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Technologically promising, room temperature luminescent columnar liquid crystals derived from *s*-triazine core: molecular design, synthesis and characterization

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ABSTRACT

Three fold Horner-Wadsworth-Emmons (HWS) reaction of triphosphonate with achiral/chiral 3,4,5-tris(alkoxy)benzaldehydes yield novel achiral/chiral star-shaped liquid crystals (LCs), in which three fluorophore arms such as 1,2,3-tris(alkoxy)-5-styrylbenzenes are tethered to a central *s*-triazine core. These LCs, the first of their kind, display a columnar liquid crystalline phase over a wide temperature range existing between well below and above the room temperature, which is evidenced by optical and calorimetric studies. Besides, they show photoluminescence both in solution and mesomorphic states. Thus, given their self-organization into fluid one-dimensional columnar array coupled with light generating capability, these organic ordered-fluids can be regarded as novel media for advanced technological applications.

Since 1977 when Chandasekhar et al.[1] discovered columnar (Col) liquid crystal (LC) phases in benzene-hexa-*n*-alkanoates, there has been a phenomenal growth in research activity relating to the rational molecular design and synthesis of structurally diverse organic molecules capable of exhibiting such mesophase(s).[2] This is because Col phases, generally formed by the spontaneous self-assembly of shape-anisotropic π-conjugated molecules into fluid columnar stacks, are highly anisotropic and ordered structures with extensive π-orbital overlap leading to a high degree of uniaxial charge-carrier mobilities. Besides, they can be readily and repeatedly processed from the isotropic melt of mesogens to eliminate structural/electronic defects when compared to single-crystals or inorganic semiconductors used in technological applications.[2,3] They have been recognized as potential media for hole- and electron-transports given the fact that the measured charge-carrier mobility value in some Col LCs exceeds 1 $cm^2 V^{-1} s^{-1}$.[4] Thus, Col phases hold immense promise in electronic devices such as photovoltaic cells,[3] field effect transistors[5] and organic light emitting devices (OLEDs).[6]

Their usage in fabricating OLEDs is especially significant if an additional parameter such as the transport of excitation energy, the luminescence behavior, is incorporated in the constituent mesogens; in fact, the intrinsic photoluminescence property enables the Col phases to serve as emissive layers as well in OLEDs. Thus, in recent years there has been a growing interest in developing luminescent organic molecules exhibiting columnar behavior where a large variety of shape-anisometric motifs bearing fluorophores have been reported.[7] Among these, 1,3,5-triazine-based LCs[8] appear to be suitable substances in view of the fact that 1,3,5-triazine core possesses strong electron affinity when compared to other aromatic rings.[9] Although a large number of triazine-based compounds have been prepared,[8] the efforts in design and synthesis of such functional materials capable of exhibiting luminescent Col phase existing between well below, and above the ambient temperature, a vital feature required for device performance, are absolutely necessary.

In order to achieve these goals, C_3-symmetric three-armed star-shaped compounds **Ia** and **IIa–b** have been rationally designed, synthesized, and probed for their physical properties. Scheme 1 depicts the general molecular structure of these systems. As can be seen, they contain three 1,2,3-tris(alkoxy)-5-styrylbenzenes, as fluorophore arms, linked covalently to a central electron-deficient 1,3,5-triazine core. Here, styryl arms not only accounted for the effective conjugation but also serve as electron-rich cores as they possess electron-donating branched alkoxy tails. These branched alkoxy chains have been especially chosen given the experimental observation that they reduce melting (crystal-to-Col phase) transition temperatures and thus, widen the thermal range of the required LC phase. They are also known to lower the clearing (Col-to-isotropic liquid phase) transition temperatures.[2,10] In fact,

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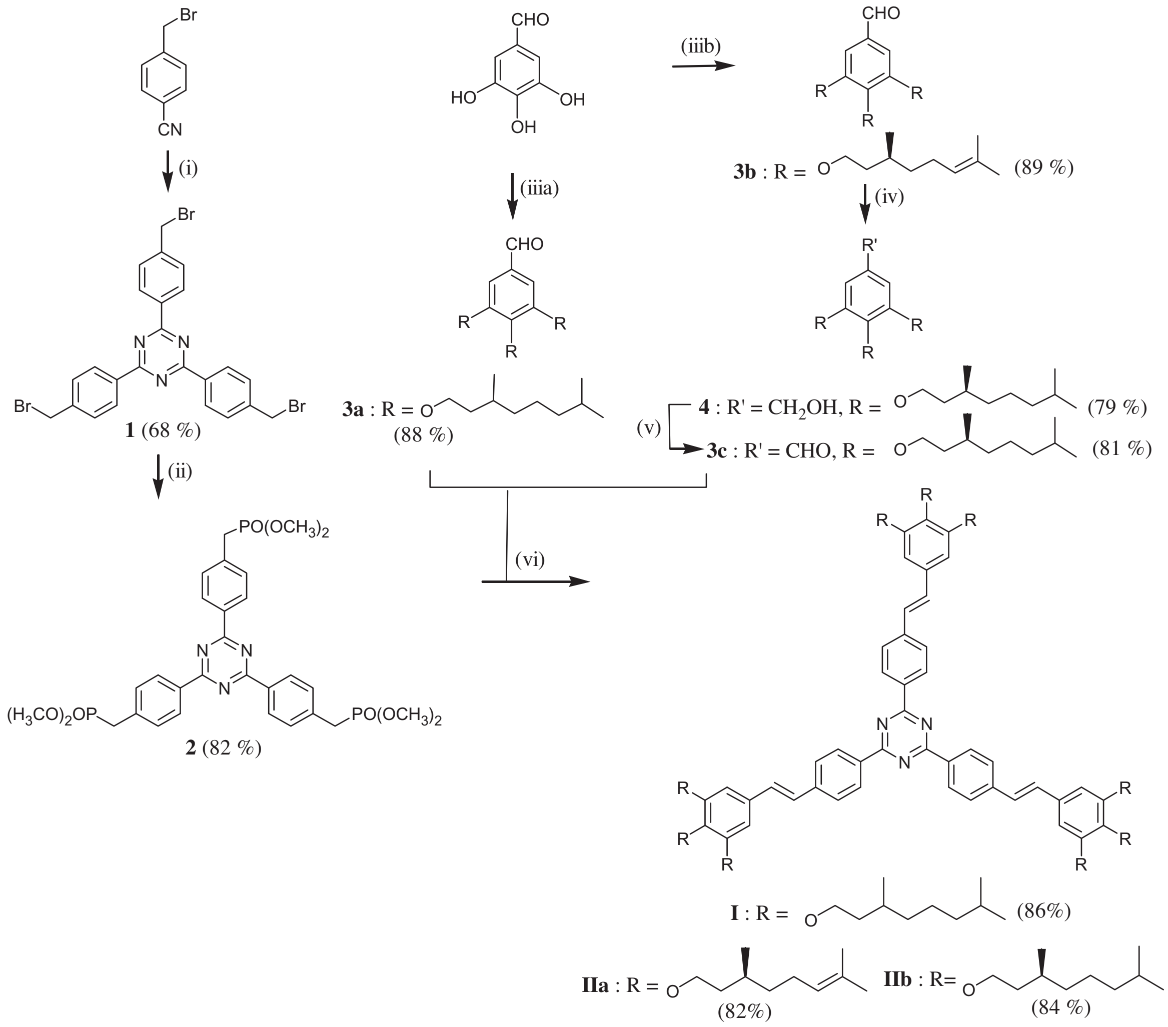

Scheme 1. Reagents and conditions: (i) CF_3SO_3H, CH_2Cl_2, 0 °C, 12 h. (ii) Trimethyl phosphite, reflux, 5 h. (iiia) 1-Bromo-3,7-dimethyloctane, anhyd. K_2CO_3, DMF 80 °C, 12 h. (iiib) (*S*)-(+)-Citronellyl bromide, anhyd. K_2CO_3, DMF 80 oC, 12h. (iv) H_2/Pd–C, abs. EtOH, rt, 8h. (v) PCC, CH_2Cl_2, rt, 1 h. (vi) *n*-BuLi, THF, 12 h.

we opted to employ branched achiral, (3,7-dimethyloctan-1-oxy) and chiral [(*S*)-3,7-dimethyloct-6-en-1-oxyand (*S*)-3,7-dimethyloctan-1-oxy] to realize both achiral and chiral star-shaped compounds and to understand the structure-property correlation. In essence, the molecular design, which represents the first of its kind, consists of 1,3,5-triazine core and styryl arms substituted with branched achiral/chiral terminal tails.

Specifically designed target C_3 symmetric compounds **I** (achiral) and **IIa–b** (chiral) have been prepared by the route outlined in Scheme 1. Cyclotrimerization of 4-(bromomethyl)-benzonitrile upon treating with trifluoromethanesulfonic acid yields 2,4,6-tris(4-(bromomethyl)phenyl)-1,3,5-triazine (**1**).[11a] The Arbuzov reaction of **1** and trimethyl phosphite under reflux for 12 h affords the key intermediate, hexamethyl (4,4’,4”-(1,3,5-triazine-2,4,6-triyl)tris-(4,1-phenylene))tris(methylene)triphosph-onate (**2**), in an 82% yield.[11b] Williamsons reaction, the O-alkylation, of 3,4,5-trihydroxybenzaldehyde with 1-bromo-3,7-dimethyloctane and (*S*)-(+)-citronellyl bromide furnish 3,4,5-tris(3,7-dimethyloctyloxy)benzaldehyde (**3a**)[8] and 3,4,5-tris((*S*)-3,7-dimethyloct-6-enyloxy)benzaldehyde (**3b**), respectively. Subjecting aldehyde **3b** to Pd/C-catalyzed hydrogenation gives (3,4,5-tris((*S*)-3,7-dimethyloctyloxy)phenyl)methanol (**4**) which oxidizes in the presence of PCC yielding 3,4,5-tris((*S*)-3,7-dimethyloctyloxy)benzaldehyde (**3c**).[12] In the key step of synthesis, the reaction of triphosphonate **2** under Horner-Wadsworth-Emmons conditions (HWS) with aldehydes **3a–c** furnish the necessary star-shaped target compounds **I** and **IIa–b** in good yields (82-86%). These compounds have been fully characterized with the help of spectroscopic viz., UV–vis, FT-IR, ^1H and ^{13}C NMR, MS, techniques, and microanalytical data.

As expected, they show nearly similar spectral (UV–vis, IR, ^1H and ^{13}C NMR) patterns. The ^1H and ^{13}C NMR spectra are especially found to contain the anticipated spectral patterns that assist in elucidating the proposed structures of the compounds unambiguously. For example, olefinic protons of the styryl moiety resonate as a quartet at δ 7.17–7.22 with the vicinal coupling constant (J) of 16–16.4 Hz, indicating the *trans* configuration of the double bond; the 18 aromatic protons appear at δ 8.77–8.78 (d, 6H, J = 8.4 Hz), 7.7–7.71- (d, 6H, J = 8.4-8.48 Hz) and 6.79 (s, 6H). However, the mesogen **IIa** shows an additional multiplet pattern in the region δ 5.11–5.14 arising due to olefinic proton of the peripheral alkoxy tails. The ^{13}C spectra (downfield from the $CDCl_3$ peaks; a 1:1:1 triplet at $\delta = 77$) of mesogens **I** and **IIb** show the expected eleven signals; while the spectrum of **IIa** possesses four peaks additionally. Notably, the signal at δ 171.15 commonly found in all the three spectra arises due to the carbons of *s*-triazine core.

The synthesized compounds **I** and **IIa–b** have been examined for their LC properties with the help of multiple, complementary experimental techniques. First, the occurrence of LC behavior in these compounds at room temperature (rt) was immediately apparent as they were isolated as a sticky yellow mass, which could be readily spread with the aid of a glass rod/spatula. To corroborate this observation both polarizing optical microscope (POM) and differential scanning calorimeter (DSC) investigations were performed on the samples. The results of these studies of compounds **I** and **IIa–b** have been summarized in Table 1 and discussed in more detail in the following paragraphs.

The textural patterns of the samples confined between untreated, clean glass substrates were observed by POM. The sheared (mechanically stressed) samples at rt exhibit nonspecific, highly birefringent pattern. However, on heating the samples till their clearing temperature followed by cooling gradually, they show a mesophase having specific, informative textural pattern emanating strikingly from the dark background of isotropic liquid. For example, when a thin film of compound **I** is gradually cooled from the isotropic phase, the LC phase sets in at 71.9 °C manifesting optically, as shown in Figure 1, in the form of a pattern featuring the combination of mosaics with elongated birefringent defects and homeotropic domains. This pattern is well-known to be an important signature and conclusive evidence for the occurrence of Col phase.[2] On lowering the sample temperature further, neither any other textural change nor crystallization of the sample were seen till room temperature implying that the Col phase once formed upon cooling from the isotropic phase, crystallizes by no means instead it remains unaltered. The chiral compounds **IIa** and **IIb** exhibit analogous behavior with the exception that mosaic and homeotropic domains in the optical texture of Col phase appear relatively tiny.

In all the cases, the extent of occurrence of the mesophase below the ambient temperature could not be determined in the optical study due to limitations of the experimental setup. However, this information could be obtained with the help of calorimetric study. In the DSC traces, obtained during the first heating-cooling cycles, as shown in Figure 2, no exothermic (from just below the Iso-Col to −40 °C) or endothermic (from −40 °C to near the Col-Iso transition) peaks exist for these three samples. Most importantly, these features of DSC traces found to be highly reproducible for any number of heating-cooling cycles indicate clearly that these compounds stabilize Col phase below and above the room temperature. Further, the chemical stability of the samples has been ascertained by taking DSC scans after keeping the samples very close to their clearing temperatures for 6–7 h and noted that the transition temperatures agree well with the previous runs. It is immediately apparent from the results accumulated in Table 1 that the phase transition temperatures and thus, the thermal width of Col phase of the three compounds vary significantly although their peripheral branched-alkoxy tails possess an identical carbon skeleton. That is, compound **I** possessing achiral branched (3,7-dimethyloctan-1-oxy) tail shows higher clearing temperature and thus, wider thermal range of Col phase when compared to that of chiral analogues **IIa** and **IIb**. Among the chiral compounds **IIa** and **IIb**, the former (with olefinic-bond in the chiral tail) stabilizes the Col phase over a slightly higher thermal range than the latter (without olefinic-bond in the chiral tail). These findings clearly suggest that the presence or absence of molecular chirality and double bond greatly affect the phase behavior of the star-shaped mesogens.

The photophysical characteristics of the synthesized star-shaped mesogens have been studied both in solution and fluid Col states at room temperature by UV–vis absorption and

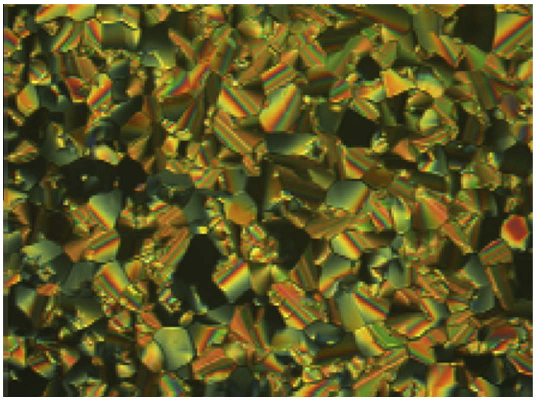

Figure 1. Optical texture of the Col phase shown by **I** at 70 °C.

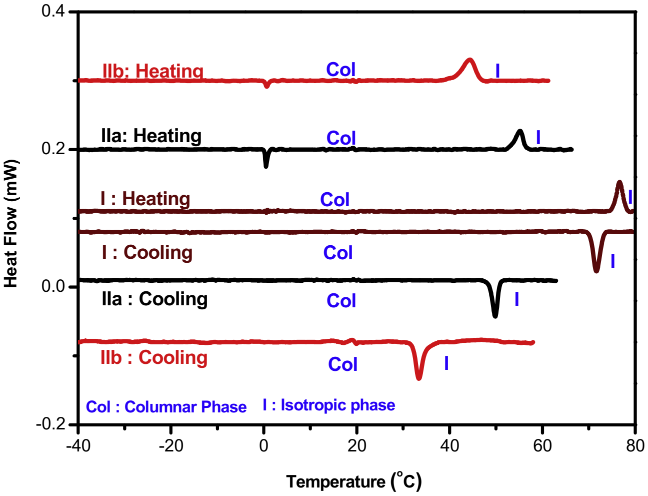

Figure 2. DSC thermograms of mesogens **I** and **IIa–b**.

Table 1

Phase transition temperatures (°C)[a] and associated enthalpies (J/g), and photophysical (absorption and emission) properties of **I** and **IIa–b**. Col = Columnar phase; Iso = Isotropic phase, rt = room temperature

Compound	Phase sequence	Dichloromethane solution [c]			Columnar LC phase at rt		
	Heating; cooling	Absorption λ_{max} (nm)	Emission [d] λ_{max} (nm)	Stokes shift (nm)	Absorption λ_{max} (nm)	Emission [d] λ_{max} (nm)	Stokes shift (nm)
I	Col 76.6 (0.5) I; I 71.9 (0.55) Col [b]	290 [e], 383	543	160	291 [e], 376	509	133
IIa	Col 55.2 (0.49) I; I 49.9 (0.75) Col [b]	289 [e], 381	542	161	293 [e], 376	508	132
IIb	Col 44.4 (0.42) I; I 33.3 (0.83) Col [b]	292 [e], 381	542	161	289 [e], 378	508	130

[a] Peak temperatures in the DSC traces recorded during the first heating-cooling cycles at 5 °C/min.
[b] No other phase transition was observed till −40 °C.
[c] Micro molar concentration.
[d] Excitation wavelength (λ_{ex}) = 380 nm.
[e] Shoulder adjoining the main (intense) peak.

photoluminescence. The results have been accumulated in Table 1. The absorption and luminescence spectra of solutions in CH_2Cl_2 of compounds **I** and **IIa–b** were found to be nearly identical, as shown in the top panels of Figure 3. In fact, the spectral pattern and the absorption and emission intensity appear to be independent of the concentration of compounds in solution within the working concentration ranging from 5.5×10^{-6} to 6.5×10^{-6} mol L^{-1}. As can be seen in the top panel of Figure 3, all the three mesogens show two absorption maxima centered around 290 nm and 380 nm corresponding to the π–π^* and n–π^* transitions originating due to high absorption coefficients; this means that these mesogens readily absorb photons. By irradiating these solutions with 380 nm light, fluorescence maximum occurs at around 540 nm. This is in agreement with the general observation that the emission occurs at a longer wavelength than the absorption. The visually perceivable green light in the emissive state has been shown in the inset of Figure 3. In all the cases, the Stokes shift, the difference between positions of the band maxima of the absorption, and emission spectra, were found to be nearly 160 nm (Table 1). The absorption and emission spectra of fluid Col phase at rt have been recorded for the mesogens held between two quartz plates. They show two absorption bands analogous to the solution state (see the lower left-portion of Fig. 3 and Table 1). As shown in the lower right-portion of Figure 3, upon excitation with 380 nm light, they exhibit an intense broad signal with photoluminescence maximum at 508 nm; the inset of Figure 3 shows visually perceived green light in the emissive state evidencing the preservation of optical properties in fluid columnar assembly. It can be seen that the emission band of the fluid phase appears at a relatively lower wavelength when compared to that of solution state. This blue-shift can be attributed to the degree of intermolecular interactions within the Col structure (local order) and the thickness (viscosity) of the sample. Specifically, such a blue-shift observed earlier in the Col phase has been assumed to be associated with the lowering of the magnitude of disorder along the column and a decrease in the ability of the molecules to form self-quenching aggregates.[13] Seemingly, the large Stokes shift values of these films are of the same magnitude as in solution. These results point toward the high charge transfer efficiency and conformation relaxation in the excited state of the molecules. On the whole, Stokes shifts of the absorption and emission wavelengths are almost identical implying that photophysical properties of the three mesogens are the same. It may also be pointed out here that the Col phase of the chiral compounds **IIa–b** was found to be CD inactive implying that molecular chirality has not facilitated molecular organization in helical fashion in the LC (Col) phase.

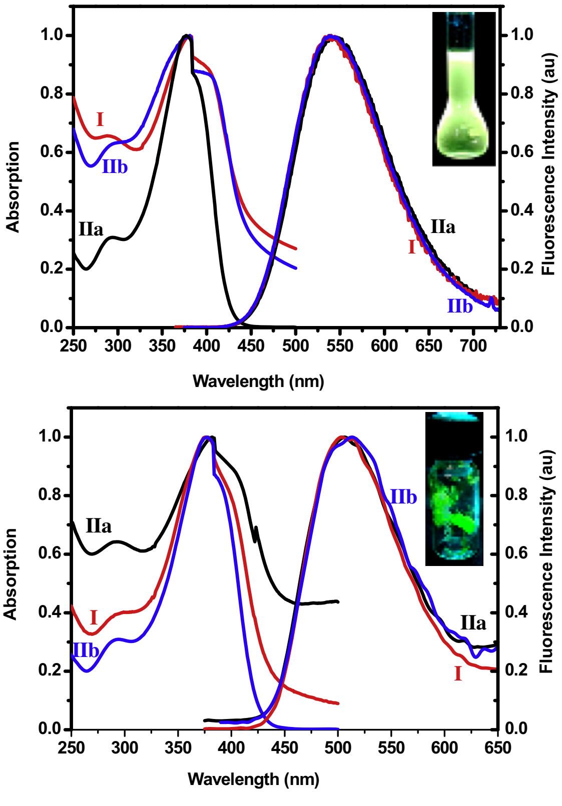

Figure 3. UV–vis absorption (left regions) and emission (right portions) spectra of compounds **I** and **IIa–b** in their solution (top panel) and mesomorphic (lower panel) states. Insets in the top and bottom panels show the pictures of solution and Col states respectively, as seen after the illumination of the light of 354 nm.

In summary, the first examples of photoluminescent, room temperature Col LCs derived from a combination of *s*-triazine and styrylbenzene cores have been prepared by three fold HWS reaction of triphosphonate with achiral/chiral aldehydes, and characterized. The thermal width of the Col phase, which is remarkably high, depends on the nature of the peripheral alkoxy tails. Whereas the photophysical properties found to be independent of such a structural parameter as all the three mesogens behave analogously in this respect with a large Stokes shifts both in solution and mesomorphic states. These mesogens and /or their future variants might thus turn out to be appropriate candidates for various technological applications.

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