Journal of Photochemistry and Photobiology A: Chemistry 207 (2009) 73–78

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Indane-1,3-dione and cholesterol containing butadiene derivatives: Photoresponsive liquid crystalline glasses for imaging applications

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ARTICLE INFO

Article history:
Available online 28 November 2008

Keywords:
Photoresponsive liquid crystals
Imaging
Polarised photoluminescence

ABSTRACT

Synthesis, thermo-optical and glass forming properties of a series of photoresponsive luminescent mesogenic materials containing a butadiene moiety linked to a cholesterol group (**CBIN**, **CBIN8** and **CBIN12**) as well as colour imaging devices based on them are described. These molecules exhibited relatively high fluorescence quantum efficiency in the solid and liquid crystalline states. The cholesteric phase was observed to be the major phase in these molecules and the pitch of cholesteric helix was sensitive to external stimuli such as temperature and light, making it possible to tune their iridescent colour in the visible region. The colour reflected by the cholesteric films could be stabilized by converting them to the glassy state by sudden cooling from their cholesteric phase to ~0 °C. Selective exposure of the material in its liquid crystalline phase to light resulted in *trans–cis* photoisomerization of the butadiene chromophore. Consequently the pitch of the irradiated portion changed depending upon the intensity of the illuminating light. The coloured images thus formed could be stored for long periods by converting the films to glasses by sudden cooling. The images stored in the glassy state were stable over long periods of time (>one year).

1. Introduction

Supramolecular chemistry deals mainly with molecules that are held together by various non-covalent interactions such as π–π stacking, H-bonding, ionic interactions and solvophobic interactions [1]. Supramolecular materials which respond to external stimuli such as heat, light and electricity are specially attractive for the design of functional materials [2]. Such systems can be useful in a wide range of emerging applications, including ultra-fast optical switches, rewritable colour imaging devices as well as in temperature, pressure and chemo-sensing devices [3]. Even though photoresponsive materials such as liquid crystals, gels and vesicles have been well studied, creation of new materials which can compete efficiently with existing systems pose a considerable challenge [4].

With respect to design of stimuli sensitive materials, liquid crystals (LCs) evoke significant interest, since their cooperative behaviour and long range order play an important role in amplifying relatively weak external stimuli. Cholesteric liquid crystals (CLCs) form an important class, which possess the inherent property of selective reflection of wavelengths due to their helical superstructure originating either from intrinsic chirality of the LC molecules or due to the presence of chiral dopants [5]. The wavelength of light reflected by such materials depends on the pitch length of the helix, which in turn is highly sensitive to external stimuli such as temperature, pressure and the presence of impurities [6]. The flowing nature of the LC phase however makes such materials inefficient for long term information storage. Non-polymeric CLCs, which can be stabilized into a glassy state, while retaining their supramolecular ordering, can be used to overcome this problem. Recently glass forming LCs and in particular chiral nematic (N*) glasses have been attracting increasing attention in view of their potential application as optical filters, polarizers and lasing materials [7]. It has recently been shown that some dicholesteryl esters doped with photoresponsive chromophores such as azobenzene or diphenylbutadiene derivatives could be utilized for light induced recording of full colour images [8]. Recent studies have also shown that inherently photoactive LCs possess several advantages over doped systems [9]. This is mainly because films drawn from inherently photoactive LCs essentially consist of pure materials with well-defined molecular weights where the problem of dilution of the photochrome does not exist. This can result in much faster switching times and enhanced stability of the film [9c,d]. Earlier efforts in the design of inherently photoactive liquid crystals for recording colour images

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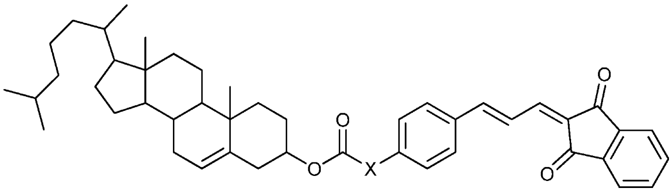
doi:10.1016/j.jphotochem.2008.11.009



CBIN : X = -O-
CBIN8 : X = -O-$(CH_2)_8$O-
CBIN12 : X = -O-$(CH_2)_{12}$O-

Chart 1.

met with only partial success [10]. Although a light induced smectic to N* phase transition was observed in cholesterol-azobenzene linked systems, the rapid thermal *cis–trans* isomerization of the azobenzene moiety resulted in a loss of the recorded image. Moreover these materials did not form stable LC glasses. Introduction of diphenyl butadiene as the photochromic unit, led to materials with an improved glass forming property [10b]. Another area of current interest is the construction of low molecular weight π-conjugated molecules which possess intense fluorescence in the solid-state [11]. Such types of molecules are useful for designing OLEDs [11b,c,d].

Keeping these points in mind we have designed a new system in which cholesterol is linked to a indane dione based butadiene chromophore via oligomethylene spacers (Chart 1). Introduction of cholesterol moiety induces liquid crystalline phases in these systems and all the three derivatives reported here exhibit enantiotropic N* liquid crystalline phase over a wide range of temperature. Here, we describe the liquid crystalline and glass forming properties as well as thermal and photochemical control of the cholesteric reflection wavelengths in these derivatives. In addition to this, films of **CBIN8** and **CBIN12** formed from their melt showed a significant enhancement in fluorescence compared to that of their solution and these aspects as well as polarized emission from the films have been examined.

2. Results and discussion

2.1. Synthesis

Compounds **CBIN**, **CBIN8** and **CBIN12** were synthesized by a multi-step process [12] and their structures were established by FT-IR, ^{1}H, ^{13}C NMR, HRMS and Elemental analysis. ^{1}H NMR analysis revealed that the compounds existed as their *E* isomers [12].

2.2. Photophysical properties in solution

Table 1
Absorption and emission characteristics of, **CBIN**, **CBIN8** and **CBIN12** in solvents of varying polarity.

Compound	Solvent	Absorption λ_{max} (nm)	Emission	
			λ_{max} (nm)	Φ_F ($\times 10^3$)
CBIN	Heptane	378	461	0.3
	Toluene	387	429	0.9
	Chloroform	387	463	0.6
	Tetrahydrofuran	382	482	0.5
CBIN8	Heptane	420	472	1.0
	Toluene	426	483	9.3
	Chloroform	436	523	2.0
	Tetrahydrofuran	421	515	1.4
CBIN12	Heptane	419	494	2.0
	Toluene	435	500	2.2
	Chloroform	428	532	3.0
	Tetrahydrofuran	422	494	2.4

Table 2
Fluorescence maxima (λ_{max}) and quantum yields (Φ_F) of cholesterol derivatives in the thin film.

Compound	λ_{max} (nm)	Φ_F	Fluorescence lifetime (ns)		
			τ_1	τ_2	τ_3
CBIN8	630	0.14	1.55	4.15	4.53
CBIN12	630	0.12	0.3	1.02	4.16

All the three derivatives (**CBIN**, **CBIN8** and **CBIN12**) showed a strong absorption in the 350–500 nm regions with absorption maxima at ~420 nm (Fig. 1a). Although the absorption spectrum was found to be independent of solvent polarity, the fluorescence spectra of all the derivatives were found to undergo a red-shift with increase in solvent polarity (Fig. 1b) which was indicative of emission arising from an intramolecular charge transfer state as observed in several donor–acceptor-substituted butadienes reported earlier [13]. These derivatives were only weakly fluorescent in solution. The absorption, emission maxima and quantum yields of fluorescence of the derivatives in different solvents are provided in Table 1.

2.3. Photophysical properties of thin films

The solid-state absorption spectrum of these derivatives exhibited a broad band (200–600 nm). Fig. 2a shows the reflectance absorption spectra of **CBIN12**. A ten-fold enhancement of fluorescence in the solid-state compared to that in solution was observed for both **CBIN8** and **CBIN12**. The solid-state emission was also much broader ranging from 500 to 780 nm with λ_{max} ~ 630 nm (Fig. 2b). The fluorescence properties of the thin films of these derivatives are summarized in Table 2. The fluorescence lifetimes measured from the thin films indicated a tri-exponential decay.

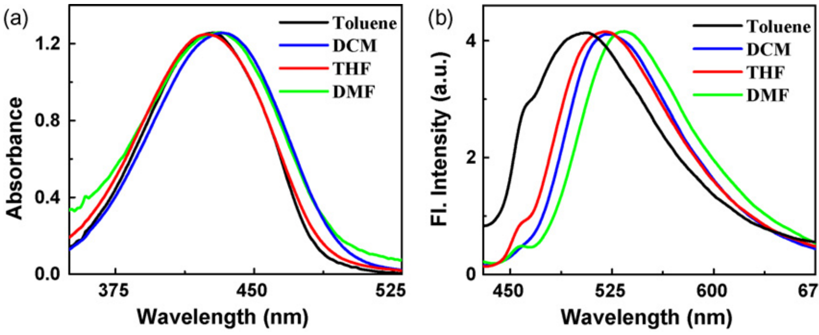


Fig. 1. (a) Absorption and (b) emission spectra of **CBIN8** in solvents of varying polarity.

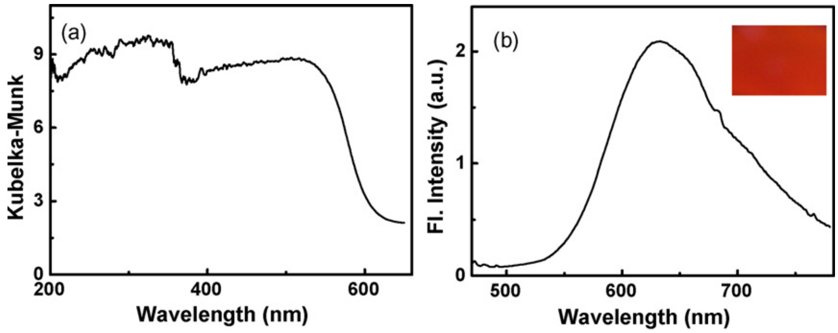


Fig. 2. (a) The reflectance absorption spectrum and (b) fluorescence spectrum of a thin film of **CBIN12** (λ_{ex} = 420 nm). Inset shows the photograph of a fluorescent thin film of **CBIN12** under 365 nm light illumination.

Table 3
Melting points, phase sequences, phase transition temperatures, phase transition enthalpy changes, phase transition entropy changes in the heating and cooling cycles of the derivatives.

Sample code	Heating cycle, °C (ΔH, kJ/mol, ΔS, J/mol/K)	Cooling cycle, °C (ΔH, kJ/mol, ΔS, J/mol/K)
CBIN	Cr1 99 Sm^a (7.5, 15.72) 204^a N* 238 I (dec.)	–
CBIN8	Cr1 83 Sm 110 Cr2 145 (9.0, 21.53) N* 169^a (5.4, 12.22) I	I 165^a (3.59, 8.2) N* 104 Sm 80 G
CBIN12	Cr1^a 81 Sm 97 Cr2^a 147 (15.89, 37.83) N* 150 I	I 144 (0.61, 1.5) N* 92 Sm 72 (4.58, G)

[a] As observed by DSC; Cr, Crystal; Sm, Smectic; N*, Chiral nematic; and I, Isotropic.

The changes in absorption and emission properties of **CBIN8** and **CBIN12** on going from solution to the solid-state could be attributed to aggregation in the solid-state [14,15] as observed for some diphenylbutadiene derivatives earlier [13c,11h]. For example, the broadening of absorption in the solid-state compared to that in solution could be attributed formation of H- and J-type aggregates, since a sum of the absorption of the monomer species and the H- and J-type aggregates could lead to a broad absorption in the solid-state. Planarization of the molecules in the solid-state, [16] resulting in improved charge transfer between the donor and acceptor groups could also contribute to broadening of the absorption spectra and red-shift in the emission spectra.

2.4. Phase transition behaviour

The mesomorphic properties of the **CBIN** derivatives were investigated by polarized light optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). The transition temperatures and corresponding enthalpy values are summarized in Table 3.

With the exception of **CBIN**, which decomposed above its isotropization temperature, the other derivatives showed enantiotropic (thermodynamically stable) LC properties exhibiting smectic (SmA) and chiral nematic (N*) phases. For example, cooling the isotropic liquid of **CBIN8** resulted in the formation of N* phase, which could be confirmed by the iridescent colours exhibited by the cholesterics, and the fan-like textures observed by POM (Fig. 3b). On further cooling, a smectic phase characterized by homeotropic texture was observed (Fig. 3c). XRD measurements of this smectic phase showed a sharp low angle peak accompanied by a diffuse peak at a wider angle. Interlayer distances (*d*) calculated from XRD were found to be significantly larger than the calculated length of the molecule (*l*). The d/l values were observed to be ~1.5 indicating an interdigitated layer like arrangement as observed in diphenyl butadienes reported earlier.

An unusual behaviour was observed in the phase transition of **CBIN8** in the heating cycle. On heating a thin film of **CBIN8**, POM studies indicated that the crystalline texture (Cr1) observed initially melted to form a smectic phase characterized by its focal-conic texture with homeotropic areas. Further heating resulted in the formation of spherulite crystals (Cr2), which again transformed into the N* phase at 145 °C and finally isotropized at 169 °C. A similar reemergence of the crystal phase was reported earlier for molecules consisting of a cholesterol moiety linked to an alkoxy-cyano-substituted diphenylbutadiene [11b]. The Cr1-Sm-Cr2 transition which was also observed in the heating cycle of **CBIN8** was reproducible and was observed both for samples crystallized from solvents and for super cooled solids. This transition from a relatively less ordered smectic phase to a highly ordered crystalline phase in the heating cycles of **CBIN8** was confirmed by DSC, which showed a clear exotherm corresponding to the smectic-to-crystal transformation (Fig. 4). Similar observation was made with the **CBIN12** also.

Fig. 3. Polarized photomicrographs of **CBIN8** in (a) smectic phase (91 °C, heating cycle); (b) cholesteric phase (165 °C, cooling cycle) and (c) smectic phase (99 °C, cooling cycle).

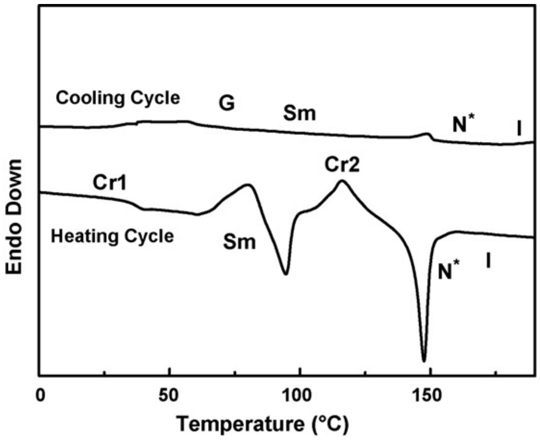


Fig. 4. DSC trace of **CBIN8** in the cooling/heating cycle, at 5 °C/min.

XRD measurements of **CBIN8** indicated that the interlayer distance (d) was the same for the Sm phases, which appear before and after the Cr phase. The XRD pattern of Cr1 was broad indicative of a glassy nature (Fig. 5a). This form could probably be a metastable state or frustrated crystal wherein the molecules are not highly ordered. On heating, the sample could initially melt to the smectic phase, wherein the molecules have the freedom to move. On further heating the molecules could reorient to form highly ordered crystals (Cr2). The crystalline nature of this form was indicated by the sharp peaks observed in its XRD pattern (Fig. 5b).

2.5. Formation of LC glasses

CBIN8 and **CBIN12** formed stable transparent glassy LCs when they were suddenly cooled from their LC state to ~0 °C (Fig. 6). The glassy LCs obtained by cooling from the LC phases were stable for several months at room temperature.

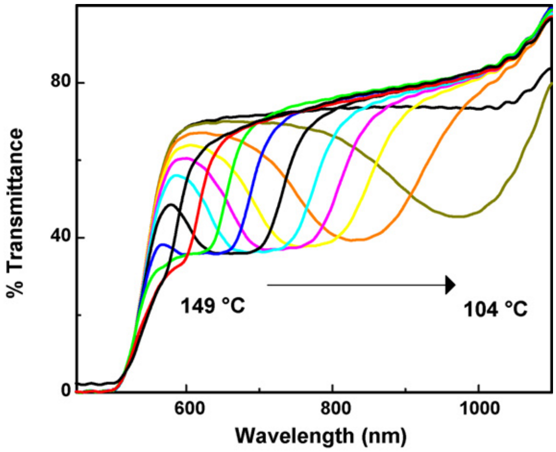


Fig. 7. Changes in the reflection band of cholesteric phase of **CBIN12** with decreasing temperature in the cooling cycle.

The reflection induced by the helical arrangement in CLCs satisfies the equation:

$$\lambda_{\max} = np$$

where $\lambda_{\max}$ is the reflection maximum; p, the pitch of the helix and n, the refractive index. Generally, the pitch of cholesteric helix decreases with increasing temperature. The reflection band maximum of **CBIN12** film showed a shift from 564 to 973 nm on changing the temperature from 149 to 104 °C (Fig. 7).

2.6. Photomodulation of reflected light

Photoisomerization of the diphenylbutadiene chromophore is known to result in the formation of stable *cis* isomers [13c]. When the material held in the cholesteric LC state was irradiated with 400 nm light, photoinduced formation of the *cis* isomer led to a

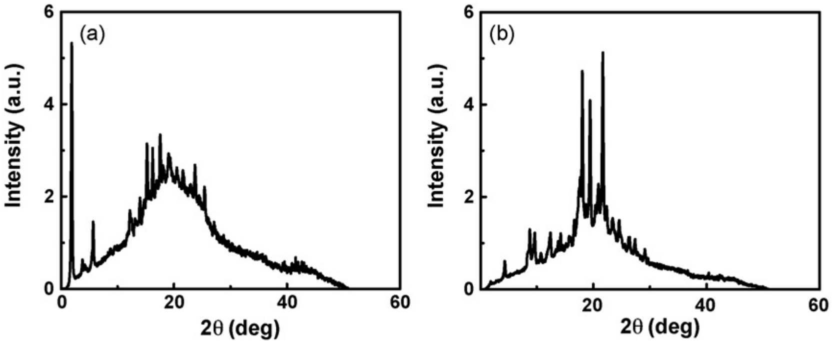


Fig. 5. XRD pattern of **CBIN8** in (a) Cr1 (80 °C) and (b) Cr2 (110 °C) phase.

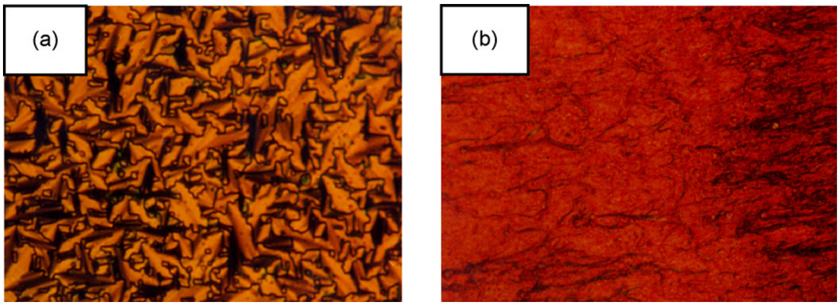


Fig. 6. Polarized photomicrographs of **CBIN12** in (a) N* (141 °C) and (b) N* glassy state (freezing from 122 to ~0 °C).

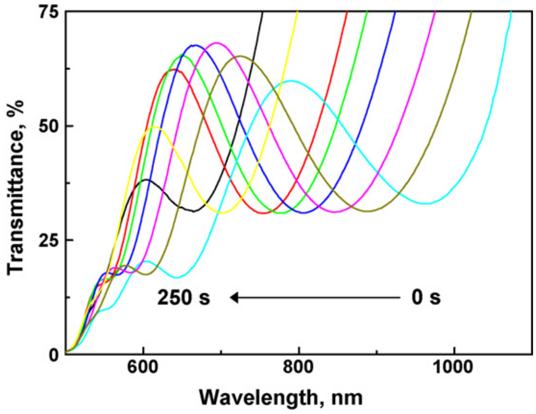


Fig. 8. Photoinduced changes of cholesteric reflection in a film of **CBIN8**.

shortening of the pitch of the N* helix. As a result a blue-shift of the reflectance band from the NIR to visible region of the spectrum was observed [6a]. Using this procedure the colour of the N* film could be photochemically tuned over the visible region (Fig. 8). The photochemically induced colour in the cholesteric films could be stabilized in the glassy state by quenching them from the respective temperatures into an ice cold temperature. The images thus formed were very stable and could be stored over long periods of time (>one year).

2.7. Polarized luminescence

Recently, active chiral nematic liquid crystals, which emit light rather than modulate an external light source, have attracted substantial interest [7c]. Chiral nematic liquid crystals represent a very promising coherent or incoherent source of circularly polarized light for applications in displays, optical information processing and storage [17]. The helical structure suppresses photoluminescence (PL) of one sense of circular polarization when the emission spectrum overlaps the selective reflective band of the helix. PL with the opposite sense of polarization is transmitted so that the output is circularly polarized [18]. Fig. 9 shows the circularly polarized photoluminescence spectra of the **CBIN12** cholesteric glass (prepared by cooling the cholesteric film suddenly from 130 to ~0 °C by dropping into an ice bath) on excitation with 532 nm light and the more intense luminescence is observed for right circularly polarized light which confirmed the left-handedness of the **CBIN12** helix.

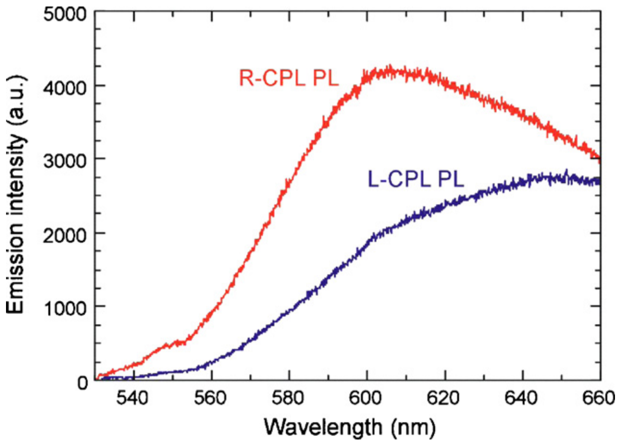


Fig. 9. Circularly polarized photoluminescence spectra of the **CBIN12** cholesteric glass by excitation with 532 nm light. The red and blue curves are right-CPL and left-CPL spectra.

The circular dissymmetry factor is defined by

$$g_e = \frac{2(I_L - I_R)}{(I_L + I_R)}$$

where $I_{R(L)}$ is the detected intensity when the fast axis of the wave plate is rotated by ±45° with respect to the transmission axis of the analyzer. The detected light is predominantly right- (left-) hand polarized in these configurations but may contain linearly polarized and unpolarized components. The PL is completely circularly polarized when $|g_e| = 2$.

A maximum g_e value of 1.3 is obtained from a luminescent chiral nematic poly(para-phenylene) [19]. The calculated g_e value for **CBIN12** at 610 nm was 0.66.

3. Conclusions

The molecules described herein form a versatile class of photoresponsive materials with multifunctional properties. **CBIN8** and **CBIN12** showed a broad absorption band (500–780 nm) and enhanced red-emission in their solid-state ($\Phi_F \sim 14\%$) when compared to that in solution ($\Phi_F \sim 10^{-3}$). These inherently photoresponsive liquid crystals form stable, clear N* glasses and could be used for imaging purposes. The solid-state luminescent properties of with enhanced emission compared to solution state was reported and chiral fluorescent glasses were prepared. Circularly polarized photoluminescence was observed from properly aligned cholesteric glasses and the cholesteric helix was found to be left-handed.

4. Experimental

The reagents and materials for synthesis were used as obtained from Aldrich and S.D. Fine Chemicals. Dry solvents were used wherever necessary and were prepared using reported drying procedures. Melting points are uncorrected and were determined on a Mel-Temp II melting point apparatus. IR spectra were recorded on an IR Prestige-21 series of Shimadzu FT-IR spectrometer. ^{1}H NMR spectra were recorded on Bruker DPX 300 MHz spectrometer using tetramethylsilane (TMS) as the internal standard and chloroform-*d* ($CDCl_3$), DMSO-d_6, and acetone-d_6 as the solvent. The coupling constant (*J*) values of 16 Hz for the olefinic protons in ^{1}H NMR spectrum of all derivatives, confirmed their *E* stereochemistry of the butadiene derivatives. High Resolution Mass Spectral Analysis (HRMS) was obtained from JEOL JMS600 instrument. Elemental analyses were carried out using ThermoFinnigan FLASH EA 1112 CHNS Analyzer. Fluorescence quantum yields in solution state with reproducibility of around 10%, were determined by comparison with 10-methylacridinium trifluoromethane sulphonate in water ($\Phi_f = 0.99$). Phase transitions were observed using a Nikon HFX 35A Optiphot-2 polarized light optical microscope, equipped with a Linkam THMS 600 heating and freezing stage connected to a Linkam TP92 temperature programmer. Differential scanning calorimetric studies were performed using a Seiko Instrument SSC5200. For the preparation of N* glassy LCs, the sample was sandwiched between two thin glass plates and heated to the cholesteric temperature, following which it was suddenly cooled by dropping the film into an ice bath. A super high pressure mercury lamp (200 W) equipped with a DLP® (1024 × 764 dots, Texas Instruments) was employed for colour image recording. The intensity of light at each dot was modulated by the digital micromirror device (DMD) following the image data provided as a jpeg file from a personal computer. The sample was irradiated through the appropriate set of optical filters transmitting light at around 400 nm. X-Ray diffraction patterns were measured using a Rigaku diffractometer (Type 4037) with graded d-space elliptical side-by-side multilayer optics, monochromated Cu Kα radiation (40 kV, 30 mA) and imaging plate

(R-Axis IV). The samples were put in quartz capillary tubes (1.5 mm diameter, 0.01 mm wall thickness) and positioned on a hot stage. The samples were heated to their isotropic phase, cooled to the mesophase and then exposed to a radiation beam of 150 mm camera length. Measurements of solid-state photoluminescence were carried out using the front face emission scan mode on a SPEX Fluorolog F112X Spectrofluorimeter. Solid-state fluorescence quantum efficiency was measured using an integrating sphere in a SPEX Fluorolog Spectrofluorimeter. The PL quantum yield in thin films (Φ_{film}) was determined using a calibrated integrating sphere system. The Xe-arc lamp was used to excite the thin-film sample placed in the sphere with 445 nm as the excitation wavelength. Samples were prepared by heating the material placed between two glass coverslips, which was heated above the respective melting points to make good film and cooled to room temperature. The quantum yield was determined by comparing the spectral intensities of the lamp and the sample emission as reported in the literature [20]. Using this experimental set-up and the integrating sphere system, solid-state fluorescence quantum yield of thin film of the standard green OLED material tris-8-hydroxyquinolinolato Aluminum (Alq$_3$) was determined to be $19 \pm 2\%$, which is consistent with previously reported values [21].

Acknowledgements

The research grants from Japanese Society for Promotion of Science (JSPS) and the travel support from the Department of Science and Technology (DST), India under an Indo-Japanese Scientific Collaborative Project (IJCSP) programme are gratefully acknowledged. N.S.S.K., S.A. and K.V.R., thank CSIR, Government of India, for research fellowships. This is contribution No. 270 from NIIST-PPG.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.11.009.

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