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## Room temperature columnar liquid crystalline self-assembly of acidochromic, luminescent, star-shaped molecules with cyanovinylene chromophores

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**Abstract** Two new star-shaped tris(*N*-salicylideneanilines) (TSANs) incorporated with cyanovinylene chromophores were prepared through a multistep synthesis. The position of the cyano group was altered in the target molecules, to understand its impact on the photophysical and thermotropic behavior, in comparison to the stilbene derivative without a cyano group. The presence of the cyano group enhanced the mesophase range in comparison to the non-cyano stilbene derivative. Further, this enhanced intermolecular interactions led to the stabilization of columnar rectangular phase in comparison to the columnar hexagonal phase of simple stilbene derivative. These compounds exhibited the freezing of columnar phase in a glassy state, which is beneficial from the device fabrication point of view. Thus the introduction of cyano group within the molecular structure of a star-shaped TSAN enhanced the intermolecular interactions and also altered the luminescence behavior. Such ordered luminescent molecular assemblies, which stabilize the columnar order over a long range are promising from the viewpoint of emissive displays. These compounds can be utilized for the sensing of volatile acids in solution at very low concentration (in parts per billion level) or in thin film state, either by fluorescence switching or quenching.

#### Introduction

Stilbene based molecules are gaining importance in material science due to their unique photophysical and photochemical properties. The energy levels of the vinylene chromophore in the molecular structure can be easily tuned by the appropriate molecular design aimed towards specific applications like organic light emitting diodes, solar cells, photoconductors, nonlinear optically (NLO) active materials, photoswitchable materials.<sup>1-4</sup> The ease of synthesis, structural tunability and planar molecular structure made them compatible in the design of self-assembled supramolecular structures like gels and liquid crystals.<sup>5-6</sup> The cyanostilbene chromophore is a widely studied molecular motif due to its interesting photophysical and aggregation behavior. This has also served as a fluorophore, which suppress the non-radiative decay due to the restriction of intramolecular rotations (RIR) and also led to the favorable arrangement of the

molecules in bulk or self-assembled structures that cooperatively led to an enhancement of emission.<sup>7</sup> This enhancement in the emission due to the aggregation in contrast to their solution state emission, is termed as aggregation induced emission (AIE).<sup>8</sup> Development of molecular materials to overcome the aggregation caused quenching (ACQ) of luminescence will be a desirable quality from the viewpoint of organic light emitting diodes (OLEDs).

Columnar (Col) liquid crystals (LCs) formed by the one-dimensional (1D) stacking of shape anisotropic molecules are interesting towards the application in organic electronics. They can be compared to 'molecular wires' due to the 1D stacking of central conjugated cores surrounded by the peripheral sheath of alkyl chains. They are termed as the next alternatives in comparison to organic single crystals and amorphous polymers.<sup>9</sup> Even though they lack the high charge carrier mobility in comparison to single crystals, they are far better in comparison to amorphous polymers, along with a good solution processability. Thus there are several nonconventional molecular designs that are utilized to stabilize functional Col phases, which are suitable for applications like OLEDs, solar cells or organic field effect transistors.<sup>10</sup> The design of emissive Col LCs suitable for the application in OLEDs, always comes with a hurdle of ACQ, due to the increased intermolecular interaction in Col phase.

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Recently, the topic of luminescent liquid crystals (LLCs) are attracting increasing attention,<sup>11</sup> as a new class of optical materials to overcome the inherent low brightness and poor energy efficiency of conventional LCs used in displays.<sup>12</sup> Development of such materials is of paramount importance in the advancement of anisotropic LEDs, polarized lasers, information storage devices, sensors or one-dimensional conductors.<sup>13</sup> However, having highly emissive molecules in solution does not guarantee the same in the condensed state due to the ACQ effect.<sup>14</sup>Recently an interesting phenomenon named as aggregation induced enhanced emission (AIEE) was reported in silole derivatives<sup>15</sup> and  $\alpha$ -cyanostilbenic derivatives.<sup>16</sup> The solutions of these molecules exhibited high fluorescence quantum yields in aggregated state in comparison to the monomers in dilute solution state. Motivated by this fact, several AIEE active molecular motifs were introduced in the liquid crystal design, to combine the beneficial AIEE property with the self-organizing behavior of LCs.<sup>12a</sup> Several liquid crystals based on  $\alpha$ -cyanostilbenic derivatives were synthesized.<sup>17-19</sup> Such molecules displayed multistimuli responsive behavior.

Tris(*N*-salicylideneanilines) (TSANs) are getting acceptance from investigators as a valuable molecular motif to realize variety of self-assemblies. With a meticulous molecular

design, one can achieve variety of functional materials, due to its synthetic flexibility and hence the tunability of the properties. There are numerous reports on the application of TSANs based molecular structures designed towards the molecular switches,<sup>20</sup> chemosensors,<sup>21</sup> covalent organic microporous structures,<sup>22</sup> and chiral catalysts.<sup>23</sup> We have reported a number of Col LCs based on TSANs whose photophysical and thermal behavior can be tuned by the appropriate molecular design.<sup>24</sup> Recently we have reported several TSANs containing *trans*-stilbene chromophore stabilizing Col phase and bright green luminescence.<sup>24f,h</sup> This motivated us to study the corresponding cyanostilbene derivatives.



**Figure 1.** Molecular structures of the stilbene based TSANs ( $ST^{24f,h} \alpha$ -CNST and  $\beta$ -CNST), and their thermal behavior (based on the cooling scans from DSC)

In the present report we are providing the synthesis, characterization, thermal and photophysical behavior of star-shaped TSANs comprising cyanostilbene moieties. Here the position of cyano group with respect to the phenyl group near to the central core was varied. The molecule with the cyano group in  $\alpha$ -position to the phenyl group was termed as  $\alpha$ -CNST and the molecule with the cyano group in the  $\beta$ -position to the phenyl group was termed as  $\beta$ -CNST (Fig.1). Considering the presence of three basic amine protons in conjugation with cyanovinylene fluorophore, we envisaged that the photophysical properties of the molecule can be modulated by protonation. Such molecules can be used as sensors for the detection of trace amount of acids. It is surprising to notice that such reports are not there with TSANs, and we decided to explore their acidochromic behavior towards the development of a chemosensor.

#### Synthesis and characterization

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The target TSANs were synthesized as briefed in Scheme 1. 1,3,5-Triformyl phloroglucinol, the key intermediate was synthesized by Duff's reaction.<sup>20,24</sup> Ethyl-3,4,5-tri(*n*-

#### Scheme 1. Synthesis of star-shaped TSANs



**Reagents and Conditions:** (i) LAH, THF, RT, 2 h (95 %); (ii) SOCl<sub>2</sub>, dry dichloromethane, room temperature (95%); (iii) NaCN, benzyltriethylammonium chloride, Dry DMF, 65 °C, 72 h (75%); (iv) 4-Nitrobenzaldehyde, dry ethanol+chloroform (1:1), NaOEt, room emperature, 3 h (70 %); (v) Zinc powder, HCOONH<sub>4</sub>, THF-CH<sub>3</sub>OH (2:1), room temperature, 1 h (60-70 %); (vi) (PCC) Pyridinium chlorochromate:silica gel, dichloromethane, room temperature, 1 h (75%); (vii) 4-nitrophenylacetonitrile, ethanol, piperidine (75%); (viii) 1,3,5-triformylphloroglucinol, Methanol, reflux, 6 h (67-68%).

dodecyloxy)benzoate was synthesized as reported earlier.<sup>24g</sup> This ester was reduced to corresponding alcohol **2** on treatment with lithium aluminium hydride (LAH). This alcohol was oxidized to corresponding aldehyde **7** on treatment with pyridinium chlorochromate (PCC). This aldehyde on treatment with 4-nitrobenzyl cyanide, in presence of piperidine as a base resulted in the formation of nitro compound **8**. The nitro group was selectively reduced with the help of zinc powder in presence of ammonium formate at room temperature to yield corresponding amine **9** in good yield. This amine was refluxed with 1,3,5-triformyl phloroglucinol to give the tris(*N*-salicylideneanilines) denoted as  $\alpha$ -CNST. The constitutional isomer of this compound was prepared in the following way. The benzyl alcohol **2** was converted into its chloride derivative **3** on treatment with thionyl chloride. Heating this chloride with sodium cyanide in presence of benyltriethylammonium chloride in dry DMF at 65 °C over three days yielded corresponding benzyl cyanide **4** in good yield. This was treated with 4-nitrobenzaldehyde in the presence of base to provide the nitro compound **5**. This compound was reduced to corresponding amine **6** as mentioned earlier. Finally this amine was condensed with 1,3,5-triformyl phloroglucinol to provide the target TSANs denoted as  $\beta$ -CNST.

Both the target molecules existed as an inseparable mixture of  $C_{3h}$  and  $C_s$  geometrical isomers of keto-enamine tautomer, with the  $C_s$  isomer in higher amount<sup>24f,h</sup> (Table 1) as evidenced by <sup>1</sup>H NMR spectra (See SI). In particular, the proton spectra showed multiple peaks between  $\delta$  8.7-8.9 and  $\delta$  13.1-13.5 which are arising due to the resonance of vinylic and secondary amine protons respectively, and their coupling. As given in Fig.S23, the region viz,  $\delta$ 13.1-13.5 consisted of four doublets arising from the resonance of an amine proton (H<sub>a</sub>) of  $C_{3h}$ isomer and three analogous amine protons (H<sub>c</sub>, H<sub>g</sub> and H<sub>e</sub>) of C<sub>s</sub> isomer. The enamine region viz.,  $\delta$  8.7-8.9 also consisted of four doublets, arising from the resonance of a proton (H<sub>b</sub>) of C<sub>3h</sub> isomer and three protons (H<sub>d</sub>, H<sub>f</sub> and H<sub>h</sub>) of  $C_s$  isomer. The integration of H<sub>a</sub> against H<sub>c</sub>, H<sub>g</sub> and He of amine protons or Hb vs Hd, Hf and Hh of enamine protons can be considered to calculate the ratio of two isomers. In the present work, we have considered amine protons for estimating the ratio of the two isomers, because of the better separation of peaks (Fig. S23). Molecular structures were further confirmed by <sup>13</sup>C NMR, IR and MALDI-TOF mass spectrometry. Stilbene based TSANs (ST) without cyano functional group bearing nine *n*-dodecyloxy chains was also prepared as reported earlier<sup>24f,h</sup> for the comparison of the photophysical properties with respect to  $\alpha$ -CNST and  $\beta$ -CNST.

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#### **Thermal behavior**

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The liquid crystalline phase assignment of the TSANs, phase transitions, associated enthalpies with these transitions are provided in Table 1 and graphically represented in Figure 1. The data obtained from X-ray diffraction (XRD) studies are presented in Table 2. The thermal behavior of compound **ST** was reported earlier<sup>24f,h</sup> and to visualize the impact of cyano substitution (*a*-CNST and *β*-CNST), it is included in Table 1 and Figure 1.

<b>Fable 1.</b> Phase transition temperatu	ires <sup>a</sup> (°C) and corre	sponding enthalpies	(kJ/mol) of DLCs
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Phase sequence					
Entry $(C_{3h}: C_s)^{b}$	2 <sup>nd</sup> Heating	1 <sup>st</sup> Cooling			
<b>ST</b> <sup>d</sup> (1:2.41)	Cr 66.5 (1.5) Col <sub>h</sub> 199.5 (1.6) I	I 196.5 (1.4) $\operatorname{Col}_{h}^{c}$			
<b>α-CNST</b> (1: 2.9)	Col <sub>r2</sub> 187.9 (14.1) Col <sub>r1</sub> 219.2 (2) I	I 212.8 (2.6) Col <sub>r1</sub> 183.5 (15.2) Col <sub>r2</sub> <sup>c</sup>			
<b>β-CNST</b> (1:2.5)	Col <sub>r2</sub> 220.4 (25.2) Col <sub>r1</sub> 237.8 (8.4) I	I 233 (6.8) Col <sub>r1</sub> 215 (18.6) Col <sub>r2</sub> <sup>c</sup>			

<sup>a</sup>Peak temperatures in the DSC thermograms obtained during the second heating and first cooling cycles at 5 °C/min. <sup>b</sup>Ratio obtained from <sup>1</sup>H NMR; <sup>c</sup>Crystallization was not observed till room temperature. <sup>d</sup>Reported in reference 24f,h. Cr: Crystal phase; Col<sub>h</sub>: Columnar hexagonal phase; Col<sub>r</sub>: Columnar rectangular phase; I: Isotropic phase.



**Figure 2.** POM image of compound in  $Col_{r1}$  phase at 194 °C (a); in  $Col_{r2}$  phase at 177 °C (b); frozen  $Col_{r2}$  phase at 25 °C (c).



**Figure 3.** DSC scans of compound *a*-CNST obtained for second heating (red trace) and first cooling (blue trace) (a); XRD profile depicting the intensity against the 2 $\theta$  obtained for the Col<sub>r1</sub> phase of compound *a*-CNST at 200 °C (inset provides the image patterns obtained) (b).

Compounds <sup>a</sup>	Phase	$d_{\rm obs}(\rm \AA)$	Lattice parameters (Å),		
$(D/\text{\AA})$	(T/°C)		Lattice area $S$ (Å <sup>2</sup> ),		
	Symmetry		Molecular volume $V(A^3)$		
	Col <sub>r1</sub>	41.51	a = 22.9; b = 41.51;		
a-CNST	(200)	22.90	S = 950.6, V = 4809.9,		
(56.8)	p2mm	$5.06(h_a)$	Z = 1.2		
		39.78	a = 28.7;		
	Col <sub>r2</sub>	28.7	b = 39.78;		
	(140)	23.01	S = 1141.69,		
	p2mm	11.45	$V = 569^{7}/,$		
		$4.99(h_a)$	Z = 1.4		
		39.68	a = 27.75;		
	Col <sub>r2</sub>	27.75	b = 39.68;		
	(25)	22.55	S = 1101.12,		
	p2mm	11.64	V = 5494.6,		
		$4.99(h_a)$	Z = 1.3		
	Col <sub>r1</sub>	39.74	a = 21.02; b = 39.74;		
β-CNST	(225)	21.02	S = 835.33,		
	p2mm	$4.94(h_a)$	V = 4126.55,		
(56.8)		20.72	Z = 1.		
× /	Cal	39.72	a = 22.05; b = 39.72; c = 208.86		
	(140)	22.63	V = 4314.55		
	n2mm	11.63	Z = 1.1		
	<i>P</i>	$4.8(h_a)$			
	Cal	39.75	a = 27.17; b = 39.75;		
	$Col_{r2}$	22.43	S = 1080.0, V = 5130.03		
	(23)	11.67	V = 5150.05, Z = 1.3		
	p∠mm	$4.75(h_a)$	L = 1.5.		
<sup>a</sup> The diameter (	D) of the disk (	estimated from	n Chem 3D Pro 8.0 molecular		
model software from Cambridge Soft). dobs: spacing observed; dcal:					
spacing calculated (deduced from the lattice parameters; $a$ for Col <sub>h</sub> phase).					
The spacings marked $h_a$ correspond to diffuse reflection in the wide-angle					
lattice parameters obtained for Col phase. Z indicates the number of					
molecules per	columnar slice	of thickness	$h_{-}$ estimated from the lattice		

**Table 2.** Results of (*hkl*) indexation of XRD profiles of the compounds at a given temperature  $(T/^{\circ}C)$  of mesophase.

Stilbene based TSAN with nine *n*-dodecyloxy chains exhibited a Col phase with hexagonal symmetry over a wide thermal range starting from ambient temperature to  $\approx 200$  °C. TSAN *a*-**CNST** was a waxy solid that was shearable and looked briefringent under polarizing optical microscope (POM). On heating it with the help of programmable hot stage showed a transition to more birefringent and fluidic structure in accordance with a transition noticed by differential scanning calorimeter (DSC) at 188 °C with an enthalpy change of 14.1 kJ/mol. This was transformed to an isotropic liquid at  $\approx 219$  °C ( $\Delta H = 2$  kJ/mol) (Fig.3a). On cooling the isotropic liquid, a transition to a bright mosaic pattern was noticed at 212 °C, which exhibited a reduction in the brightness at around 184 °C. This mosaic texture disappeared over further cooling and

area S and the volume V.

transformed into a dark colored texture with the remnants of high temperature mosaic pattern, which remained unaltered at room temperature (RT) (Fig.2a-c). No signs of crystallization were noticed in DSC scans, even though the sample was not shearable at room temperature. This is probably a transition to the glassy state (Fig.3a). Though the POM texture resembled the Col phase, the symmetry of the columnar arrangement can be understood only with the help of XRD studies, and hence the XRD scans were collected at different temperatures. Powder XRD pattern obtained at 200 °C, on cooling from the isotropic liquid exhibited a sharp peak with a d-spacing of 41.51 Å along with a peak corresponding to a d- spacing of 22.9 Å (Fig.3b, Table 2). At wide angle a diffused peak corresponding to a *d*-spacing of 5.06 Å was observed, which corresponds the packing of flexible alkyl tails. Peaks at the low angle can be indexed into the (01) (10) Miller indices of a rectangular lattice with lattice parameters a = 22.9 Å; b = 41.51 Å. The values calculated for the lattice area and lattice volume were found to be 950.6 Å<sup>2</sup> and 4809.9 Å<sup>3</sup>. The number of molecules present in the unit rectangular cell (Z) was found to be approximately one. As noticed in the DSC scans there was a transition at 212 °C ( $\Delta H = 2.6$  kJ/mol), which prompted us to conduct the XRD at a temperature lower than this. The XRD pattern obtained at 140 °C showed several peaks at low to mid angle region corresponding to *d*-spacings of 39.78, 28.7, 23.01 and 11.45 Å that can be indexed in to the Miller indices (01), (10), (11) and (22) of a rectangular lattice. The low temperature rectangular structure is different from the high temperature one with a larger lattice area and larger cell volume (Table 2 and Fig.S26). In order to distinguish these two different Col<sub>r</sub> phases, we have named the high temperature one as Col<sub>r1</sub>

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**Figure 4.** Schematic showing the self-assembly of compound  $\alpha$ -CNST in Col<sub>r</sub> phase of *p2mm* symmetry (Derived from the XRD pattern obtained at 25 °C, only  $C_{3h}$  isomer shown for the sake of clarity)

phase, while the low temperature one as  $\text{Col}_{r2}$  phase. Similar reflections were observed for the diffraction pattern obtained at room temperature (Table 2, Fig.S26), which showed the existence of  $\text{Col}_{r2}$  phase with out any crystallization, however in a glassy state. The self-assembly of *a*-**CNST** in  $\text{Col}_r$  phase of *p2mm* symmetry can be represented as shown in Fig.4.

Constitutional isomer  $\beta$ -CNST was also a waxy solid which showed similar phase transitions, but with a higher isotropic temperature of 238 °C. The optical texture had rectilinear defects arising from the homeotropic domains (Fig.5a), which is commonly observed for Col phase. A transition was noticed at 215 °C ( $\Delta H = 18.6$  kJ/mol), with a decreased birefringence in the optical texture (Fig.5b). This remained as such till room temperature without a sign of crystallization. It has to be noted that cooling at a slower rate (1°C/min) provided a nice homeotropically aligned Col<sub>r</sub> phase with the fern like domains growing at right angles to each other (Fig.S27). Powder XRD studies were conducted at different temperature intervals. The XRD pattern obtained at 225 °C confirmed the Col<sub>r</sub> phase (Fig.5c and Table 2). The diffraction patterns obtained at 140 °C and RT showed the existence of another Col<sub>r</sub> phase (Fig.S28). The self-assembly of  $\beta$ -CNST in Col<sub>r</sub> phase of p2mm symmetry can be represented as shown in Fig.S29.



**Figure 5.** POM image of compound  $\beta$ -CNST in Col<sub>r2</sub> phase at 150 °C (a); DSC scans of compound  $\beta$ -CNST obtained for second heating (heating: black trace) and first cooling (cooling: red trace) (b); XRD profiles depicting the intensity against the 20 obtained for the Col<sub>r2</sub> phase of compound  $\beta$ -CNST at 225 °C (inset provides the image pattern obtained) (c).

Similar to the case of  $\alpha$ -CNST, we have denoted the high temperature and low temperature Col phases as Col<sub>r1</sub> and Col<sub>r2</sub> phases. In comparison to  $\alpha$ -CNST,  $\beta$ -CNST exhibited higher clearing temperature and enhanced mesophase range, which confirms the enhanced intermolecular

interactions due to this substitution. The introduction of cyano group in the molecular structure led to the stabilization of  $Col_r$  phase in comparison to TSANs without a cyano group, *i.e.* **ST**, which again confirmed the enhanced intermolecular interactions in these molecules due to the polar cyano group.

#### **Photophysical behavior**

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Photophysical properties of the TSANs,  $\alpha$ -CNST and  $\beta$ -CNST were studied in solutions and in thin films and compared with that of ST (Table 3). The absorption spectra of compounds in chloroform solutions displayed two bands, which are due to  $n-\pi^*$  and  $\pi-\pi^*$  transitions.  $\alpha$ -CNST exhibited blue shifted bands in comparison to ST, while  $\beta$ -CNST exhibited a red shifted band. Between the two cyanostilbene derivatives,  $\beta$ -CNST exhibited a red shifted absorption band (Fig.6a). Emission spectra of ST and  $\beta$ -CNST exhibited a single emission maximum centered at 517-519 nm along with a shoulder band at longer wavelength. In comparison, the emission spectrum of  $\alpha$ -CNST was blue shifted with an emission maximum at 504 nm. The thin films of the samples were prepared by spin coating of the solutions in chloroform on quartz plates. The emission spectra of these films showed red shifted bands in comparison to solutions due to the formation of aggregates.<sup>25</sup> The emission spectra of  $\beta$ -CNST were red-shifted in comparison to that of ST and  $\alpha$ -CNST in the thin film state (Fig.6b). Fluorescence lifetime measurements at micromolar concentrations and thin films revealed the existence of three different species. The species in the solution state showed lower lifetime in comparison to the same in thin film state, which points to the formation of aggregates (See SI, Table S2-3 and Fig.S31). However the aggregates do not show any sort of enhanced emission in comparison to the solution state (Fig. S32). Both the solutions and thin films showed visually perceivable emission on exciting with the UV light of long wavelength (Fig.S33). The relative quantum yields of these compounds were measured in solution as reported earlier (Table 3).<sup>25</sup> The quantum yields were in the range of 0.26-0.3. The optical band gap calculated from the absorption onset values were found to be in the range of 2.5-2.6 eV.



**Figure 6.** Normalized absorption spectra of compounds (solid line) and emission spectra (broken line) in CHCl<sub>3</sub> solution (a); normalized absorption spectra of compounds (solid line) and emission spectra (broken line) obtained for the thin films prepared by spin coating in CHCl<sub>3</sub> solution (b);

Solution				Thin film				
Entry	Absorption	Emission <sup>b</sup>	Stokes shift	$\phi^{\mathrm{f}}$	$\lambda_{onset}$	$\Delta E_{g, opt}^{d}$	Absorption <sup>g</sup>	Emission <sup>e,g</sup>
	(nm)	(nm)	$(cm^{-1})$		(nm)		(nm)	(nm)
ST	357, 441	517	3333	0.30	497	2.50	376, 436	560
a-CNST	359, 437	504	3042	0.28	487	2.55	439	559
β-CNST	369, 449	519	3004	0.26	504	2.46	456	575
<sup>a</sup> Micromolar solutions in CHCl <sub>3</sub> . <sup>b</sup> Excited at the respective absorption maxima. <sup>c</sup> Band gap was determined from								
the red edge of the longest wave length in the UV-Vis absorption spectra. ${}^{d}\Delta E_{g}$ (eV) = 1242.37/(wavelength in								
nm), <sup>e</sup> Excited at the respective absorption maxima in thin film state, <sup>f</sup> Relative quantum yields are calculated with								
respect tetrakis(octyl)-1H-phenanthro[1,10,9,8]carbazole-3,4,9,10-tetracarboxylate in THF solution as the								

Table 3. Photophysical<sup>a</sup> properties of TSANs in solution and thin film state.

#### Acidochromism

standard, <sup>g</sup>Prepared by spin coating of the sample.

Considering the presence of a basic N atom in conjugation with a cyanovinylene chromophore, we envisioned that these compounds might act as good proton acceptors and the protonation may change the extent of electron delocalization. This would affect the optical properties, specially the fluorescence of these compounds, which can be beneficial in the detection of acids. Due to the high solubility and strong acidity of the trifluroacetic acid (TFA), it was chosen to protonate the TSANs. As seen from the Fig.7a and c, the emission intensities of compounds  $\alpha$ -CNST and  $\beta$ -CNST were reduced by the addition of trifluoroacetic acid (TFA)

along with a red shift (26-33 nm). The red shift was more in the case of  $\alpha$ -CNST thus the emission color change from green to yellow was more prominent under UV light of long wavelength (Fig.S35). However, the absorption spectra of these compounds showed only a small blue shift (Fig.S34). It is interesting to note that gradual neutralization with the triethylamine recovered the original green emission, which was confirmed by fluorimetric titration (Fig.7b and d). Similar experiment was done for the spin-coated thin films too, but with vapors of TFA and TEA. Due to the low emission intensity, the emission change was not visually detectable, but the fluorescence spectrum revealed the change in the emission (Fig.8 and Fig.S36). Treating the films with vapors of TEA showed emission shift to the original position only in the case of  $\alpha$ -CNST, while the original emission maximum was not recovered in the case of  $\beta$ -CNST. However in both the cases the emission intensity was increased after neutralizing the films with TEA vapors (Fig.8b,d). From the luminescence quenching in response to TFA addition, we calculated the limit of detection (LOD) for TFA in solution. The LOD determined for  $\beta$ -CNST

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**Figure 7.** Change the emission spectra of compound  $\alpha$ -CNST with the gradual addition of TFA (a); recovery of the emission by neutralization with TEA (b); Change the emission spectra of compound  $\beta$ -CNST with the gradual addition of TFA (c); recovery of the emission by neutralization with TEA (d).



**Figure 8.** Change the emission spectra of the thin film of compound  $\alpha$ -CNST on exposure to TFA vapors (a); recovery of the emission by neutralization with TEA vapors (b); Change the emission spectra of compound  $\beta$ -CNST on exposure to TFA vapors (c); recovery of the emission by neutralization with TEA vapors (d).

was 48.34 parts per billion (ppb), while for *α*-CNST the LOD was found to be 78.89 ppb (See SI, Fig.S38 and S39).

In order to make a simple handheld device to detect the acid vapors by naked eye we have placed the solution used for the preparation of films on a TLC plate with the help of a dropper (See the word 'IIT' in Fig.S37). Under the UV light of long wavelength these letters have shown bright yellow emission. Placing the droplets of TFA over the word 'IIT' quenched the emission along with a redshift as seen under UV light. After few minutes the droplets of TEA placed on this word showed the recovery of the yellow emission instantly. Thus these compounds can be utilized as volatile acid sensors in solution as well as in thin film state either by switching or by quenching of the emission without the need of any sophisticated instrumentation.

#### Conclusions

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In this paper we have prepared two novel star-shaped TSANs through a multistep synthesis to incorporate a cyanovinylene chromophore between the two unsymmetrically substituted benzene rings. The position of the cyano group was altered and the target molecules were compared with the stilbene derivative for their thermal and photophysical behavior. The presence of the cyano group enhanced the mesophase range in comparison to the non-cyano stilbene derivative. Further, enhanced intermolecular interactions led to the stabilization of Col<sub>r</sub> phase in comparison to the columnar hexagonal phase of simple stilbene derivative. These compounds exhibited the freezing of Col phase in a glassy state, which is beneficial from the device fabrication point of view. These compounds exhibited different absorption and emission behavior in comparison to the stilbene based TSANs reported earlier. The solution state emission of  $\alpha$ -CNST was blue shifted in comparison to stilbene based TSANs (ST), while the  $\beta$ -CNST exhibited a red shifted emission band in comparison to that of ST. These compounds were emissive in the thin film state also, which means that they are emissive in Col phase. In the solid thin films,  $\alpha$ -CNST exhibited a similar emission as compound ST, but a red shifted emission was observed for  $\beta$ -CNST. Thus the stabilization of room temperature Col phase along with the emissive nature is promising from the viewpoint of emissive displays. These compounds showed the ability to detect the volatile acids in solution as well as thin film state with an emission switching or by quenching. Specially, in solution state, they could sense the volatile acid like trifluoroacetic acid in parts per billion levels by fluorescence switching. It is interesting to note that they recover their original emission on neutralization with a base.

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Conflicts of interest statement. There are no conflicts of interest to declare

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