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Introduction

Ferroelectricity is an important property for new functional and smart materials. Ferroelectric materials exhibit electric properties that are useful in modern optoelectronics, especially in liquid crystal display, and they have seen rapid growth in recent years. Ferroelectric and antiferroelectric properties arising from various forms of liquid crystals, including calamitic, bent-shaped and polymeric molecules, is an intense research area in liquid crystals.^{1–12} Niori *et al.*¹ first reported ferroelectric switching behavior from achiral bent-core molecules in the smectic phase. Later, the long axes of the BC molecules were found to be tilted with respect to the layer normal in the lamellar B₂ phase with antiferroelectric properties.¹³

In general, most of the bent-shaped mesogens, derived from a 1,3-phenylene core with five aromatic rings, were found to form numerous mesophases. These bent-shaped mesogens exhibit a variety of phases (B_1 – B_8) and these B phases are called banana phases, which depend on the nature of the mesogen and terminal alkyl chain. Among them, electro-switching has been observed for the B_2 , B_5 and B_7 phases. The bent-core molecules with shorter terminal alkyl chains exhibit the B_1 phase, which has a columnar structure (Col_r) and is generally non-switchable. Polar switching, however, can only be observed for long terminal alkyl chain compounds exhibiting the B_2 and B_7 phases with a lamellar structure. The switching properties in the lamellar phase of bent-core compounds is ascribed to polar

Photo and electrically switchable B7 mesophase exhibiting asymmetric bent-core liquid crystals[†]

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The first bent-core liquid crystal materials with a photo-active azo linkage exhibiting the B_7 mesophase are reported. The lower homologues of the bent-core compounds display the B_1 phase and higher homologues show the B_7 mesophase. The mesomorphic properties were characterized using polarized optical microscopy, differential scanning calorimetry and X-ray diffraction. The B_7 phase of these materials establishes ferroelectric switching characteristics with anticlinic organization (SmC_AP_F) of the molecules in the layers. The bent-core molecules with an azo linkage are important for photoisomerization studies, which indicate *trans* to *cis* isomerization at 30 s, whereas the reverse processes take place over 40 s in chloroform.

character and supramolecular chirality. The switchable mesophase is attributed to the efficient packing of bent molecules into smectic layers. In addition to the polar order, if the long axes of molecules are tilted with respect to the layer normal, the phase is designated as a SmCP phase (where P stands for polar order). If the polarizations in adjacent layers are the same, the SmCP phase behaves as a ferroelectric phase. Whereas if the polarizations in adjacent layers alternate from layer to layer, the SmCP phase behaves as an antiferroelectric phase. The B₂ phase has four types of arrangements based on orientation of tilt and polarization in successive layers, which results in SmC_sP_A, SmC_AP_A, SmC_sP_F and SmC_AP_F configurations where the subscripts S and A of C, and F and A of P, denote synclinic, anticlinic, ferroelectric and antiferroelectric configuration, respectively.¹⁴⁻¹⁶

Pelzl *et al.*¹⁷ first reported B_7 phase being of particular interest because of its unusual nucleation as well as its beautiful optical textures. The B_7 phase forms screw-like, telephone-wire nuclei, beaded filaments, striped focal conics, banana leaf-like and circular domains and checkerboard textural elements.¹⁷⁻¹⁹ Recently, two different models of the structure of the switchable B_7 phase have been proposed using either modulated/undulated layered SmCP or SmCPG (G denotes general model, which explained a double tilted SmCG structure) phases.^{7,19}

Bent-shaped liquid crystals composed of azo and imino linkages have barely been studied.^{21–24} Furthermore, bent-core compounds possessing these linkages have so far not been reported to exhibit the B_7 phase. In the present work, we report the first example of azo compounds exhibiting the B_7 mesophase. The homologous series bent-core compounds are constructed using different linking groups, such as azo, imino, ester and biphenyl moieties. As azobenzene is considered to be a prototype molecular switch, the incorporation of an azo

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 $\begin{array}{l} Reagent: i) \ NaNO_2 \ / \ HCl \ / \ 0^{\circ}C, \ NaOH;, \ ii), \ v) \ K_2CO_3 \ / \ Kl \ / \ Acetone, \ Br-C_nH_{2n+1}; \ iii) \ HCl \ / \ Ethanol \ / \ Reflux; \\ iv) \ Ethanol \ / \ Con.H_2SO_4 \ / \ reflux; \ vi) \ NaOH/Ethanol \ / \ Reflux; \ Vii) \ DCC/DMAP/DCM; \ Viii) \ EtoH/reflux \ Acetone \$

Scheme 1 Synthetic route followed for the preparation of bent-core compounds (8a–8d).

linkage into the bent-core molecule is one of the important developments in switchable organic molecules.^{15,25–29} An imino linkage was introduced in these molecules, as it had been found to be more conducive to mesomorphism. The compounds with shorter alkyl chains exhibited the B_1 phase, while the compounds with relatively longer alkyl chains showed the B_7 mesophase. The observed mesophase is further confirmed by DSC analysis and X-ray diffraction studies. The photo and electrical switching properties of compounds were studied by UV/Vis spectrophotometry and an electro-optical method, respectively.

The bent-core compounds (8a-8d) were prepared by following the synthetic pathway shown in Scheme 1. (4-(4'-Hydroxyphenylazo)phenyl)acetamide $(1)^{21,30}$ was obtained by diazo coupling reaction of 4-aminophenylacetamide with phenol using NaNO₂/HCl, NaOH at 0 °C, alkylated by Williamson ether synthesis with an even number alkyl bromide (n = 6, 8, 10)and 12) to obtain (4-(4'-n-alkyloxyphenylazo) phenyl)acetamide $(2a-2d)^{21}$ and further 4-(4'-n-alkyloxyphenylazo)aniline $(3a-3d)^{31}$ was obtained by hydrolysis of 2a-2d. Simultaneously, ethyl 4'-hydroxy biphenyl-4-carboxylate $(4)^{21}$ was prepared by esterification of 4'-hydroxybiphenyl-4-carboxylic acid and ethanol with conc. sulfuric acid. Then compound (4) was alkylated with an even number alkyl bromide (n = 6, 8, 10 and 12) to obtain ethyl 4'-n-alkyloxybiphenyl-4-carboxylate (5a-5d)²² followed by hydrolysis of (5a-5d) to obtain ethyl 4'-n-alkyloxybiphenyl-4carboxylic acid (6a-6d).²² Further, the 3-formylphenyl 4'-n-alkyloxy biphenyl-4-carboxylate (7a-7d) was obtained by esterification reaction of 3-hydroxy benzaldehyde with 6a-6d using DCC and DMAP as a catalyst. Finally, the target compounds of 3-((4-((4'-n-alkyloxyphenyl)diazenyl)phenylimino)methyl) phenyl 4'-n-alkyloxybiphenyl-4-carboxylate (8a-8d)²² were synthesized by Schiff's-base reaction using amine (3a-3d) and aldehyde (7a-7d).²² Detailed syntheses of 7a-7d and 8a-8d are given in the Experimental.

Results and discussions

Mesomorphic properties of the compounds

The mesophase behaviors of the compounds (8a-8d) were investigated using DSC and POM analysis. The homologous series of asymmetric bent-core compounds (8a-8d) consist of a five-ring aromatic core and terminal alkyl chains on both sides with even numbers of carbon atoms (6, 8, 10 and 12). The transition temperatures and the associated enthalpy values are summarized in Table 1. A DSC thermogram of the compounds (8a-8d) is shown in Fig. 1. DSC thermograms of the compounds were measured at the rate of 5 $^{\circ}$ C min⁻¹. The compounds 8a, 8b and 8c indicate three endo and two exo peaks during heating and cooling. The lowest temperature, intermediate and highest temperature peaks correspond to crystal-crystal, crystal-liquid crystal and liquid crystal-isotropic transition, respectively. Compound 8d shows two crystalline phases both on heating and cooling. DSC analysis revealed that the clearing temperature of the compounds decreases on increasing the terminal chain length and the mesophases of all the compounds are enantiotropic in nature.

POM textural observations of the four compounds (**8a–8d**) were carried out in order to identify the different mesophases. Among these homologous series of compounds, the compounds with shorter alkyl chains (**8a** and **8b**) show the B_1 phase, as expected. The POM texture of compound **8a** in the B_1 phase is shown in Fig. 2a. Compound **8b** displays a typical fan-type texture (Fig. 2b–d) of the B_1 phase upon cooling from the isotropic state, which on further cooling transforms to a crystalline phase (Fig. 2e).³² Usually, the B_1 phase is substituted by the lamellar B_2 phase on increasing the length of terminal alkyl chains and this transition depends on the ratio of core size to the chain length.^{33,34} In our case, the higher homologues (compounds **8c** and **8d**) with relatively longer alkyl chains exhibit B_7 mesophases, which are depicted in Fig. 2f and 3,

Table 1 Phase transition temperatures (°C) and enthalpies $[J g^{-1}]$ of compounds **(8a–8d)**

Sample code/ alkyl chain length	DSC (°C)									
	Cr ₁	Heating Cooling	Cr ₂	Heating Cooling	B ₁	Heating Cooling	B ₇	Heating Cooling	I	
8a/6	*	142.2 [08.4]	*	178.4 [14.3] 165.4 [16.4]	*	180.2 [15.2] 175.2 [21.3]			*	
8b/8	*	137.9 [09.4]	*	[10.4] 172.1 [24.4] 154.9 [26.5]	*	[21.3] 175.9 [22.3] 171.4 [31.1]	_		*	
8c/10	*	121.1 [09.8]	*	167.0 [40.0] 153.3 [38.7]	_		*	171.3 [36.3] 168.1 [42.0]	*	
8d/12	*	98.4 [05.1] 61.7 [06.4]	*	121.1 [40.8] 142.4 [26.6]			*	167.7 [33.0] 165.3 [17.4]	*	

Note: Cr and Cr_2 = crystalline phases; B_7 = polar tilted lamellar phase; B_1 = rectangular columnar (Col_r) phase; I = isotropic phase. (* = phase exists; — = phase does not exist).



Fig. 1 DSC thermograms of compounds (8a-8d).



Fig. 2 A microphotograph of the B₁ phase of compounds observed from POM, (a) B₁ phase of compound **8a** at 175 °C, (b) isotropic transforming into B₁ phase of compound **8b** at 169 °C, (c) developing of fan like texture of B₁ phase of compound **8b** at 167 °C, (d) typical fan-type texture of B₁ phase of compound **8b** at 165 °C and (e) crystallization at 154 °C and (f) circular and oval fan-shaped domains in the B₇ phase at 165 °C of compound **8c** (magnification: 20×).

respectively. This new type of mesophase is exhibited during the slow cooling from an isotropic liquid in which helical filaments and single- and double-winded helical patterns were observed (Fig. 3), this is the characteristic observation for the B₇ phase. The molecular arrangement in the B7 phase is intermediate between that of the B₁ and B₂ phases.^{6,7} Interestingly, many fascinating and spectacular textures, like helical filaments, striped focal conics or fan-shaped, oval domains, myelinic and checkerboard textures have been observed in the B7 phase.^{18,19} Fig. 3 exhibits the growth of spiral filaments, circular, oval and fan-shaped domains in the B7 phase on cooling the compound 8d from the isotropic phase. The equidistant stripes in the circular domain or in the fan-shaped texture or equidistant concentric circles are clearly the result of a helicoidal periodicity. This periodicity is probably due to a twisted distribution of the molecular tilt, which corresponds to the pitch of helical structure, as in the chiral SmC* phase.¹⁷ Generally, the biphenyl moiety is rigid in nature, the presence of azo and imino linkages and a biphenyl ring in the bentshaped molecule form stronger asymmetry, which might be responsible for the B7 phase. Thus stronger asymmetry, rigidity and longer methylene chain of the bent-core compounds favor stabilization of the B7 phase.



Fig. 3 The POM microphotographs of compound **8d** showing the growth of spiral filaments at 164 °C, myelinic, circular, oval and fan-shaped domains in the B_7 phase at 160 °C (magnification: 50×).

X-ray diffraction studies

Compounds 8a and 8b, exhibiting B1 mesophase as indicated, were further examined using XRD analysis. For example, the powder XRD profile of compound **8b** exhibits four reflections in the small angle region with spacing d1 = 39.58 Å, d2 = 36.97 Å, d3 = 23.03 Å, d4 =20.38 Å and a diffuse peak in the wide angle region with spacing d5 = 4.58 Å. These small angle peaks at d1, d2, d3, d4 could be indexed as (11), (20), (02) and (22) planes of a center rectangular columnar structure, respectively. Thus, this phase is a rectangular columnar B₁ mesophase with columnar lattice constants a = 73.94 Å and b = 46.86 Å. The X-ray diffraction profile of compound **8b** at 160 °C is shown in Fig. 4. Compounds 8c and 8d, exhibiting B₇ mesophase as indicated in the POM observations, were further investigated using XRD analysis. As a representative, compound 8d is described in details. The 2D XRD pattern of compound 8d at 160 °C is shown Fig. 5. In the small angle region, two reflections at d1 = 42.22 Å and d2 = 22.62 Å with the ratio of spacing as 1:1/2indicate a lamellar or smectic type ordering with layer spacing as 42.22 Å.²⁰ Furthermore, a diffuse peak in the wide-angle region with d spacing of 4.67 Å is ascribed to liquid like in-plane order of molecules in the layer. The tilt angle calculated from the observed layer, spacing from XRD pattern and molecular length estimated



Fig. 4 The X-ray diffraction intensity profile for the B_1 phase obtained for the compound ${\bf 8b}$ at 160 °C.



Fig. 5 The XRD profile in the B_7 phase of compound 8d at 160 °C. The inset shows the profile in the logarithmic scale and a 2D image of the XRD pattern.

from the molecular formula is found to be about 41.3° . However the longer wavelength modulations of the layers in the B₇ phase are not detected in our XRD measurements.²⁰

Electro-optical investigations

To ascertain the effect of electric field on the mesophases of these bent-core molecules (8a-8d), detailed electro-optical investigations have been carried out. ITO coated homemade cells treated with polyimide were used for these experiments. The sample thickness of 8 µm was adjusted with suitable Mylar spacers and sample was filled in the cell by capillary action in isotropic phase. The sample was cooled slowly from the isotropic phase (1 °C min⁻¹) under a low frequency electric field to obtain a planar alignment of the sample. The current responses were measured across a 1 k Ω resistance connected in series with the sample cell under the application of a triangular wave voltage (53 V, 75 Hz). The current responses observed in the mesophase of compounds 8a and 8b indicated the absence of spontaneous polarization and B1 phase of these compounds was further confirmed by the electro-optical measurements. In contrast, however, interesting electro-optical effects were observed for the mesophase of compounds 8c and 8d. The compound 8d exhibited different textures on applying different electric field, as represented in S4 (ESI[†]), which form a needle, fan and distorted fan texture at 43 V, 53 V and 63 V, respectively. Among these the voltage at 53 is the optimum voltage to form the fan texture. The switching current response (Fig. 6) in the mesophase of the compound 8d shows a single polarization current peak for each half period of applied electric field. This single peak could possibly indicate ferroelectric switching behavior of the mesophase; the single peak disappears in the isotropic state confirming ferroelectric switching. The same is also verified by observing that the field induced polarized state remains stable even under very low frequency at 0.5 Hz. The single polarization current peak observed in this experiment further supported the B₇ character of the mesophase as B₇ phase generally found to exhibit only ferroelectric switching characteristics.7 This type of switching behavior is indicative of regions with supramolecular chirality with an anticlinic-ferroelectric



Fig. 6 The switching current response in the B_7 phase of the compound 8d showing a single polarization current peak for each half period of applied electric field.

arrangement (SmC_AP_F) of the molecules. These observations were quite similar to those obtained for the B₇ mesophase exhibited by compounds, reported earlier.^{7,20} Similar electro-switching responses were also found for compound **8c** (ESI,[†] S5). The spontaneous polarization (*P*s) for the B₇ phases of compound **8c** and **8d** has been found as 10 nC cm⁻² and 15 nC cm⁻², respectively.

Photo-switching studies of bent-core compounds

The photo-switching properties of compound 8a were measured in chloroform using UV/Visible spectroscopy in the absence and presence of UV light exposure at different time intervals. The absorption spectra of compound 8a is carried out in chloroform; $C = 1.3 \times 10^{-5}$ M. The absorption spectra of compound 8a shows absorption maxima at 307 nm, 378 nm and a shoulder band around 477 nm, as shown in Fig. 7. The absorbance in the UV region at 378 nm corresponds to the π - π * transition of the E isomer, which is usually stronger and a weak absorbance in the visible region around 477 nm represents the $n-\pi^*$ transition of the Z isomer. The absorption spectra of compounds 8a-8d are shown in the ESI⁺ (S6). The absorption spectra are similar for all the compounds because of their similar molecular structure, the only difference is in the alkyl chain, which does not alter the electronic transitions. Consequently, compound 8a alone was considered for photoisomerization study.15,27

Sample **8a** was illuminated with UV light, resulting in a decrease in the absorbance at 378 nm with an increase at 477 nm, suggesting the transformation of *E* to *Z* isomer. After 30 s exposure of UV light, there is no change in absorption spectra, which confirms photo saturation of the $E \rightarrow Z$ isomerization processes. Fig. 7 displays the *E*/*Z* photoisomerization of compound **8a** upon exposure to UV light. Two isobestic points at 338 and 447 nm are noted from Fig. 7, confirming the photoisomerization processes.^{15,27} A structural conformational change of compound **8a** during UV/Visible irradiation is represented in S7 (ESI[†]). The *Z* isomer of compound **8a** can



Fig. 7 (a) Absorption spectra of compound **8a** with different exposure times to UV light (b) the absorption spectra of the shoulder band of compound **8a** and (c) the time dependence photoisomerization curve of *E* isomer of compound **8a** measured at 378 nm.

be converted to the *E* isomer by shining visible light or keeping the solution in the dark. The *Z* isomer of sample **8a** is illuminated by 520 nm light; with subsequent time intervals resulting in an increase in the absorbance at 378 nm with a decrease at 477 nm. There is no change in the absorption after 40 s, which confirms the reversible *E*/*Z*-forms of compound **8a** upon UV/Visible light illumination of the photoisomerization reaction represented in S8 (ESI†). Similarly, the *Z* isomer is slowly converted to the *E* isomer when it is placed in the dark and this process is known as the "thermal back reaction".^{15,21,24} The bent-core compounds **8a–8d** exhibit very strong photoisomerization phenomena with UV as well as visible light illumination and these are also thermally reversible. The photoisomerization behavior of compound **8d** during UV as well as visible light illumination is given in the ESI† S9 and S10.

Comparison of the mesophase and photoisomerization behavior of compounds with similar structures

The mesomorphic properties of the compound (8d) can be compared with our previously reported^{21,24} unsymmetrical bent-core compounds with similar structures, as shown in Table 2.



It can be seen from Table 2 that compound C (8d) exhibits the B_7 phase, whereas compounds A and B display the B_2 phase. In this asymmetric BC compound A was synthesized with sixrings using different linking groups, azo, imine and ester, which show the B_2 phase with a higher transition temperature.

 Table 2
 Influence of linkage groups on mesophase behavior of five-ring bentcore compounds

Subs	stituents			
n	No. of aromatic ring/X	Р	Mesophase/ reference	
12	6/-N=CH-Ar-COO-	Y = COO	B ₂ /21	
12	5/-N=CH-	Y = COO	$B_2/24$	
12	5/-N=CH-	Biphenyl	B ₇	
	Subs n 12 12 12 12	Substituents No. of aromatic n ring/X 12 6/–N=CH–Ar–COO– 12 5/–N=CH– 12 5/–N=CH–	SubstituentsNo. of aromatic n P12 $6/-N$ =CH-Ar-COO- 12Y = COO Y = COO 1212 $5/-N$ =CH- Biphenyl	

We intended to study the effect of the number of aromatic rings of compound A, thus compound B was synthesized with fivering. We observed that the B2 mesophase was once again retained, similarly the higher homologues exhibit the B2 phase and the lower ones exhibit the B_1 phase and the transition temperature also reduced. From compounds A and B, the number of aromatic ring was decreased from six to five, reducing the rigidity, hence the transition temperature decreased. Furthermore, compound C was synthesized by the introduction of a biphenyl ring, which exhibited the unusual B7 mesophase. Here, the presence of azo, imine and biphenyl moieties are highly asymmetric and the biphenyl moiety is relatively rigid in nature. This suggests that the presence of a sequence of azo, imine linkage groups and a biphenyl ring in bent-core molecules might be responsible for the B₇ mesophase. Thus stronger asymmetry, rigidity and higher homologues of bent-core compounds favor stabilization of the B₇ phase.

The photo-isomerization behavior of compound **8a** can be compared with similar five-aromatic ring containing bent-core compounds, which have been reported earlier.²⁷ The photoisomerization studies reveal that the compound **8a** testifies to *E* to *Z* and *Z* to *E* isomerization taking place at 30 s and 40 s, whereas reported compounds were recorded at 50 s and 60 s, respectively.²⁷ Though all are five-aromatic ring containing BC compounds, compound **8a** has faster photo-isomerization. This may be attributed to the nature of the linking group (-CH=N-) in the azobenzene as well as the rigidity of the biphenyl moiety. The time taken for photoisomerization depends on the nature of the linking group (electron withdrawing group/donating group) and size of the substituent in the azobenzene moiety.³⁵ The faster isomerization process is a key factor for optical data storage applications.

Conclusion

We have presented the synthesis of asymmetric bent-core mesogens with variable terminal chain lengths and their mesomorphic, photo induced isomerization and electro-optical switching properties were analyzed. Mesomorphic behavior and physical properties strongly depend on the symmetry of the molecules. In this series, shorter chain homologues exhibit a rectangular columnar B_1 phase and the higher homologues exhibit the B_7 phase. The stronger asymmetry and rigidity of the bent-core molecules appear to favor the stabilization of the B_7 phase. The B_7 mesophase shows the ferroelectric-anticlinic

Paper

organization (SmC_AP_F) of molecules in the layers. The photoisomerization properties of compound **8a** revealed that *E* to *Z* isomerization takes place after 30 s, whereas the reverse process takes place after 40 s in chloroform as solvent. All the compounds establish photo-induced as well as thermally reversible switching behavior. The photo-isomerization process and ferroelectric switching behavior of bent-core compounds might be exploited in the fields of optical data storage devices, molecular switches and pyroelectric materials.

Experimental

Materials

4-Aminophenylacetamide (Sigma-Aldrich, India), phenol, sodium nitrate, potassium hydroxide, 4'-hydroxybiphenyl-4carboxylic acid, sodium hydroxide, potassium carbonate, hydrochloric acid (Merck, India), 3-hydroxybenzaldehyde, potassium iodide, *N*,*N*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) (Aldrich), were used as received. Solvents such as ethanol, dichloromethane, ethyl acetate, chloroform and acetone were purified by the reported procedure.³⁰

Instrumentation

The infrared spectra of compounds were obtained from Perkin Elmer FT-IR spectrometer using KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl₃ with TMS as an internal standard. DSC measurements were performed at a heating rate of 5 °C min⁻¹, and samples taken in an aluminum pan with a pierced lid, in a dry nitrogen atmosphere with an empty pan as reference on a TA instrument (model Q 10). The LC texture of compounds were observed using a Euromex polarizing optical microscope (POM) equipped with a Linkem HFS91 heating stage and a TP-93 temperature programmer. Samples were placed in between two thin glass cover slips and melted with heating and cooling at the rate of 2 $^{\circ}$ C min⁻¹. The photographs were taken with a Canon 1000 D camera. The field induced LC textures of compounds were observed by a Nikon microscope and spontaneous polarization (Ps) of the B_7 phase was measured by a triangular wave method in a planner-aligned cell using a digital oscilloscope (Agilent, model MSO6012A) and an arbitrary waveform generator (Agilent, model 33220A) coupled with a power amplifier (Trek, model 601). X-ray diffraction (XRD) studies of non-oriented samples filled in Lindemann capillary (diameter 0.7 mm) were performed using Cu-Ka radiation from a rotating anode generator (Rigaku Ultrax-18) with a graphite crystal as monochromator. The diffraction pattern of each sample was recorded on a 2D image plate (Marresearch). Some of the XRD measurements were performed using 1D-XRD using Pan Analytical-DY1042-Empyreau XRD with PDS and Pix cell. The absorbance spectra of compounds were measured on a Shimadzu UV-1650 spectrophotometer using chloroform as solvent. The photoisomerization of azobenzene between the E and Z-form was carried out, using a 6 W high-pressure Hg lamp (Sankyo, Japan) for UV (365 nm), (Hitachi, Japan) for visible light illumination (520 nm).

Synthetic procedures

Synthesis of 3-formylphenyl 4'-hexyloxybiphenyl-4-carboxylate (7a). The 3-formylphenyl 4'-hexyloxybiphenyl-4-carboxylate was synthesized by esterification reaction of hexyloxybiphenyl-4-carboxylic acid (0.04 mol) with 3-hydroxybenzaldehyde (0.4 mol) using dicyclohexylcarbodiimide (DCC) (0.4 mol) and 5% wt of 4-dimethylaminopyridine (DMAP) used as a catalyst in methylene chloride (DCM) (200 mL). The resultant mixture was stirred for 12 h at room temperature under a nitrogen atmosphere. After completion of reaction, the precipitated byproduct urea was filtered out, then the filtrate was evaporated and product was purified by silica gel column using chloroform as eluent. After recrystallization in ethanol, 3-formylphenyl 4'-6-hexyloxybiphenyl-4-carboxylate (yield: 95%) was obtained as a white powder. A similar procedure was adopted for preparation of the other members of the even number alkyl series, such as octyl, decyl and dodecyl (7b-7d).

7a: $C_{26}H_{26}O_4$; calcd C, 77.59; H, 6.49; O, 15.90; found C, 77.18; H, 6.48; O, 16.34. FT-IR; 2992, 2921, 1772, 1727, 1603, 1467, 1399, 1274, 1234. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 9.86 (m, 1H, -Ar-CHO), 8.24 (m, 2H, -Ar-H), 7.77-7.63 (m, 4H, -Ar-H), 7.43-7.33 (m, 4H, -Ar-H), 6.86 (m, 2H, -Ar-H), 3.96 (m, 2H, -OCH₂-), 1.71 (d, 2H, -CH₂-), 1.31-1.27 (dd, 4H, -CH₂-), 0.98 (m, 3H, -CH₃). ¹³C NMR (CDCl₃, 400 MHz), δ (ppm): 190.9, 165.1, 156.4, 151.8, 141.7, 137.1, 130.4, 129.8, 128.4, 127.4, 114.1, 68.2, 31.9, 29.7, 25.7 and 14.1.

Synthesis of 3-((4-(4'-hexyloxyphenylazo)phenylimino) methyl) phenyl 4'-hexyloxybiphenyl-4-carboxylate (8a). The synthetic procedure for 3-((4-(4'-hexyloxyphenylazo)phenylimino)methyl) phenyl 4'-hexyloxybiphenyl-4-carboxylate (8a) was as follows: 4-(4'-hexyloxyphenylazo)aniline (3a) (0.0064 mol) and 3-formylphenyl 4'-hexloxybiphenyl-4-carboxylate (0.0064 mol) were dissolved in ethanol (50 mL) and the reaction mixture was refluxed until a yellow color solid precipitated out. After completion of the reaction, the desired product was filtered out and washed with ethanol, then the product was recrystallized from ethanol to obtain a yellowish brown powdery compound 8a (yield: 71%). A similar procedure was adopted for the preparation of the other members of the even number alkyl series, such as octyl, decyl and dodecyl (8b–8c).

8a: $C_{44}H_{47}N_3O_4$; calcd C, 77.50; N, 6.16; H, 6.95; O, 9.39; found C, 77.38; H, 6.88; N, 6.36 O, 9.38. FT-IR; 3042, 2933, 2860, 1735, 1405, 1244, 2001, 842. ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 8.54 (s, H, -CH=N-), 8.27 (m, 2H, -Ar-H), 7.95 (m, 2H, -Ar-H), 7.90 (m, 2H, -Ar-H), 7.66 (m, 2H, -Ar-H), 7.50 (m, 2H, -Ar-H), 7.42 (m, 2H, -Ar-H), 7.37-31 (m, 2H, -Ar-H), 7.30 (m, 2H, -Ar-H), 7.02 (m, 2H, -Ar-H), 6.91 (m, 2H, -Ar-H), 4.06 (m, 4H, -OCH₂-), 1.86 (d, 4H, -CH₂-), 1.51-1.45 (dd, 12H, -CH₂-), 0.88 (m, 6H, -CH₃). ¹³C NMR (CDCl₃, 400 MHz): 165.2, 159.7, 155.4, 151.4, 144.3, 141.7, 132.1, 130.6, 129.4, 127.6, 126.4, 123.6, 122.9, 120.4, 114.2, 68.3, 32.1, 29.5, 25.7 and 14.4.

Syntheses of compounds 1 to **6a–6d** were followed based on previous reports. $^{\rm 21,22}$

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