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New para-substituted non-symmetric isoflavones for their fast photo-switching ability: Synthesis and their liquid crystal characterization

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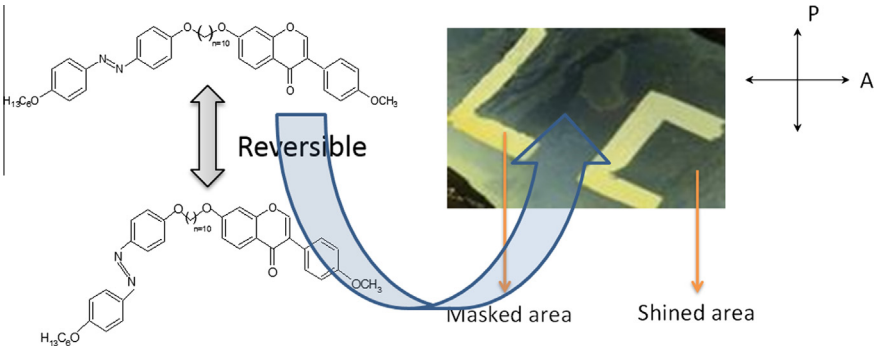
HIGHLIGHTS

- First time fast photo switching values were reported for isoflavone based azodyes.
- Both ON and Off times were very promising.
- Unsymmetrical nature is suggested as the main reason for the behaviour.

GRAPHICAL ABSTRACT



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ABSTRACT

The first example of non-symmetric isoflavone-based fast photo-switchable liquid crystals with different functional groups at the *terminal* position were synthesized and characterized. Polarizing optical microscopy study revealed that the compounds showed least ordered nematic phase. Optical photo switching study exhibited very fast photoisomerization effect in solution. The *E–Z* and *Z–E* conversion occurred around 3–5 s and 40–700 s respectively. This is also the first example of *para*-substituted non-symmetric isoflavone liquid crystals exhibiting very fast photo switching property in solution. Argument based on non-symmetrical behaviour might be the reason for the observed behaviour.

Introduction

The liquid crystals are known for self-assembling with respect to the external aid. Tacitly, oligomeric liquid crystals have heed in research due to their peculiar properties as compared with other low molecular weight liquid crystals [1–4]. Now a days photo-induced properties have greater attention due to their molecular alignment with respect to the incident light [5,6]. The photochromism phenomenon is observed ascribed to variation in the electronic spectra of azobenzene molecules. In other words, *cis-trans* isomerization is the backbone for the photochromism studies [7]. However, the optical data storage device concept is coming up by light induced studies on photo-sensitive compounds [8]. Clearly, azobenzene molecules are showing a strong tendency of photoisomerization with the illumination of UV light and visible light of

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suitable wavelengths [9]. The more stable *trans* configuration of N=N in the azodyes [10], isomerizes to form *cis*-isomer in presence of 365 nm UV light. It is observed in the previously reported journals, azobenzene group is either chemically bonded to liquid crystal molecules or physically mixed with the liquid crystals as dopants. The phase changes are very essential factor in the photo-induced studies for the application point of view. The order to disordered state transition is commonly observed in light sensitive materials, when the light of suitable wavelength is illuminated on that [11]. But, Prasad et al. reported the reverse process using same UV light irradiation [12] where disorder to order transition is reported.

Azobenzene liquid crystals are the best materials among other photo-sensitive compounds for the device fabrication, due to their photochromic properties. Hence, lot of bent-core azodyes are reported in the fields of photoisomerization and photochromism [12,13]. Also, photo-polymerization of azobenzene based liquid crystals are reported from last few decades [14,15]. Along with this, some of the acrylate monomers containing banana shape also reported due to their photo-cross-linking behaviour [16,17]. However, photo-cross-linking in bent core and oligomeric liquid crystals are interesting topics in liquid crystal research [18–21].

The present investigation focuses on the synthesis and photo-isomerization behaviour of four new, non-symmetric liquid crystals incorporating different *para*-substituted isoflavones and azobenzene chromophores connected via a flexible methylene spacer. According to literature, materials derived from biological sources such as glycolipids have gained much interest in liquid crystal research [22]. However, isoflavone has been rarely used as a molecular fragment in the design of new liquid crystalline materials [23–26]. Isoflavones are water-soluble compounds found in many plants. They comprise of a class of naturally occurring organic compounds related to flavonoids and their derivatives are made up of the large number of natural isoflavonoids [27].

Here in these investigations, the optical behaviour of synthesized materials was studied in solution. Also, we have created the optical storage device using guest–host system on solids. The isoflavone dye (guest) is mixed with the liquid crystalline material E7 (room temperature liquid crystal act like host) for measuring the thermal back relaxation. This guest–host effects in liquid crystals with azo dyes could be provides a path for the exploration of systems for obtaining fast switching light shutters.

Experimental

Synthetic procedures

4-[(4′-Hexyloxyphenyl)diazenyl]phenol (I)

Compound **I** was synthesized according to the reported method [28] from 4-hexyloxyaniline (3.35 mmol, 1 equiv.), concentrated hydrochloric acid (2 mL), water (15 mL) and cooled to 0 °C. After the solution was neutralized to pH = 8 with a dilute sodium hydroxide solution. Sodium nitrite (4.08 mmol, 1.2 equiv.) in cold water (12 mL) was added drop wise to the solution and the mixture was stirred at 0 °C for 1 h. Phenol (4.02 mmol, 1.2 equiv.) in cold ethanol (12 mL) was then added drop wise to the solution and stirred at 0 °C for 1 h. The solution was neutralized with a diluted sodium hydroxide until pH become 6–7. The mixture was stirred for 1 h at 0 °C. Finally, the distilled water (30 mL) was added to the mixture and the precipitate was filtered off and treated with chloroform.

Reddish yellow coloured solid; R_f = 0.4 (40% $CHCl_3$–EtOH); yield: 75%. IR (KBr Pellet) ν_{max} in cm^{-1}: 3186 (OH), 2954, 2920 (CH_2 aliphatic), 1600 (C=C), 1499 (N=N), 1249 (C—O ether). ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.01 Hz, 4H, Ar), δ 6.90 (d, J = 8.12 Hz, 4H, Ar), δ 4.07 (t, J = 4.11 Hz, 2H, OCH_2), δ 1.10–1.90 (m, 8H, CH_2), δ 0.89 (t, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.6, 160.7, 144.3, 145.3, 114.7, 116.2, 123.6, 124.4, 116.2, 68.7, 29.6, 25.6, 31.8, 22.7, 14.1; MS (FAB+): m/z for $C_{18}H_{22}N_2O_2$, calculated: 298.38. Found: 298.16; elementary analysis: calculated (found) %: C 62.47 (62.81), H 7.21 (7.15), Br 17.32 (17.13), N 6.07, (6.01), O 6.93 (6.58).

1-[4-(n-Bromodecyloxy)phenyl]-2-(4′-hexyloxyphenyl)diazene (IIa)

Compound **IIa** was synthesized according to the reported method [29]. Compound **I** (1.93 mmol, 1 equiv.), potassium carbonate anhydrous (5.79 mmol, 3 equiv.) and dibromodecane (5.79 mmol, 3 equiv.) in acetone (20 mL) and refluxed for 6 h. Afterwards, it was poured into ice-cold water and acidified with dilute hydrochloric acid (pH < 5). The precipitate was filtered off and was crystallised from methanol/chloroform (10:2).

A similar procedure was adopted for the synthesis of compound IIb.

Bright yellow coloured solid; R_f = 0.45 (60% $CHCl_3$–MeOH); yield: 70%; IR (KBr Pellet) ν_{max} in cm^{-1}: 2954, 2850 (CH_2 aliphatic), 1602 (C=C), 1497 (N=N), 1246 (C—O ether). ^1H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.11 Hz, 4H, Ar), δ 6.99 (d, J = 8.01 Hz 4H, Ar), δ 4.09 (t, J = 4.12 Hz, 4H, OCH_2), δ 3.45 (t, J = 4.01 Hz, 2H, CH_2Br), δ 1.12–1.98 (m, 24H, CH_2), δ 0.89 (t, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl3): δ 1616.6, 144.3, 114.7, 123.6, 33.7, 68.7, 32.6, 29.6, 28.0, 25.9, 28.6, 31.8, 22.7, 14.1; MS (FAB+): m/z for $C_{28}H_{41}BrN_2O_2$, calculated: 517.54. Found: 516.23; elemental analysis: calculated (found) %: C 64.98 (7.02), H 7.98 (7.86), Br 15.44 (14.99), N 5.41 (5.23), O 6.18 (6.14).

7-Hydroxy-3-(4′-fluorophenyl)-4H-1-benzopyran-4-one (IIIa)

Compound **IIIa** was synthesized according to the reported procedures [30,31]. 4-fluorophenylacetic acid (11.7 mmol, 1 equiv.), resorcinol (12.87 mmol, 1.1 equiv.) in $BF_3{\cdot}Et_2O$ (30 mL) and heated for 4 h at 70–75 °C under nitrogen atmosphere. The reaction mixture was then cooled to room temperature. Then dry DMF and $MeSO_2Cl$ (35.1 mmol, 3 equiv.) were added and heated at 75–80 °C for 1.5 h (distillation of DMF was done by using anhydrous $CaCl_2$). The reaction mixture was poured into ice cold water. Then filtered the precipitate obtained.

A light reddish yellow coloured solid; yield = 59%. IR (KBr) ν_{max} in cm^{-1}: 3193 (OH), 1641 (C=O) and 1598 (C=C). ^1H NMR (400 MHz, DMSO-d_6): δ 10.85 (s, 1H, OH), δ 8.41 (s, 1H, H) and δ 6.89–7.99 (d, J = 8.11 Hz, 7H, Ar). ^{13}C NMR (100 MHz, CDCl3): δ 162.1, 158.6, 153.2, 175.3, 165.0, 123.5, 118.2, 115.4, 101.4, 128.2, 128.0; MS (FAB+): m/z for $C_{15}H_9FO_3$, calculated: 256.23. Found: 256.05; elemental analysis: calculated (found) %: C 70.31 (70.85), H 3.54 (3.42), F 7.41 (7.25), O 18.73 (18.64).

Similar procedures were adopted for the preparation of compounds **IIIb–IIIc** by replacing compound **IIIa** with compounds **IIIb** and **IIIc**, respectively.

7-[{4-[(4′-Hexyloxyphenyl) diazenyl]phenoxy}decyloxy]-3-(4′-fluorophenyl)-4H-1 benzopyran-4-one (IVa)

Compound **IVa** was synthesized according to the method reported in literature [32] from a mixture of compounds **IIa**, (0.58 mmol, 1 equiv.), **IIIa**, (0.64 mmol, 1.1 equiv.), potassium carbonate (1.16 mmol, 2.0 equiv.) and a catalytic amount of KI in acetone (20 mL) refluxed for 18 h. Afterwards, it was poured into ice-cold water and acidified with dilute hydrochloric acid (pH < 5). The precipitate was filtered off and was crystallised from methanol/chloroform (10:2).

A pale yellow coloured solid; yield = 59%. IR (KBr Pellet) ν_{max} in cm^{-1}: 2919, 2851 (CH_2 aliphatic), 1642 (C=O), 1602 (C=C), 1447 (N=N), 1244 (C—O). ^1H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, J = 8.9 Hz, 1H, Ar,), δ 7.92 (s, 1H, Ar), δ 7.90 (d, J = 8.9 Hz, 2H, Ar), δ 7.85 (d, J = 8.9 Hz, 2H, Ar), δ 7.55–7.52 (m, 2H, Ar), δ 7.12 (t, J = 8.7 Hz, 3H, Ar), δ 6.98 (d, J = 8.9 Hz, 4H, Ar), δ 6.84 (d, J = 2.3 Hz, 1H, Ar), δ 4.07–4.02 (m, J = 4.23 Hz, 6H, OCH_2), δ 1.87–1.78 (m, 6H,

CH_2), δ 1.49–1.45 (m, 6H, CH_2), δ 1.36–1.34 (m, 12H, CH_2), δ 0.92 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (100 Hz, $CDCl_3$): δ 162.1, 157.8, 153.2, 175.3, 165.9, 161.6, 144.3, 123.5, 117.2, 128.1, 115.4, 100.3, 1147, 109.1, 127.4, 115.4, 68.7, 29.6, 25.9, 31.8, 22.7, 14.1; MS (FAB+): *m*/*z* for $C_{43}H_{49}FN_2O_5$, calculated: 692.86. Found: 692.35; elemental analysis: calculated (found) %: C 74.54 (74.63), H 7.13 (6.92), F 2.74 (2.58), N 4.04 (3.97), O 11.55 (11.56).

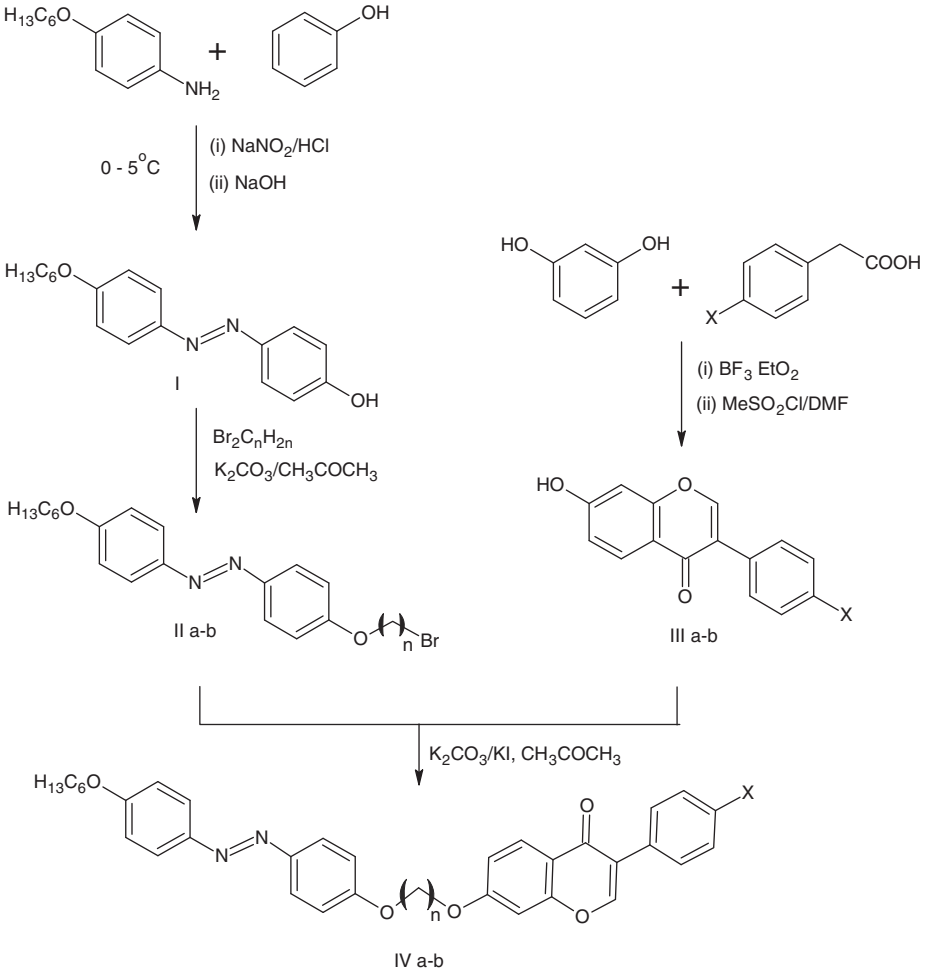
Similar procedure was followed to synthesis the compounds **IV(b–d)**.

Compound ***IVb***

A pale yellow solid; yield 65%; IR (KBr Pellet) ν_{max} in cm^{-1}: 2937, 2919, 2851 (CH_2 aliphatic), 1643 (C═O), 1601 (C═C), 1446 (N═N), 1252 (C—O). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.9 Hz, 1H, Ar), δ 7.91 (s, 1H, Ar), δ 7.86 (d, *J* = 8.9 Hz, 2H, Ar), δ 7.85 (d, *J* = 8.9 Hz, 2H, Ar), δ 7.50 (d, *J* = 8.8 Hz, 2H, Ar), δ 6.99–6.96 (m, 7H, Ar), δ 6.83 (d, *J* = 2.4 Hz, 1H, Ar), δ 4.06–4.02 (m, *J* = 7.11 Hz 6H, OCH_2), δ 3.84 (s, 3H, OCH_3), δ 1.86–1.80 (m, 6H, CH_2), δ 1.49–1.47 (m, 6H, CH_2), δ 1.36–1.34 (m, 12H, CH_2), δ 0.92 (t, *J* = 7.0 Hz, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.9, 163.6, 161.2, 161.1, 159.6, 158.0, 152.0, 147.0, 146.9, 130.1, 127.7, 124.9, 124.3, 118.3, 114.9, 114.7, 114.4, 114.0, 100.6, 68.7, 68.4, 68.3, 55.4, 31.6, 29.5, 29.4, 29.3, 29.2, 29.0, 26.1, 26.0, 25.7, 22.6, 14.0; MS (FAB+): *m*/*z* for $C_{44}H_{52}N_2O_6$, calculated: 704.89, found: 704.31; elemental analysis: calculated (found)%: C 74.54 (74.61), H 7.44 (7.37), N 3.97 (3.86), O 13.62 (13.71).

Compound ***IVc***

A pale yellow coloured solid; yield 55%; IR (KBr Pellet) ν_{max} in cm^{-1}: 2939, 2863 (CH_2 aliphatic), 1641 (C═O), 1603 (C═C), 1446



Where,

Compounds	n	X
IIa	6	
IIb	10	
IIIa		F
IIIb		Br
IIIc		OCH_3

Where,

Compounds	n	X
IVa	10	F
IVb	10	OCH_3
IVc	6	F
IVd	6	Br

Scheme 1. Synthetic routes for the formation of 7-[{4-[(4′-hexyloxyphenyl) diazenyl]phenoxy}alkyloxy]-3-(4′substitutedphenyl)-4H-1-benzopyran-4-ones.

(N=N), 1242 (C—O). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.20 (d, J = 8.9 Hz, 1H, Ar), δ 7.92 (s, 1H, Ar), δ 7.87 (d, J = 8.9 Hz, 2H, Ar), δ 7.85 (d, J = 8.9 Hz, 2H, Ar), δ 7.55–7.52 (m, 2H, Ar), δ 7.12 (t, J = 8.7 Hz, 2H, Ar), δ 7.01–6.98 (m, 5H, Ar), δ 6.84 (d, J = 2.4 Hz, 1H, Ar), δ 4.09 (t, J = 6.4 Hz, 2H, OCH_2), δ 4.07 (t, J = 4.0 Hz, 2H, OCH_2), δ 4.03 (t, J = 6.6 Hz, 2H, OCH_2), δ 1.90–1.82 (m, 4H, CH_2), δ 1.61–1.5 (m, 8H, CH_2), δ 1.37–1.35 (m, 4H, CH_2), δ 0.92 (t, J = 3.4 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.6, 163.6, 161.8, 161.2, 161.0, 158.0, 152.4, 147.0, 146.9, 130.7, 130.6, 127.9, 127.8, 124.4, 124.3, 118.2, 115.5, 115.3, 115.0, 114.7, 114.6, 100.7, 68.6, 68.4, 68.0, 31.6, 29.2, 29.1, 28.9, 25.8, 25.7, 25.6, 22.6, 14.0; MS (FAB+): m/z for $C_{39}H_{41}FN_2O_5$, calculated: 636.75, found: 636.29; elemental analysis: calculated (found) %: C 73.56 (73.84), H 6.49 (6.58), F 2.98 (2.84), N 4.40 (4.31), O 12.56 (12.48).

*Compound **IVd***

A pale yellow coloured solid; yield = 63%; IR (KBr Pellet) ν_{max} in cm^{-1}: 2935, 2860 (CH_2 aliphatic), 1637 (C=O), 1602 (C=C), 1442 (N=N), 1251 (C—O). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, J = 8.9 Hz, 1H, Ar), δ 7.93 (s, 1H, Ar), δ 7.86 (d, J = 8.9 Hz, 2H, Ar), δ 7.85 (d, J = 8.9 Hz, 2H, Ar), δ 7.55–7.52 (m, 2H, Ar), δ 7.49 (d, J = 8.2 Hz, 2H, Ar), δ 7.02–6.97 (m, 5H, Ar), δ 6.83 (d, J = 2.3 Hz, 1H, Ar), δ 4.08–4.02 (m, J = 4.32 Hz 6H, OCH_2), δ 1.87–1.80 (m, 4H, CH_2), δ 1.48–1.43 (m, 8H, CH_2), δ 1.38–1.35 (m, 4H, CH_2), δ 0.91 (t, J = 3.1 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.3, 163.7, 161.2, 161.1, 158.0, 152.5, 146.9, 146.8, 131.6, 130.9, 130.6, 127.8, 124.3, 124.2, 122.3, 118.2, 115.1, 114.7, 114.6, 114.3, 100.7, 68.6, 68.4, 68.30, 31.6, 29.2, 29.1, 27.9, 25.8, 25.7, 25.6, 22.6, 14.0; MS (FAB+): m/z for $C_{39}H_{41}FN_2O_5$, calculated: 697.66, found: 696.17; elemental analysis: calculated (found) %: C 67.14 (67.25), H 5.92 (5.81), Br 11.45 (11.36), N 4.02 (3.89), O 11.47 (11.38).

Sample preparation for photoswitching study

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 ^{1}H NMR (500 MHz), ^{13}C NMR (125 MHz) by Bruker. Also, CHN elemental analyser (Leco & Co) was used. UV/Vis absorption spectra were recorded using UV–Visible spectrophotometer obtained from Ocean Optics (HR2000+). For photo-switching studies in solutions, the synthesized liquid crystals were dissolved in chloroform at concentration of $C = 1.2 \times 10^{-5}$ mol L^{-1}. Photo-switching behaviour of the azobenzene containing isoflavone moiety was investigated by illuminating with OMNICURE S2000 UV source equipped with 365 nm filter with 5 mW/cm^2 intensity. Heat filter is added just before the sample to avoid any heat radiation arising from the sample. The photo switching studies in solids, the synthesized liquid crystals were mixed with room temperature liquid crystals E7 to make guest–host system. 5% of isoflavone based azo dyes were physically mixed with 95% E7 at 80 °C (isotropic temperature of E7). The mixture is filled into the previously sandwiched (ITO + polyimide coated) glass substrates, unidirectionally rubbed cell at isotropic temperature (~80 °C). Qualities of the cells were observed under optical polarizing microscope.

Optical and thermal investigation

Thermal behaviour of all the compounds was studied using polarized optical microscopy (POM Olympus BX-51). Liquid crystalline phase is observed through optical polarizing microscope under 1 °C/min cooling using *Linkam Hotstage*.

Results and discussions

Material synthesis

The synthetic scheme of new materials is depicted in Scheme 1. The compounds were synthesized according to the reported procedures [28]. Compounds were purified on silica gel (60–120) by column chromatography and recrystallized from Ethanol:Chloroform (30:70) and are characterized by ^{1}H, ^{13}C NMR and FTIR.

Structures of compounds **IVa–IVd** in the present investigations were given in Fig. 1.

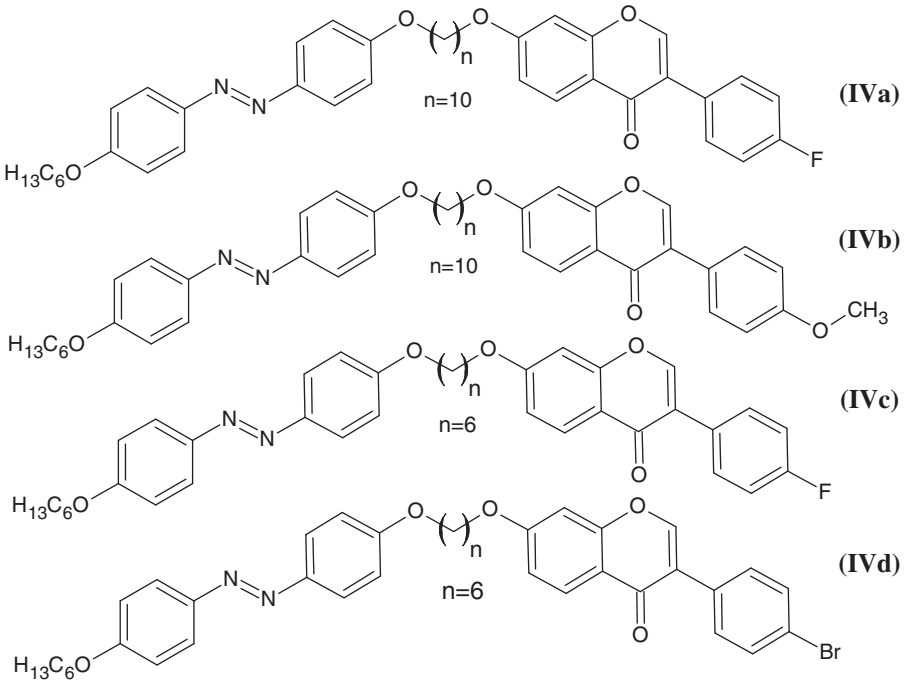


Fig. 1. Chemical structures of the compounds studied in these investigations.

Mesomorphic properties

The thermal behaviour of all the compounds was studied using polarized optical microscopy (POM). The synthesized compounds are isoflavone compounds (IVa–IVd) consist of five rings, aromatic compounds includes the terminal ethers and hetero atoms.

Phase transition temperatures with the nematic-isotropic temperatures are given in Table 1. The POM of the compounds was measured at a rate of 1 °C min^{-1}. Fig. 2 showing the nematic phase of the compound IVb at 202.4 °C. All the four compounds showed the nematic phase and the ranges are given in Table 1.

Photoswitching behaviour

All synthesized compounds showed similar absorption spectra due to their similar molecular structures. The difference is the alkyl chain length (n = 6 and 10) and end group substituents (X = F, OCH_3 and Br) in all the four compounds, which do not alter the electronic transitions (see Fig. 3).

The absorption spectra of compounds **IVa–IVd** are shown in Fig. 3. Consequently, compounds **IVa–IVd** was considered for

Table 1
Phase transition temperature (T/°C) for different compounds exhibiting liquid crystalline phases. (Abbreviations: Cr = crystal, N = nematic, I = isotropic phase).

Comp.	Scan	Phase transition (°C)
IVa	Cool	I 183.6 N 179.3 Cr 150.6
IVb	Cool	I 204.5 N 199.7 Cr 134.8
IVc	Cool	I 214.6 N 208.3 Cr 162.6
IVd	Cool	I 200.7 N 194.2 Cr 114.2

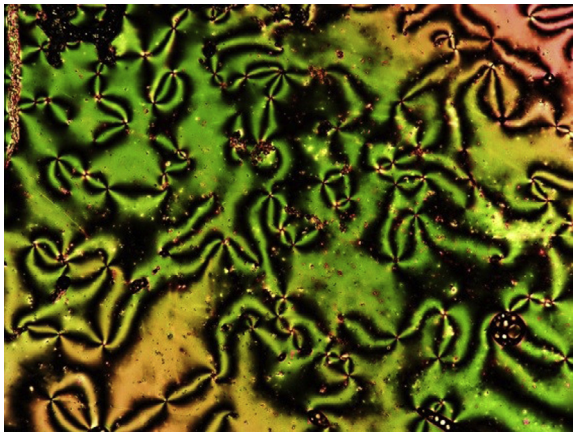


Fig. 2. Polarized optical micrographs obtained from cooling of isotropic phases showing schlieren texture observed for compound 'IVb' at 202.4 °C on cooling from isotropic melt.

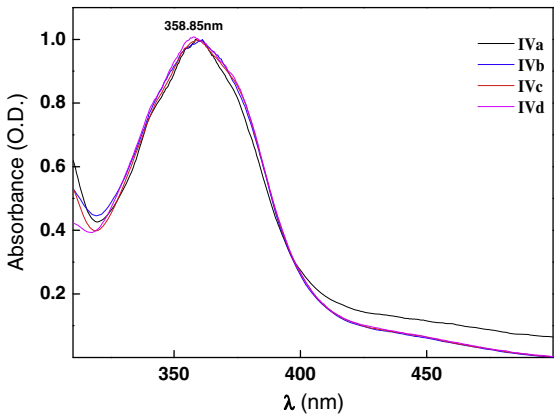


Fig. 3. Absorption spectra before irradiation of the UV light for the compounds IVa–IVd showing similar transition peaks.

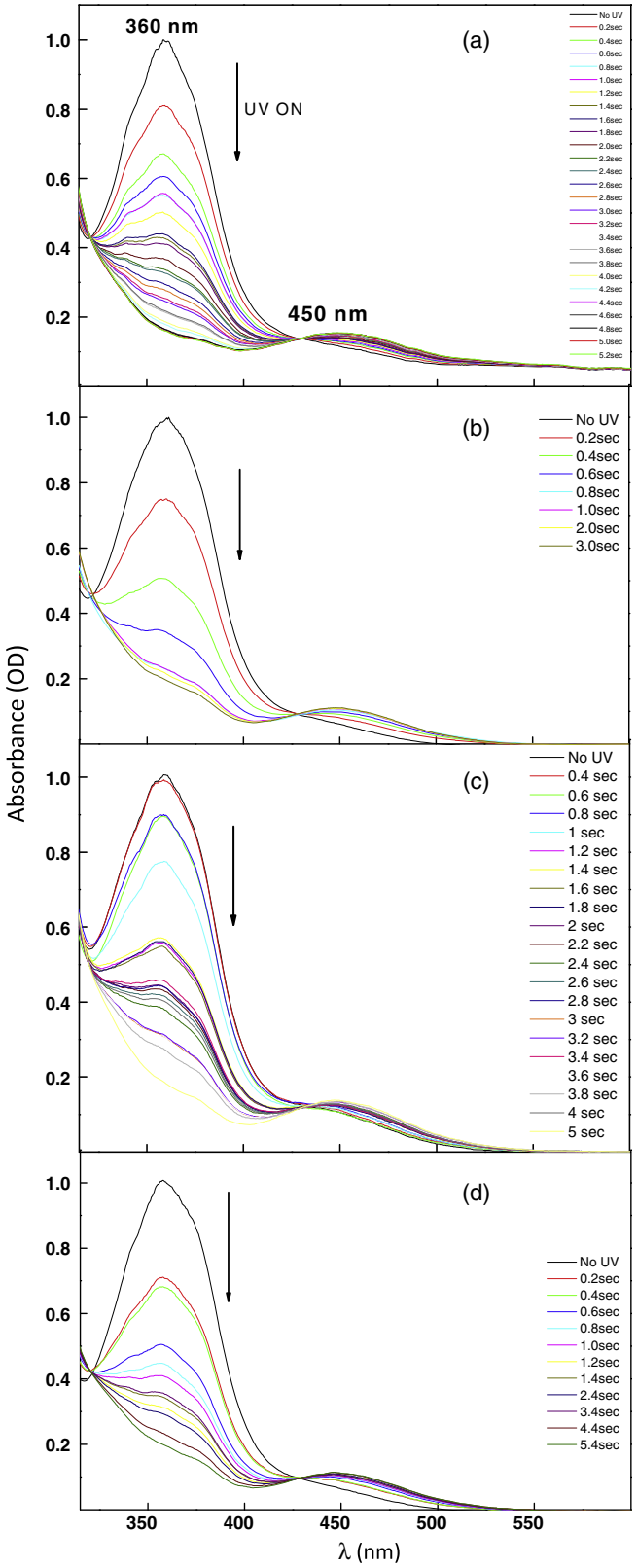


Fig. 4. Showing the absorbance data of all the samples investigated here respectively as IVa–IVd.

photoisomerization study. Photo-switching studies were initially performed in solution and then with liquid crystal cells. It gives an idea of the materials behaviour with respect to UV light. Also, these results are indispensable for creating optical storage devices.

Fig. 4a–d depicts the absorption spectra of **IVa** ($n = 10$ and X = F) and **IVb** ($n = 10$ and X = OCH_3) and **IVc** ($n = 6$ and X = F) and **IVd** ($n = 6$ and X = Br) respectively before and after UV illumination. The absorption spectra of compound **IVa–IVd** showed two absorbance maxima one at ~365 nm and the other at ~450 nm. The absorption spectra of compound was carried out in chloroform solution having concentration, $C = 1.2 \times 10^{-5}$ mol L^{-1}. The strong absorbance in the UV region at ~365 nm corresponds to π–π^* transition of the *E* isomer (*trans isomer*) and the week absorption at 450 nm corresponds to n–π^* transition of the *Z* isomer (*cis isomer*).

The compound **IVa–IVd** was illuminated with UV light having 365 nm filter with UV intensity of 5 mW/cm^2 at different time intervals and immediately the absorption spectra were recorded. The absorption maximum at 365 nm decreases due to *E*/*Z* photoisomerization, which leads to *E* isomer transformed to *Z* isomer. After ~4 s illumination, there is no change in absorption spectrum confirms the photo saturation of *E*/*Z* isomerization process as shown in Fig. 5. Data extracted from Fig. 4 and absorption values with different UV exposure times were recorded. Curves shows that photo-saturation occurs within 1 s of time for sample **IVb** and 2 s for sample **IVd** and ~4 s for sample **IVa** and **IVc** which is very fast as compared with nematic to isotropic phase involved photoisomerization [33].

The reverse transformation from *Z* to *E* can be brought by two methods, one by keeping the solution in dark and other by illuminating white light of higher wavelength. The first method is well known as thermal back relaxation. Fig. 6a–d shows the thermal back relaxation process for the compounds investigated here. Here back relaxation is measured at peak wavelength ~365 nm. Fig. 7 shows the *Z*–*E* absorption of compound **IVa–IVd** as a function of thermal back relaxation time in which data was extracted from Fig. 6 absorption values after exposed to UV light for 6 s (which is above photo-saturation values) were recorded. On the other hand, back relaxation takes place within 90 s for sample **IVb**, ~400 s of time for sample **IVa** and **IVc**, 700 s for sample **IVd** which is also quiet fast back relaxation as compared with earlier reported on isoflavones. Specially for compound **IVb** having UV ON: 1 s and UV Off: 90 s containing fluorine substitution in their structure is unique and showing very fast back relaxation as compared with earlier reported isoflavone based compounds.

It is necessary to investigate the photosensitivity to check the feasibility of the isoflavones interns of UV intensity. Here, we have used **IVb** for the investigations, this compound exhibited fast photoswitching behaviour. Fig. 8 shows the changes in back relaxation time with respect to illumination of different UV intensity (365 nm filter is used). One can clearly see that molecules relax very fast when UV intensity increases. When intensity is around 17 mW/cm^2, both UV ON and UV Off take place around the same time.

The rate of thermal back relaxation depends on the geometry of the dimers. Although exact reason for this fast thermal back relaxation is difficult to predict. But, we speculate the following reasons in this study. The thermal back relaxation is very fast, when the *Z*-isomer is at metastable state. It is due to steric repulsion of the two bulky phenyl rings which are positioned on the same side (dihedral angle = 0°). However, the *E*-isomers are thermodynamically stable as steric repulsion is minimal with the two phenyl rings 180° apart [ ].

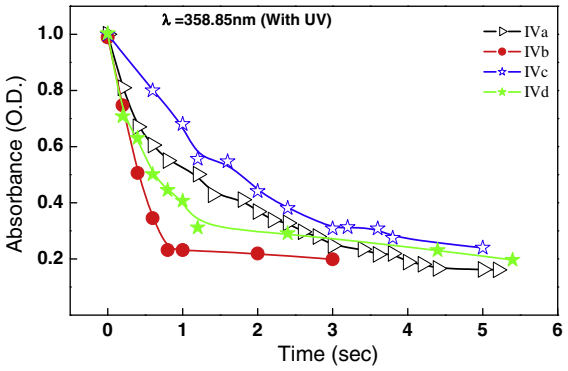


Fig. 5. Showing *E*–*Z* isomerization in presence of UV irradiation with respect to exposure time. Data is compared with compounds IVa–IVd respectively.

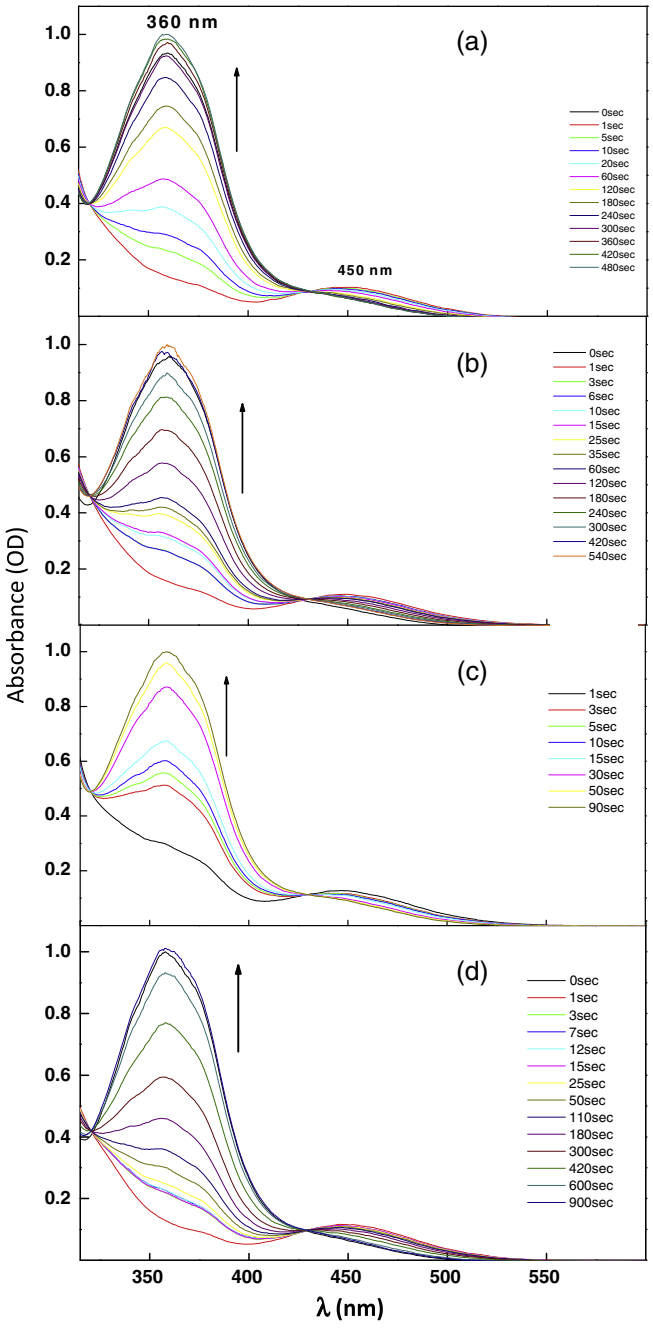


Fig. 6. Showing the thermal back relaxation data of all the samples investigated here namely IV (a), IV (b), IV (c), and IV (d). One can see 2 peaks, one at ~365 nm and another at 450 nm.

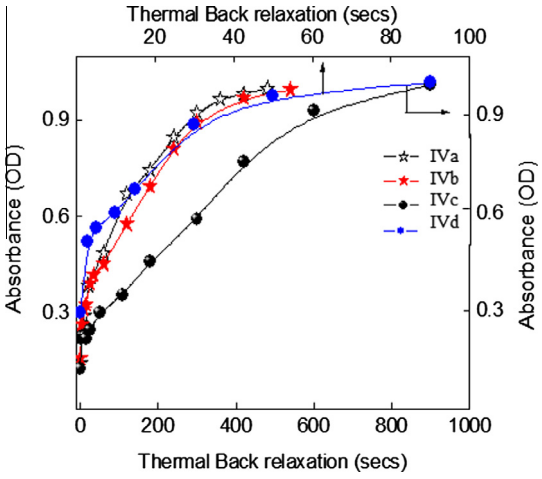


Fig. 7. Thermal back relaxation time for the compound IVb as a function of UV light intensity showing slow back relaxation (lower intensity) to fast thermal back relaxation (higher intensity).

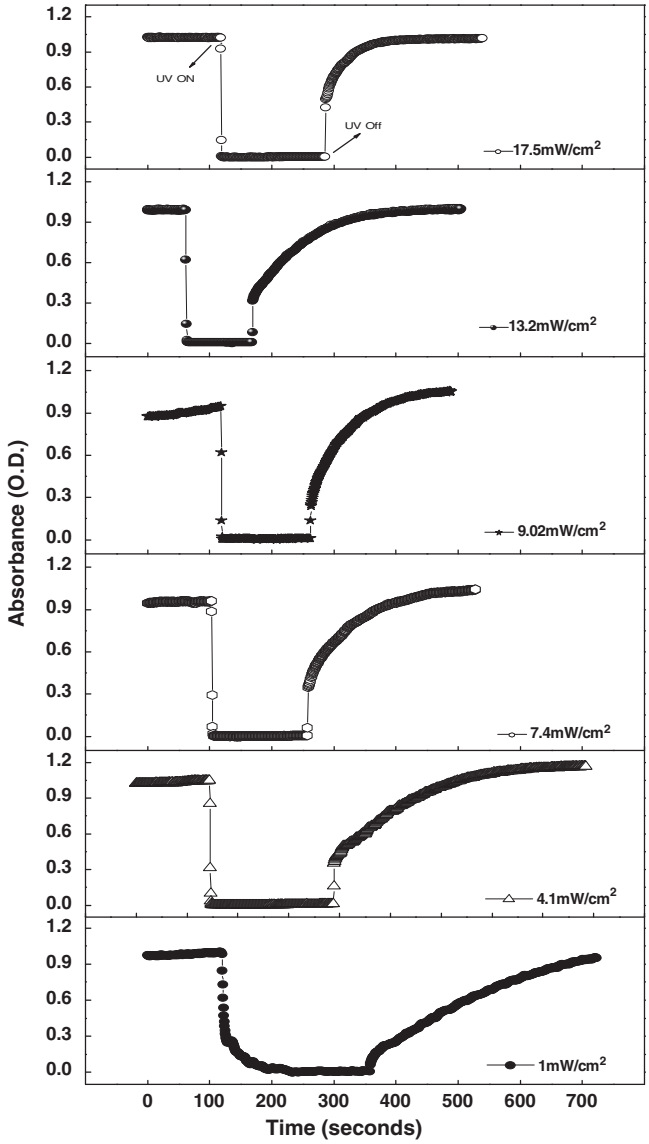


Fig. 8. *Z–E* photoisomerization of the compounds **IVa–IVd**. One can see that photo-saturated thermal back relaxation time is around ~90 s for the compound IVc, ~400 s for the compounds IVa and IVb and around 700 s for the compound IVd.

Another creative thinking might be the asymmetric (non-symmetric) effect play an important role in the study of photo-switching nature. There are two asymmetric groups attached on both the sides of azo moiety. Such as bulky isoflavone with alkyl chain and a small p-substituted benzene at another side. This asymmetric effect on the anisotropic azo moiety containing isoflavones might be responsible for fast photoswitching behaviour.

Spectral investigations on solid films were also recorded as a function of UV illumination. Here guest–host effect is employed. Where E7 (room temperature nematic liquid crystal) was used as host and isoflavone based liquid crystals were used as guest systems.

The cells were prepared by polyimide coating and rubbed it unidirectionally. These cells were filled with the guest–host mixture at isotropic temperature of the mixture. UV/Vis spectral data were recorded using Spectrophotometer.

Fig. 9 shows the UV ON and UV Off (thermal back relaxation) process for the compound **IVb**. Peak wavelength is ~360 nm and data is generated from peak absorbance at 360 nm as a function of exposure time. One can clearly observe that *E–Z* conversion takes around 3 s whereas thermal back relaxation takes around 40 min. Which is very fast as compared to earlier published results [1]. This is also the first report for showing fast photoswitching behaviour of isoflavones on solids.

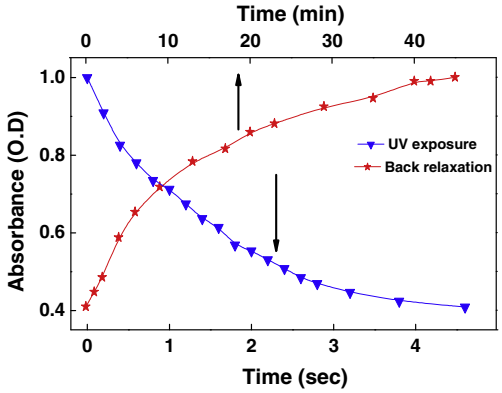


Fig. 9. Behaviour of the compound-IVb with respect to time, in presence of UV light (studied with LC filled cells).

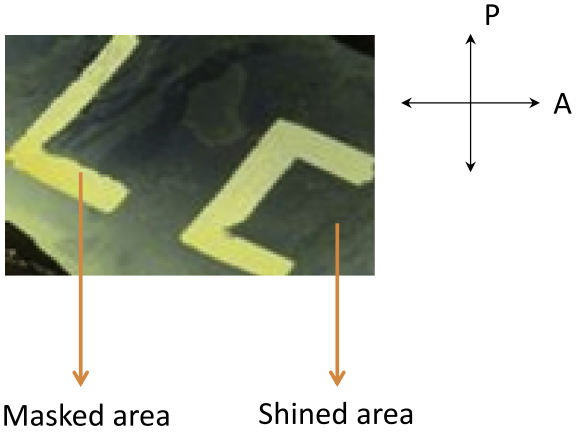


Fig. 10. Demonstration of optical pattern storage capability of the device based on the principle described in this article observed under the crossed polarizers. The sample was kept at room temperature and illuminated with UV radiation through a photo masks. The dark regions are the molecules are exposed to UV radiation and the bright regions are where the radiation is masked. P and A were the polarizer and analyser.

A demonstration of the efficiency of the materials showed here. An optical storage device (see Fig. 10) that is fabricated by using the above mentioned method. The guest–host mixture was illuminated with UV light of 8 mW/cm^2 intensity through a standard mask for 5 min. Bright regions is the area which is masked and the dark region is the area which is illuminated with UV radiation.

Material transforms from order to disorder state with the illumination of UV light giving high contrast between bright and dark states. Research is in progress to stabilize these materials to use it as permanent optical storage devices by incorporating polymeric chains to photo-polymerize the structure.

Conclusions

New isoflavone based liquid crystals with azobenzene moieties were synthesized. POM showed that all four compounds have nematic phases. The photoswitching properties of compound **IVa–IVb** showed *trans* to *cis* isomerization around **1–4** s. Whereas reverse process took place around **40–700** s in solutions. These materials show much faster back relaxation than so far reported materials. Thus, the photoswitching behaviour of these materials may be suitably exploited in the field of optical data storage device and in molecular switches, which needs fast photo-switching. Indeed, so far no isoflavone based azo compounds reported which showed very fast switching property in solutions as well as in solids.

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