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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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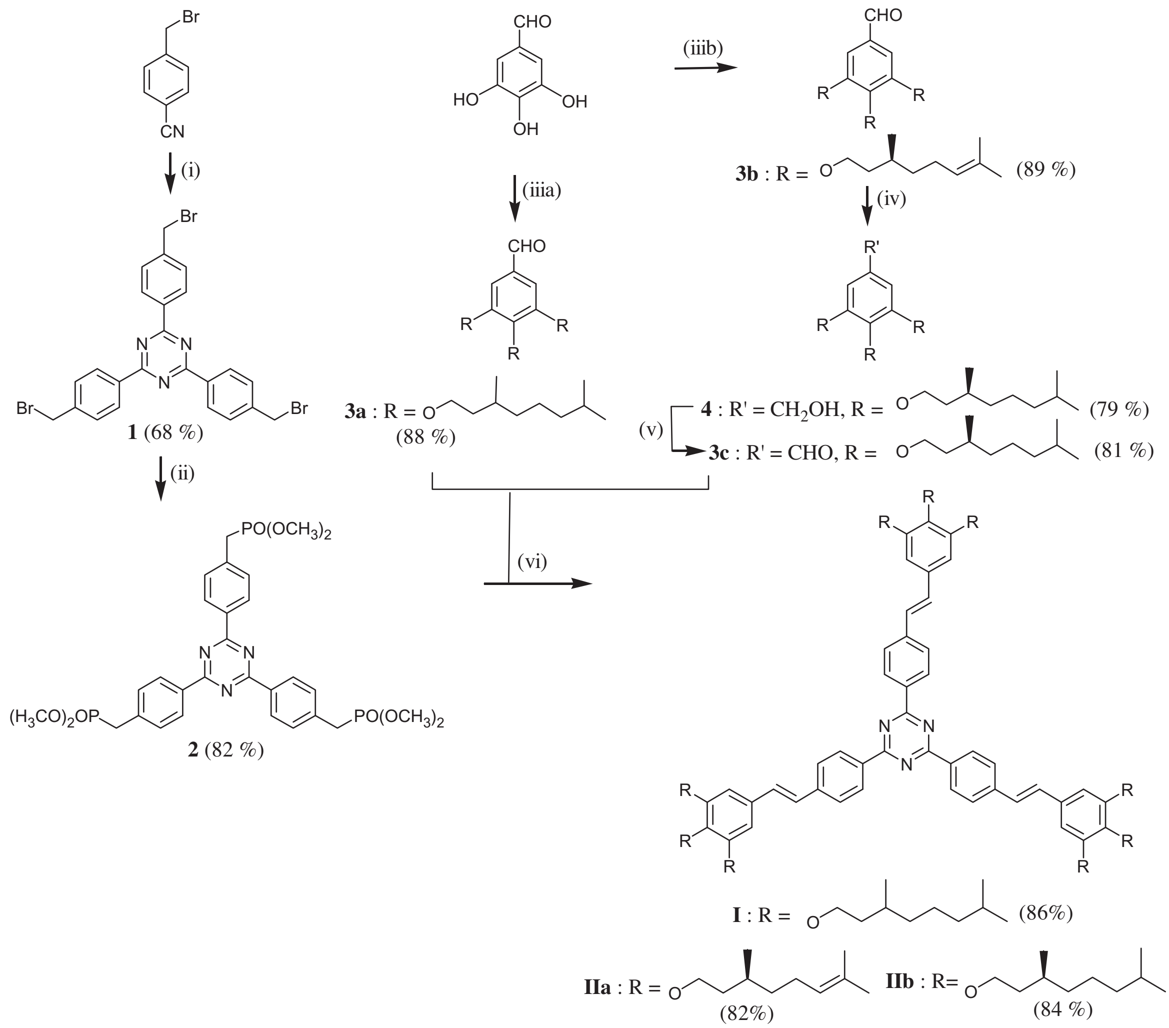

Scheme 1. Reagents and conditions: (i) CF_3SO_3H, CH_2Cl_2, 0 °C, 12 h. (ii) Trimethyl phosphite, reflux, 5 h. (iiia) 1-Bromo-3,7-dimethyloctane, anhyd. K_2CO_3, DMF 80 °C, 12 h. (iiib) (*S*)-(+)-Citronellyl bromide, anhyd. K_2CO_3, DMF 80 oC, 12h. (iv) H_2/Pd–C, abs. EtOH, rt, 8h. (v) PCC, CH_2Cl_2, 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, ^{1}H and ^{13}C NMR, MS, techniques, and microanalytical data.

As expected, they show nearly similar spectral (UV–vis, IR, ^{1}H and ^{13}C NMR) patterns. The ^{1}H 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 δ = 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