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# Aromatic $\pi$ - $\pi$ Driven Supergelation, Aggregation Induced Emission and Columnar Self-assembly of Star-shaped 1,2,4-Oxadiazole Derivatives

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Abstract: A new family of star shaped 1,2,4-oxadiazole derivatives with the variation in the number of the flexible peripheral tails have been synthesized and characterized. It is interesting to note that the number of flexible tails in the periphery dictated the self-assembly and the photophysical behavior. The compound with three flexible tails stabilized a crystalline state with lamellar packing, and did not show organogelation, but showed blue emission in crystalline and thin film state. The compound with six flexible tails stabilized hexagonal columnar liquid crystalline state and it showed the ability to gelate in nonpolar solvents at a concentration less than 1 weight percent; qualifying it as a supergelator, where  $\pi$ - $\pi$ interactions play a major role. This phenomenon is very rare, in comparison to earlier reports where the supergelation is supported by H-bonding interactions. Besides the capability to form self-standing, moldable gel, this compound also exhibited aggregation-induced emission (AIE), which persisted even in xerogel state. X-ray diffraction studies unraveled the rectangular columnar self-assembly in the gel state. The columnar order and emissive nature in the liquid crystal and xerogel state makes this molecule promising for the application in emissive displays. Compounds with nine alkyl tails stabilized long range columnar hexagonal phase. This report emphasizes the importance of various non-covalent interactions in deciding the nature of self-assembly.

# Introduction

The self-assembly of organic molecules into well-defined hierarchical superstructures that perform various functions requires a 'bottom-up' approach from the molecular level. Incorporation of the functional units in the molecular structure alone will not guarantee the anticipated outcome. In order to have a preferred outcome, behavior of the molecular aggregates in bulk or in a medium matters. Liquid crystals (LC) are one such example of engineered molecular materials, which are the resultant of the spontaneous self-assembly of shape anisotropic molecules. This state of the matter possess an intermediate order and mobility between solids and liquids.<sup>1</sup> The driving force for such assembly is mainly nanophase segregation between the incompatible molecular subunits in addition to other secondary interactions like H-bonding,  $\pi$ - $\pi$  interactions, ionic, hydrophilic or hydrophobic interactions. With a careful molecular design one can predict the outcome of the self-assembly of such shape anisotropic molecules. Gelators are another class of molecules with

specific structural features, which immobilize large amount of solvents when they selfassemble.<sup>2</sup> They may gelate organic or aqueous solvents. The self-assembly of such molecules to form gels is assisted by weak forces like H-bonding,  $\pi$ - $\pi$  interactions, hydrophobichydrophilic or van der Waals interactions. This class of materials is showing promise for the application in optoelectronics,<sup>3</sup> templates for the growth of inorganic nanostructures,<sup>4</sup> fluorescent sensors<sup>5</sup> and controlled release systems. Usually the ability of organogelators to gelate large volume of solvent comes from the presence of certain functional groups like amide, alcohol, carboxylic acid, aromatic units, steroid moieties and aliphatic chains etc.<sup>2</sup> Gelation brings about drastic changes in the electronic and optical properties. For example, fluorescent molecules that are emissive as monomers may not be emissive in aggregated state due to aggregation induced quenching of fluorescence. Organogels which show aggregation induced emission (AIE) due to their supramolecular self-assembly in gel state form an important class of materials from the view point of solid state lighting.<sup>6</sup> Though there are several reports on AIE active molecules which emit across the whole visible region.<sup>7</sup> there is dearth in the solid state blue emitters. Blue light emitters form an integral part of the full color display devices and also form a vital cog in white light emitting devices.<sup>8</sup> Hence there are lot of efforts on building solid-state blue light emitters by the introduction of functional moieties which will help to generate AIE.<sup>9</sup> Among gelators, there is a class of supergelators which at very low concentration (less than 1 wt %) yield self-standing, self-healing and moldable gels.<sup>10</sup> A common structural feature of these molecules is the ability to form strong Hbonding.<sup>11</sup> There is a single report so far on a polycatenar type supergelator without such Hbonding but mainly stabilized by  $\pi$ - $\pi$  interaction.<sup>12</sup> The presence of two heterocyclic (1.3.4oxadiazole) units might have increased the intermolecular  $\pi$ - $\pi$  interactions to stabilize the aggregation. This observation encouraged us to incorporate heterocyclic moieties in our molecular design that might enhance the  $\pi$ - $\pi$  interactions to stabilize gelation.<sup>12</sup> Synthesis of such supergelators is challenging, as there is no proven design principle.

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Integration of heterocyclic moieties in the molecular architecture of thermotropic liquid crystals is a rewarding task as it can bring about a large change in their thermal and physical properties. This stems from the polarizability of heteroatoms like nitrogen, oxygen and sulfur atoms. There is an increased interest in the design of highly  $\pi$ -conjugated liquid crystals bearing heterocycles<sup>13</sup> due to the enormous possibilities they offer. Liquid crystalline self-assemblies derived from electron deficient heteroaromatic rings are potential candidates for organic light-emitting diodes (OLEDs),<sup>14</sup> by offering good charge-transporting property and strong fluorescence. Especially 1,3,4-oxadiazole moieties are well-known for their

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excellent electron-accepting behavior and fluorescence and hence been incorporated in the core structure of calamitic and discotic LCs, to obtain the conductive smectic or columnar mesophases respectively.<sup>13, 32</sup> In spite of the good emissive nature and high thermal endurance of 1,2,4-oxadiazole unit, the reports on its incorporation in LC design the absorption spectra are taken scarce, unlike its 1,3,4-isomer. This is probably due to the synthetic difficulty in comparison to 1.3.4-oxadiazole derivatives. The asymmetric ring of 1.2.4-oxadiazole moieties provides a strong lateral dipole, which leads to the stabilization of different LC phases than those obtained from corresponding 1,3,4-isomers.<sup>15,17-24</sup> Asymmetrical substitution of 1,2,4oxadiazole could be another tuning handle to modify their material property. In comparison to 1,2,5- and 1,3,4-oxadiazole derivatives, asymmetrically substituted 1,2,4-oxadiazole derivatives are known for their high band gap and known to possess high S<sub>1</sub> and T<sub>1</sub> energies, which is beneficial for the design of high triplet energy host materials for efficient phosphorescent OLEDs (PHOLEDs).<sup>16</sup> PHOLEDs are known for their higher efficiency in comparison to OLEDs as they harvest both the singlet and triplet excitons. According to literature 1,2,4-oxadiazole derivatives have a moderate thermal stability (decompose around 300 °C) than their 1,3,4-oxadiazole isomers, <sup>17</sup> but they exhibit lower melting points and a wider mesophase range.<sup>18</sup> There are many reports on banana shaped, <sup>19</sup> bent shaped liquid crystals, <sup>17, 20, 21, 22</sup> supramolecular liquid crystals, <sup>23</sup> chiral calamitic liquid crystals <sup>24</sup> based on 1,2,4-oxadiazole derivatives. In the case of bent compounds the bending angle provided by the 1,2,4-oxadiazole core is 140° which slightly more than that of 1,3,4-oxadiazole core (134°) and hence they are anticipated to show some interesting properties like biaxial nematic behavior.<sup>19a</sup> Apart from the bent polycatenars reported by Gallardo et. al.,<sup>20a</sup> there are no reports on molecules based on 1,2,4-oxadiazoles exhibiting columnar phases. Though columnar (Col) phases formed by the one-dimensional stacking of disc-like molecules were discovered in 1977,<sup>25</sup> consequently many different non-conventional molecular designs like polycatenars, dendrimers, metallomesogens, bent shaped molecules, oligomers, polymers, macrocycles and star shaped molecules were identified to stabilize Col phases.<sup>1</sup> Columnar phases are of technological importance in recent times because of their potential application in organic electronic devices like solar cells, field effect transistors and OLEDs as they provide one-dimensional pathway for the movement of charge carriers along the columns.<sup>26</sup>

Star shaped mesogens or 'hekates' are formed by the covalent linking of three arms symmetrically to a central core.<sup>27</sup> Shape-persistent star shaped mesogens are obtained on connecting the three rigid arms to central core through linkers. Their lack of shape anisotropy to exhibit mesophases is compensated by the nanophase segregation of chemically or

physically different molecular subunits and their tendency of efficient space filling. Compared to the synthetic difficulty associated with discotics this molecular design is advantageous due to the inherent synthetic flexibility. Thus the Col phases can be incorporated with other functional properties like hole or electron transport, nonlinear optical activity or fluorescence. Apart from this aspect, star shaped molecules are capable of exhibiting a rich variety of mesophases like nematic, columnar, cubic or soft crystal phases, because of their peculiar structure and tunable molecular design. The presence of the voids between the arms of the molecular structure helps to avoid the crystallization of mesophases and promote the glassy state. Columnar phases with glassy nature are important as they allow the movement of charge carriers through them with the simultaneous restriction of ionic impurities.<sup>28</sup> In the context of the application of Col phases to OLEDs, it is important to prepare molecules, which stabilize Col phase along with the preserved solid-state luminescence. This is because aggregation quenching of luminescence in Col phase is detrimental to the device performance.

In this paper we report the first examples of star shaped molecules containing three 1,2,4-oxadiazole heterocyclic moieties attached to the 1, 3 and 5 positions of the central benzene ring. These molecules exhibit  $Col_h$  phase over a wide range. Most importantly one of these molecules shows supergelation in hydrocarbon solvents. Gel and xerogel show aggregation-induced emission behavior with blue emission, while the dilute solutions containing solvated monomers is weakly emissive.

# **Results and discussion**

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**Synthesis and Characterization.** The synthetic method for the preparation of the target molecules is presented in scheme 1. The synthetic methods for ethyl gallate, 3,4,5-trialkoxyethyl gallate are same as reported earlier.<sup>29a-c</sup> 3,4,5-Trialkoxy ethyl gallates (**6c-d**) and 3,4-dialkoxy benzaldehyde (**4b**) were obtained by the *O*-alkylation of ethyl gallate and 3,4-dihydroxy benzaldehyde respectively following Williamson's protocol. Compounds **6c-d** were reduced to respective 3,4,5-trialkoxy benzyl alcohols (**5c-d**) by lithium aluminium hydride (LAH) in dry THF. Further oxidation of 3,4,5-trialkoxy benzyl alcohols (**5c-d**) using



Scheme 1. Synthesis of star shaped 1,2,4-oxadiazole derivatives. Reagents and conditions: (i) 1-Bromoalkanes, anhyd. $K_2CO_3$ , DMF, 80 °C, 12 h (70-90%); (ii) LAH, THF, 0 °C to rt, 12 h (75-80%); (iii) PCC, DCM, rt, 1 h (70-81%); (iv) NH<sub>2</sub>OH·HCl, DMSO, reflux, 3 h (70-80%); (v) NH<sub>2</sub>OH.HCl, triethylamine, CH<sub>3</sub>CN, reflux, 24 h (70-85%); (vi) trimesic acid chloride, pyridine, 6 h, reflux(55-60%).

pyridinium chlorochromate (PCC) gave 3,4,5-trialkoxy benzaldehydes (4c-d).<sup>29b</sup> These benzaldehyde derivatives (4b-d) were converted to their respective nitriles (3b-d) upon heating with hydroxylamine hydrochloride in DMSO at 100 °C for 3h.<sup>30</sup> *p*-Hydroxy benzonitrile was converted to *p*-alkoxy benzonitrile (3a) by Williamson's protocol. Further reflux of nitrile (3a-d) with hydroxylamine hydrochloride in ethanol led to benzamidoxime intermediates (2a-d), which on further refluxing with trimesylchloride in pyridine afforded 1,3,5-benzene substituted 1,2,4-oxadiazole derivatives (1a-d).<sup>31</sup> The structures of all the intermediates and target molecules were confirmed using <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR spectroscopy and ESI-HRMS or MALDI-TOF analysis.

The <sup>1</sup>H NMR spectra of oxadiazole derivatives **1a-d** exhibited low field signals ( $\delta = 9.15$  ppm for **1a**) for the protons on central benzene ring in comparison to that of the previously reported<sup>32</sup> star shaped molecules with 1,3,4-oxadiazole arms ( $\delta = 8.95$  ppm), which is due to the more electron withdrawing nature of 1,2,4-oxadiazole units. Similarly, the <sup>13</sup>C NMR of 1,2,4-oxadiazole derivatives **1a-d** exhibited low field signals at 173 ppm and 169 ppm for the heterocyclic carbons in comparison to the heterocyclic carbons of the 1,3,4-oxadiazole derivatives (signals at 169 ppm and 165 ppm)(See the supporting information (SI) for the details).

**Thermal behavior.** The target molecules were probed for their thermal behavior with the help of thermogravimetric analysis (TGA), Polarizing Optical Microscopy (POM) and Differential Scanning Calorimetry (DSC). The TGA studies of compounds **1a-d** showed good thermal stability at least upto  $\approx 300$  °C and complete degradation occurred at around 600 °C, as evidenced by TGA (See the SI). The thermotropic LC behavior of the compounds is summarized in table 1. A comparison between the thermal behaviors of the earlier reported regioisomers<sup>32</sup> of the present series is furnished in Fig. 1.

Table 1. Phase transition temperatures <sup>a</sup> (°C) and corresponding enthalpies (kJ/mol) of DLCs

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	Phase sequence	
	2 <sup>nd</sup> Heating	1 <sup>st</sup> Cooling
1a	Cr 128.8 (375.6) I	I 82.9 (332.3) Cr
1b	Cr 106.7 (340.2) Col <sub>h</sub> 112.4 (13.8) I	I 111.4 (15.1) Col <sub>h</sub> 75.8 (349) Cr
1c	Cr 12.9 (100.2) Col <sub>h</sub> 160.0 (26.5) I	I 158.9 (26.3) Col <sub>h</sub> 3.8 (42.8) Cr
1d	Cr <sub>1</sub> 22.0 (137.4) Cr <sub>2</sub> 42.0 (607.6) Cr <sub>3</sub> 60.0 (751.2)	I 149.3 (40) Col <sub>h</sub> 12.1 (65.1) Cr
	Col <sub>h</sub> 150.6 (40.0) I	

Peak temperatures in the DSC thermograms obtained during the second heating and first cooling cycles at 5  $^{\circ}$ C/min. Cr = Crystal phase; Col<sub>h</sub> = Columnar hexagonal phase; I = Isotropic phase.



Figure 1. Bargraph summarizing the thermal behavior of compounds  $Ia-c^{32}$  and 1a-d (first heating cycle, temperature range of the Col<sub>h</sub> phase is mentioned on the bars)

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Compound **1a** with three *n*-decyloxy tails turned out to be a crystalline compound, as in the case of corresponding 1,3,4-oxadiazole derivative **Ia**.<sup>32</sup> The flexibility provided by three alkoxy tails is not sufficient to stabilize liquid crystalllinity. Compound **1b** with six *n*-decyloxy tails exhibited an improved thermal behavior with an enantiotropic columnar hexagonal phase (Col<sub>h</sub>) phase over a short thermal range (6 degrees in heating cycle). On cooling from the isotropic liquid state, a mosaic texture interspersed with homeotropic domain (Fig.2a) was found, before reaching crystallization at  $\approx 76^{\circ}$  (Fig.2b).



**Figure 2.** Photomicrograph of texture as seen by POM for the Col<sub>h</sub> phase of compound **1b** at 85 °C (a); DSC traces obtained for the first cooling (upper trace) and second heating (lower trace) cycles of **1b** at a rate of 5 °C min<sup>-1</sup> (b) and XRD profiles depicting the intensity against the  $2\theta$  obtained for the Col<sub>h</sub> phase of compound **1b** at 100 °C and 85 °C (inset shows the XRD image patterns obtained) (c)

The compound was investigated further with the help of XRD studies to understand the symmetry of the mesophase. Powder XRD patterns obtained at 100 °C and at 85 °C (Fig. 2b) were almost similar. The XRD pattern obtained at 100 °C exhibited a sharp single peak at low angle ( $2\theta \approx 3^{\circ}$ ), along with two diffused peaks at wide angle ( $2\theta \approx 16-28^{\circ}$ ). The first diffused peak is corresponding to the packing of flexible alkyl tails, while the second one corresponds to the packing of discs within the column, *i.e.* intracolumnar distance. The intracolumnar distance was found to be 3.29 Å, which was quiet low without any secondary interactions.<sup>3</sup> It is to be noted that, the regioisomeric compounds **Ib-c** did not show any peak corresponding to core-core stacking,<sup>32</sup> thus confirming the enhanced core-core interaction in the case of 1,2,4-oxadiazole derivatives (**1b-d**). This enhanced core-core interaction with low intracolumnar distance is beneficial to one-dimensional charge carrier mobility.<sup>26</sup> The sharp single peak points that the phase under investigation is Col<sub>h</sub> phase. Even though it is not unambiguous to assign hexagonal symmetry for Col phase with a single peak in the low angle, there are many instances in literature, where in the phase was assigned as Col<sub>h</sub> because of the minimum in the



**Figure 3.** Self-organization of compound **1b** in hexagonal columnar  $(Col_h)$  lattice. Space filling energy minimized (all-*trans*) molecular model of **1b** derived from molecular mechanics (MM2) method.

Table 2. Results of (hkl)	indexation of XRD	profiles of the	compounds at a	given te	emperature
(T) of mesophase					

Compound	Phase	$d_{\rm obs}(\rm \AA)$	$d_{\rm cal}({\rm \AA})$	Miller	Lattice parameters (Å), Lattice area S		
	$(T/^{\circ}C)$			indices	$(A^2)$ , Molecular volume $V(A^3)$		
( <i>D</i> /A)	-			hkl			
1b	Col <sub>h</sub>	30.64	30.64	100	a = 35.38, S = 1084.1, V = 3566.5,		
	(100)	$4.48(h_a)$			Z = 1.48		
(42.21)	C 1	$3.29(h_c)$	20.62	100			
, ,	$\operatorname{Col}_{h}$	30.63	30.63	100	a = 35.37, S = 1084.4, V = 3564.3,		
	(85)	$4.51(n_a)$			Z = 1.48		
10	Cal	$3.29(n_c)$	20 62	100	a = 22.05 S = 0.45.0 V = 2.112		
IC	(145)	26.02	26.02	100	u = 55.05, 5 = 945.9, v = 5112,		
	(143)	$\frac{4.03}{3.29} \begin{pmatrix} n_a \end{pmatrix}$			L = 0.98		
(42)	Col	28.63	29.63	100	a = 33.06 S = 946.5 V = 3114		
	(80)	$4.55(h_{a})$	27.05	100	Z = 0.98		
	()	$3.28(h_c)$					
	Col <sub>h</sub>	29.60	29.60	100	a = 34.18, S = 1011.7, V = 3328.6,		
	(25)	$4.40(h_a)$			Z = 1.05		
		$3.29(h_c)$					
1d	Col <sub>h</sub>	29.62	32.83	100	a = 34.2, S = 1013, V = 3332.8,		
	(130)	$4.57(h_a)$			Z = 0.93		
(42.8)	C 1	$3.29(h_c)$	20 (2	100	a = 34.8, S = 1053.1, V = 3464.6,		
, í	$Col_h$	30.62	28.63	100	Z = 0.96		
	(100)	$(4.31 (h_a))$					
	Col	30.63	29.60	100	a = 35.4, S = 1083.1, V = 3563.3		
	(50)	$443(h_{-})$	27.00	100	Z = 1		
	(00)	$3.29(h_a)$					
	Col <sub>h</sub>	32.83	32.83	100	a = 37.9 $S = 1244.6$ $V = 4107.2$		
	(25)	$4.36(h_a)$			7-11		
		$3.30(h_c)$			L = 1.1		

<sup>a</sup>The diameter (D) of the disk (estimated from Chem 3D Pro 8.0 molecular model software from Cambridge Soft).  $d_{obs}$ : spacing observed;  $d_{cal}$ : spacing calculated (deduced from the lattice parameters; *a* for Col<sub>h</sub> phase). The spacings marked  $h_a$  and  $h_c$  correspond to diffuse reflections in the wide-angle region arising from correlations between the alkyl chains and core regions, respectively. *Z* indicates the number of molecules per columnar slice of thickness  $h_c$ , estimated from the lattice area *S* and the volume *V*.

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form factor.<sup>32, 34</sup> Hexagonal cell parameter '*a*' was calculated from  $d_{100}$  and was found to be 35.38 Å. The value of '*a*' is 15% less than the molecular diameter of compound **1b** (Table 2) which may be due to the interdigitation of peripheral alkyl chains or folding of alkyl chains in mesophase (Fig.3). The number of molecules forming the columnar slice, which is denoted as *Z* was found to be 1.48. This is difficult to explain considering the star shaped molecular structure.<sup>32</sup> Such *Z* value (*Z* >1) is often found in polycatenars and explained due to the side-by-side packing of two molecules to form a disc.<sup>13d</sup>



**Figure 4.** Photomicrographs of textures as seen by POM for the Col<sub>h</sub> phase of compound **1c** at 135 °C (a); at 25 °C (b); XRD profiles depicting the intensity against the  $2\theta$  obtained for the Col<sub>h</sub> phase of compound **1c** at 145 °C, 80 °C and 25 °C (c).

Compound **1c** with nine *n*-decyloxy tails showed an improved mesophase range with an isotropic temperature around 160 °C. On cooling the isotropic liquid, mosaic texture develops from the homeotropic region (Fig. 4a). This is a regular textural pattern associated with Col phases in literature. Most notably the compound crystallized at around 4 °C as confirmed by the DSC thermogams (Fig.S42c). The optical texture observed at room temperature (RT) also showed similar textural pattern showing no signs of crystallization at RT (Fig.4b). Powder

XRD studies carried out at higher temperature and room temperature showed similar diffraction pattern (Table 2, Fig.4c), which shows that the Col<sub>h</sub> phase is stable for a temperature range of 155 degrees including room temperature. The number of molecules present in unit cell 'Z' in the case of compound 1c was found to be 1. It must be noted that in the case of compound **1b**; which is having six alkyl tails, the value of Z was 1.48. The molecular diameter is almost same as that of compound **1c**. This difference between the two molecules may be due to the increase in the number of peripheral alkyl chains in the case of compound 1c when compared to compound 1b. The last compound of the series 1d, which is having nine dodecyloxy chains also exhibited Col<sub>h</sub> phase but with a slight decrease in the mesophase range in comparison to its decyloxy homologue, due to an increase in the melting and a decrease in clearing temperature (Table 1 and Fig.1). Thus the increase in the peripheral chain length decreased the thermal range of the mesophase. The POM image was characteristic of the Col<sub>h</sub> phase with large spherulites (Fig.5a and b), which persisted till room temperature. In DSC thermograms of the first cooling scan crystallization was seen at 12 °C (Fig. S42d). The XRD patterns obtained at different temperatures corroborated the POM and DSC observations confirming the type and thermal range of the  $Col_h$  phase (Table 2)

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**Figure 5.** Photomicrographs of textures as seen by POM for the Col<sub>h</sub> phase of compound 1d at 125 °C (a); at 30 °C (b); and XRD profiles depicting the intensity against the  $2\theta$  obtained for the Col<sub>h</sub> phase of compound 1d at 130 °C, 100 °C, 50 °C and 25 °C (c).

# Photophysical and electrochemical studies

Photphysical properties of the star-shaped molecules **1a-d** in micromolar THF solution are depicted in Table 3. We expected a significant difference in their photophysical properties due to the difference in substitution pattern. Absorbance and fluorescence spectra of the compounds **1a-d** were measured in micromolar THF solutions (Fig. 6). As can be seen, the absorption spectra of hekates **1a-d** showed absorption maximum centered around 278 nm, which was not dependent on their substitution pattern. The absorption maxima of hekates **1a-d** with respect to their 1,3,4-oxadiazole counterparts **Ia-c** exhibited a hypsochromic shift (absorption maxima 312-324 nm).<sup>32</sup>

Table 3. Photophysical <sup>a</sup> and electrochemical <sup>c</sup> properties of star-shaped molecules

DLCs	Absorption	Emission	Stoke's	$\lambda_{onset}$	Emission <sup>i</sup>	$\Delta E_{g, opt}^{d, e}$	E <sub>10x</sub> <sup>f</sup>	E <sub>HOMO</sub> d, h	E <sub>LUMO</sub> <sup>d, g</sup>
	(nm)	° (nm)	shift (nm)	(nm)	(nm)				
1a	278	299	21	294	410	4.23	1.97	-6.31	-2.08
1b	278	314	36	295	484	4.21	1.83	-6.17	-1.96
1c	279	311	32	294	502	4.22	1.97	-6.31	-2.09
1d	278	309	31	294	496	4.23			

<sup>a</sup> Micromolar solutions in THF. <sup>b</sup> Excited at the respective absorption maxima. <sup>c</sup> Experimental conditions: Micromolar DCM solutions, Ag/AgNO<sub>3</sub> as reference electrode, glassy carbon as working electrode, platinum wire as counter electrode, TBAP (0.1 M) as a supporting electrolyte, room temperature. <sup>d</sup> In electron volts (eV). <sup>e</sup> Band gap was determined from the red edge of the longest wave length ( $\lambda_{onset}$ ) in the UV-Vis absorption spectra using the relation  $\Delta E_{g, opt} = 1242.37 / \lambda_{onset}$ . <sup>f</sup> In volts (V). <sup>g</sup> Estimated from the formula  $E_{LUMO} = E_{HOMO} + E_{g, opt}$ . <sup>h</sup> Estimated from the onset reduction peak values by using  $E_{HOMO} = -(4.8 - E_{1/2,Fc,Fc+} + E_{ox, onset})$  eV. <sup>i</sup> Emission obtained by exciting the thin films at their absorption maxima in solution.



**Figure 6.** Normalized absorption (solid line) and emission spectra (dotted line) in micromolar THF solution obtained for **1a-d** (a); Normalized emission spectra of thin films of compounds **1a-d** (excited at the absorption maxima obtained in solution state), inset shows the images of these thin films under UV light of long wavelength (365 nm) (b).

Based on the resemblance to the previously reported 1,2,4-oxadiazole derivatives<sup>20</sup> the single absorption band observed with these molecules could be due to  $\pi$ - $\pi$ \* transition of the aromatic system. Optical bandgaps of these systems were estimated from the red edge of the absorption spectra. These compounds **1a-d** showed a larger band gap of 4.2 eV, in comparison to their 1,3,4-oxadiazole derivatives (3.4-3.5 eV).<sup>32</sup> Emission spectra obtained by exciting the solutions of these compounds at their absorption maxima showed emission maxima centered around 299-314 nm. The emission spectra were red shifted on increasing the number of peripheral alkyl chains.

The emission intensity was less in solution state and we could not measure the relative quantum yield of these compounds with respect to standard compound. We were interested to study the emissive nature of these molecules in solid state. The thin films of the compounds were prepared by slow cooling of the isotropic liquids of the samples sandwiched between the glass coverslips. They showed a red-shifted emission and excitation spectra (Fig. 6b; Table 2 and Fig.S47 in SI), which points to the formation of aggregates. The red-shifted excitation and emission spectra of the thin films in comparison to the respective spectra in solution state at micromolar concentration points to the formation of J-aggregates<sup>35</sup>

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Energy levels of frontier molecular orbitals (HOMO and LUMO) of the star shaped molecules were obtained by cyclic voltammetry (CV) and the data are tabulated in table 3. We have chosen compounds **1a-c** for carrying out CV studies. All the compounds exhibited irreversible oxidation and reduction waves (See Fig. S49). The optical band gap  $E_{g}$ , <sub>opt</sub> was estimated from the red edge of the absorption spectra. Energy levels of LUMO and HOMO were determined by using the formulae  $E_{LUMO} = E_{HOMO} + E_{g, opt}$  and  $E_{HOMO} = -(4.8 - E_{1/2,Fc,Fc+} + E_{ox, onset})$  eV. Compounds **1a-c** exhibited LUMO levels of -2.08 eV, -1.96 eV and -2.09 eV, and HOMO levels of -6.31 eV, -6.17 eV and -6.31 eV. In comparison to their 1,3,4-oxadiazole counterparts these compounds showed lower LUMO and HOMO levels and higher band gaps. The higher band gap is the most challenging material property pursued in the advancement of deep blue PHOLEDs.<sup>36</sup> Considering this the present series of compounds are good candidates for such applications.

**Gelation studies.** The compounds were investigated for their ability to aggregate in solutions of hexane, decane, dodecane, hexadecane, chloroform, dichloromethane, ethanol, dimethylsulfoxide (DMSO), *n*-butanol, tetrahydrofuran, benzene, toluene and *m*-xylene. Except for compound **1b** with six decyloxy chains, none of the compounds exhibited gelforming ability. Compound **1b** formed gels in solvents like hexane, decane, dodecane and

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hexadecane and confirmed by the inversion of the glass vial (Fig. 7c, Table 3 in SI). This compound was soluble in chloroform, dichloromethane and tetrahydrofuran, while it was insoluble in DMSO. Compound **1b** got precipitated in solvents like ethanol and *n*-butanol. Compound **1a** with three decyloxy chains did not form any gel in dodecane and same with the case of compound **1c** and **1d** with nine alkoxy chains. Compound **1b** with six decyloxy chains stabilized the gel formation in dodecane with very low critical gelation concentration (CGC) of 0.52 wt %. In literature it is well-known that the molecules which undergo gelation at concentrations lower than 1 wt% are usually classified as super gelators.<sup>10</sup> The supergelation capability of compound **1b** was further confirmed by the formation of self-standing gels (Fig. 7e)



**Figure 7.** Emission spectra showing an increase in the emission intensity with time on gelation (a); Normalized emission spectra showing a red shift on gelation (b); Images showing the gel formation with respect to time in daylight (c); Images showing the gel formation under the UV light (365 nm) with respect to time (d); Self standing gel in daylight (left) and under UV light (365 nm) (e); Plot showing the change in the emission intensity at emission maximum with respect to time (f).

The organogel was formed within 150 seconds after dissolving in dodecane (Fig.7c,d). The formation of gel was probed by fluorescence spectroscopy by plotting the fluorescence intensity at emission maximum against the time taken for gelation in seconds. The emission intensity increases with the time and reaches saturation at 220 seconds (Fig. 7a,b,f). Visually this change is apparent on irradiating the solution at these time intervals with the UV light of

long wavelength ( $\lambda = 365$  nm) (Fig. 7d). Normalized emission spectra showed a red shift in the emission maxima from 426 nm to 442 nm (Fig.7b).

To the best of our knowledge, compound **1b** is the first star shaped supergelator with out any supportive H-bonding in its molecular structure. In literature few metal-organic gels,<sup>37</sup> organic-inorganic hybrids,<sup>38</sup> polypeptides,<sup>39</sup> sugars <sup>40</sup> and polymers<sup>41</sup> show such super gelation property. This can be explained as below. From the XRD data of the xerogel of compound 1b it is shown that the molecules self-assemble to form rectangular columnar phase, while in the bulk state the molecules self-assemble to form hexagonal columnar phase. In both cases  $\pi$ - $\pi$  interactions play a major role in supporting columnar self-assembly. The Hbond that is observed in the case of crystalline compound 1a is between the aromatic hydrogen of one molecule and the heterocyclic nitrogen of the other molecule. This hydrogen bonding is only possible, if the molecules arrange in an antiparallel lamellar structure (Fig.18a). Thus we can conclude that H-bond does not play a role in the columnar selfassemblies found in liquid crystal and gel state. Apart from  $\pi$ - $\pi$  interactions, other factors like number and position of the peripheral alkyl chains also have vital role in the gelation, aided by weak forces like van der Waals force. Till date there is a single report on supergelation, where  $\pi$ - $\pi$  interactions play a major role and this is found in 1,3,4-oxadiazole based polycatenar.<sup>12</sup> We also like to point out that rod-like systems are more conducive to form organogels than the star shaped molecules in the absence of supporting interactions like Hbonding and one can find many examples in literature.<sup>2</sup>

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**Figure 8.** Emission spectra showing an increase in the emission intensity on decreasing the temperature due to gelation (a); Normalized emission spectra showing a red shift on gelation (b); Plot showing the change in emission intensity on decreasing the temperature (c); Reproducible reversibility of emission intensity in solution to gel interconversion (d).

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Formation of organogel was also confirmed by measuring the emission spectra of the solution as a function of decreasing temperature. The emission intensity increased on decreasing the temperature upto 40 °C with a red shift from 426 nm to 452 nm (Fig. 8a,b and c). There is a huge increase (four fold) in the luminescence intensity in gel state in comparison to the solution state emission (Fig.7a and 8a). But we should note that this increase in luminescence intensity is seen when the solution is above CGC (3.4 mM in dodecane). When the concentration of the solution is very less for example at 20  $\mu$ M, where the monomers are greater in number in comparison to aggregates, the difference between the luminescence intensity is twelve fold (Fig. 9b). Thus this is a phenomenon of aggregation-induced emission. The emission spectra showed a red shift upon gelation (Fig. 8c and S46), which was similar to the observation in Fig.7b. This gel formation was reversible for many cycles of heating and cooling as evidenced by the change in the emission intensity at emission maximum (Fig. 8d).



**Figure 9.** Normalized absorption spectra of compound **1b** in dodecane at 4 mM (red trace) and 20  $\mu$ M (blue trace) concentration (a); Emission spectra of compound **1b** in dodecane at 4 mM (red trace) and 20  $\mu$ M (black trace) concentration (b); The fluorescence decay of compound **1b** in dodecane at 4 mM (red trace) and 20  $\mu$ M (blue trace) concentrations (green trace is instrument response function: IRF;  $\lambda_{exc} = 290$  nm) (c); Dynamic light scattering curve observed for compound **1b** in dodecane in micromolar concentration (d).

Fluorescence lifetimes of the excited species formed in the 20  $\mu$ M and 4 mM dodecane solutions were measured by monitoring at their emission maxima (426 nm for dilute solution and 442 nm for the concentrated solution). The solution with lower concentration showed biexponential decay with two excited species  $[T_1 = 3.4 \text{ ns} (87\%), T_2 = 15 \text{ ns} (13\%)].$ The solution with higher concentration showed the same set of excited state species, where the excited state species with higher lifetime was in higher amount [ $T_1 = 3.4$  ns (10%),  $T_2 =$ 15 ns (90%)] (Fig. 9c). The species with lower lifetime was solvated monomer, whereas the species with the higher lifetime is formed due to aggregation. Dynamic light scattering experiments carried out for compound 1b in dodecane in milimolar concentration showed the presence of aggregates of 300 nm size (Fig.9d). The absorption spectrum obtained at higher concentration (4 mM) has shown a blue shift compared to the solution at lower concentration  $(20 \ \mu\text{M})$  (Fig. 9a). This shows that the aggregates formed during gelation are of H-type aggregates where the molecules are arranged one above the other in cofacial or parallel manner. Excitonic splitting in these aggregates leads to a high-energy transition and a low energy forbidden transition. In such systems the absorption spectra is dominated by the highenergy band leading to a blue shifted absorption band with respect to monomer absorption band. This also leads to strong red shift in the fluorescence from low energy band.<sup>41</sup> Eventhough H-aggregates are supposed to exhibit reduced luminescence than in solution, here the situation is exactly opposite of the expected. In literature there are limited reports on luminescent H-aggregates.<sup>43</sup> Usually this luminescence by H-aggregates is accounted for the excimer species or due to a slight rotation of two exciton-coupled molecules in the excited state. We should note that the annealed thin films showed the formation of J-aggregates. Thus there is a J- to H-type conversion was seen on moving from solid to gel state. Similar H-type aggregation of star shaped molecules on gelation in hydrocarbon solvents was reported by Das et al. 44

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**Figure 10.** Moldability of organogel of **1b** in dodecane (1.5 wt%) into different shapes like cube (a); cylinder (b); trigonal prism (c) seen under day light; under UV light (365 nm) (d); ability to sustain the weight (e); Photograph of gel after standing for 45 days in daylight and under UV light (365 nm) (f); Plots of  $T_{gel}$  vs concentration for compound **1b** in dodecane (g).

The self-standing gel showed an incredible stability on keeping inverted for a period of more than a month (Fig.10f). When we taken the gel in small amount and kept it inverted shrinkage of gel was observed over a period of 25 days but shape was retained. (See SI Fig. S50). This indicated another level of self-organization of the xerogel architecture in the absence of solvent. The luminescence remained same in spite of the change in the structure of the gel. We have investigated the thermal stability of the gel with respect to concentration by 'dropping ball' method,<sup>45</sup> which showed a gradual increase (Fig.10g) on increasing the concentration. The gel prepared at 1.5 wt % concentration showed higher mechanical strength and could be molded into any shape as shown in Fig.10a-d and the luminescence remained unchanged.

Extensive microscopy was carried out to understand the superstructure of the gel formed from compound **1b**. The surface morphology of the xerogels of **1b** obtained from the organogel in dodecane was studied with the help of field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM). Scanning electron microscopy (SEM) images of the xerogels obtained by evaporating the 1 mM dodecane solutions of compound **1b** showed the entangled network of fibers (Fig.11). AFM microscopy was carried out on a drop casted film (**1b** in dodecane, 1mM) and allowing the solvent to evaporate to get a xerogel film. The AFM images



Figure 11. SEM images obtained for compound 1b at 1mM dodecane solution (a); an expanded region of the first image (b) (scale bar is  $1\mu m$ ).

showed a very dense network of fibers (Fig. 12a). The same experiment carried out by drop casting a solution at lower concentration  $(1 \times 10^{-5} \text{ M})$ , helped us to look at the individual fiber in detail (Fig. 12b). The fibers are of several micrometers in length, with heights of 30-40 nm and thickness of around 185 nm (Fig. 12c and d). Transmission electron microscopy (TEM) images of the gels (1mM dodecane solution) showed interwoven network of fibers of diameter 30-40 nm (Fig. 13). These SEM, AFM and TEM images of the gels were further supported by fluorescence microscopy and optical microscopy studies (see the SI, Fig. S40 and S48).



**Figure 12.** AFM images obtained for compound **1b** at 1mM dodecane solution (scale bar is 1  $\mu$ m) (a); at 1 x 10<sup>-5</sup> M (scale bar is 2 $\mu$ m) (b); Expanded regions of figure 12b and showing the height profiles of the individual fibers (c); Expanded regions of figure 12b and showing the thickness of an individual fiber (d).



**Figure 13.** TEM images obtained for compound **1b** at 1mM dodecane solution (scale bar is 5  $\mu$ m) (a); an expanded regions of figure 13a showing entangled fibers (scale bar is 1  $\mu$ m) (b)

Further the structure of the xerogel was studied with the help of powder X-ray diffraction studies carried out on a thin film of the compound **1b** prepared by drop casting the 1 mM solution on a glass slide. The XRD pattern of the xerogel film (Fig. 14a) showed many peaks centered at 30.61, 24.91, 10.67, 9.11, 7.11 6.18, 5.96, 5.42, 5.05, 3.79. This may be due to the strong intermolecular interactions of the adjacent molecules in xerogel state. The ratio of reciprocal *d*-spacings clearly rules out a lamellar order of the molecules, but strongly suggests columnar rectangular structure in particular. The lattice parameters '*a*' and '*b*' of the unit rectangular cell was found to be 61.22 and 27.26 Å, respectively (details are in

supporting information). The columnar arrangement of these molecules in the nanofibers of the xerogel is also supported by the birefringent texture obtained for the xerogel state (Fig. 14b). Thus we can represent the hierarchical self-assembly of these star shaped molecules in bulk and gel state as shown in the figure 15.



**Figure 14.** XRD profile depicting the intensity against the  $2\theta$  obtained for the Col<sub>r</sub> phase of compound **1b** in xerogel state (inset shows the XRD image pattern obtained) (a) POM image of the xerogel showing a birefringent texture (b).



Figure 15. Schematic representation showing the supramolecular hierarchical organization of compound 1b.

#### **Rheological studies**

To obtain further insights into the dynamic mechanical properties of the organogel formed from compound **1b** in dodecane, we performed dynamic frequency sweep experiments (at constant stress) to measure the rheological response, as characterized by G\* ( $\omega$ ) = G' ( $\omega$ ) + iG" ( $\omega$ ), where G' is the storage modulus, G" is the loss modulus and  $\omega$  is

the angular frequency.<sup>46</sup> These measurements are advantageous as the final details of the gel structure remain perfect due to small dormation (*i.e.* small stress). Figure 16a, shows measurements of G' and G" for the gels containing 0.52 wt% of compound **1b** in dodecane as a function of  $\omega$  (at 25 °C using 0.2 kPa stress). We make two observations from Figure 16a.



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**Figure 16.** Angular frequency (rad s<sup>-1</sup>) dependence of G' and G" obtained with small stress amplitudes: (a) 0.52 wt% of compound **1b** in dodecane at 25 °C using 0.2 kPa stress. (b) Stress dependence of G' and G" of the same gel **1b** measured at constant frequency (at 25 °C, and frequency at 0.1 Hz). (c) Thixotropic nature of organogel of **1b** (3.4 mM) in *n*-dodecane at 25 °C (Deformation; stress: 0.1 to 100 Pa, time: 300 s, angular frequency: 10 Hz; Recovery; Stress: 1 Pa, time: 300 s; angular frequency: 10 Hz.) (d) Five continuous cycles of measurement for **1b** (3.4 mM) to prove that gel is thixotropic.

First, G' is greater than G" over the entire range of frequency measurements, indicating that the LC gel behaves as a solid-like, viscoelastic material. Second, G' and G'' are weakly dependent on frequency. It should also be noted that even at the lowest frequency (the limit of the instrument) we did not see liquid like behaviour of the gel (*i.e.* G">G'). This confirms that gel nature of these materials in which structural relaxation is very large.

Past studies have also demonstrated that the dynamics of the sol-gels lead to characteristic features in non-linear rheological measurements. To establish this non-linear viscoelastic regime, we performed stress amplitude dependence of the storage and loss

moduli. Figure 16b shows stress-dependent nonlinear measurements of the gel at a fixed frequency of 0.1 Hz. We note two features in Figure 16b. First, at low strain amplitudes G' is nearly constant, suggesting a linear viscoelastic regime. In this regime, G'> G" which is consistent with the solid like behavior of the gel. Second, above a critical stress value (2.8 kPa), both G' and G" became strain dependent and leads ultimately to the observation of viscoelastic liquid-like behaviors at high stress (G">G'). This signifies a deformation driven transition from a viscoelastic solid to viscoelastic liquid.

The thixotropic nature of the gel was also examined by studying the recovery of the destroyed gel. Two continuous processes, *i.e.* deformation and recovery were followed step by step to understand the thixotropic nature (Figure 16c). A varying stress from 0.2 to 3 kPa at an angular frequency of 10 Hz for 300 s was applied for the deformation step and the values of G' was monitored as a function of time for 300 s. In the recovery process, the storage modulus G' was monitored as a function of same time interval (300 s) for a low shear stress of 0.2 kPa while keeping the same angular frequency (10 Hz). This experiment was repeated five times and the results are shown in Figure 16d. The results show that the gel recovered immediately after removing the applied stress.

#### Single crystal XRD studies

We were curious to know how these 1,2,4-oxadiazole based molecules self-assemble in crystalline state. We thought that this knowledge would help us in unraveling the association of these molecules in liquid crystalline and gel self-assemblies. Even though, we desired the crystallization of compound **1b**, unfortunately except compound **1a**, none of the compounds in this series crystallized in any solvents. Nevertheless crystal structure of compound **1a** provided some valuable insights into the self-assembly of this series of molecules, as we discuss in the following (Table 4 in SI).

Slow evaporation of  $CH_2Cl_2$  solution of **1a** at room temperature afforded colorless rectangular prism like crystals suitable for single crystal X-ray diffraction determination (Fig.17b); the crystallographic data are summarized in the SI section. The star-shaped molecule of **1a** has a diameter of 43.11Å and its oxadiazole ring is roughly coplanar with central benzene rings and two peripheral benzene rings (Fig.17a). Neighboring pair of



**Figure 17.** ORTEP representation of the compound of **1a** (a); Image of a crystal of **1a** under day light (b); Image of a crystal under UV light ( $\lambda = 365 \text{ nm}$ ) (c).

molecules is aligned in an alternating anti-parallel manner augmented by two sets of  $\pi^{-}\pi$ stacking interactions.<sup>47</sup> First one is (stacking distance of 4.50Å) between the centroid of the oxadiazole ring of one molecule and the same of the neighboring molecule. Second one is between the centroid of the central benzene ring of one molecule and centroid of the peripheral benzene ring of other molecule (stacking distance of 4.03 Å) (Fig.18b). Further there is a lateral non covalent C-H...N interaction between the hydrogen atom (H29) of the peripheral benzene ring of one molecule, with the nitrogen atom (N2) of the oxadiazole ring of another molecule ( $d_{CH...N} = 2.628$  Å) (Fig.18a). The restriction of the intramolecular rotation would be restricted by the van der Waals interaction of long alkyl chains from the neighbouring molecule leading to interdigitation<sup>48</sup> (Fig.S54). In addition there is hydrophobic interactions (2.394Å) between terminal *n*-decyl chains of the next row. As a result, this alternate packing of molecules, leads to a repeating lamellar distance of 26.95 Å (Fig 18a and Fig. S55). The heteroatoms in the five membered rings were preferentially co-planar with the carbon and nitrogen atoms to form a planar  $\pi$ -conjugation system. The comparison of C-O, N-O and C-N bond distances and angles of the hetrocyclic ring of **1a** has been made and the results are summarized in Table 4 (SI).



Figure 18. Crystallographic packing structure of compound 1a, side view showing Hbonding, hydrophobic interactions and lamellar packing (a) and simplified top view showing  $\pi$ -stacking interactions (b).

Compound **1a** is almost nonfluorescent in solution but a significant enhancement in the emission intensity in thin film was observed, emitting blue fluorescence (Fig. 5b) upon exposure to UV light ( $\lambda_{ex}$ = 365nm). Interestingly, similar behavior was observed with the single crystal too (Fig.17c). Presumably, inhibition of the intramolecular rotation helps in the planarization of the molecule in the crystalline state of compound **1a**, thus enhancing the fluorescence due to push-pull mechanism. In addition, this arrangement prevents the aggregation quenching. Thus  $\pi^{-..}\pi$  stacking, lateral H-bonding, van der Waal's interaction and hydrophobic interactions of alkyl tails as a whole leads to lamellar packing in the crystal structure. In the case of compound **1b** with six alkyl tails, the increased number of alkyl chains enhances the disorder at periphery, while maintaining the planarity of the central aromatic core; which allows the columnar stacking. Increase in the number of alkyl tails helps in the stabilization of liquid crystallinity and organogelation in hydrocarbons due to increased fluidity (Fig. S56). Thus with the increase in the number of alkyl chains, molecules move from lamellar packing in the crystalline state to columnar packing in liquid crystalline and gel state as in the case of **1b**. Further increase in the number of alkyl tails disrupts this subtle balance, as in the case of compound **1c** and **1d**, which exhibit only columnar LC phase, but lose the ability to undergo gelation. Similar behavior was observed in the recently reported series of macrocycles, where the number of peripheral tails played a major role in deciding the type and thermal range of the mesophase.<sup>49</sup>

# Conclusion

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We have reported a new class of star shaped 1,2,4-oxadiazole derivatives stabilizing hexagonal columnar phase over a broad temperature range. Their thermal behavior was analyzed with the help of polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction studies. The number and length of the peripheral chains affected the mesophase stability and the thermal range. Compound with three peripheral tails was crystalline and showed the lamellar packing as evidenced from single crystal XRD studies. The compounds required at least six alkyl tails at the periphery to stabilize the columnar hexagonal mesophase. The thermal range of the mesophase increased with the number of alkyl chains. Increase in the chain length reduced the thermal range of the columnar hexagonal phase. All the compounds showed weak fluorescence in solution state but strong emission in solid state. In the solid-state emission the compounds showed a red shift with the increase in the number of peripheral chains. The compound with six alkyl chains showed the ability to self-assemble into freestanding gels in nonpolar solvents. This is a first example of a star-shaped supergelator, which form a self-standing gel where attractive  $\pi$ - $\pi$  interactions play a major role. At higher concentration this compound forms a mechanically stable, moldable gel. Another property of technological importance is that the compound shows aggregationinduced blue light emission, which is twelve times greater than the monomer emission. By photophysical studies of thin films and gels it is revealed that in the former case this compound forms J-aggregate, while in the later case it forms H-aggregates. Rheological studies confirmed the thixotropic nature of the gel. The xerogels were characterized with the help of scanning electron microscopy, transmission electron microscopy, atomic force miscroscopy, fluorescence microscopy and polarizing optical microscopy. These microscopic techniques confirmed a highly interwoven network of fibers. Fluorescent microscopy revealed

that these fibers were fluorescent due to the aggregation-induced emission phenomenon. Polarizing optical microscopy of the xerogel films showed a birefringent texture, which is evidence to the anisotropic nature of self-assembly. X-ray diffraction studies revealed that the molecules are organized form a Col phase with rectangular symmetry. Considering the dearth of wide band gap, solid-state blue light emitting organic materials, these star shaped molecules are promising, due to their emissive nature in the aggregated state and columnar self-assembly. They have a bright potential in the field of solid-state emissive displays.

# **Supporting Information**

Synthesis and characterization details of intermediates and final compounds, <sup>1</sup>H and <sup>13</sup>C NMR spectra, POM images, DSC and TGA thermograms, XRD plots, details related to photophysical, electrochemical, gelation and single crystal XRD studies.

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