

# Photochromic liquid crystal (PLC) : A brief history of 1-Alkyl-2-(arylo)imidazoles

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## ARTICLE INFO

### Keywords:

Photochromism  
Liquid crystals  
Azobenzenes  
1-Alkyl-2-(arylo)imidazoles  
POM  
DSC

## ABSTRACT

Photochromism and Liquid Crystals are mainly dominated by the change of structure/orientation upon optical/thermal stimulation. Upon light absorption photochromic molecules show reversible structural change with eligible spectral features. The molecules who transform from the orientational more ordered to less ordered arrangement by thermal/physical stimuli show the properties of LC or mesogen. Photochromic responses in LCs encourage re-alignments upon light irradiation and various other properties of the materials. Photochromism is a disorder phenomenon while LC is an ordered orientation; hence, the design of single molecule having two contradicting properties is challenging. Azobenzenes belong to unique class of photochrome and undergo trans-cis photoisomerization while presence of long aliphatic chains sometime induces the LC properties. In our research, a series of substituted aryloimidazoles are designed and some of them are susceptible to optical stimulation and a few of the long alkyl substituted 1-Alkyl-2-(arylo)imidazoles ( $R_{aai}-C_nH_{2n}$ ) show thermally controlled LC behaviour.

## 1. Introduction

Photochromism is the reversible structural change of inorganic/organic molecules/materials with change of colour, dipole moment and spectral characteristics [1–4] and in the liquid crystals the molecules undergo change of ordered orientation with thermal stimulation [5–7]. The photochromic materials are used in making of toys, cosmetics, sunglasses, defence materials, thermal sensors, optical switches and memories, data storage, filters, auto-developing photography, invisible ink/writing and many others.

Liquid crystal (mesogen) displays intermediate phase behaviour of crystalline solid and isotropic liquid. These are widely used in calculators, digital watches, oscillaographic systems, television displays and in making toys and decorative materials. Inclusion of photochromic motif in the mesogens develops a unique opportunity but highly intricate to change of external stimuli to regulate novel optical properties, ferroelectric behaviour, the induction of chirality, the photo-regulation of the oscillation wavelength of mirrorless lasers etc.

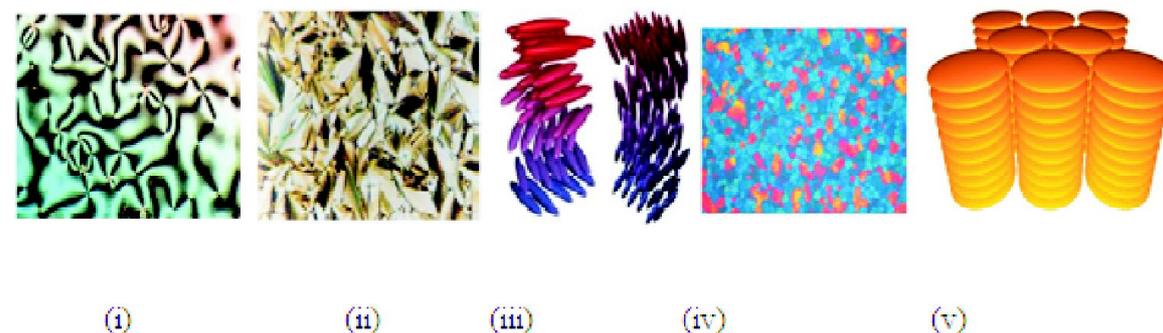
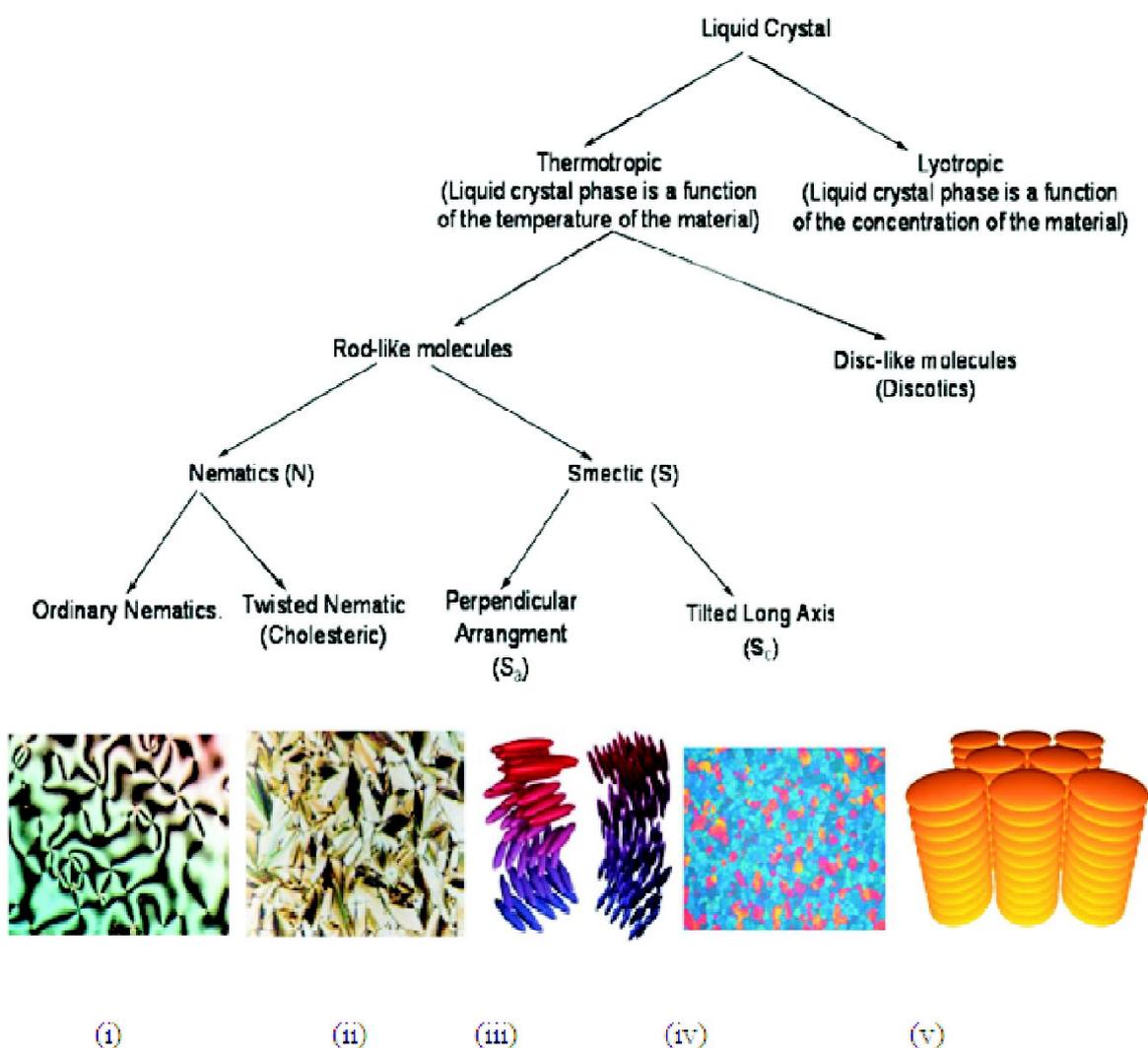
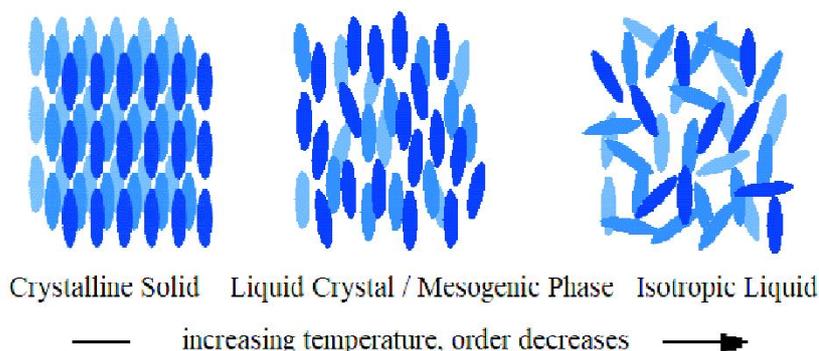
## 2. Liquid Crystal (LC)

Liquid Crystals (LCs) are defined as intermediate state of matter which exists in between solid (crystalline) and liquid (isotropic)

phases and shows temperature/stress dependent properties of each state [5–7]. It is considered as unique “mesophase”. In the LC phases the molecules possess some orientational or positional order but with a lower degree of organisation compared with a crystalline solid that is known as anisotropic intermolecular interactions. The LC possesses liquid-like flowing behaviour, but more viscous than isotropic liquid due to their positional order. The molecules in the LC phase are sensitive to external stimuli, like temperature, electric and magnetic fields. Recently liquid-crystalline single molecules or polymers containing photochromic motifs are of much attraction because of their applications in multicolour display devices, for sensing temperature of hot spots, heat flow mapping, stress distribution pattern measurement, smart window, spy devices etc.

The photo-controlled phase transitions of some liquid crystal of chiral molecules such as asymmetric azobenzene, show potential applications in dye-sensitised solar cells, ordered reaction media and ion transport systems. Liquid crystals show crystalline phase properties below certain temperature ( $T_c$ ) and upon heating at above  $T_c$ , isotropic fluid behaviour is observed (Fig. 1). In crystalline phase the material shows positional and orientational order of crystalline phase. Liquid crystals (LCs) are of two categories: lyotropic and thermotropic compounds. Thermotropic LCs show heat/thermal dependent phase change; lyo-

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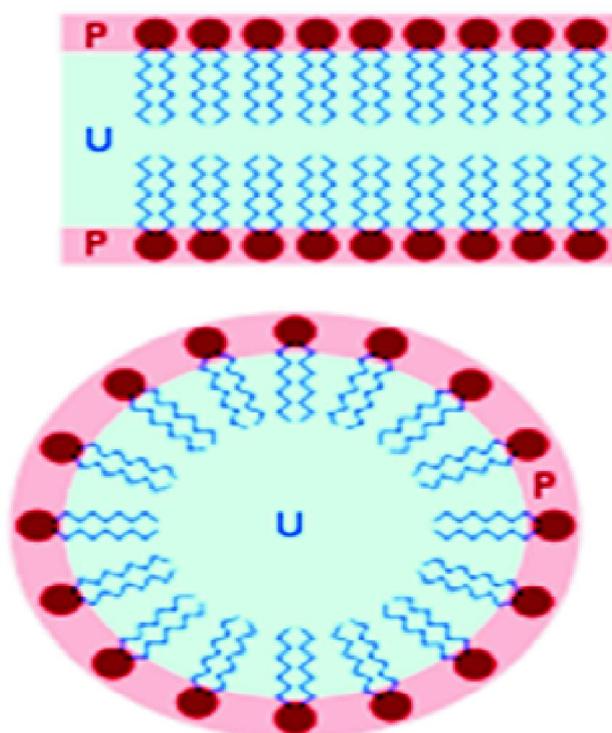


Schlieren texture of (i) Nematic, (ii) Smectic, (iii) Chiral, (iv) Blue and (v) Discotic Phase

Fig. 1. Liquid crystal phases and classification.

tropic LCs are formed by mixing with an isotropic solvent. Thermotropic LC's are Nematic (thread like, N), Smectic (Soap bubble type, Sm), Chiral Phase, Blue Phase and Discotic Phase. A Nematic LC phase has orientational order but no positional order and

has been used in many stimuli (strain, temperature, light, and electric fields) responsive elastomers [5,8]. Lyotropic LC phase may have space to fill the solvents to provide fluidity to the system (Fig. 2).



**Fig. 2.** Lyotropic LC : surfactant molecules (red heads) are in contact with water and the tails are immersed in oil (blue) [bilayer (upper) and micelle (lower)].

### 3. Photochromes

The molecules or materials those are sensitive to irradiated light by changing colour and associated with structure/redox states are defined as photochromes [1–3]. Use of Sunglass in the sunny days is common application of photochromes.

#### 3.1. Inorganic photochromes

First generation photochromic lenses use AgX (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) during 1970s [9]; light irradiation has reduced to metallic Ag which causes grey colour of glass. It is reoxidised upon removal of light (Table 1) or by Cu<sup>2+</sup>.

**Table 1**

Doped inorganic compounds in photochromic glasses and their changes

Inorganic photochrome	Redox reaction	Visible colour change
AgX	Ag <sup>+</sup> → Ag(0) Ag + Cu <sup>++</sup> → Ag <sup>+</sup> + Cu <sup>+</sup>	Grey
Co(III) salts	Co <sup>3+</sup> → Co <sup>2+</sup>	Blue
Fe(III) salts	Fe <sup>3+</sup> → Fe <sup>2+</sup>	Brown
Mn(III) salts	Mn <sup>3+</sup> → Mn <sup>2+</sup>	Violet
Eu <sup>2+</sup> /Ce <sup>3+</sup> and Ti <sup>4+</sup>	Eu <sup>2+</sup> /Ce <sup>3+</sup> + Ti <sup>4+</sup> → Eu <sup>3+</sup> /Ce <sup>4+</sup> + Ti <sup>3+</sup>	Reversible pink-red

Different transition metal, lanthanides, nontransition metal complexes like Fe(III), Co(III), Mn(III), Eu<sup>2+</sup>/Ce<sup>3+</sup> + Ti<sup>4+</sup>, Sn/Sb may be doped to generate multiple color in the glasses. Besides Au nano of different size doped in glass shows different colour- yellow to blue.

#### 3.2. Organic photochromes

Organic photochromes include spiropyrans, diarylethenes, and photochromic quinones, azobenzenes, azopyridines etc. are mixed with the plastic or thinly coated on the surface of the plastic to make photochromic lenses, sensing processors etc. which are lighter and therefore more comfortable to wear. Photochromes regulate many light sensitive reversible physical processes such as optical memories and switches, variable electrical current, membrane transportation of ions, etc. For this purpose, organic photochromes are incorporated in polymers, liquid crystalline materials, or other matrices [10–12].



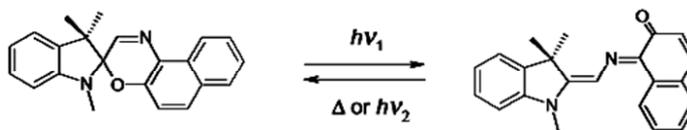
**Table 2**

List of organic photochromes

Sl. No.	Family of photochrome	Structural changes before and after light irradiation Closed vs open form
1	Spiropyrans	

Table-2 (contd.)

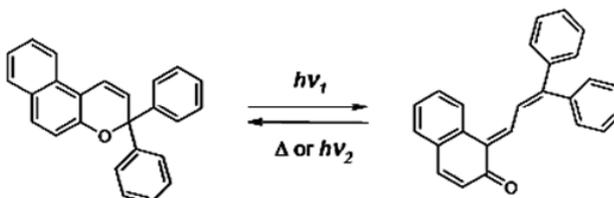
2 Spirooxazines



Colorless

Blue

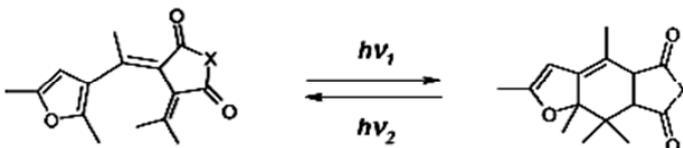
3 Chromenes



Colorless

Intense Blue

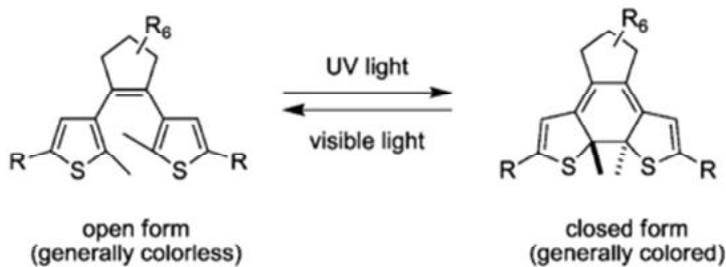
4 Fulgides (X = O); fulgimides (X = NR)



Colorless/light green

Blue

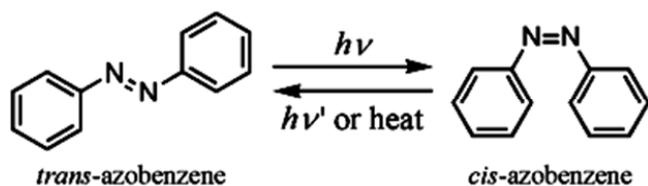
5 Diarylethenes



Colorless

Light Pink

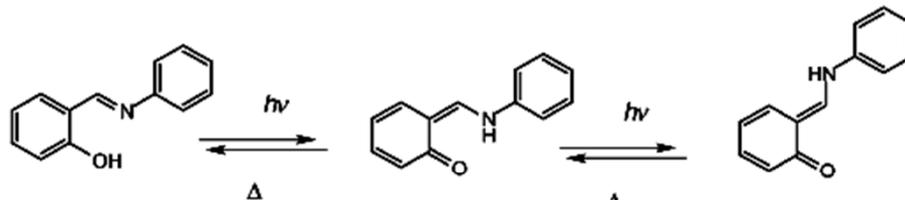
6 Azobenzenes



Orange yellow

Orange/Red

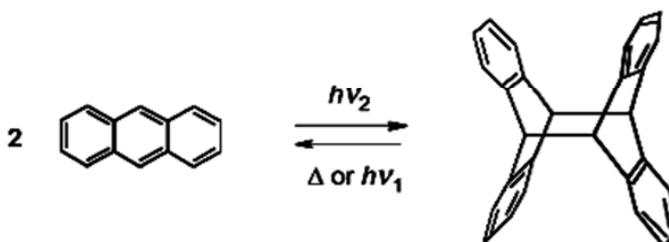
7 Anils and related compounds



Colorless/yellow

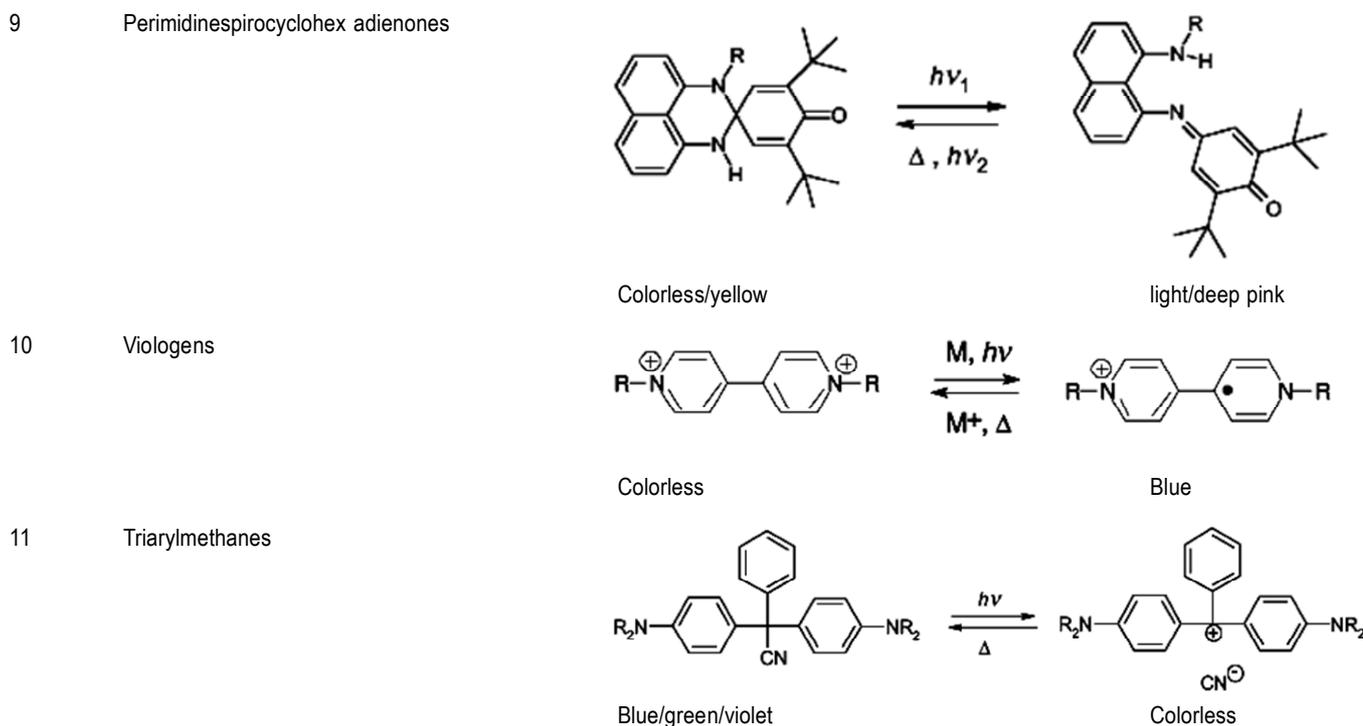
Orange

8 Anthracene



Colorless

Blue



### 3.3. Azo photochromes

Photochromism is defined as 'reversible transformation of a molecular entity between two isomeric forms resulting in different absorption spectra, induced in one or both directions by absorption of electromagnetic radiation. The spectral change is typically, but not necessarily, of visible colour and is accompanied by differences in other physical properties.' [1–3]. G. S. Hartley (1937) reported the cis-trans isomerization of aromatic azo dyes on absorbing UV light [13] followed by publications on the derivatives of azobenzene which is considered the best characterized photoswitches [14–19]. Trans-Azobenzene shows a weak  $n-\pi^*$  band  $\sim 420$  nm and a strong  $\pi-\pi^*$  transition  $\sim 320$  nm. Cis-Azobenzene has a stronger  $n-\pi^*$  band also near 430 nm and shorter wavelength band at 280 nm (Fig. 3).

The cis-trans (Z-to-E) isomerization of phenylazopyridines was reported by Ellis V. Brown and G. Richard Granneman in 1975 [20]. Advantage of azopyridine derivatives is their coordination to a metal ion and hydrogen bonding through the pyridyl-N and/or the azo-N group. First report of photoisomerization of azoimidazole appears in 2003 [21] by T. Majima and subsequent publication appeared in 2005 by Otsuki, Sinha in 2005 [22]. Arylazoimidazole possesses two eligible N-donor centres (imidazolyl-N and azo-N) to constitute azoimine ( $-N=N-C=N-$ ) chelated geometry and/or monodentate imidazolyl-N coordination complexes [23–40]. Photochromic properties are examined by

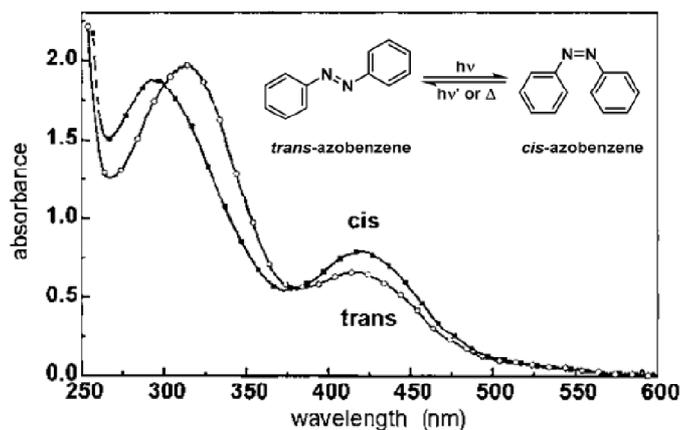


Fig. 3. Photochromism azobenzene in Hexane.

optical and thermal relaxation routes. Upon light absorption in the UV region ( $\sim 360$  nm) the stable rod shaped trans-configuration of the photochrome ( $R_{aaiR}$ ) undergoes structural change either through N-Ar bond rotation or the cleavage of  $-N=N-$  followed by rotation to energetically higher stage of cis-configuration. The metal complexes of  $R_{aaiR}$  in general having longer M-N(azo) distances of diamagnetic configuration (Zn(II), Cd(II), Hg(II), Pb(II), Cu(I), Ag(I), Pd(II)) show photoinduced trans  $\rightarrow$  cis isomerization [41–57] (Figs. 4–6). The photoisomerization rate and quantum yield are largely influenced by the effective mass and the rigidity of the matrix about the photochrome. Solvent polarity, pH of the medium, presence of ions or molecules in the media also influence the photochromic process. In some

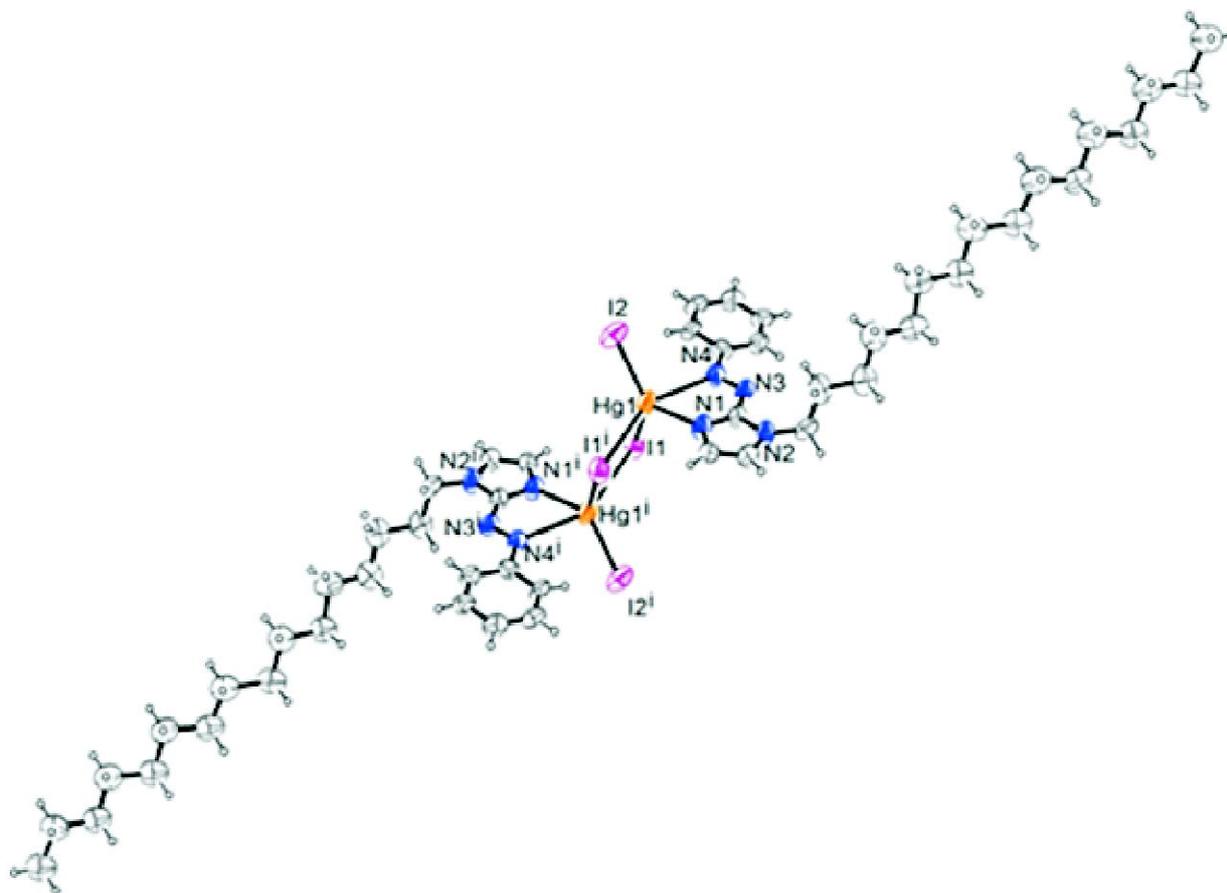


Fig. 4. The molecular Structure of  $[\text{Hg}(\text{Haai-C}_{16}\text{H}_{33})(\mu\text{-I})(\text{I})]_2$  (4a) where azo bond (-N-N-) is in transoid configuration.

cases the optimised geometries/Single Crystal X-Ray Structure parameters of the complexes have been used for DFT computation and the molecular functions and their electronic energy have been used to explain the photochromic properties.

#### 4. Photochromic Liquid Crystals (PLCs)

Upon attaching photochromic units to LC materials may impose an optical property to the mesogenic efficiency towards storage and modulation to the external stimuli, such as heat, electric fields, and light [58–60]. Photoisomerisation is a disorder process where ordered rod like trans-azo is transformed to bent or V-shaped less ordered cis-azo structure. LC is an orientational ordered property of molecules. Therefore PLC (photochromic liquid crystal) is the transformation of orientational more ordered to less ordered arrangement and is highly sensitive to physical stimuli and chemical composition.

Azobenzene appended Liquid Crystals (LCs) have attracted much attention due to their photo-induced, photo-switchable, and elastic properties. Upon attachment of photochromic function to

LCs can employ large effects on their properties. Induction of both photochromism and liquid crystalline properties in the same molecule can exercise an opportunity to make a material useful for many practical applications viz., technology for imaging, materials for optical storage, integrated optical devices, laser and NLO (non-linear optical) materials [61,62]. Most studies have focused on varying the length of the alkyl chain or introduction of other substitution patterns [63–67] (e.g. pendant hydroxyl group on the alkyl chain, functionalised aryl groups, amide groups and pendant mesogenic groups) in the backbone of azobenzene. Increase in molecular length-to-breadth of the substituents amplifies the entropy chain; enhances thermal stability, and diminishes the clearing temperature of LC phase. Moreover, the azo linking increases the linearity of the molecule and this characteristic able to induce the mesophase transition.

#### 5. Arylazoimidazole and their complexes : Mesogens and Metallomesogens

Imidazole is abundant in biology and chemistry. Attachment

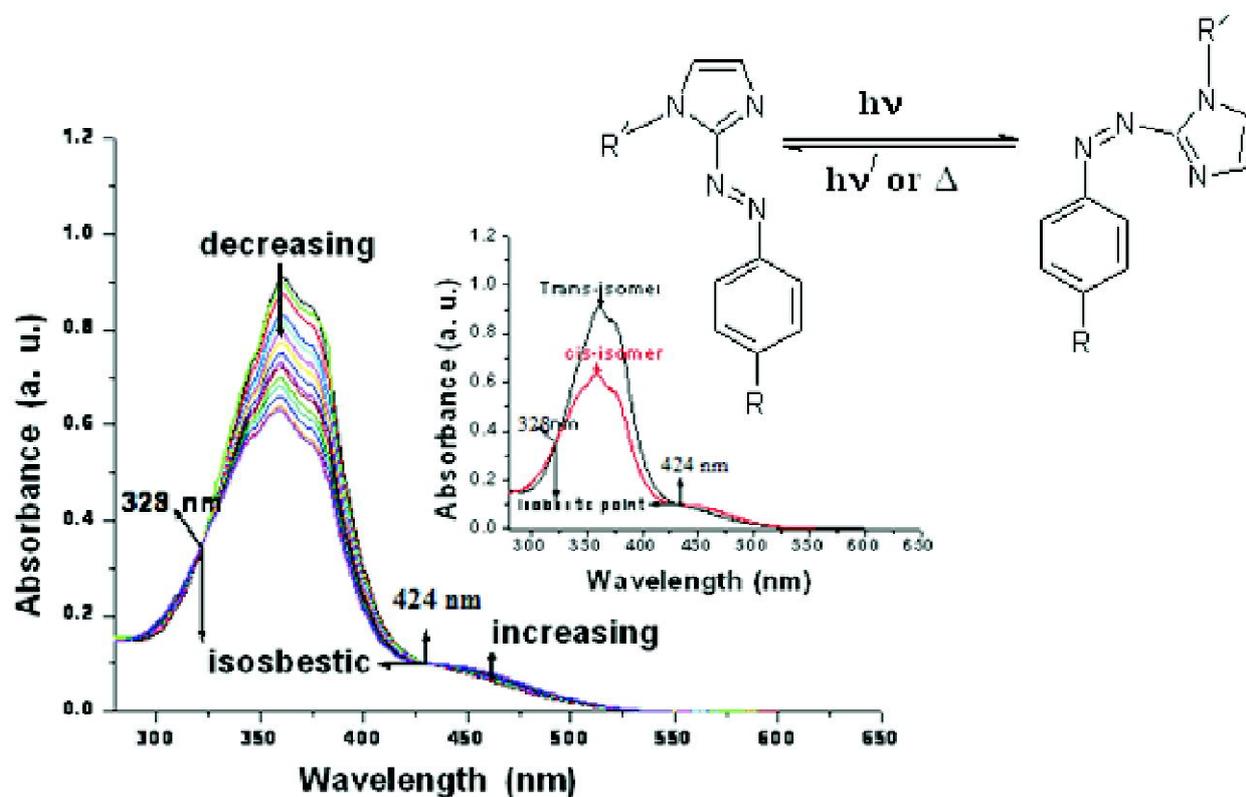


Fig. 5. Spectral changes of Haai-C<sub>10</sub>H<sub>21</sub> in MeOH on irradiating light at 362 nm for 3 min interval at 25°C. E (trans) and Z (cis) the photochrome is shown in inset.

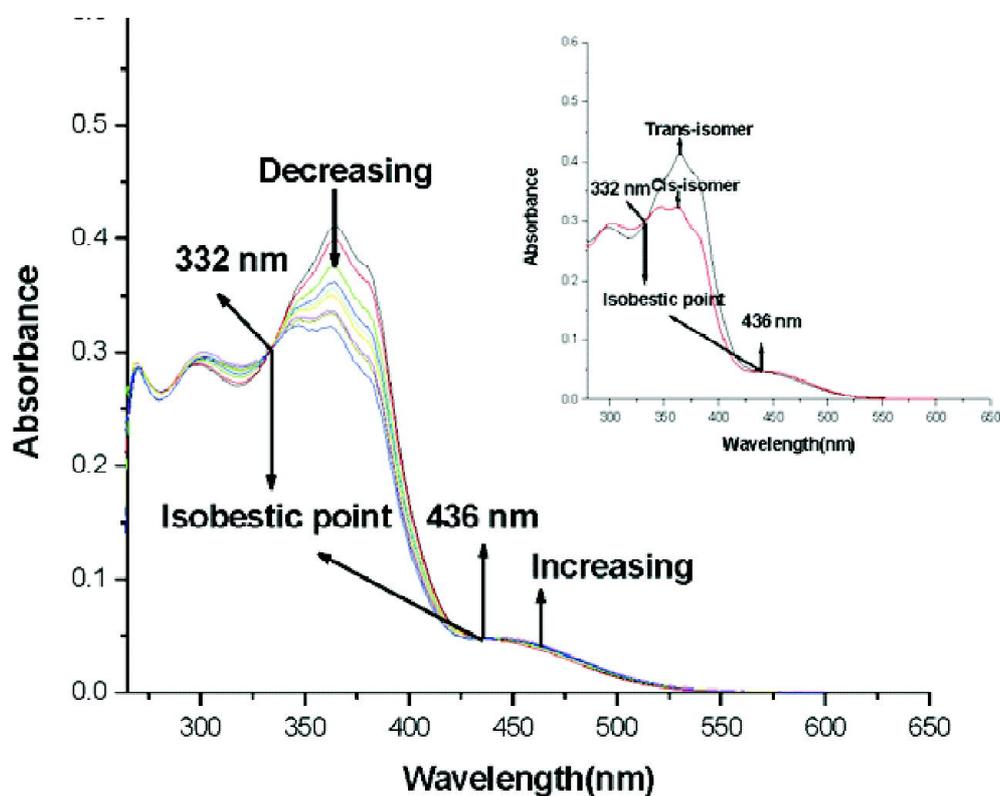
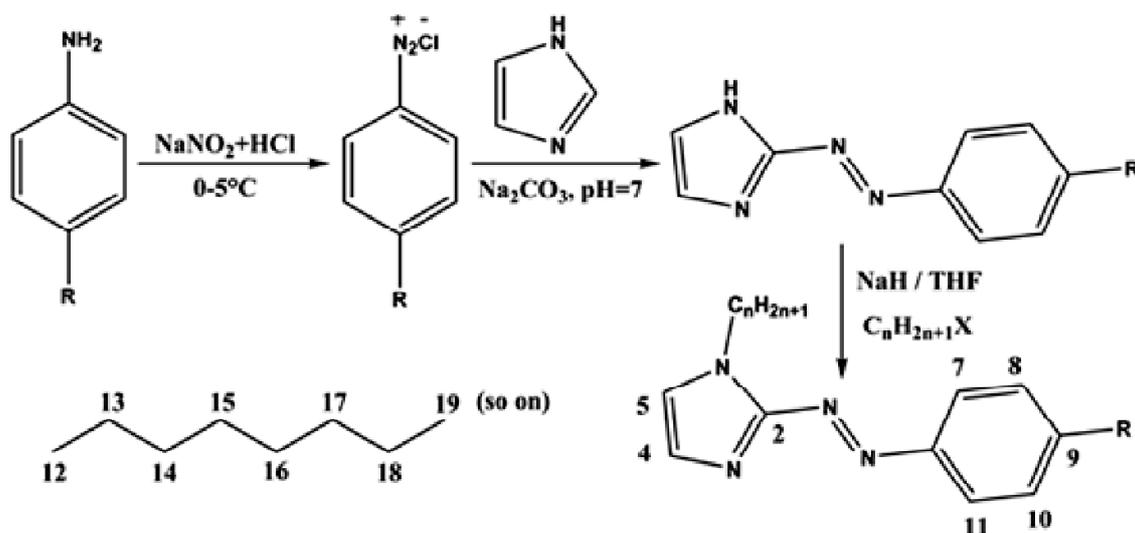


Fig. 6. The UV-Vis spectroscopic change of [Hg(Haai-C<sub>16</sub>H<sub>33</sub>)( $\mu$ -I)I]<sub>2</sub> in DMF solution; irradiation at 368 nm at 5 min interval at 25°C repeatedly. The spectra of Z (cis) and trans (E) isomer of the complex is shown in inset.



R = H (a), Me(b);  $C_nH_{2n+1}$ , n = 10 (1), 16 (2), 18 (3), 22 (4)

**Scheme 1.** General synthetic process of Raai- $C_nH_{2n+1}$  (1-3).

of arylazo group ( $Ar-N=N^+$ ) to imidazole backbone has synthesized 2-(aryloxy)imidazoles. It was first prepared by Fargher and Pymen in 1919 [68] but spectral characterization was reported in 1981 and 1985 [69], respectively. In depth literature search revealed that a US patent was filed in 1998 concerning its antidepressant activity [70]. The diazotization of aromatic amines in acidic medium by  $NaNO_2$  at low temperature ( $0^\circ C - 5^\circ C$ ) followed by the coupling with imidazole in aqueous sodium carbonate solution (pH=7) isolated 2-(Aryloxy)imidazoles (RaaiH). To dry THF solution of RaaiH at ambient condition NaH was added slowly and stirred followed by the drop addition of alkyl halide ( $R^1X$ ) to synthesise 1-alkyl-2-(aryloxy)imidazole, RaaiR<sup>1</sup> or Raai- $C_nH_{2n+1}$  (Scheme 1) [53].

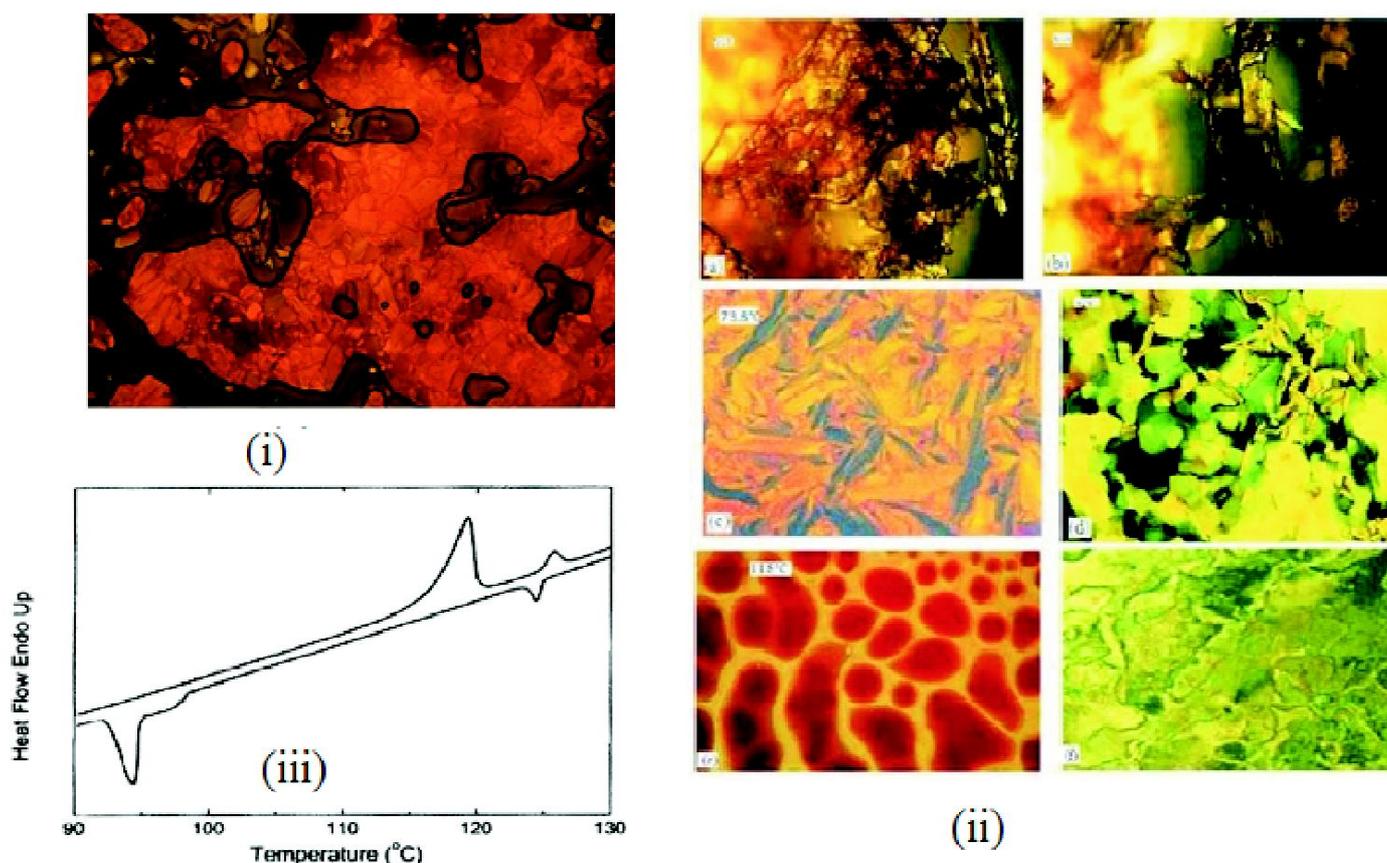
The ligands may act as either monodentate imidazolyl-N or bidentate chelating molecule. 1-Alkyl-2-(aryloxy)imidazole (Raai- $R^1$ ), has excellent  $\pi$ -acidity which could potentially influence the structure and reactivity of their complexes [23–40]. Ligand belongs to unsymmetric N,N'-chelating system where N and N' are abbreviated to N(imidazole) and N(azo) respectively. The single crystal X-ray diffraction structure of one of the complexes,  $[Hg(Haai-C_{16}H_{33})(\mu-l)(l)]_2$  (Fig. 4) shows transoid orientation of azo function ( $-N=N-$ ). However, we have not been able to isolate cis-azo oriented compound.

The effect of UV light irradiation on 1-alkyl-2-(aryloxy) imidazoles is examined and have found the photoisomerization (Fig. 5) [22]. The influence of light irradiation on the spectral changes of on  $[Hg(Haai-C_{16}H_{33})(\mu-l)(l)]_2$  in DMF solution at 368 nm at 5 min interval at  $25^\circ C$  is shown in Fig. 6. The influence of solvent,

foreign innocent molecules, pH, micelles on the photochromic activity of Raai- $C_nH_{2n+1}$  is examined [22, 41–57] and also the coordination of complexes of transition and nontransition metal ions [23–40]. Rates and quantum yield ( $\Phi$ ) of photoisomerization is largely controlled by molecular weight, chain length and selection of solvent. Photochromic quantitative parameters in Table 3 reveal that the rates of photoisomerization of Hg(II) complexes,  $[Hg(Raai-C_nH_{2n+1})(\mu-l)]_2$ , about to 20 times slower than their

**Table 3.** Parameters of photoisomerization of Raai- $C_nH_{2n+1}$  in MeOH and  $[Hg(Raai-C_nH_{2n+1})(\mu-l)]_2$  in DMF solution at  $25^\circ C$  [53,56]

Compound	$\lambda_{Abs}$ , nm	Rate of trans $\rightarrow$ cis conversion $\times 10^8 s^{-1}$	$10^9 \Phi_{trans \rightarrow cis}$
Haai- $C_{10}H_{21}$ (1a)	362	34.11	1.61
Meaai- $C_{10}H_{21}$ (1b)	363	33.12	1.43
Haai- $C_{16}H_{33}$ (2a)	360	25.81	1.37
Meaai- $C_{16}H_{33}$ (2b)	362	24.80	1.29
Haai- $C_{18}H_{37}$ (3a)	362	23.24	1.27
Meaai- $C_{18}H_{37}$ (3b)	363	22.71	1.24
Haai- $C_{22}H_{45}$ (4a)	360	20.72	1.17
Meaai- $C_{22}H_{45}$ (4b)	363	20.17	1.11
$[Hg(Haai-C_{10}H_{21})(\mu-l)]_2$ (5a)	365	1.921	0.106
$[Hg(Meaai-C_{10}H_{21})(\mu-l)]_2$ (5b)	367	1.837	0.085
$[Hg(Haai-C_{16}H_{33})(\mu-l)]_2$ (6a)	366	1.479	0.085
$[Hg(Meaai-C_{16}H_{33})(\mu-l)]_2$ (6b)	369	1.325	0.083
$[Hg(Haai-C_{18}H_{37})(\mu-l)]_2$ (7a)	367	1.321	0.079
$[Hg(Meaai-C_{18}H_{37})(\mu-l)]_2$ (7b)	368	1.232	0.078
$[Hg(Haai-C_{22}H_{45})(\mu-l)]_2$ (8a)	366	1.123	0.071
$[Hg(Meaai-C_{22}H_{45})(\mu-l)]_2$ (8b)	368	1.119	0.068



**Fig. 7.** (i) POM views of Schlieren texture of N-phase at 51.2°C of Haai-C<sub>18</sub>H<sub>37</sub> (**3a**); (ii) Phases of [Hg(Meaai-C<sub>16</sub>H<sub>33</sub>)(μ-I)I]<sub>2</sub> (**6b**) at heating phase (a) at 50.1°C (crystalline), (b) 59.3°C (melting start), (c) 73.8°C (SmA) and (d) 92°C (bananashape) and (e) isotropic phase at 118°C and (f) on cooling phase (71°C) mosaictexture; (iii) The DSC of [Hg(Haai-C<sub>16</sub>H<sub>33</sub>)(μ-I)I]<sub>2</sub> (**6a**) at the rate of 2°C min<sup>-1</sup> (94°C (exo), 118.9°C (endo), 125°C (exo), 122°C (endo)).

parent azoimidazole ligand, Raai-C<sub>n</sub>H<sub>2n+1</sub>. Because of solubility problem the experiment for the complexes, [Hg(Raai-C<sub>n</sub>H<sub>2n+1</sub>)(μ-I)I]<sub>2</sub>, are carried out in DMF solution while free ligand is soluble in methanol.

## 6. Liquid crystal property

It is difficult to predict whether long alkyl chain substituent of definite *n* in Raai-C<sub>n</sub>H<sub>2n+1</sub> could show LC property or its metal complexes. Polarized light Optical Microscopy (POM) and differential scanning calorimetry (DSC) are used to examine the LC properties of the molecules. Upon POM investigation of few compounds Haai-C<sub>18</sub>H<sub>37</sub> (**3a**) and Haai-C<sub>22</sub>H<sub>45</sub> (**4a**) show mesomorphic response (Fig. 7). The nematic (N) texture is shown by Haai-C<sub>18</sub>H<sub>37</sub> (**3a**) at 55°C (Fig. 7) while Haai-C<sub>22</sub>H<sub>45</sub> (**4a**) shows unknown Smectic (Sm) phase at 62°C and, finally shift to isotropic (I) phase [53]. Other compounds show common crystalline-isotropic transition and the DSC plots do not show significant changes. Similarly, the POM examination of [Hg(Raai-C<sub>n</sub>H<sub>2n+1</sub>)(μ-I)I]<sub>2</sub> (5-8) only [Hg(Meaai-C<sub>16</sub>H<sub>33</sub>)(μ-I)I]<sub>2</sub> (**6b**) shows

mesomorphic activity [56]. On slow heating, the crystalline solid turns to jelly phase and starts to melt at 50°C by a cloudy appearance and the process completed around 128°C which displays various types of smectic phases. A focal conic fan textures were found from 50.1°C to 71°C (Fig. 7) and SmA phase mesogene is observed at 73.8°C. The SmA → banana shaped on heating cycle at 92°C and on continuing the isotropic phase appears at 118°C. The reverse process i.e., the cooling cycles is very complex and proceed through large number of phases those are difficult to distinguish; at 71°C SmB phase Mosaic texture is observed. The differential scanning calorimetry (DSC) (Fig. 7) of this complex shows Δ*H* (26.4J/g) at 94°C and endothermic response at 118.9°C (32.1J/g) followed by a small peak at 122°C, where Δ*H* is very low (1.68 J/g) indicates a transition from crystal to Mosaic texture of smectic B textures.

## Conclusion

Attachment of photochrome to LC molecular system generates a special series of molecules who are showing light-induced

spectral features. Photochromic responses in LCs encourage re-alignments upon light irradiation and various other properties of the materials. In our research, a series of long chain alkyl substituted 1-alkyl-2-(arylo)imidazoles ( $\text{Raai-C}_n\text{H}_{2n+1}$ ) are designed and some of them are susceptible to optical stimulation. Metal complexes of  $\text{Raai-C}_n\text{H}_{2n+1}$  also exhibit light induced structural properties; however, only few of them are showing metallo-megogenic behaviour.

### Acknowledgements

My sincere thanks to Dr. Debashis Mallick, Mrinalini Datta Mahavidyapith, Birati, West Bengal and Dr. Chandana Sen, Behala College, Kolkata, West Bengal for their research contribution in this field. Financial support from Jadavpur University is gratefully acknowledged.

### Conflict of Interest

I declare no conflict of interest.

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