 0.42$ (40% CH_2Cl_2–EtOH); yield: 62%; melting point: 160.2 °C; IR (KBr pellet) γ_{max} in cm^{-1}: 3321, 1728, 1602, 1484, 1248, 1140, 829; ^1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, $J = 8.2$ Hz, 2H, Ar), δ 7.92 (d, $J = 7.5$ Hz, 2H, Ar), δ 7.88 (d, $J = 7.5$ Hz, 2H, Ar), δ 7.01 (d, $J = 8.2$ Hz, 2H, Ar), δ 5.54 (s, 1H, OH), δ 4.42 (q, $J = 7.2$ Hz, 2H, CH_2CH_3), δ 1.44 (t, 3H, CH_2CH_3).

2.3 General procedure for the preparation of azobenzene based esters

The fluorine substituted benzoic acid (15.3 mmol, 1 equiv.) was dissolved in 50 ml of dry dichloromethane. DMAP (1.40 mmol, 0.1 equiv.) were added and the mixture was stirred for 30 minutes. A solution of compound **C** (15.3 mmol, 1 equiv.) in dry dichloromethane (10 ml) was added to the mixture and DCC (23.0 mmol, 1.5 equiv.) in 10 ml of dry dichloromethane was added slowly. The mixture was stirred for 24 hours. The reaction was monitored by TLC. After completion of reaction, the precipitate was removed by filtration and the filtrate was quenched with 1.5 N hydrochloric acid. The compound was extracted two times with dichloromethane. Then it was washed with 1 N sodium hydrogen carbonate, followed by brine wash. Removed the water content by adding anhydrous sodium sulfate.[27] Finally, collected the solid crude product by evaporating dicholoromethane using rotatory evaporator. Obtained product was purified by column chromatography using chloroform : methanol (20 : 1) as eluent. The product was recrystallized from methanol : chloroform (2 : 1) to get the target compounds.

D_1. A pale yellow coloured solid; yield: 35%; melting point is 151.2 °C; IR (KBr pellet) γ_{max} in cm^{-1}: 2922, 2857, 1732, 1605, 1508, 1238, 1075, 884, 759, 604; ^1H NMR (400 MHz, $CDCl_3$): δ 8.29–8.25 (m, 4H, Ar), 8.06–8.03 (m, 4H, Ar), 7.96–7.94 (m, 5H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.32 (ester C=O), 165.29–115.8 (Ar–C); MS (FAB+): *m*/*z* for $C_{19}H_{13}FN_2O_2$, calculated: 320.32. Found: 320.13; elemental analysis: calculated (found) %: C 71.24 (71.29), H 4.09 (3.97), F 5.93 (5.97), N 8.75 (8.68), O 9.99 (9.91).

D_2. A pale yellow coloured solid; yield: 35%; melting point is 167.35 °C; IR (KBr pellet) γ_{max} in cm^{-1}: 1742, 1706, 1602, 1508, 1278, 1196, 1067, 1015, 875, 755, 684; ^1H-NMR (400 MHz, $CDCl_3$): δ 8.22–7.21 (m, 12H, Ar), 4.45 (q, 2H, OCH_2), 1.46 (t, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.07 (ester C=O), 163.86–115.87 (Ar–C), 61.32 (OCH_2), 14.35 (CH_3).

E_1. A pale yellow colored solid; yield: 35%; melting point is 168.7 °C; IR (KBr pellet) γ_{max} in cm^{-1}: 1742, 1595, 1442, 1335, 1212, 1116, 983, 864, 802, 687; ^1H-NMR (400 MHz, $CDCl_3$): δ 8.06–7.39 (m, 12H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.08 (ester C=O), 163.95–109.11 (Ar–C); MS (FAB+): *m*/*z* for $C_{22}H_{17}FN_2O_4$, calculated: 392.38. Found: 391.23.

E_2. A pale yellow coloured solid; yield: 35%; melting point is 170.1 °C; IR (KBr pellet) γ_{max} in cm^{-1}: 1737, 1705, 1625, 1596, 1447, 1337, 1280, 1222, 1124, 1024, 870, 800, 642; ^1H-NMR (400 MHz, $CDCl_3$): δ 8.24–7.02 (m, 11H, Ar), 4.45 (q, 2H, OCH_2), 1.46 (t, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.05 (ester C=O), 161.97–109.38 (Ar–C), 61.34 (OCH_3), 14.53 (CH_3).

2.4 Characterization

The structures of the intermediates and desired products were confirmed by spectroscopic methods: IR spectra were recorded using a "Perkin Elmer (670) FTIR spectrometer" and ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) by Bruker. Also, CHN elemental analyser (Leco & Co) was used. Optical textures were obtained by using Olympus BX 51 polarizing optical microscope equipped with a Linkam Hotstage. Sample were prepared on glass slide and covered with coverslip. **D_1**, **D_2**, **E_1**, **E_2** were prepared in chloroform with fixed concentration of $\sim 1.2 \times 10^{-5}$ mol l^{-1} for photoswitching study. Photoswitching study was performed by using UV-Vis spectrophotometer (model: Ocean Optic HR 2000+). Quartz cuvettes containing the sample solutions were closed to avoid evaporation of the solvent. The absorption for all the compounds (*E*-isomers) were measured before UV irradiation. Omni Cure Series 2000 UV light source at intensity 5 mW cm^{-2} filtered through 365 nm filter and heat filter (to avoid any heat radiation arising from the source). The irradiation extended

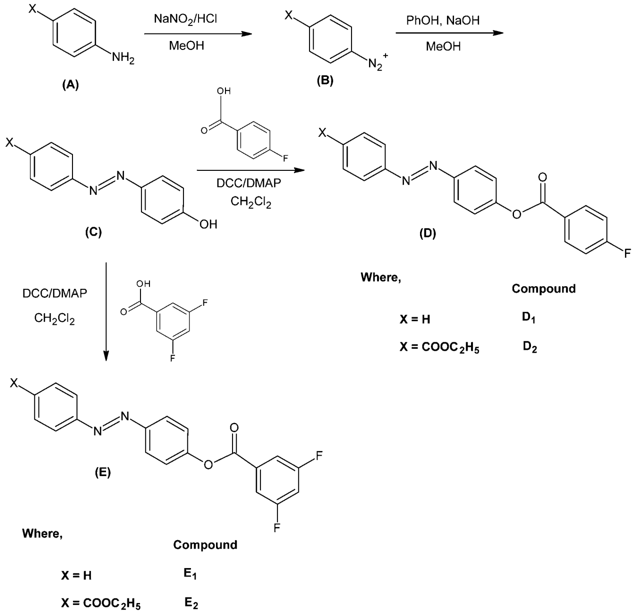


Fig. 1 Chemical structure and synthesis of fluorinated azobenzene compound.

with no disturbance until a photostationary states was attained and then, the light source was switch off. The changes in the absorption spectra at the range from 260 to 600 nm were recorded as a function of time. All these experiments have been carried out at room temperature.

3. Results and discussion

3.1 Synthesis

The synthesis of compound **D$_1$**, **D$_2$**, **E$_1$**, and **E$_2$** were performed as depicted in Fig. 1 which shows synthesis scheme.

Ethyl-4-amino benzoate (compound **A**) was diazotised by using sodium nitrite and hydrochloric acid. The diazotised nitronium ion (compound **B**) was coupled with phenol to produce *para* substituted azobenzene (compound **C**). Compound **D$_1$** and **D$_2$** having single fluorine atom was obtained by coupling compound **C** with 4-fluoro benzoic acid in the presence of DCC and DMAP as coupling agent. The synthesis of compound **E$_1$** and **E$_2$** with two fluorine atoms were performed by coupling compound **C** with 3,5-difluoro benzoic acid by DCC and DMAP. Crude products were further purified by column chromatography, followed by recrystallization from methanol. The newly synthesized compounds were characterized by IR, ^{1}H and ^{13}C NMR, and elemental analyses.

Table 1 Phase transition temperature (T/°C) for compounds D$_1$, D$_2$, E$_1$ and E$_2$[a]

Compound	Scan	Phase transitions
D$_1$	Cool	I 141.4 Cr
D$_2$	Cool	I 235.5 N 172.0 SmA 164.0 Cr
E$_1$	Cool	I 135.0 Cr
E$_2$	Cool	I 181.0 SmA 106 Cr

[a] Abbreviations: Cr = crystalline phase, N = nematic phase, SmA = smectic A phase, I = isotrophic phase.

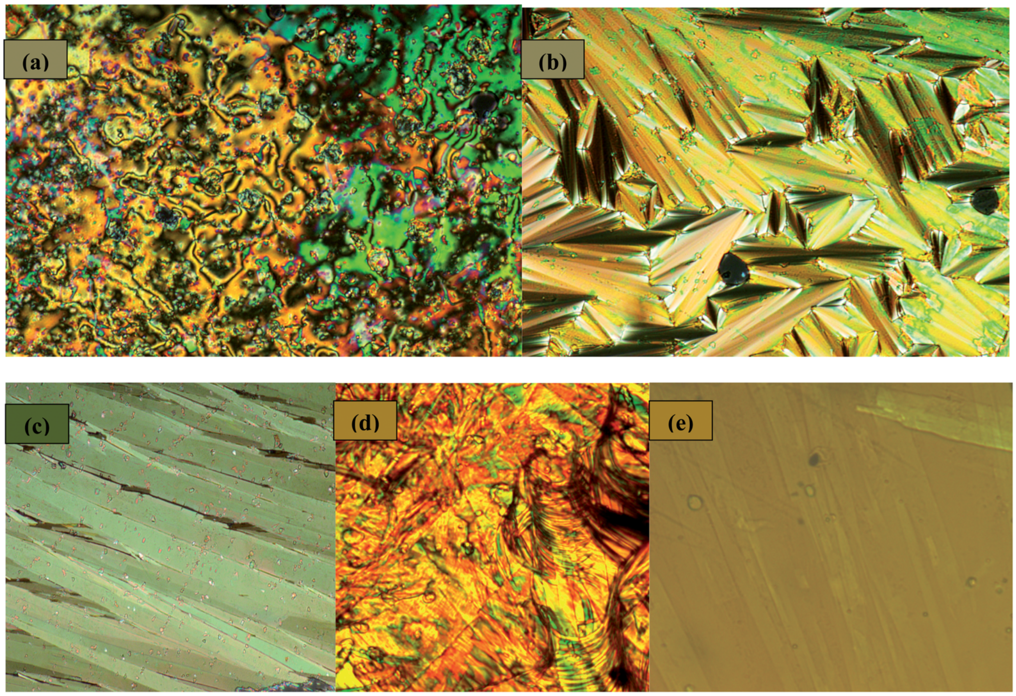


Fig. 2 Polarized optical micrographs obtained from cooling of isotropic phases of (a) nematic phase of D$_2$ at 225.5 °C (b) SmA phase of D$_2$ at 168.0 °C (c) crystalline phase of D$_2$ at 160.0 °C (d) SmA phase of E$_2$ at 181.0 °C (e) crystalline phase of E$_2$ at 106 °C.

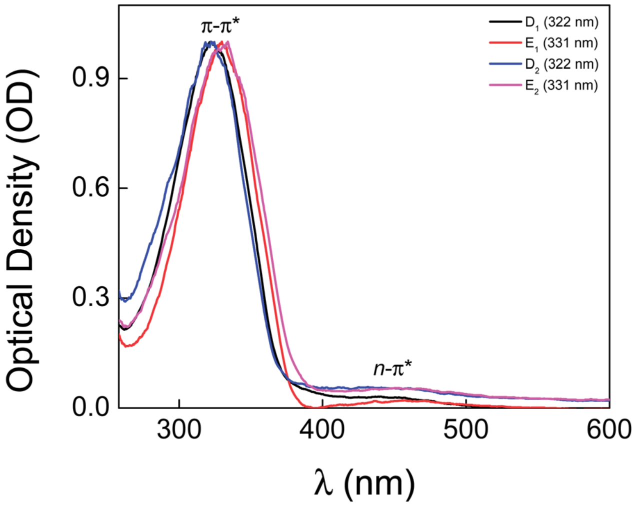


Fig. 3 Absorption spectra before illumination.

3.2 Polarizing optical microscopy (POM) studies

Liquid crystalline phases were observed in compound $\mathbf{D_2}$ using the polarizing-light optical microscope. A nematic phase (schlieren texture) was observed upon cooling from the isotropic at the rate of 2 °C per minute.

Optical texture was captured for compound $\mathbf{D_2}$ at 225.5 °C (Fig. 2a) showing typical nematic phase. On further cooling a broken fan shaped texture was observed as typical for smectic A phase. It was found at lower temperature 168 °C (Fig. 2b) whereas crystalline phase (Fig. 2c) observed on further cooling. For compound $\mathbf{E_2}$, a fan shaped texture typical for smectic A phase was observed as shown in Fig. 2d at 171 °C and at 106 °C it transforms to crystalline phase (Fig. 2e). Similar phases were found by us where we used fluorine-substituted benzoate ester (rod-shaped liquid crystals).[21] It was successfully incorporated into azobenzene as side arm linked with terminal double bonds as polymerizable functional groups. They showed smectic A and nematic phases of liquid crystal.[21] In case of compound $\mathbf{D_1}$ and $\mathbf{E_1}$ with no $-CO_2C_2H_5$ functional group, not showed any liquid crystalline phases. Thus, with $-CO_2C_2H_5$ group undoubtedly plays a major role to bring mesogenic features of the azobenzene derivatives. It should be noted that the fluorinated azobenzene compounds have lower transition temperature compare to non-fluoro compounds. Because, transition temperature decreases with the number of fluorine atom increases.[21,22]

Table 1 summarizes the mesophase behavior observed under the polarizing optical microscope. One can see the nematic and smectic phase for $\mathbf{D_2}$ compound and SmA phase for $\mathbf{E_2}$ compound and only crystalline phases for $\mathbf{D_1}$ and $\mathbf{E_1}$ compounds.

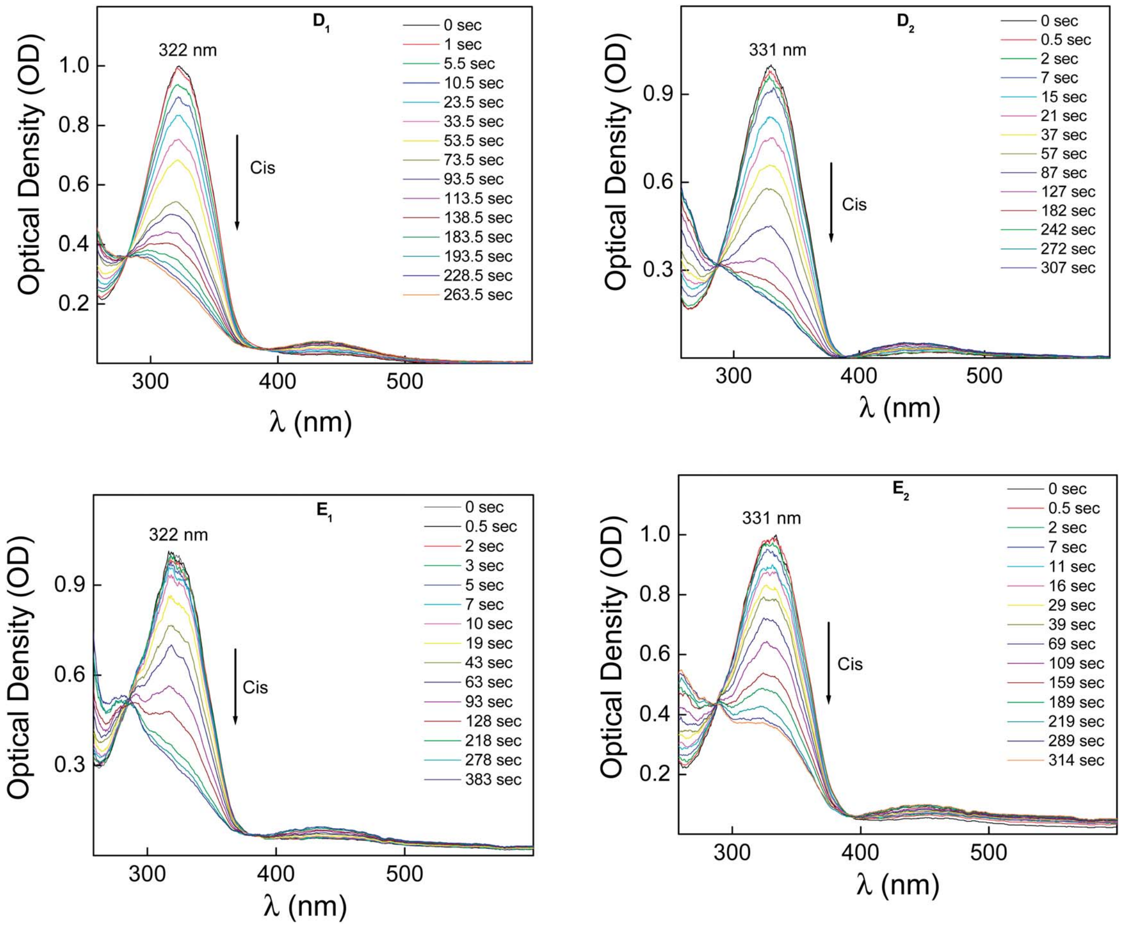


Fig. 4 Normalized absorption spectra with different exposure time of UV light with 365 nm filter for the compounds D_1, E_1, D_2, and E_2. No UV corresponds to the 0 s of UV illumination. Intensity used for the illumination is 5 mW cm^{-2}.

3.3 Photo switching studies

Photo switching studies were performed on quartz cuvette using chloroform as solvent which gives an idea of the materials behaviour with respect to UV light and also these results are indispensable for creating optical storage devices. The influence of fluorine on the π–π* absorption band position is best evaluated from the absorption spectra. Prior to illumination, a strong peak appeared at UV region correspond to π–π* transition of *E* isomer and weak peak at visible region correspond to n–π* transition of *Z* isomer[21,23] as shown in Fig. 3.

The *E* isomers of $\mathbf{D_1}$ and $\mathbf{D_2}$, which contain mono fluorine display their absorbance band at 322 nm whereas $\mathbf{E_1}$ and $\mathbf{E_2}$ which substituted with two fluorine produces absorption band at 331 nm. $\mathbf{E_1}$ and $\mathbf{E_2}$ showed bathochromic shifts with respect to $\mathbf{D_1}$ and $\mathbf{D_2}$ in the spectra. The addition of fluorine on the molecular structure of azobenzene derivatives effects the electronic spectra of the compounds. The lone pair electrons present in the –F have considerable interaction with the π system of the aromatic ring.[24]

During UV illumination, using 365 nm filter (UV intensity is around 5 mW cm^{-2}) along with heat filter to remove any heat radiation arising from the sample. Absorption peak decreases due to π–π* transition, followed by slight increase in the peak around 450 nm as a result of n–π* transition as shown in Fig. 4 ($\mathbf{D_1}$, $\mathbf{E_1}$, $\mathbf{D_2}$ and $\mathbf{E_2}$).

The wavelength at which azobenzene photoisomerization occurs depends on the particular structure of azobenzene molecules which can be attuned synthetically with substituent groups to the chromophores.[4] By all means, azobenzene molecules undergo *E*–*Z* isomerization when irradiated with light attuned to an appropriate wavelength.[25] Upon UV illumination of mono- and di-fluoro azobenzene compound, absorption was observed at their peak wavelengths, 322 nm and 331 nm respectively. Even so there were notably no changes in their *E*–*Z* isomerization time observed where all four compounds took ~4 minutes to reach photostationary state due to photo isomeric equilibrium of the *E*–*Z* isomers. That is to say the limitation in wavelength tuning did not influence the speed of *E* to *Z* isomer transition during illumination. The photo conversion efficiency (CE) of the *E*–*Z* photoisomerization is estimated from eqn (1).[26]

Table 2 Summarised *E*–*Z* photoisomerization result results

Compounds		*E*–*Z* (minutes)	CE (%)
Monofluoro	$\mathbf{D_1}$	4	72.93
	$\mathbf{D_2}$	4	80.80
Difluoro	$\mathbf{E_1}$	4	70.26
	$\mathbf{E_2}$	4	64.46

$$\mathrm{CE} = \frac{A(t_0) - A(t_\infty)}{A(t_0)} \times 100\% \tag{1}$$

Where $A(t_0)$ is absorbance before UV and $A(t_\infty)$ is absorbance after UV. Table 2 summarizes the photo conversion efficiency in these systems.

$\mathbf{D_2}$ gives 80.8% of *Z* fraction which is the highest among all four compounds whereas $\mathbf{E_2}$ gives the lowest CE which is 64.46%. $\mathbf{D_1}$ and $\mathbf{E_1}$ give 72.93% and 70.26% of CE respectively. With an increasing number of fluorine substituent, the size of the molecules increases and this change should result in an increasing free volume required for the photoisomerization. The reduced *Z* fraction observed in the case of $\mathbf{E_1}$ in comparison with $\mathbf{D_1}$ and also $\mathbf{E_2}$ in comparison with $\mathbf{D_2}$ may be explicable in terms of the sterically hindered structure of the *Z* isomer having increased number of fluorine substitution on phenyl ring. It is clear that as the *Z* isomer is sterically crowded and thermodynamically unstable, leading to the reduced *Z* fraction in the photostationary state.[27]

Thermal back relaxation occurs when molecules after attaining photo saturation state has been left in the dark where *Z* isomers transform to *E* isomers. The effect of structural modification can be observed in their thermal back relaxation

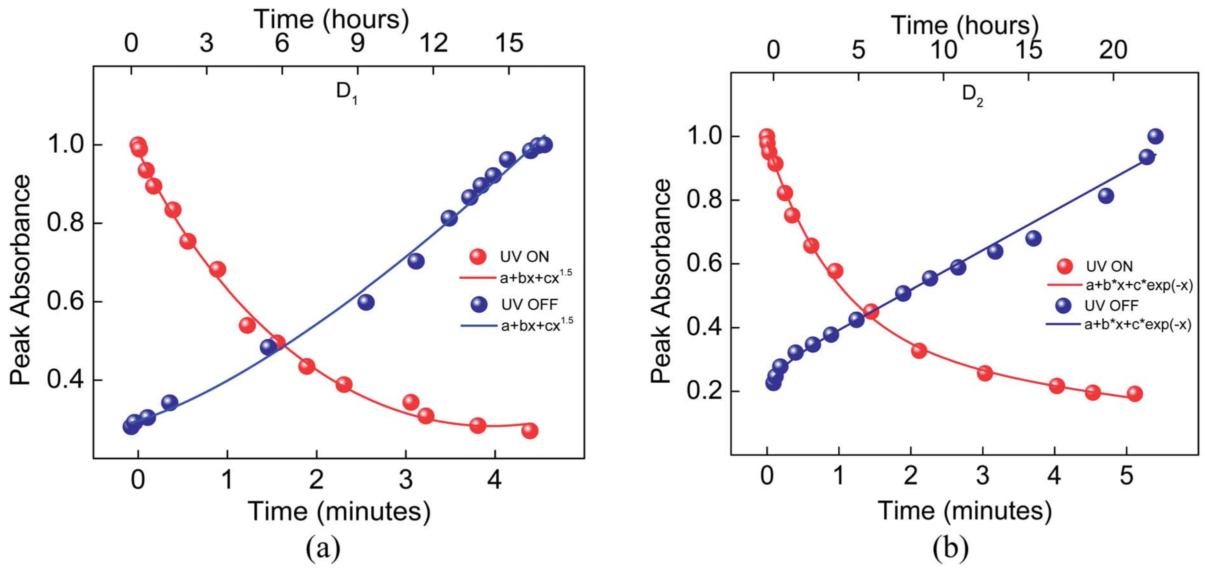
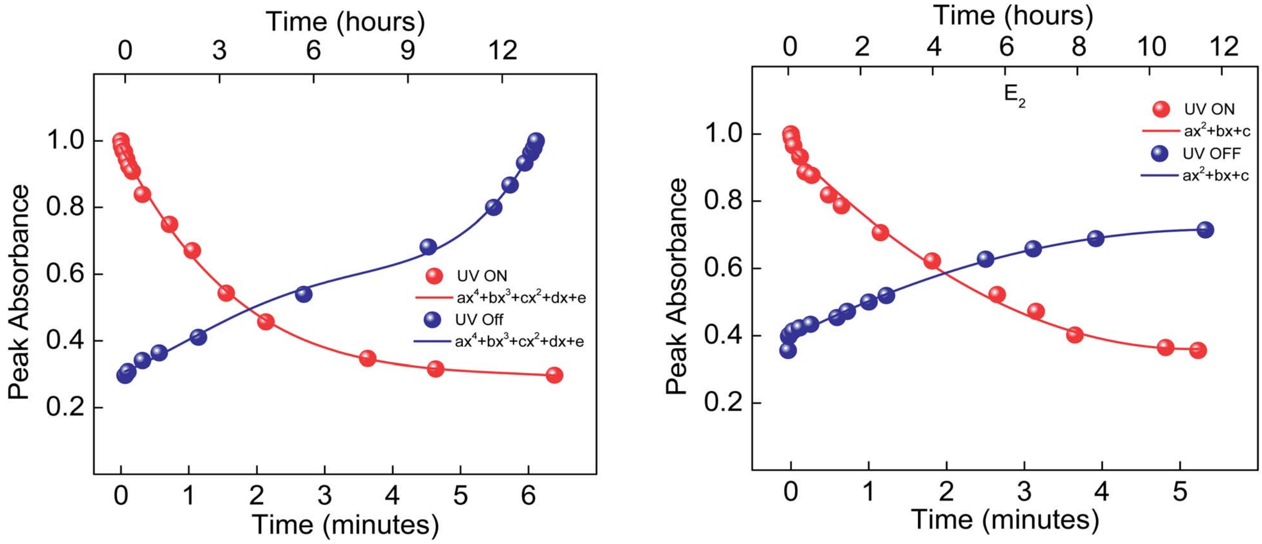


Fig. 5 Thermal back relaxation process of $\mathrm{D_1}$ and $\mathrm{D_2}$ as function of time after illuminating the material to photostationary state.

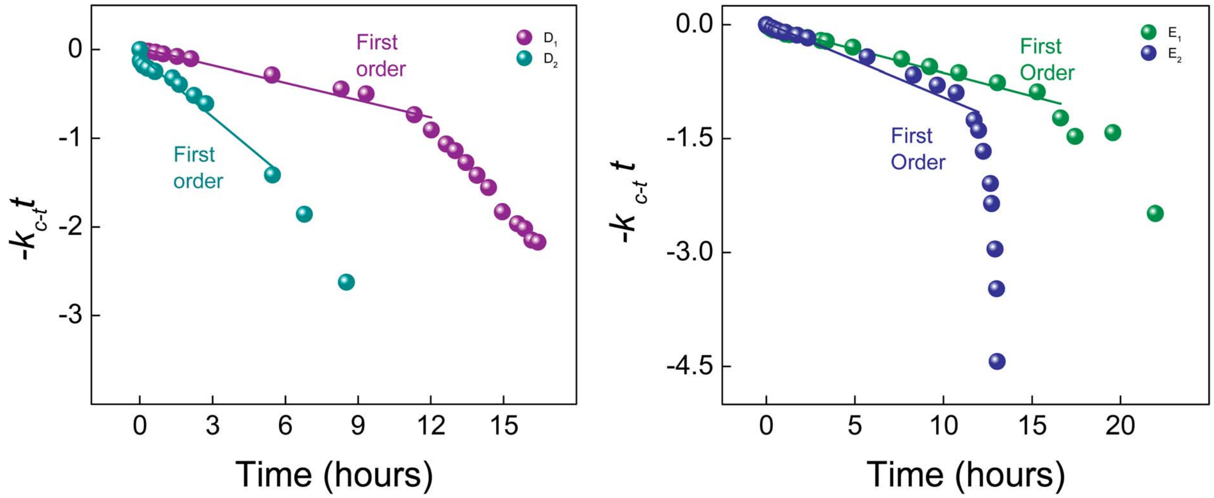


(a) (b)

Fig. 6 Thermal back relaxation process of E_1 and E_2 in the function of time after illuminating the material to photostationary state.

time. The reverse isomerisation process of $\mathbf{D_1}$ and $\mathbf{D_2}$ as a function of recovery time is as shown in Fig. 5. In case of monofluoro substitution $\mathbf{D_1}$, took about 16.42 hours to convert back to stable *trans* configuration whereas $\mathbf{D_2}$ having with $-CO_2C_2H_5$ group as functional group took around 22.48 hours. The reason of $\mathbf{D_2}$ took longer time to relax back to its original *E* configuration could be that phases involved on both sides of transitions possess layered structure (smectic phases). In fact, a similar feature was observed in another case wherein the phase involved has a layer structure.[21]

In the following, $\mathbf{D_1}$ and $\mathbf{D_2}$ will be compared with azobenzene chromophore incorporating two fluorine atoms at the terminal end. As shown in Fig. 6, diflouro-substituted molecule $\mathbf{E_1}$, shows 13.08 hours of thermal back relaxation whereas difluoro-substituted with $-CO_2C_2H_5$ group, $\mathbf{E_2}$ shows 11.55 hours of back relaxation. The presence of $COOC_2H_5$ functional group in difluoro azobenzene chromophores reduced the thermal back relaxation time to 11.55 hours. Fluorine, the most electronegative element are thought to withdraw electron density from the bonding π-type orbitals of $-N{=}N-$ double bond. This electronic effect made the $-N{=}N-$ double bond unstable and reduces the barrier for inter-conversion leading to fast thermal back relaxation when more fluorine was added.[1] Surprisingly, the $-CO_2C_2H_5$ group containing monofluoro azobenzene gives a longest *Z* isomer lifetime among the other compounds synthesized and almost double than that of difluoro-substituted azobenzene with $-CO_2C_2H_5$ group.



(a) (b)

Fig. 7 First-order plots for *Z*–*E* thermal isomerization for monofluoro-substituted and difluoro-substituted azobenzene measured at room temperature 25 °C.

For *Z–E* photo isomerization, it is necessary to measure first order plot. Fig. 7 shows the first order plot which is measured by fitting the experimental data to the eqn (2) (ref. 27) at room temperature 25 °C.

$$\ln \frac{A_\infty - A_t}{A_\infty - A_0} = -k_{c-t}t \tag{2}$$

Where A_t, A_0, and A_∞ are the absorbance at peak wavelength at time t, time zero, and infinite time, respectively. The reaction was first order in the time region indicated. But, deviated from first order in the later stage of the reaction. Mainly due to the long thermal back relaxation might affected the experimental temperature conditions, since this experiment has been carried out in solution. Here one can mainly observed the change in back relaxation time with respect to chemical structures.

Experiment concerning first order plots with respect to solid samples with different temperature where room temperature liquid crystals were mixed with these synthesized compounds is in progress and will be reported in due course.

The similar series of carboxylic acid derivative and amide based compounds were synthesized as well, to justify the effect of ester compounds which are reported in this article. The information regarding amide and carboxylic acid compounds are written in the supplementary ESI.†

4. Conclusion

Overall, the presence of fluorine and $-CO_2C_2H_5$ group in azobenzene proved to be the most important structural factors determining the liquid crystallinity and thermal back relaxation time. Based on experimental results, materials with monofluoro-substituted azobenzene esters exhibit long thermal back relaxation in comparison with difluoro-substituted counterparts. Long thermal back relaxation nearly 22 hours is the first report on fluorine-substituted esters and is strong contenders for creation of optical information storage devices.

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