Synthesis and Characterization of Naphthalene-Based Banana-Shaped Liquid Crystals for Photoswitching Properties

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(Received: Apr. 15, 2013; Accepted: Jan. 22, 2014; Published Online: Feb. 24, 2014; DOI: 10.1002/jccs.201300191)

A series of banana-shaped monomers containing naphthalene as central units, azobenzene in side arms with terminal alkenes were synthesized and characterized. Polarizing optical microscopy, DSC and X-ray diffraction measurements reveal that one compound processes a nematic phase while other four compounds exhibit B₆ phase. The absorption spectrum of *trans*-azobenzene displays high-intensity π - π * transition at 365 and low-intensity n- π * transition at 450 nm. These molecules exhibit strong photoisomerisation behaviour in solutions in which *trans* to *cis* isomerisation takes 55 seconds whereas reverse process takes about 32 hours. Such a long thermal back relaxation is useful for creation of optical image storage devices.

Keywords: Naphthalene; Azobenzene; Isomerisation; Photoswitching; Optical image storage.

INTRODUCTION

Banana phases comprises of bent core mesogenic units are very attractive and interesting not only for the fundamental aspects but also due to their unique electro-optical properties.^{1,2} In particular, the electro-optic responses of some mesophases are examined by using electro-optic devices such as a flat-panel display, light scattering electro-optical switches and electrically switchable color-tuneable reflectors.³ Azobenzene moiety is not only attractive photoactive groups but also efficient for many optical storage devices.⁴ Due to their unique *cis-trans* isomerization properties, azobenzene moieties play important role when they are mixed with anisotropic liquid crystals (for example bent core liquid crystals, BCLCs) as guest host system. BCLCs are one of the new supramolecular, functional and smart materials which have received much attention due to their interesting mesomorphism. They exhibit typical nematic, lamellar (like smectic) and columnar phase and these phases are somewhat different from the one exhibited by conventional liquid crystals (rod-like & disc-like molecules).5-7

Bent core mesogens usually comprises of five or six member phenyl rings connected by linking groups such as azobenzene, azomethine, Schiff base, ester groups etc. In most of the cases, bend of the molecular long axis results from 1,3-phenylene connection to the centre of the molecule. When azobenzene moiety is inserted between these two phenyl rings, then banana shaped liquid crystals becomes very sensitive to light. Lutfor et. al.⁸ reported bent shaped azobenzene monomers and their photoisomerization properties when they are used as guest host system along with liquid crystals. Synthesis of new azobenzenecontaining bent-shaped monomers and their photochemical properties with calamitic liquid crystals in solutions were reported.^{8,9} The photoinduced thermal back relaxation was found to be increased which is useful for creation of permanent optical storage devices.⁸

On the other hand, a field of research that is growing steadily is the photoinduced phenomenon in which the incident light brings about the molecular ordering/disordering of the liquid-crystalline system.¹⁰⁻¹³ This particular aspect of photonics, in which molecular geometry can be controlled by light, is considered as the future technology for optical storage devices.¹⁴⁻¹⁶ The heart of the phenomenon in such system is the reversible photo-induced shape transformation of the molecules containing the photo-chromic azo groups.¹⁷ Upon UV irradiation (around 365 nm, corresponding to the π - π * excitation of the azo group), the energetically more stable E or *trans* configuration, with an elongated rod-like molecular form, changes into a bent Z or *cis* configuration. The reverse transformation can be brought by illumination with visible light (in the range 400–500)

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nm, corresponding to the $n-\pi^*$ band). This latter change can also occur in the 'dark' by a process known as thermal back relaxation. Several bent-core molecules containing an azo (-N=N-) linkage have been reported for the possibility of photochromism and photoisomerization.¹⁸

This paper presents synthesis and characterization of naphthalene based liquid crystalline bent shaped monomers with azobenzene units connected via ester linkage to the core. In addition, we have studied the polarizing optical microscopic textures along with differential scanning calorimetry which gives evidences for the mesophases. We also investigated UV induced absorption studies which gives powerful insight of the light influence in the new molecules.

RESULTS AND DISCUSSION Synthesis

The synthesis and purification of compounds were performed as depicted in Scheme 1. The azobenzene containing rod-like side arms were prepared from ethyl 4-aminobenzoate. The diazonium salt of ethyl 4-aminobenzoate was prepared with sodium nitrite in the presence aqueous hydrochloric acid, which was coupled with phenol to yield ethyl 4-[(4-hydroxyphenyl)diazenyl] benzoate **1**. The reaction and purification by crystallization was performed according to our earlier paper.²⁰

Scheme 1 Synthesis of compounds 4a-e



Reagent and conditions: (i) NaNO₂, 3 equiv HCl, 2 °C; (ii) NaOH, pH 9, 2 °C; (iii) K_2CO_3 , KI, BrC_nH_{2n-1} (n = 2-6), reflux; (iv) KOH, MeOH; (v) DCC, DMAP.

Compound 1 was alkylated with 4-bromo-1-butene in the presence of potassium carbonate as base to give ethyl 4-{2-[4-(but-3-enyloxy)phenyl]diazenyl} benzoate **2a**. Other compounds (2b-e) were synthesized with the same method of compound 2a. These intermediate compounds 2a-e, having rod-shaped azobenzene units with double bond at the terminal position were found to be liquid crystalline and showed smectic A phase. Then compound 2a-e having ester groups were hydrolyzed under basic conditions to yield the acids **3a-e**. All the compounds, except **3a**, showed nematic phase. The liquid crystallinity in such compounds is induced due to hydrogen-bonded dimer formation, a phenomenon well documented in literature.9,21-26 The carboxylic acid groups are associated to form the H-bonded cyclic dimers either in crystalline and liquid crystalline phases and most of the dimers exhibited enantiotropic liquid crystalline behaviour. In the final step, two equivalents of the acid 3a-e were coupled with one equivalent of 2,7-dihydroxynaphthalene using DCC and DMAP to achieve our desired banana-shaped molecules 4a-e (Scheme 1). **Mesomorphic properties**

Thermotropic behavior of the synthesized compounds was studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction measurements at the mesophase temperature. The DSC curves were obtained during two successive heating-cooling scans at a heating/cooling rate of 5 °C min⁻¹. The POM and X-ray measurements were performed for the confirmation of phase structure of the expected compounds. The thermodynamic parameters such as the phase transition temperatures ($T/^{\circ}$ C) and enthalpy changes (Δ H/Jg⁻¹) associated with these phase transitions of the banana shaped monomers are listed in Table 1.

Compound **4a** shows enantiotropic phase sequences of Cr–N-I transitions which is confirmed by DSC and POM textural observation. On cooling, the isotropic-nematic transition appears which crystallizes at 133.1 °C (Table 1). The compound **4b-e** showed two transition peaks on heating which are attributed to the Cr–B₆ and B₆-I transitions. On cooling, again two peaks corresponding to I–B₆ and B₆-Cr transitions were observed.

DSC and POM studies reveal that compounds **4b-e** exhibited the enantiotropic phase sequences of $Cr-B_6-I$. A representative compound **4e** was used to confirm the phase structure by X-ray measurement. The thermal behaviour of all compounds **4a-e** is in accordance with literature.^{9,20,27-29} Hence, increasing the terminal chain length (**4a** vs. **4e**), as expected, decreases the transition temperature (Table 1). In addition, the odd-even effect on the isotropic temperature

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Comp	n	Scan	Phase transitions
4a	2	heat	Cr 140.5 (20.0) N 168.7 (2.7) I
		cool	I 165.0 (3.0) N 133.1 (17.7) Cr
4b	3	heat	Cr 138.6 (23.4) B ₆ 161.1 (9.5) I
		cool	I 159.7 (10.5) B ₆ 94.1 (22.8) Cr
4c	4	heat	Cr 120.1 (27.7) B ₆ 164.9 (14.1) I
		cool	I 162.3 (10.6) B ₆ 86.6 (32.1) Cr
4d	5	heat	Cr 137.9 (20.4) B ₆ 157.9 (8.3) I
		cool	I 153.5 (7.7) B ₆ 104.6 (23.2) Cr
4e	6	heat	Cr 110.8 (24.0) B ₆ 156.6 (10.7) I
		cool	I 154.4 (11.8) B ₆ 89.82 (31.4) Cr

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

Abbreviation Cr = crystal, N = nematic, $B_6 = smectic A phase$, I = isotropic phase.

was seen to compound **4a-e** where even number of alkyl carbon has higher transition temperature than odd number of alkyl carbon chain.^{20,27-29} The enthalpy changes determined by DSC are in agreement with the values usually observed for typical crystalline-nematic, nematic-isotropic, crystalline-smectic, smectic-isotropic and smectic-crystalline transitions which confirm the presence of a smectic and a nematic mesophases.^{30,31} The solid-liquid crystal or liquid crystal-solid transitions involved much more energy than the liquid crystal-isotropic liquid or liquid crystal-liquid crystal transitions.³² Similar odd-even effects have been reported in other materials.³³ Increasing terminal chain length decreases the transition temperature as usual. A large number of bent-core liquid crystalline materials derived from 2,7-dihydroxynaphthalene unit have already been reported.³³⁻³⁹ Similar to widely studied resorcinol derivatives,^{7,8,18,40} the 2,7-dihydroxynaphthalene derivatives also possess bent angle of about 120°. Depending upon peripheral and lateral substitutions, these materials exhibit a variety of mesophases such as nematic, smectic and columnar phases. The structure-property relationship in bentcore liquid crystals derived from 2,7-dihydroxynaphthalene core has been extensively discussed by several researchers.33-39

Compounds **4a-e** are comparable with other bentcore mesogens incorporating 2,7-dihydroxynaphthalene units connected with rod-like wings containing Schiff's base units.³⁸ Several series of bent-shaped mesogens based on substituted naphthalene-2,7-diol having phenylbenzoate wings and a double bond at one or at both end of the terminal chains have been reported.^{34,41} These compounds were synthesized using the long chains, but only smectic phases were observed for the ester based bent-core molecules. The fluorinated banana-shaped compounds were prepared with 2,7-dihydroxynaphthalene central unit,³³ which showed SmCP_A phases, B1-type rectangular columnar phases (Col_r) and B₆-type intercalated smectic phases (Sm_{intercal}). Here, the overall mesophase stability of the reported compounds,^{33,38} is quite similar to our compounds **4a-e**. These comparisons indicate the stabilizing effect of azobenzene units on the nematic and smectic phases of the naphthalene based banana shaped compounds.

Under the polarizing microscope, a schlieren texture as typical for nematic phase for compound **4a** was observed upon cooling from the isotropic phase. Optical textures taken for compound **4a** (n = 2) at 155 °C is shown in Fig. 1, no other phase transition on further cooling before crystallization was observed. On cooling from the isotropic phase, compound **4d** (n = 5) showed fan shaped texture and compounds **4b**, **4c** and **4e** showed broken fan shaped texture which is a typical smectic A phase corresponding to the B₆ phase showed by **4b-e**, there was no other phase transitions observed. All the transition temperatures observed under POM were matching with DSC data.

For further phase structure conformation, X-ray dif-



^{Fig. 1. Optical micrograph of (a) compound 4a taken at 155 °C and (b) compound 4b taken at 150 °C, (c) compound 4c at 152 °C, (d) compound 4d at 147 °C, (e) compound 4e at 142 °C, cooling cycle.}

fraction was carried out in the mesophase obtained upon cooling of the isotropic phase of the compound **4e** (n = 6). The intensity versus 20 plot derived from the diffraction pattern as shown in Fig. 2. The compound **4e** showed one sharp reflection at d = 26.26 Å in the lower angle region and in addition, a diffused peak in the wide-angle region with *d*-spacing of 4.29 Å at 140 °C is due to a liquid like in-plane ordering of molecules in the layers. The XRD pattern observed as typical of a B₆ intercalated mesophase due to sharp reflection is the half of the molecular length (53.77 Å).

UV-absorption study: Solutions with concentrations of 2.25×10^{-5} molL⁻¹ of **4a-e** were prepared in chloroform for UV-visible absorption studies. The spectrum of **4a** and **4e** shows three absorptions peaks with maximum absorbance at 260, 364 and 452 nm and **4d** shows also three absorptions peaks at 261, 365 and 450 nm (Fig. 3). Compound **4b** and **4c** shows also three absorptions peaks with maximum absorbance at 263, 368 and 450 nm (Fig. 3). The azobenzene monomers in the *trans* form all showed a strong band in the UV-region (~365 nm) which is attributed to the π - π * transition, and a weak band in the visible region (~450 nm) due to the n- π * transition.

Photoswitching study

A solution concentration of 5×10^{-5} mol L⁻¹ of **4c** was prepared in chloroform. The spectrum shows three absorption peaks with maximum absorbance at 261 nm, 365 nm ($\epsilon = 34.940$ L.mol⁻¹.cm⁻¹) and 445 nm. Since peak around 261 nm is non photoactive and it is not of our interest, so we did not focus our discussions on this peak. Fig.



Fig. 2. The intensity versus 2θ graph derived from X-ray diffraction for SmA_{intercal} phase of compound 4e at 140 °C.

4 shows the spectral changes by irradiation at 365 nm. The absorbance at 365 nm decreases and after 55 seconds the photostationary state of a *cis-trans* mixture is reached. By irradiation at 436 nm the absorbance at 365 nm increases until a new photostationary state is reached. The photo-chemical back reaction by irradiation at 436 nm is shown in Fig. 5.

The thermal back reaction $(cis \rightarrow trans)$ is shown in Fig. 6. After irradiation at 365 nm to photostationary state, the solution was kept in the dark and the back reaction was measured at $\lambda = 365$ nm after over 32 hours. The presence of the two isobestic points indicates the absence of side reactions. A linear correlation of ln ($E_{\infty} - E_t$) as a function of time indicates a reaction of the first order, see Fig. 7. After 1680 min the conversion degree from *cis* to *trans* was 88%. Similar photochemical switching behaviour has previously been reported to center linked bent-core azobenzene liquid crystalline polymers in which two azobenzene groups are attached to a central resorcinol unit.⁴²







Fig. 4. UV/Vis absorption spectra of **4c** in chloroform, $c = 5 \times 10^{-5} \text{ mol } \text{L}^{-1}$, irradiation at 365 nm.

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Using the materials described in this article, an optical pattern storage device is fabricated as shown in Fig. 8. Here experimental cell is filled with the mixture of guest naphthalene bent shaped molecules and the host liquid crystalline molecules (10% of guest mixed with 90% of guest 5CB). The region 1 represents UV illuminated area and region 2 represents masked region which per se not contributing in the isomerization phenomena. Pattern is illuminated with 365 nm UV light at room temperature through photo mask to create the pattern shown in the Fig. 8. One can see the good clarity between bright and dark states which enable to optical pattern storage devices.

CONCLUSIONS

Five new bent-core mesogens with azobenzene units



Fig. 5. UV/Vis absorption spectra of **4c** in chloroform, $c = 5 \times 10^{-5}$ mol L⁻¹, irradiation at 436 nm (the sample was irradiated before at 365 nm).



Fig. 6. Thermal back reaction (*cis* → *trans*) of 4c in chloroform (the solution was irradiated before at 365 nm).

containing 2,7-dihydroxynaphthalene as central bent core unit are studied. One of them showed nematic mesophase behavior and other four show B_6 phase. The double bonds can be used for preparation of polymers or silyl functionalized bent-core mesogens, whereas the presence of the azo linkage in these liquid crystals monomers is suitable for the photochromism application and *trans-cis-trans* isomerizations cycles under UV irradiation. Optical storage device using present molecules is presented which shows the capability of the discussed materials for device applications. The detail photochemical *cis-trans* isomerizations study of



Fig. 7. Thermal back reaction $(cis \rightarrow trans)$ of **4c** in chloroform, Plot of ln $(E_{\infty} - E_t)$ at $\lambda = 365$ nm as a function of time.



Fig. 8. Demonstration of optical pattern storage capability of the device based on the principle described in the article observed under the crossed polarizers (marked as P and A). The sample was kept at room temperature and illuminated with UV radiation through a mask. The dark region marked as 1 is where the molecules are in isotropic state caused by illuminating UV and the bright region marked as 2 is where the radiation is masked.

other compounds and all compounds at solid film is now in progress and will be reported in due course.

EXPERIMENTAL

Materials synthesis: Ethyl 4-[(4-hydroxyphenyl)diazenyl]benzoate (1) was synthesized according to our earlier paper.¹⁹ Other intermediate compounds such as ethyl 4-{2-[4-(but-3-enyloxy)phenyl]diazenyl}benzoate (2a), ethyl 4-{2-[4-(pent-4-enyloxy)phenyl]diazenyl}benzoate (2b), ethyl 4-{2-[4-(hex-5-enyloxy)phenyl]diazenyl}benzoate (2c), ethyl 4-{2-[4-(hept-6-enyloxy)phenyl]diazenyl}benzoate (2d), ethyl 4-{2-[4-(oct-7-enyloxy)phenyl]diazenyl}benzoate (2e), 4-{2-[4-(but-3-enyloxy)phenyl]diazenyl}benzoic acid (3a), 4-{2-[4-(pent-4-enyloxy)phenyl]diazenyl}benzoic acid (3b), 4-{2-[4-(hex-5-enyloxy)phenyl]diazenyl}benzoic acid (3c), 4-{2-[4-(hept-6-enyloxy)phenyl]diazenyl}benzoic acid (3d) and 4-{2-[4-(oct-7-enyloxy)phenyl]diazenyl}benzoic acid (3e) were synthesized according to the little modification of our earlier paper,²⁰ and see detailed synthetic procedures and analytical data in ESI. 2,7-Naphthalene bis[4-{2-[4-(but-3-enyloxy)phenyl]diazenyl}benzoate] (4a): Compound 3a (0.040 g, 0.135 mmol), 25 mL of dry dichloromethane, DMAP (4.88 mg, 0.04 mmol), 2,7-dihydroxynaphthalene (10.81 mg, 0.067 mmol), DCC (44 mg, 0.20 mmol) was added and the mixture was stirred for 24 h. Work-up procedure was followed according to earlier reported paper.²⁰ Yield of 4a: 0.015 g (31%). IR (KBr, v_{max}, cm⁻¹): 3072 (=CH₂), 2924 (CH₂), 2852 (CH₂), 1730 (C=O, ester), 1644 (C=C, vinyl), 1600, 1456 (C=C, aromatic), 1249, 1138, 1078 (C-O), 839 (C-H). ¹H NMR (CDCl₃) δ : 8.42 (d, 4H, J = 8.9 Hz), 8.02 (d, 4H, J = 8.4 Hz), 7.99 (d, 4H, J = 8.8 Hz), 7.98 (d, partially merged with 7.99 d, 2H), 7.76 (d, 2H, J = 2.1 Hz), 7.44 (dd, 2H, J = 8.2 Hz), 7.08 (d, 4H, J = 8.9 Hz), 5.97 (m, 2H, CH=), 5.25 (d, 2H, J = 12.5 Hz, =CH₂), 5.18 (d, 2H, J = 9.4 Hz, =CH₂), 4.15 (t, 4H, J = 6.8 Hz, OCH₂-), 2.62 (m, 4H, -CH₂). ¹³C NMR (CDCl₃) δ: 29.50, 69.60, 114.44, 115.21, 118.28, 118.77, 119.41, 121.33, 122.39, 124.45, 125.55, 129.23, 130.51, 131.56, 132.65, 134.51, 147.34, 149.23, 155.12, 161.22, 164.77. 2,7-Naphthalene bis[4-{2-[4-(pent-4enyloxy)phenyl]diazenyl}benzoate] (4b): Compound 4b was synthesis from **3b** according to our reported paper. Yield of **4b**: 0.018 g (35%). IR (KBr, v_{max}, cm⁻¹): 3078 (=CH₂), 2924 (CH₂), 2852 (CH₂), 1730 (vC=O, ester), 1647 (C=C, vinyl), 1600, 1456 (C=C, aromatic), 1249, 1138, 1078 (C-O), 839 (C-H). ¹H NMR $(CDCl_3)$ δ : 8.40 (d, 4H, J = 8.9 Hz), 8.02 (d, 4H, J = 8.6 Hz), 7.98 (d, 2H, J = 8.9 Hz), 7.92 (d, 2H, J = 8.9 Hz), 7.75 (dd, 2H, J = 8.2 Hz), 7.71 (d, 2H, J = 6.1 Hz), 7.43 (dd, 2H, J = 8.6 Hz), 7.06 (t, 2H, J = 8.5 Hz), 5.88 (m, 2H, CH=), 5.10 (d, 2H, J = 16.2 Hz,

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=CH₂), 5.03 (d, 2H, J = 9.8 Hz, =CH₂), 4.10 (t, 4H, J = 6.7 Hz, OCH2-), 2.18 (m, 4H, -CH2), 1.89 (m, 4H, -CH2). 2,7-Naphthalene bis[4-{2-[4-(hex-5-enyloxy)phenyl] diazenyl}benzoate] (4c): Compound 4c was synthesis from 3c according to our reported paper. Yield of **4c**: 0.020 g (37%). IR (KBr, v_{max} , cm⁻¹): 3076 (=CH₂), 2924 (CH₂), 2854 (CH₂), 1730 (C=O, ester), 1647 (C=C, vinyl), 1600, 1456 (C=C, aromatic), 1251, 1138, 1078 (C-O), 839 (C-H). ¹H NMR (CDCl₃) δ : 8.41 (d, 4H, J = 8.5 Hz), 8.02 (d, 4H, J=6.8 Hz), 8.00 (d, 4H, J=6.8 Hz), 7.98 (d, partially merged with 8.00 d, 2H), 7.44 (d, 2H, J = 8.6 Hz), 7.42 (d, 2H, J =5.5 Hz), 7.05 (d, 4H, J = 8.5 Hz), 5.89 (m, 2H), 5.13 (d, 2H, J = 16.1 Hz), 5.05 (d, 2H, J=9.4 Hz), 4.11 (t, 4H, J=6.8 Hz, OCH₂-), 2.31 (m, 4H, -CH₂), 1.97 (m, 4H, -CH₂-), 1.60 (m, 4H, -CH₂-). 2,7-Naphthalene bis[4-{2-[4-(hept-6-enyloxy)phenyl]diazenyl}benzoate] (4d): Compound 4d was synthesis from 3d according to our reported paper. Yield of 4c: 0.016 g (32%). IR (KBr, v_{max}, cm⁻¹): 3064 (=CH₂), 2924 (CH₂), 2854 (CH₂), 1730 (C=O, ester), 1653 (C=C, vinyl), 1600, 1456 (C=C, aromatic), 1249, 1138, 1078 (C-O), 839 (C-H). ¹H NMR (CDCl₃) δ: 8.41 (d, 4H, J = 8.6 Hz), 8.01 (d, 4H, J = 6.9Hz), 8.00 (d, 4H, J = 6.9 Hz), 7.98 (d, partially merged with 8.00 d, 2H), 7.76 (d, 2H, J = 8.6 Hz), 7.41 (d, 2H, J = 5.9 Hz), 7.05 (d, 4H, J = 8.6 Hz), 5.85 (m, 2H), 5.07 (d, 2H, J = 16.1 Hz), 4.99 (d, 2H, J = 9.2 Hz), 4.09 (t, 4H, J = 6.9 Hz, OCH2-), 2.14 (m, 4H, -CH2), 1.86 (m, 4H, -CH2-), 1.53 (m, 8H, -CH₂-). 2,7-Naphthalene bis[4-{2-[4-(oct-7-enyloxy)phenyl]diazenyl}benzoate] (4e): Compound 4e was synthesis from 3e according to our reported paper. Yield of 4c: 0.017 g (31.5%). IR (KBr, v_{max}, cm⁻¹): 3080 (=CH₂), 2924 (CH₂), 2852 (CH₂), 1722 (C=O, ester), 1624 (C=C, vinyl), 1602, 1456 (C=C, aromatic), 1251, 1143, 1030 (C-O), 840 (C-H). ¹H NMR (CDCl₃) δ: 8.20 (d, 4H, J = 8.6 Hz), 7.97 (d, 4H, J = 8.1 Hz), 7.93 (d, 4H, J = 6.9 Hz), 7.92 (d, partially merged with 7.93 d, 2H), 7.76 (d, 2H, J = 8.5 Hz, 7.41 (d, 2H, J = 6.2 Hz), 7.03 (d, 4H, J = 8.6 Hz), 5.85 (m, 2H), 5.84 (d, 2H, J = 16.1 Hz), 5.05 (d, 2H, J = 9.2 Hz), 4.06 (t, 4H, J = 6.8 Hz, OCH₂-), 2.08 (m, 4H, -CH₂), 1.85 (m, 4H, -CH₂-), 1.60 (m, 4H, -CH₂), 1.44 (m, 8H, -CH₂CH₂-).

Characterization: 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 ¹³C 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 Naphthalene-Based Liquid Crystals for Photoswitching Properties

a Mettler Toledo FP82HT hot stage and a FP90 central processor unit. Absorption spectra were recorded using a Perkin Elmer UV/VIS Spectrometer (Lambda 25).

Absorption spectra for photochromic study were recorded using a Shimazdu 3101 PC UV-Vis spectrometer. All the solutions were prepared and measured under air in the dark at room at temperature $(21 \pm 1 \text{ °C})$ using 1 cm quartz cells. The cells were closed to avoid the evaporation of the solvent and the solutions were stirred during the irradiation time. The solutions were irradiated at exc. = 254 nm, 365 and 436 nm respective, using a 200 watt high pressure Hg-lamp HBO 200 (NARVA Berlin, Germany) and filters IF 254, HgMon 365, HgMon 436 (Zeiss, Jena, Germany) generating monochromatic light as excitation source. Addition at 365 nm and 254 nm and Code-No. 805 (both Schott, Jena, Germany) for irradiation at 436 nm were used.

ACKNOWLEDGMENTS

This research was supported by Universiti Malaysia Pahang (RDU-100338, 120367). A special thank goes to Mrs. K. N. Vasudha for supporting many aspect regarding this work carry out.

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