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Synthesis of achiral four-ring unsymmetrically substituted toluene derived liquid crystals with a polar end group

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Achiral four-ring unsymmetrically substituted toluene-derived liquid crystals have been designed and synthesised by known and straightforward methods. All these compounds exhibit nematic phase over wide temperatures.

Keywords: bent-core; cybotactic nematic; polar moiety; liquid crystal

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1. Introduction

The discovery of bent-core or banana-shaped molecules exhibiting mesomorphism, with some of them showing macroscopic polar order viz., ferroelectricity and antiferroelectricity and spontaneous achiral symmetry breaking with the formation of chiral superstructures has stimulated liquid crystal research for further innovations [1–6]. Very recently the discovery of fluid cybotactic nematic phases [7–11] (formed by smectic C (SmC) like clusters viz., N_{cybC} phase) with ferroelectric response and field induced biaxiality in the nematic phase in bent-core mesogens derived from a symmetrical 3,5-diphenyl-1,2,4-oxadiazole unit has been reported [12]. The same phenomenon was corroborated in unsymmetrical 1,2,4-oxadiazole derivatives with a cyclohexene end moiety [13, 14]. Furthermore, the transition from normal to skewed cybotactic nematic phase exhibited by some bent-core nematic mesogens as evidenced by small angle X-ray studies [10] is correlated to a N_U–N_B phase transition by optical textures [15]. Recently Lehmann's group reported a series of oxa- thia-diazole derivatives and other biaxial V-shaped, shape-persistent molecules [16–20] exhibiting nematic mesomorphism. Weissflog *et al.* [21] reported asymmetric achiral four-ring bent-core compounds derived from *N*-benzoylpiperazine with some of them exhibiting polar properties as well as ferroelectric structures under the influence of the electric field due to the bent shape of the molecules. Fergusson and Hird reported [22, 23] low melting unsymmetrical four-ring bent-core 1,3-disubstituted phenylene derivatives. These compounds with lateral fluoro substitution and a chiral moiety at the short end of the molecule exhibit helical mesophases and higher transition temperatures than their unsubstituted compounds, which is distinctly different behaviour from that of the known liquid crystals of linear molecular architectures. Recently we reported [24, 25] unsymmetrical four-ring bent-core compounds exhibiting layered phases with spontaneously chiral and polar layers, including their polarisation splay modulated and layer undulated phase variants.

The aims of this research in angular achiral unsymmetrical four-ring molecular architectures are many and wide ranging. The objectives have origins in basic structure–property relationships in the development of wide range nematic phases with multi-functional characteristics viz., ferroelectric response, field induced biaxiality and photo-switchable devices. The molecules possessing an azobenzene moiety undergo a reversible *cis–trans* isomerisation process upon illumination with light. Hence the azo-benzene liquid crystals are among the most promising materials for photo-switchable devices. In this communication we report achiral unsymmetrical four-ring bent-core compounds, possessing photo-responsive azo linkage and a polar moiety at one end of the molecule, and exhibiting a nematic phase over a wide temperature range.

2. Results and discussion

The methodology adopted in the designed molecules (Scheme 1) for the material to exhibit liquid crystalline behaviour is as follows.

The four-ring molecule possesses one -OH group in one of the wings, located to stabilise the imine linkage of the molecule through intramolecular hydrogen-bonding, which deviates significantly from the typical symmetrical and/or V-shape of other bent core molecules. The molecule consists of three different linkages viz., a photochromic azo group, an ester linkage and salicylidene moiety between the four phenyl rings. The tail end of this unusual bent-core liquid crystal was based on a 4-*n*-alkoxysalicylaldehyde

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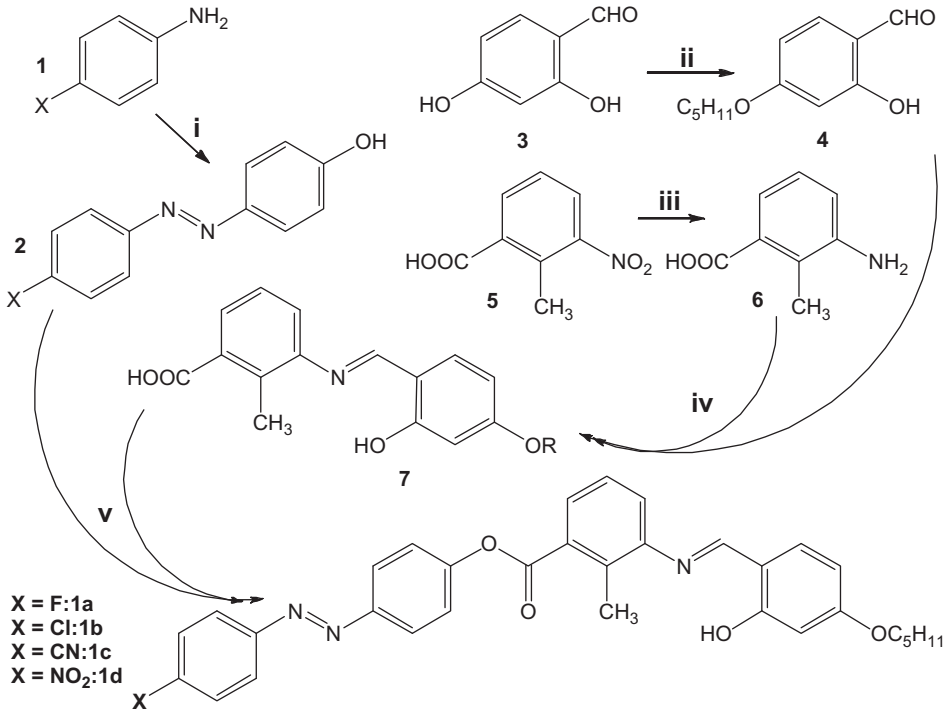

Scheme 1. Synthetic details of compounds **1a–d**. Reagents and conditions: i. HCl, $NaNO_2$, 0–5°C, phenol, NaOH; ii. dry acetone, $KHCO_3$, $C_5H_{11}Br$, Kl; iii. 10% Pd/C, H_2, EtOAc stirring 48 h; iv. absolute EtOH, AcOH, Δ, 6 h; v. DCC, DMAP, DCM, stirring 48 h.

moiety at one end whereas the bent core platform was designed by the coupling of 4-substituted phenol with 3-substituted -2-methylbenzoic acid. The other end of the molecule is substituted with a polar substituent. The Fourier transform infrared (FTIR) stretching band at around 3192–3197 cm^{-1} assigned to $\nu_{O\text{-}H\text{–}N}$ confirmed the presence of intramolecular hydrogen-bonding in all the compounds. The introduction of an *ortho* hydroxyl group in the benzylidene moiety not only enhances the stability of the imines through intramolecular hydrogen-bonding to overcome the hydrolytic instability of the molecules towards moisture but also enhances the transverse dipole-moment. Hence the salicylidene aniline core present in these compounds promotes thermal stability, which is confirmed by FTIR. The resorcylidene aniline core, present in calamitic ferroelectric liquid crystals, actually seems superior to the benzylidene aniline core with respect to mesogenicity, and is more stable towards hydrolysis. This core also played a key role in the first discovery of antiferroelectric material from achiral molecules, being the core present in the pioneering Soto–Bustamante–Blinov anticlinic bilayer antiferroelectric material ($SmAP_A$) [26–30].

The 4-*n*-alkoxysalicylaldehydes were synthesised by Williamson etherification of 2,4-dihydroxybenzaldehyde with 1-bromoalkane using $KHCO_3$ as base. In attempting to devise a strategy for the synthesis of bent-shaped molecules, we reasoned that the angular 3,4′-disubstituted biphenyl central unit [31, 32] can be separated by an ester linkage which can still be sufficiently bent-shaped and unsymmetrical to match the perturbation produced in the form of a shape factor by the introduction of a bridging group between two phenyl rings to yield a unsymmetrical molecule. The bent core at the centre 3-amino 2-methylbenzoicacid was obtained by 10% Pd-C catalysed reduction of 3-nitro 2-methylbenzoic acid. 3-Amino 2-methylbenzoic acid was condensed with 4-*n*-alkoxy-salicylaldehyde in the presence of acetic acid to yield 2-methyl 3-*N*-(4-*n*-pentyloxysalicylidene)amino benzoic acid. The other part of the molecule 4-fluorophenylazophenol was obtained by the diazotisation reaction of 4-fluoroaniline.

The modification of the angular 3,4′-disubstituted biphenyl unit with the introduction of an ester linkage (viz., a COO moiety) between the phenyl units leads to structural variation of polar groups in bent core molecules and hence can promote a broad range of interesting variations [2–4] in their mesogenic properties. Any substituent *ortho* to the ester linkage separating the two phenyl rings may substantially change the conformation of the molecule depending on the size,

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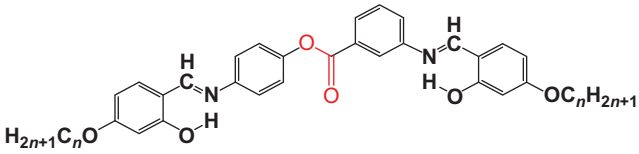
polarity and direction of substituents, and molecular interactions. Hence the desired unsymmetrical achiral bent-core compounds were obtained by *O*-acylation of 4-fluorophenylazophenol with 2-methyl 3-(*N*-(4-*n*-pentyloxysalicylidene)amino benzoic acid using dicyclohexylcarbodiimide (DCC) as condensing agent and 4-dimethylaminopyridine (DMAP) as catalyst.

As a part of our work on four ring bent-core systems, we modified the central core with a methyl substituent replacing the H-atom in the *ortho* (bay) position to the ester moiety in the central bent core. Furthermore the four ring molecule possesses an unequal distribution of aromatic rings in the two wings, which manifests in the unsymmetrical bent-shaped molecule and hence can be regarded as true hockey stick molecules bordering the bent core and calamitic molecules. The parent compounds viz., 4-(*N*-4′-*n*-alkyloxysalicylidene)-aminophenyl 3-(*N*-4′-*n*-alkyloxysalicyli-dene)amino benzoates [24, 33] (Figure 1) without the 2-methyl group substituted with alkyl chains at both ends of the molecule exhibited polarisation-modulated layer undulated $B7/B1_{RevTilted}$ phases. The mesomorphism started only with nonyloxy derivative. The lower homologues are non-mesomorphic.

The transition temperatures, transition enthalpies and associated entropies of the phase transitions are presented in Table 1. The differential scanning calorimetry (DSC) thermogram of a representative compound **1b** is presented in Figure 2. Representative textures of the mesomorphic phases of compounds **1–4** is shown in Figure 3. All the compounds exhibit nematic droplets texture in nematic (N) phase during transformation from nematic–isotropic (N–I) phase transition on cooling from isotropic (I) phase.

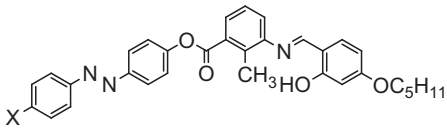
The clearing temperature T_{NI} of all the materials was found to decrease when the brightness of the microscope lamp was varied, indicating sensitivity to light. The change in the shape of the azo compounds from the linear rod-like shape (*trans*-isomer) to the bend-like shape (*cis*-isomer), in presence of external field viz. polarising optical microscopy (POM) light, leads to a local disorder in the sample that is related to a change in the molecular dimensions. Few molecules



RN-*n*: ***n* = 9, 10, 11, 12, 13, 14, 15, 16, 18**

Figure 1. Structure of 4-(*N*-4′-*n*-alkyloxysalicylidene)aminophenyl [3-(*N*-4′-*n*-alkyloxysalicylidene)aminobenzoate.

Table 1. Phase transition temperatures (°C) of compounds **1a, 1b, 1c** and **1d** recorded for second heating (first row) and second cooling (second row) cycles at 5°C/min from DSC and confirmed by polarising optical microscopy (POM). The enthalpies (ΔH in kJ/mol) and entropies (ΔS in J/mol/K) are presented in parentheses.



Compound	Substituent X	Phase transition temperatures (enthalpy, entropy)
1a	F	Cr 149.6 (38.2, 90.5) N 159.3 (0.224, 0.52) Iso Cr 71.4 (19.1, 55.5) N 156.7 (0.262, 0.61) Iso
1b	Cl	Cr 138.6 (51.2, 124.6) N 179.6 (0.197, 0.43) Iso Cr 90.8 (18.3, 50.3) N 174.9 (0.205, 0.46) Iso
1c	CN	Cr 146.1 (54.6, 130.3) N 217.7 (0.292, 0.596) Iso Cr 78.2 (10.2, 29.1) N 216.0*POM Iso
1d	NO_2	Cr 140.5 (50.9, 123.0) N 210.8 (0.536, 0.918) Iso Cr *(supercooled) N 203.1 (0.234, 0.491) Iso

*The transition could not be detected by DSC.

in the bulk undergo the molecular transition from the *trans* state to the *cis* state on absorbing the appropriate photon for transition and affecting the T_{NI} of the bulk sample. The change in molecular geometry viz., E-Z isomerism (Figure 4a) disturbs the molecular packing and polar order of the phase [34–36].

Hence thermodynamically, the *cis*-isomer acts as an impurity which reduces the phase transition temperature; this is similar to the observations reported earlier [37–40]. Qualitative studies revealed the textural changes after exposure to visible light and a decrease in T_{NI}. Extinction of the nematic phase texture occurs at T_{NI} on exposure to the transmitted light of the polarising optical microscope and T_{NI} decreases by 1–3°C. The decrease in T_{NI} is also dependent on the film thickness due to photoisomerisation. The ultraviolet (UV)–visible spectra of compound **1c** in chloroform solution (1×10^{-4} M) revealed two absorption peaks at 385 nm and 441 nm, which can be attributed to π–π^* and n–π^* transitions of the azo chromophore, respectively. The absorption peak at 441 nm (UV-visible spectra of the solutions; Figure 4) increases upon illumination with the microscope light as a function of time, reflecting the increased E-isomer concentration. Systematic

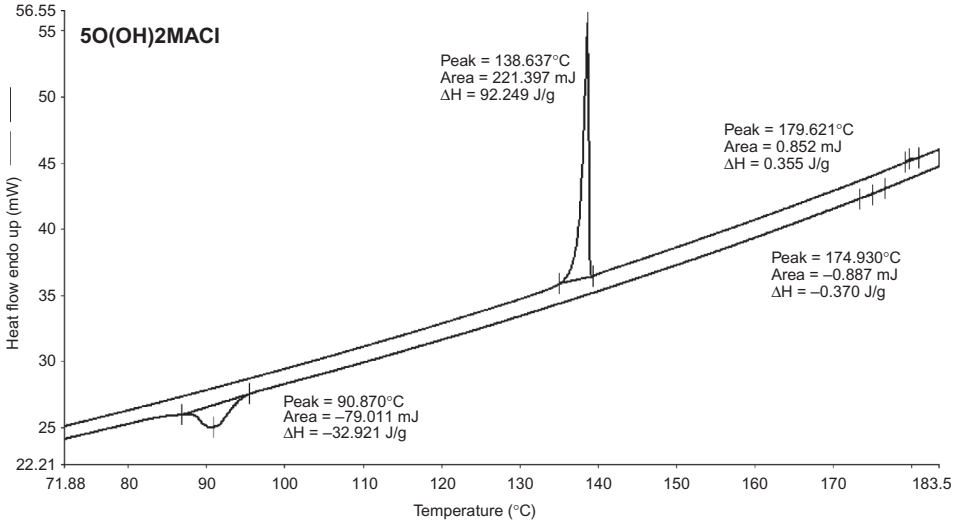


Figure 2. Representative differential scanning calorimetry of compound **1b** in the second heating and cooling cycle at 5°C/min.

quantitative studies related to photo-isomerisation and thermal-isomerisation are in progress. On further cooling, they exhibit marble or schlieren textures in nematic phase indicating a predominantly homogeneously alignment. On further cooling exhibit a slow transformation to a homeotropic alignment initially over small areas, which subsequently spreads to the entire area under observation as shown in Figure 3, predominantly.

Similar observations of such textural changes are reported in nematic phases exhibited by bent-core compounds as a signature of growth of cybotactic SmC clusters in the cybotactic nematic phase (Nc_{ybC}) [8]. We have also observed a similar transformation from classical nematic phase to growth of cybotactic clusters characteristic of the cybotactic nematic phase (Nc_{ybC}) in other bent-core compounds exhibiting nematic phase [41, 42]. These homeotropic regions exhibit transient birefringent textures either by shearing or tapping. Differential scanning calorimetric investigations also complement phase transitions observed by POM investigations. The nematic–isotropic phase transition enthalpies are of the order of 0.2–0.5 kJ/mol for all the compounds and are in the typical range usually observed for the phase transitions of bent-core compounds.

3. Conclusions

The reported compounds represent the first examples of unsymmetrically substituted bent-core mesogens bordering the calamitic and symmetrical five-ring bent-core compounds and can be regarded as a new class of materials exhibiting liquid crystal phases occurring at the boundary between classical rod-like and bent-shape molecules. Achiral unsymmetrical four-ring bent-core liquid crystals possessing a polar group at one end and an alkyloxy moiety at the other end have been designed and synthesised by simple and straightforward synthetic procedures. All the compounds exhibit exclusively nematic phase over a wide temperature range suppressing the undesired smectic phases. Further investigations by X-ray diffraction (XRD), electro-optical methods and dielectric spectroscopy to investigate the detailed structure of these nematic phases are in progress to explore the possible applications of these materials.

4. Experimental

All the chemicals were procured from M/s Alfa Aesar, Aldrich or Tokyo Kasei Kogyo Co. Ltd. The solvents and reagents are of AR grade, and were distilled and dried before use. Micro analysis of C and H elements were determined on a Carlo-Erba 1106 elemental analyser. Infrared (IR) spectra were recorded on Shimadzu IR Prestige-21, FTIR-8400S (ν_{max} in cm^{-1}) on KBr disks. ^1H nuclear magnetic resonance spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ (chemical shift δ in parts per million) solution with TMS as internal standard. The liquid crystalline properties were observed and characterised using a polarising microscope (Nikon optiphot-2-pol attached with hot and cold stage HCS302, with STC200 temperature controller configured for HCS302 from INSTEC Inc., USA). The phase transition temperatures and associated enthalpies were recorded using a differential scanning calorimeter (Perkin-Elmer Pyris-1 system) with a heating/cooling rate of 5°C/min.

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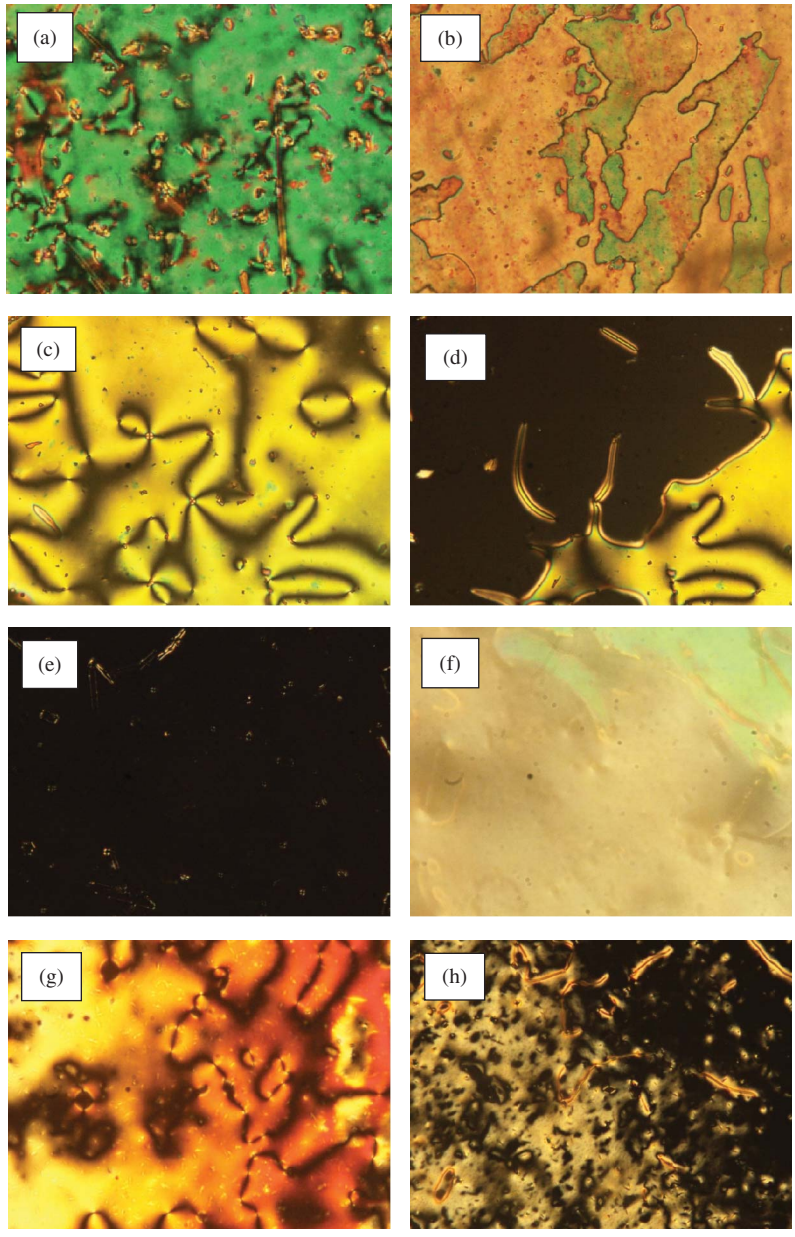

Figure 3. Microphotographs of compounds **1a–1d** in nematic phase in cooling cycle: (a) Schlieren texture of **1a** at 156.1°C; (b) marble texture of **1b** at 164°C; (c) Schlieren texture of **1c** at 216°C; (d and e) transformation of **1c** to homeotropic texture at 206°C; (f) **1c** birefringent texture upon tapping at 168°C; (g) Schlieren texture of **1d** at 200°C; and (h) slow transformation of **1d** to homeotropic texture at 198°C which subsequently turns into dark region like **1c** but on tapping exhibited birefringent texture.

4.1 Synthetic procedures

*4.1.1 4-*n*-Pentyloxysalicylaldehyde (4)*

The synthesis of 4-pentyloxy-2-hydroxy benzaldehyde (Scheme 1) viz., monoalkylation was performed using a modification of the literature procedure to improve the product yield. 2,4-Dihydroxybenzaldehyde (10 g, 72.4 mmol), 1-bromopentane (11.2 ml, 75 mmol), $KHCO_3$ (6.30 g, 75 mmol) and KI (catalytic amount) were mixed in dry acetone (250 ml) and the mixture was refluxed for 48 hours. It was then filtered hot to remove the insoluble solid. To neutralise the warm solution, dilute HCl was added, which was then extracted twice with $CHCl_3$ (100ml). The combined extracts were concentrated to give a purple solid. The product was purified by column chromatography using silica gel (60–120 mesh) eluting with a mixture of chloroform and hexane (vol./vol. 1/1) followed by evaporation of solvent. It gave the product as a pale yellow liquid. Yield = 10.6 g, (70%), IR ν_{max} in cm^{-1}: 1666 ($\nu_{C=O}$, aldehyde), 3449 ($\nu_{O\text{-}H}$, H-bonded);

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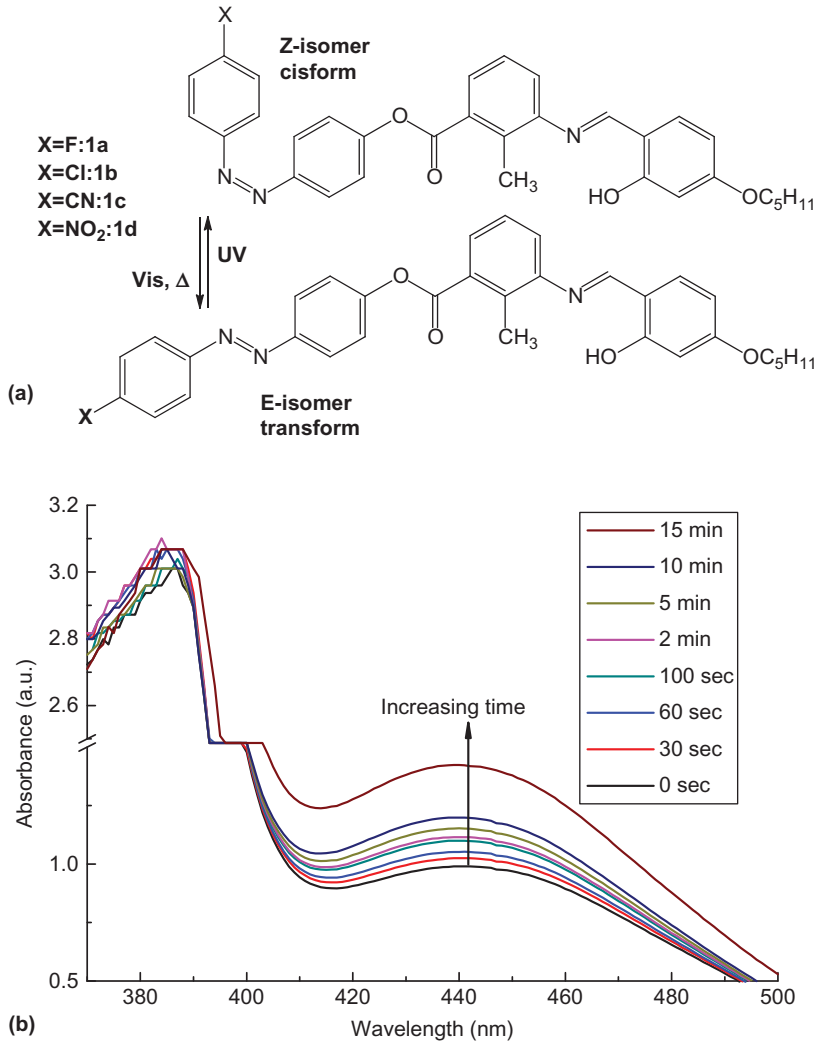

Figure 4. (a) Molecular structure of E and Z isomers. (b) Spectral changes under microscopic light irradiation of the solution of compound **1c** in chloroform (c = 1×10^{-4}M)

^{1}H-NMR($CDCl_3$, 300 MHz): δ = 11.41 (s, 1H, -**OH**); 9.66 (s, 1H, -**CH**=O); 7.40 (d, 1H, J = 8.8 Hz, Ar**H**); 6.51 (d, 1H, J = 8.9 Hz, Ar**H**); 6.61 (d, 1H, J = 8.7 Hz, Ar**H**); 4.03 (t, 2H, J = 7.8 Hz, -O-**CH_2**-); 1.65 (q, 2H, J = 6.6 Hz, - OCH_2-**CH_2**-); 1.38–1.20 (m, 4H, -**$(CH_2)_2$**-); 0.88 (t, 3H, J = 6.6 Hz, -**CH_3**).

*4.1.2 2-Methyl 3-N-(4-*n*-pentyloxysalicylidene) amino benzoic acid (7)*

An ethanolic solution of 2-methyl 3-aminobenzoic acid (0.45g, 3 mmol) was added to an ethanolic solution (20 ml) of 4-*n*-pentyloxysalicylaldehyde (0.64g, 3 mmol). The mixture was refluxed with a few drops of glacial acetic acid as catalyst for six hours to yield the yellow coloured Schiff's base. The precipitate was collected by filtration from the hot solution and recrystallised several times from absolute ethanol to give a pure compound. Yield = 0.8 g, (84%). IR ν_{max} in cm^{-1}: 1618 ($\nu_{CH=N}$, imine); 1719 ($\nu_{C=O}$, acid), 3425(ν_{O-H}, H-bonded); ^{1}H NMR($CDCl_3$, 400 MHz): δ = 13.49 (s, 1H, -**OH**); 9.99 (s, 1H, -CO**OH**); 8.35 (s, 1H, -**CH**=N-); 7.88 (d, 1H, J = 8.4Hz, Ar**H**); 7.33 (t, 1H, J = 8.0 Hz, Ar**H**); 7.46 (d, 1H, J = 8.4Hz, Ar**H**); 2.46 (s, 3H, Ar-**CH_3**); 7.29 (d, J = 7.8 Hz, 1H, Ar**H**); 6.98 (d, 1H, J = 8.4 Hz, Ar**H**); 6.43 (s, 1H, Ar**H**); 4.03 (t, 2H, J = 7.8Hz, - O-**CH_2**-); 1.57 (q, 2H, -O-CH_2-**CH_2**-); 1.29–1.21 (m, 4H, -O-$(CH_2)_2$-**$(CH_2)_2$**-); 0.88 (t, 3H, J = 7.8Hz, -O-$(CH_2)_4$-**CH_3**).

4.2 Preparation of 4-hydroxy 4′-fluoro azobenzene

The 4-hydroxy 4′-fluoro azobenzene was synthesised by the diazocoupling reaction of 4-fluoroaniline with phenol. To 4-fluoroaniline (1.11 g, 10 mmol) were added 10 ml of distilled water containing hydrochloric

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acid (12M, 2.5 ml, 30 mmol) and the mixture was heated to dissolve the contents. The solution was then cooled to 0°C. To the resulting stirred mixture cooled at 0°C was added, dropwise, a solution of sodium nitrite (0.76 g, 11 mmol) in 10 mL of water. The resulting diazonium chloride was consecutively coupled with an alkaline solution of phenol (0.94 g, 10 mmol) in 10 ml of water containing 0.80 g (20 mmol) of sodium hydroxide with constant stirring. The azo dye which formed immediately as a yellow precipitate was filtered, washed several times with water and dissolved in diethyl ether, and the resulting organic solution dried over anhydrous sodium sulphate. The crude product obtained after removal of the solvent under reduced pressure was purified by recrystallisation from cold hexane, precipitate was filtered and washed with water and methanol and dried in vacuum. Yield 1.62 g (75%). 4-Hydroxy 4′-chloroazobenzene, 4-hydroxy 4′-cyanoazobenzene, and 4-hydroxy 4′-nitro azobenzene were prepared following the same procedure to obtain the desired products in quantitative yield.

4.3 General procedure for the synthesis of compounds 1a–1d

Appropriate compound **2** (2 mmol of 4-hydroxy 4′-fluoroazobenzene, or 4-hydroxy 4′-chloroazobenzene, or 4-hydroxy 4′-cyanoazobenzene or 4-hydroxy-4′-nitroazobenzene) and 2-methyl 3-(*N*-(4-*n*-pentyloxysalicylidene)amino benzoic acid **7** (0.68 g, 2 mmol) and 4-dimethylamino pyridine (DMAP) (4 mg, 0.02 mmol) were dissolved in dry dichloromethane (DCM) (50 mL) under inert atmosphere. A solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC) (0.49 g, 2.4 mmol) in DCM (20 ml) was added to the above mixture and the mixture was stirred at room temperature for 48 hours. The precipitate *N*,*N*′-dicyclohexylurea was removed by filtration and the solvent DCM was evaporated to get the residue from the filtrate. The solid residue was purified by column chromatography on silica gel using hexane/chloroform (9:1) as eluent followed by recrystallisation from absolute ethanol to afford the pure product as a yellowish solid better than 70% yield.

Compound **1a:** IR ν_{max} in cm^{-1}: 1614 ($\nu_{CH=N}$, imine); 1735 ($\nu_{C=O}$, ester), 3197 (ν_{O-H}, H-bonded); ^1H NMR($CDCl_3$, 400 MHz): $\delta = 13.51$ (s, 1H, **-OH**); 8.46 (s, 1H, **-CH**=N-); 8.02–7.93 (m, 6H, ArH); 7.42–7.30 (m, 6H, Ar**H**); 6.54 (d, 2H, $J = 6.4$, Ar**H**); 4.01 (t, 2H, $J = 6.8$Hz, -O-**CH_2**-); 2.69 (s, 3H, Ar-**CH_3**); 1.84–1.38 (m, 6H, -**$(CH_2)_3$**-); 0.93 (t, 3H, -**CH_3**). Elemental analysis calculated for $C_{32}H_{30}FN_3O_4$: C, 71.23; H, 5.60; N, 7.79 % Found: C, 71.11; H, 5.55; N, 7.38 %.

Compound **1b:** IR ν_{max} in cm^{-1}: 1637 ($\nu_{CH=N}$, imine); 1732 ($\nu_{C=O}$, ester), 3192 (ν_{O-H}, H-bonded); ^1H NMR($CDCl_3$, 400 MHz): $\delta = 13.50$ (s, 1H, **-OH**); 8.45 (s, 1H, **-CH**=N-); 8.03–7.48 (m, 6H, ArH); 7.42–7.26 (m, 6H, Ar**H**); 6.51 (d, 2H, $J = 7.8$, Ar**H**); 4.0 (t, 2H, $J = 6.8$Hz, -O-**CH_2**-); 2.68 (s, 3H, Ar-**CH_3**); 1.83–1.38 (m, 6H, -**$(CH_2)_3$**-); 0.92 (t, 3H, -**CH_3**). Elemental analysis calculated for $C_{32}H_{30}ClN_3O_4$: C, 69.12; H, 5.44; N, 7.56 % Found: C, 68.98; H, 5.19; N, 7.09 %.

Compound **1c:** IR ν_{max} in cm^{-1}: 1631 ($\nu_{CH=N}$, imine); 1743 ($\nu_{C=O}$, ester), 2225 ($\nu_{C\equiv N}$, cyano), 3192 (ν_{O-H}, H-bonded); ^1H NMR($CDCl_3$, 400 MHz): $\delta = 13.48$ (s, 1H, **-OH**); 8.45 (s, 1H, **-CH**=N-); 8.07–7.82 (m, 6H, ArH); 7.44–7.26 (m, 6H, Ar**H**); 6.53 (d, 2H, $J = 7.8$, Ar**H**); 4.0 (t, 2H, $J = 6.8$Hz, -O-**CH_2**-); 2.68 (s, 3H, Ar-**CH_3**); 1.85–1.36 (m, 6H, -**$(CH_2)_3$**-); 0.92 (t, 3H, -**CH_3**). Elemental analysis calculated for $C_{33}H_{30}N_4O_4$: C, 72.51; H, 5.53; N, 10.25 % Found: C, 72.13; H, 5.22; N, 9.89 %.

Compound **1d:** IR ν_{max} in cm^{-1}: 1637 ($\nu_{CH=N}$, imine); 1734 ($\nu_{C=O}$, ester), 3197 (ν_{O-H}, H-bonded); ^1H NMR($CDCl_3$, 400 MHz): $\delta = 13.48$ (s, 1H, **-OH**); 8.45 (s, 1H, **-CH**=N-); 8.41–8.00 (m, 6H, ArH); 7.46–7.26 (m, 6H, Ar**H**); 6.54 (d, 2H, $J = 7.8$, Ar**H**); 4.0 (t, 2H, $J = 6.8$Hz, -O-**CH_2**-); 2.69 (s, 3H, Ar-**CH_3**); 1.83–1.36 (m, 6H, -**$(CH_2)_3$**-); 0.92 (t, 3H, -**CH_3**). Elemental analysis calculated for $C_{32}H_{30}N_4O_6$: C, 67.83; H, 5.34; N, 9.89 % Found: C, 67.07; H, 5.15; N, 9.17 %.

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