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Light emitting, star-shaped tris(*N*-salicylideneaniline) discotic liquid crystals bearing *trans*-stilbene fluorophores: synthesis and characterization

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A B S T R A C T

Star-shaped tris(*N*-salicylideneaniline) discotics possessing *trans*-stilbene fluorophores have been synthesized by condensing 1,3,5-triformylphloroglucinol with 4-(alkoxystyryl)benzen-amines, and characterized. ^{1}H and 2D ^{1}H–^{1}H COSY NMR experiments reveal their occurrence in two inseparable keto-enamine tautomeric forms featuring C_{3h} and C_s rotational symmetries. Their columnar liquid crystal behavior has been ascertained unequivocally with the aid of a polarizing optical microscope and a differential scanning calorimeter. Photoluminescence property has been examined both in solution and columnar states. Green light emission observed in the solution state is especially noteworthy. Thus, intrinsic self-assembly into a fluid columnar state exhibiting light emission property clearly illustrates their significance in technological applications.

In the past few decades, π-conjugated organic compounds, such as small molecules (monomers), oligomers and polymers, have been extensively studied[1] because of their ability to serve as an essential chemical component in the fabrication of devices viz., organic light emitting diodes (OLEDs),[2] photovoltaic cells,[3] field effect transistors (FETs)[4] etc. Molecular crystals derived from such substances are especially promising as they exhibit light absorption and emission in the visible region, photoconductivity, and electrical conductivity, and thus behave like semiconductors. Given the fact that electronic transport in semiconductors is often perturbed by residual impurities and/or chemical or morphological defects, accomplishing organic crystals free from such errors is rather essential. [1a] As is well known, realizing ultrapure and defect free organic crystals is extremely difficult as their synthesis involves multiple steps.[1] However, molecular self-organization phenomenon has been regarded as one of the important and alternative strategies for the development of supramolecular structures facilitating directional charge transport and photophysical properties.[5–7]

Columnar (Col) liquid crystal (LC) phases,[6] discovered by Chandrasekhar and co-workers in 1977,[7] are one of the best-known and most widely studied examples of such supramolecular structures. They, being highly anisotropic and ordered structures, have attracted much attention not only for their use in designing electronic and optoelectronic devices[6,8] but also for academic reasons.[6] In general, they are formed by the self-assembly of disc-like molecules, discotics, into indefinitely long columnar stacks that in turn aggregate into two-dimensional (2D) lattices of different symmetries.[6,7] Notably, individual columns of the phase serve as molecular wires as the central aromatic core of the constituent discotics act as the conducting unit, while peripheral flexible tails behave as an insulator. In other words, the extensive π-orbital overlap of the discotics within the column leads to a high degree of uniaxial charge-carrier mobilities. In fact, Col phases possess a remarkable ability to transport electrons[9] and holes.[10] Another important aspect is that they can be easily processed from the isotropic liquid phase of discotics to lessen/eliminate the structural/electronic defects. [6] Thus, Col phases can be used as the media in OLEDs,[11] solar cells[12] and FETs.[13] Discotics have been also used as the electron and hole transport layers in device fabrication.[8,11] Most importantly, for the purpose of using them as emissive layer as well, there have been constant efforts in realizing discotics exhibiting high fluorescence.[6,8,14,15]

In this work, we report the synthesis and characterization of novel fluorescent discotics derived from tris(*N*-salicylideneaniline) [TSANs] where an electron accepting central core, cyclohexane-1,3,5-trione, is substituted, for the first time, with *trans*-stilbene fluorophores. For some time now, we have been working on discotic TSANs to reveal their structure-property correlations.[16–18] Such compounds are rather special as they can be readily obtained in good quantities through simple, high yielding synthetic steps, and most appreciably, they exhibit fluid/frozen columnar supramolecular structures capable of displaying tunable photoluminescence.[16–20]

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Thus, the design of present work originated from the fact that TSANs provide unique ways to infuse and tune both luminescence and molecular material features. For example, we have demonstrated that a TSAN appended with three fluorophore 1,3,4-oxadiazole arms displays emissive characteristics both in solution and Col phase.[17] Notably, solution emitted intensive blue fluorescence, while glassy/fluid Col phase displayed light emission behavior with inherent 2D order. In continuation of this work we chose to introduce a stilbene core as it is one of the most widely explored conjugated organic systems in devising luminescent materials.[21] Precisely, we intended to append three stilbene cores with dialkoxy and trialkoxy tails, as fluorophore arms, to a central cyclohexane-1,3,5-trione core so as to realize scarcely reported fluorescent discotic LCs. The molecular structures of the accomplished discotic TSANs, **Ia–c** and **IIa–c**, existing in two inseparable keto-enamine tautomeric forms, are shown in Figure 1.

The synthetic steps adopted to realize the target TSANs and their precursors are shown in Scheme 1. The benzylic bromination of 4-nitrotoluene with *N*-bromosuccinimide (NBS) in the presence of catalytic amount of azobisisobutyronitrile (AIBN) afforded 4-nitrobenzyl bromide (**1**) in 80% yield; the Michaelis–Arbuzov reaction of this bromide with triethyl phosphite yielded diethyl(4-nitrobenzyl)phosphonate (**2**). Horner–Wadsworth–Emmons (HWE) reaction between 3,4-dialkoxybenzaldehydes (**3a–c**) and **2** in the presence of lithium diisopropyl amide (LDA in THF at −78 °C furnished 1,2-bis(alkoxy)-4-(4-nitrostyryl)-benzenes (**4a–c**) which on reduction with indium powder in hydrochloric acid at room temperature yielded 4-(3,4-bis(alkoxy)styryl)benzenamines (**5a–c**). Ethyl 3,4,5-trialkoxy-benzoates (**6a–c**) were treated with lithium aluminium hydride (LAH) in THF at 0 °C to obtain (3,4,5-tris(alkoxy)phenyl)-methanols (**7a–c**) which upon oxidation with pyridinium chlorochromate (PCC) in dichloromethane gave 3,4,5-trialkoxy-benzaldehydes (**8a–c**). Subsequent reaction of these aldehydes with phosphonate **2** under HWE reaction conditions resulted in the formation of 4-(3,4,5-tris(alkoxy)styryl)nitrobenzenes (**9a–c**) which upon subjecting to reduction yielded 4-(3,4,5-tris(alkoxy)-styryl)benzeneamines (**10a–c**). Finally, three folds of amines **5a–c** and **10a–c** were respectively, reacted with 1,3,5-triformylphloroglucinol in refluxing ethanol to accomplish the target TSANs **Ia–c** and **IIa–c** as dull yellow crystalline samples, which were repeatedly recrystallized from ethanol until constant melting and clearing temperatures were observed. Pure, bright yellowish, solid samples thus obtained were fully characterized on the basis of microanalyses and UV–Vis, FTIR and NMR spectral data.

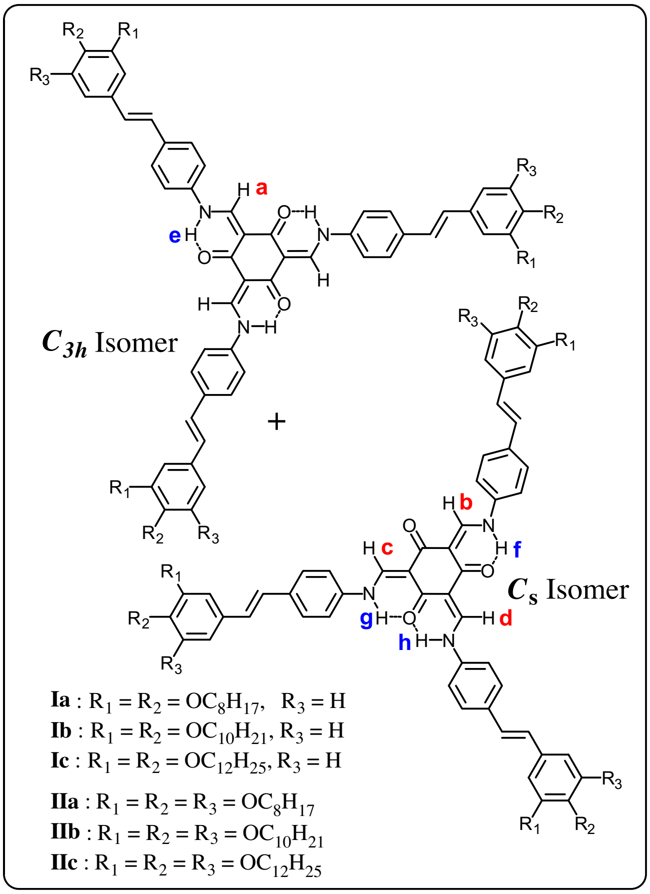
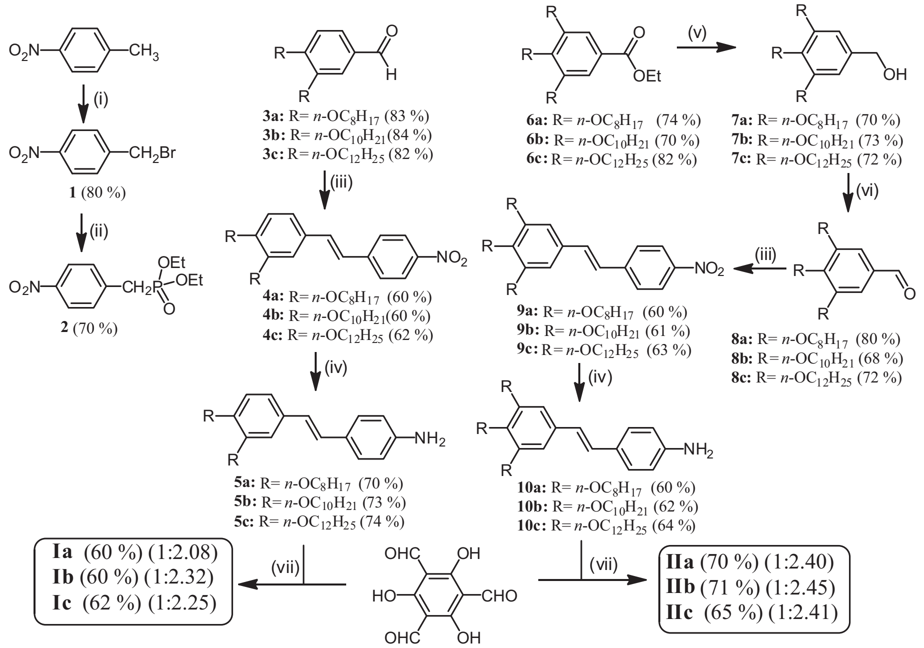


Figure 1. The molecular structure of discotic TSANs existing in two inseparable keto-enamine tautomeric (C_{3h} and C_s) forms.

The IR spectra of the TSANs showed two prominent, sharp bands in the region of 1618–1620 and 1513–1574 cm^{-1}, perhaps assignable, respectively, to the C=O and C=C groups of the central, highly conjugated core. The ^{1}H NMR spectra recorded in CDCl$_3$ were well resolved and found to possess the expected spectral pattern. Notably, as shown in Figure 2, as a representative case, multiple peaks were observed in the region of δ 8.7–9.0 and 13–13.5 due to enamine and 2°-amine protons and their coupling. The former region comprised of two distinct doublets as well as two merged doublets (with varying intensities), all arising due to the resonance of a proton (H**a**) of C_{3h} isomer and three protons (H**b**, H**c** and H**d**) of C_s form. While the latter region consisted of three distinct doublets differing in their relative intensities; each of these originate due to the resonance of an amine proton (H**e**) of C_{3h} isomer and three analogous protons (H**f**, H**g** and H**h**) of C_s isomer. ^{1}H–^{1}H COSY NMR spectrum (see inset of Fig. 2) further evidenced the coupling among the enamine and the NH protons.[16–19] The identified NMR peaks and patterns are in good agreement with those reported for discotic TSANs existing in an inseparable mixture of two keto-enamine tautomeric forms having C_{3h} and C_s symmetries.[16–19] It may be noted here that the integrations of the amine peaks have been considered for estimating the ratio of the two geometrical isomers and is shown against each discotic TSAN in Scheme 1. The occurrence of these discotics in keto-enamine (NH) form, instead of enol-imine (OH) form, can be interpreted in terms of electronic factors such as localization/delocalization of electrons and the extent/strength of H-bonding leading to the generation of an additional, thermally and hydrolytically stable, *pseudo*-aromatic ring. Precisely, the strong electron-pulling ability of the central ring and electron-pushing nature of substituents over the imine functionality leads to a substantial withdrawal of the negative charge from the oxygen atom in the OH group facilitating the proton transfer to the nitrogen atom of the imine group leading to the formation of NH isomers.

Liquid crystal behavior of the synthesized discotics was investigated by two complementary experimental techniques: (i) polarizing optical microscopy (POM) and (ii) differential scanning calorimetry (DSC). The results emanating from these studies are accumulated in Table 1. From these results it can be seen that all the TSANs exhibit enantiotropic LC behavior, in particular, Col phase that was ascertained by the observation of characteristic optical textures. The crystalline sample **Ia**, held between two untreated glass substrates, upon heating melts into Col mesophase at about 125 °C that transforms into isotropic state at ~218 °C. On cooling from the isotropic liquid, the transition to Col phase occurs at ~215 °C, which grows as a fern leaf (Fig. 3a); such a textural pattern is commonly seen for the columnar phase.[6] On further cooling, it develops into large pseudo focal conic fans covering the field of view and supercools till it reaches room temperature (RT) where it becomes highly viscous. The DSC traces of the first heating-cooling cycles corroborate the optical observation



Scheme 1. Reagents and conditions: (i) NBS, AIBN, CCl_4, reflux, 6 h; (ii) triethyl phosphite, 130 °C, 6 h; (iii) **2**, LDA, THF, −78 °C to rt, 12 h; (iv) indium powder, concd HCl, THF (1:9), rt, 2 h; (v) LAH, THF, 0 °C to rt, 12 h; (vi) PCC, DCM, rt, 1 h; (vii) ethanol, 80 °C, 6 h.

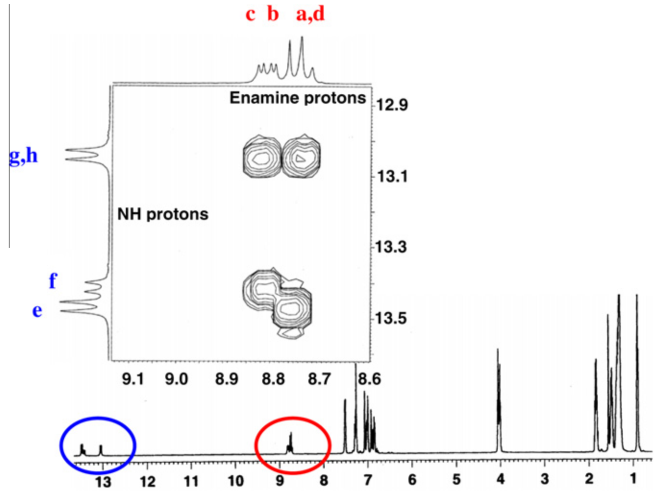


Figure 2. ^{1}H NMR spectrum of discotic **Ia** in $CDCl_3$; inset shows the ^{1}H–^{1}H COSY NMR spectrum of the same compound where the coupling among enamine and amine protons can be seen.

Table 1
Phase transition temperatures (°C)[a] and associated enthalpies (J/g), of star-shaped discotics **Ia–c** and **IIa–c**. Cr = Crystal; Col = Columnar phase; Iso = Isotropic phase

TSANs	Phase sequence Heating; cooling
Ia	Cr 125.6 [20.2] Col 218.4 [1] I; I 214.9 [0.9] Col 1.3 [0.6] Cr
Ib	Cr 111.2 [8.1] Col 229.2 [1.2] I; I 226.6 [1][b] Col
Ic	Cr 107 [35.3] Col 239.5 [1.7] I; I 237 [1.5][b] Col
IIa	Cr 72.4 [1.4] Col 240.4 [1.1] I; I 236.3 [1.1][b] Col
IIb	Cr 70.1 [1.4] Col 226.2 [1.4] I; I 220 [1.2][b] Col
IIc	Cr 66.5 [1.5] Col 199.5 [1.6] I; I 196.5 [1.4][b] Col

[a] Peak temperatures in the DSC traces obtained during the first heating—cooling cycles at 5 °C/min.

[b] The Col phase did not crystallize up to −50 °C.

(Fig. 3b); importantly, the cooling trace indicated that the Col phase transforms in to crystal state at ~1 °C. The higher members **Ib** and **Ic** showed an identical behavior. That is, the observed optical textural pattern for the mesophase of these two discotics was indistinguishable to the one seen for **Ia**. In fact the mesophases of these three compounds could be well mixed and thus, it is logical to adjudge that compounds **Ia**, **Ib** and **Ic** stabilize a Col phase of the same nature. However, it may be remarked here that the Col phase of **Ib** and **Ic**, unlike in the case of **Ia**, does not crystallize and instead it supercools well below the RT (−50 °C). Next three discotic TSANs, **IIa**, **IIb** and **IIc** derived from 3,4,5-tri-alkoxystilbene cores, display mosaic textural pattern upon cooling from their isotropic liquid state. Figure 4a depicts, as a representative case, such a pattern observed for discotic **IIa**. No textural change was observed even when the samples were cooled down to RT. However, the samples lose their fluidity at about 60 °C suggesting that Col phase freezes into the glassy state at about this temperature. The frozen Col state remains unchanged till −50 °C as evidenced by DSC traces, for example see Fig. 4b. Thus, compounds **IIa–c** behave identically with the exception that their melting temperature (T_m) and clearing temperature (T_c) decrease with the increase in the length of terminal tails. Overall, it is immediately apparent that TSANs **Ia–c** show higher T_m values when compared to that of **IIa–c**. This disparity originates because **Ia–c** comprise six peripheral chains while **IIa–c** possess nine.

These star-shaped discotics are anticipated to exhibit photophysical properties as they are made by tethering three fluorophore arms with an electron accepting central core. Thus, the optical absorption and fluorescence behavior of **Ia** and **IIa**, as representative cases, were studied in solution and mesophase. The top panels of Figure 5a,b show the UV–Vis and photoluminescence spectra of **Ia** and **IIa** in solution (THF). The absorption spectra (blue traces) of the two compounds show two bands at about 350 nm and 440 nm corresponding to π–π^* and n–π^* transitions. Upon irradiation with 440 nm light, emission maxima occur at around 510 nm and 505 nm (top panel, orange traces) for **Ia** and **IIa**, respectively. Solutions of the compounds, placed in quartz cuvettes, before, and after light irradiation are shown in the inset of

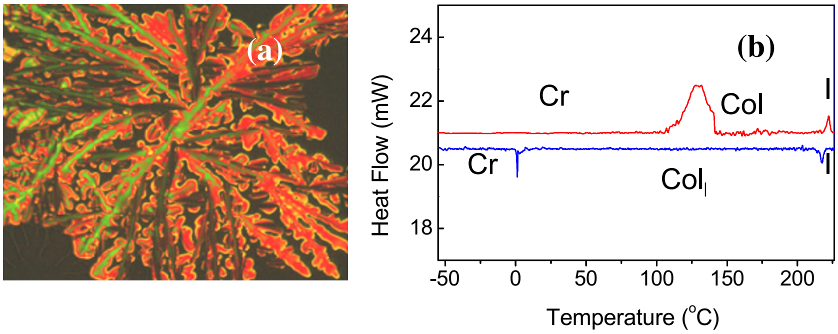


Figure 3. (a) Microphotograph of the optical texture observed for the Col phase of **Ia** at 211 °C. (b) DSC traces of the first heating-cooling cycles obtained for **Ia**.

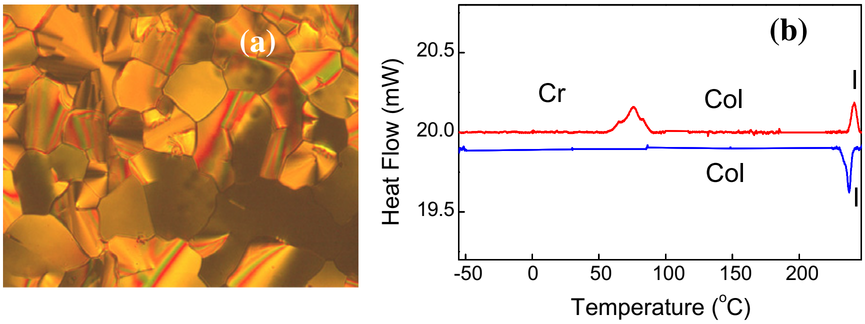


Figure 4. (a) Photomicrograph of the mosaic texture for the Col phase of **IIa** at 78 °C. (b) DSC traces of the first heating-cooling cycles recorded for **IIa**.

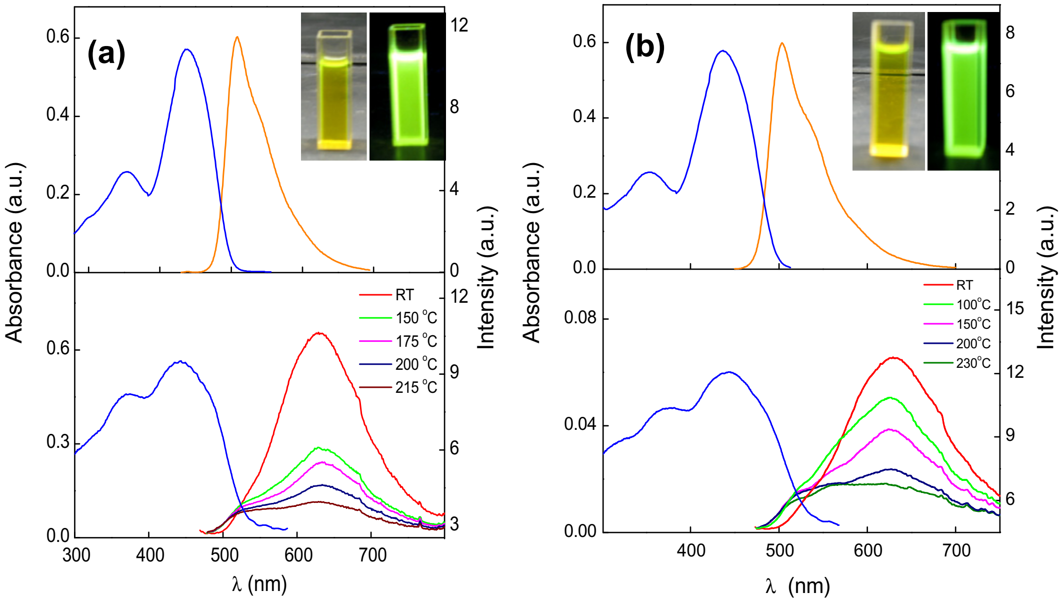


Figure 5. UV–Vis (left peaks) and emission (right peaks) spectra of **Ia** and **IIa** in their solution (top panels) and Col phase (lower panels). Insets show the pictures of solution as seen before and after illumination with 365 nm light.

Table 2
Photophysical properties of discotics **Ia** and **IIa**

	THF solution[a]			Glassy film		
TSANs	Absorption[b]	Emission[b,c]	Stokes shift[b]	Absorption[b]	Emission[b,c]	Stokes shift[b]
Ia	353, 442	510	68	366, 442	629	187
IIa	353, 440	505	65	370, 444	629	185

[a] micromolar solutions in THF.
[b] Wavelengths (nm).
[c] The excitation wavelength λ_{ex} = 440 nm.

top panels of Figure 5a,b where the visually perceivable green light in the emissive state can be seen. As shown in Table 2, the Stokes shifts, the difference between positions of the band maxima of the absorption and emission spectra, were found to be nearly over 60 nm. The lower panels of Figure 5a,b illustrate the absorption spectra of the frozen Col phase (blue traces) and the photoluminescence spectra recorded at different temperatures while cooling the Col phase from isotropic phase till RT. Analogous to the solution spectra, the UV–Vis spectra of the frozen Col state at RT display two absorption bands. Upon excitation with 440 nm light, both the films, at RT, show a broad emission band at 629 nm with a negligible shoulder (see red traces of lower panels of Figure 5a,b). The emission spectra of the fluid Col phase, recorded at four different temperatures, exhibit, as shown in the right hand side of lower panels of Fig. 5a,b, a broad emission band at around 630 nm. It can be seen that the intensity of the emission peak increases progressively with the decrease in the temperature; this can be attributed to breaking of larger columnar stacks into smaller ones and thermally activated radiationless processes.[22]

Apparently, the emission maxima of the neat/frozen Col phase, when compared to the solution, exhibit a strong bathochromic (red) shift that can be attributed to the strong co-facial proximity of C_{3h} and C_s isomers within the Col structure and perhaps the presence of excimers/aggregates. Generally, the excimers are regarded as molecular dimers or a stoichiometric complex with associated excited electronic states, dissociative ground states, and structure-less emission spectra.[23] In essence, the intimate overlap of the discotic cores in the fluid columnar/glassy state brings the energy levels closer and thus, a large red shift in the emission maxima occurs. Besides, to some extent, the thickness of the sample also contributes to the shift in emission wavelength. Therefore, for very thin (spin coated or vacuum deposited) samples there is the possibility that emission might shift toward the blue region. These results clearly illustrate the photoluminescence property of the present discotics both in solution and mesomorphic state and thus, further substantiate our view that discotic TSANs hold promise for diverse technological applications.

In conclusion, the synthesis and characterization of new discotic LCs derived from tris(*N*-salicylideneaniline)s are reported. The novelty of these discotics stems from the fact that three stilbene fluorophores, varying in the number and length of terminal chains, are joined to an electron accepting central core. All six compounds, occurring in two inseparable keto-enamine tautomeric forms featuring C_{3h} and C_s rotational symmetries, show Col LC behavior. Their solutions and fluid/glassy Col phases exhibit photoluminescence. In view of the fact that these TSANs stabilize light emissive Col phase, aided by the self-assembly of two tautomeric forms, they can be regarded as technologically important organic substances.

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