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# Liquid Crystalline Star-shaped Supergelator Exhibiting Aggregation Induced Blue light Emission

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Abstract: A family of closely related star shaped stilbene based molecules containing an amide linkage are synthesized and their self-assembly in liquid crystalline and gel state was investigated. The number and position of the peripheral alkyl tails were systematically varied to understand the structure-property relation. Interestingly one of the molecules with seven peipheral chains was bimesomorphic exhibiting columnar hexagonal and columnar rectangular phase, while rest of them stabilized room temperature columnar hexagonal phase. The self-assembly of these molecules in liquid crystalline and organogel state is extremely sensitive to the position and number of alkoxy tails in the periphery. Two of the compounds with six and seven peripheral tails exhibited supergelation behavior in long-chain hydrocarbon solvents. One of these compounds with seven alkyl chains was investigated further and it has shown higher stability and moldability in the gel state. The xerogel of the same compound was characterized with the help of extensive microscopic and X-ray diffraction studies. The nanofibres in the xerogel are found to consist of molecules arranged in a lamellar fashion. Furthermore, this compound shows very weak emission in solution, but show aggregation induced emission property in the gel state. Considering the dearth of solid-state blue light emitting organic materials, this molecular design is promising where the self-assembly and emission in the aggregated state can be preserved. The unsymmetric design to lower the phase transition temperatures. The presence of amide bond helps to stabilize columnar packing over a long range due to its polarity and intermolecular hydrogen bonding in addition to promoting organogelation.

#### Introduction

Molecular self-assembly plays a crucial role in the development of functional soft materials.¹ There are various functional supramolecules like dendrimers, peptosomes, microcapsules, micelles, organogels and liquid crystalline materials, which are formed through molecular self-assembly. Organogels and liquid crystals are one such example where the engineered molecules exhibit the desired functions in the self-assembled state. Columnar liquid crystalline (Col LC) self-assembly of disc shaped molecules was discovered in 1977,² and this unique one-dimensional (1D) self-assembly has got the potential in the development of organic light emitting diodes (OLED),³ organic field effect transistors (OFETs),⁴ organic photovoltaics (OPVs),⁵ gas sensors and lubricants.⁶ The efficiency of these devices depends on the

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intermolecular order, which help in the charge migration along the columnar phases.^{6,7} Thus the molecular design principle of Col LCs involves the utilization of various secondary interactions like H-bonding,  $\pi$ - $\pi$  interactions, ionic, hydrophilic and hydrophobic interactions etc. apart from the molecular shape anisotropy that leads to the nanoseggregation of incompatible molecular subunits.^{8,9} After the discovery of Col phase in disc shaped molecules, there were many different non-conventional molecular designs to stabilize Col phases. Shape persistent star shaped mesogens¹⁰⁻¹³ or 'hekates'¹¹⁻¹² are one of the non-conventional LCs formed by the covalent linking of three rigid arms symmetrically to a central core through linkers. Their lack of shape anisotropy to exhibit mesophases is compensated by the nanophase segregation of chemically/physically different molecular subunits and their tendency of efficient space filling. More recently, propeller-like 1,3,5-triphenyl benzenes exhibiting ordered columnar phases are reported.¹³ Inherent synthetic flexibility and the easy incorporation of the properties like hole/electron transport, nonlinear optical activity, fluorescence and the ability to exhibit a rich variety of mesophases like nematic, columnar, cubic or soft crystal phases are the uniqueness of hekates in comparison to discotics. The presence of the voids between the arms of these star shaped molecules promote the glassy state.¹¹⁻¹² Columnar phases with glassy nature are important as they allow the movement of charge carriers with the simultaneous restriction on ionic impurities.¹⁴ In the context of the application of Col phases towards OLEDs, it is important to stabilize Col phase along with the preserved solid-state luminescence. This is because aggregation quenching of luminescence is detrimental to the device performance. Similarly organogels are the three dimensional network of the entangled supramolecular fibres which is formed by self assembly of low molecular weight gelator, entrapping a large volume of the solvent.^{15,16} The 1D self-assembly of the molecules in the form of fibers has got a great potential in the area of optoelectronics, controlled drug release ¹⁷ energy transfer ^{18, 19} sensing²⁰ and security.^{21, 22}

Both the self-assemblies *i.e.* Col LCs and organogels can be designed and tuned to have properties like long-range order and high charge-carrier mobility in addition to their inherent properties like self-healing ability, ease of processing, high solubility to enhance their application in the fabrication of electronic devices.^{8-9, 15-16} These self-assemblies bring anisotropies in the physical properties, for example the conductivity along the column is more, while that across the column is less in many orders. The emission may be more in the bulk state if the molecules form slip-stacked

 or J-type aggregates, while it gets quenched when they form cofacial or H-type aggregates.²³ The aggregation caused quenching (ACQ) due to the non-radiative decay of the excited state is a notorious problem in decreasing the luminescence efficiency in aggregates, which have strong  $\pi$ - $\pi$  interaction. Since the planar structure of the molecule is a prerequisite for the stabilization of Col phase and vital for charge migration, this is a delicate problem to address. Thus the design should include an option to preserve both columnar order as well as emissive nature.

There is a class of molecules which show the phenomenon of aggregation induced emission (AIE), where the luminescence quenching is avoided due to the restricted rotation of the fluorophores. Hence there is flurry of activity to synthesize molecules that exhibit AIE phenomenon in the whole visible region ²⁴ and eventually targeted their application in solid-state emissive displays. Inspite of these efforts, the molecules which exhibit aggregation induced blue light emission are very rare. Further columnar self-assembly of such molecules is a challenging task. Considering the scarcity and the vital role in the construction of full color display and white light emission²⁵⁻²⁷ developing such molecules, which combine columnar self-assembly, blue emission and AIE phenomenon is of foremost importance. Again the absence of a general protocol makes molecular design complicated and demanding.

It will be ideal if a molecule exhibits LC behavior and the ability to undergo gelation maintaining the same order. Such compounds are suitable candidates for the applications in optoelectronic devices.²⁸⁻²⁹ In order to achieve this the molecule should have the ability to self-assemble into columnar aggregates and the interaction of these aggregates with the solvents must not destabilize the columnar self-assembly. Incorporation of functionalities like amide, hydroxyl, acid, large aromatic units and steroid moieties often known to support gelation and in few case less than 1 weight % of molecule is sufficient to gelate large volume of slovents. Such compounds are known as supergelators.³⁰ There are some reports on fluorescent amide derivatives which employ the hydrogen bonding to form large 3D entangled networks, which help in entrapping the solvent.³¹⁻³²

Though there are some reports on the mesogens containing amide units are reported, their gelation properties are not explored in detail. It should be noted that such molecules with amide units stabilized wide mesophase range including room temperature.³³ Stabilizing room temperature Col phase is also another factor, which

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will enhance the performance of the semiconductor, as most of them crystallize at room temperature leading to defects, which might act as charge traps. Amide units are incorporated as linking units between the central core and peripheral tails in the case of discotics to overcome the coulombic repulsion between the cores resulting in reduced intracolumnar distance and hence resulting in high charge-carrier mobility. ³⁴ Recently there has been a report where the introduction of amide units stabilized a ferroelectrically switching Col phase.³⁵

*trans*-Stilbene unit has been excellent known for its properties,³⁶ and has found many commercial photochemical/photophysical applications viz., optical brightener, laser dyes and in the fabrication of OLEDs, photoresists, photoconductive devices, optical switching and non linear optics (NLO). Coya et. al. fabricated a blue OLED from that 1,3,5-tris(3,4,5-tris(dodecyloxy)styryl benzene, but the molecules were crystalline at room temperature.³⁷ Lehman *et. al.* reported a star shaped stilbene based molecule which stabilized the Col phase over a thermal range of 37 degrees.³⁸ Yelamaggad *et. al.* reported the star shaped molecules based on *trans*-stilbene stabilizing the Col_b phase, but the compound is a green light emitter in solution and further red shift was seen in solid state.^{39,40}

In this report we have designed a star shaped molecule where the central benzene ring is connected with two *trans*-stilbene fluorophores at alternate positions, while the other meta-position is occupied by peripherally substituted alkoxy benzene connected through an amide linkage. Peripherally substituted *trans*-stilbenes were chosen for their emissive nature, while amide linkage was introduced as a possible means to achieve room temperature liquid crystallinity and gelation. Further variation in the structure was carried out, by varying the number of alkyl tails in these peripheral rings to tune the thermal and gelation behavior (Fig. 1).



Figure 1. Bargraph summarizing the thermal behavior of compounds 1a-e (second heating cycle)

## **Results and discussion**

**Synthesis and Characterization.** The synthetic route for the preparation of the target molecules is depicted in scheme 1 and 2 (See the SI for experimental and characterization data).



Scheme 1. Synthesis of key-intermediate1,3-bis(diethoxyphosphoryl)methyl)-5-nitro benzene (8). Reagents and conditions: i) KMnO₄, aq. NaOH, reflux, 6 days (58%); ii) HNO₃, H₂SO₄, reflux, 24 h (73%); iii) NaBH₄, BF₃.Et₂O, dry THF, 16h, rt (89%); iv) PBr₃, dry THF, 24 h (97%); v) Triethylphosphite, 130°C, 6 h, N₂(70%).

m-Xylene was subjected to oxidation by refluxing in a alkaline aqueous solution of  $KMnO_4$  to obtain isophthalic acid (12) which was nitrated by heating with the nitration mixture to get 5-nitro benzene-1,3-dioic acid (11). This compound was reduced with NaBH₄ in presence of Lewis acid BF₃.Et₂O to get 3,5-bis-(hydroxymethyl) nitrobenzene (10). This alcohol was further reacted with  $PBr_3$  to obtain 3,5-bis-(bromomethyl)nitrobenzene (9). The Michaelis-Arbuzov reaction of compound (9) with the triethylphosphite furnished 1,3bis((diethoxyphosphoryl)methyl)-5-nitrobenzene (8). The requisite aldehyde (4a-b) were prepared in quantitative yields by different methods as follows; (i) 3,4,decyloxy benzaldehyde (4a) was prepared by *O*-alkylation of 3,4dihydroxybenzaldehyde with *n*-bromodecane following Williamson's etherification

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Scheme 2. Reagents and Conditions: i)1-Bromodecane, anhyd.  $K_2CO_3$ , DMF, 80 °C, 24h (70-80%) ii) LAH, THF, 0 °C to rt, 12 h (75%); iii) PCC, DCM, rt, 4h (70-80%); iv) 10% NaOH(aq), Ethanol, reflux, 6 h (76 - 80%); v) 3,5(bis((diethoxyphosphoryl)methyl)1-nitrobenzene, NaH, dry THF, 0 °C - rt (53-60%); vi) Zn, HCOONH₄, THF + Methanol (1:1), 1 h, rt (80-90%); vii) (a) (**6a-c**), SOCl₂, DMF (catalytic), 4 h, reflux; (b) acid chlorides of **6a-c**, dry THF, Et₃N, 6 h, reflux (52 - 76%).

protocol, (ii) 3.4,5-tridecyloxy benzaldehyde (4b) was synthesized, by the oxidation of 3,4,5-tridecyloxy benzyl alcohol (5b) using pyridiniumchlorochromate which in turn was obtained by the reduction of ethyl 3,4,5-tridecyloxy benzoate (7b). The Wittig-Horner reaction of these benzaldehydes (4a-b) with the phosphonate ester (8) in the presence of NaH in THF at 0 °C furnished (E)-1,3-bis(3,4-bis(decyloxy)styry))-5-nitrobenzene (3a) and (E)-5-(3-(3,4,5-tris(decyloxy)styryl)-5-nitrostyryl)-1,2,3tris(decyloxy)benzene (3b) respectively. These nitro products were converted to corresponding key amines, (E)-3,5- bis(3,4-bis(decyloxy)styrl) benzenamine (2a) and (E)-3,5-bis(3,4,5-tris(decyloxy)styrl) benzenamine (2b) respectively. Finally, the aminostyryl compound 2a was subjected to react with 3,4-didecyloxy benzoyl chloride and 3,4,5-tridecyloxybenzoyl chloride to obtain the target molecules (1a) and (1b) respectively. These acid chlorides were obtained by refluxing the corresponding acids **6a** and **6b** with SOCl₂ in presence of catalytic amount of anhydrous DMF. The reaction mixture was subjected to distillation to remove the excess thionyl chloride to furnish the acid chlorides and the residue obtained was used as such for the next step. Similarly the aminostyryl compound **2b** was reacted with 3.4-didecyloxy benzoyl chloride and 3,4,5-tridecyloxy benzovl chloride to obtain the target molecules (1d) and (1e) respectively. 4-Decyloxybenzoyl chloride was reacted with aminostyryl compound **2b** to give the target molecules **1c**.

**Thermal behavior.** The target molecules were probed for their thermal behavior with the help of polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Further the nature of the mesophase is confirmed with the help of X-ray diffraction (XRD) studies. The thermotropic LC behavior of the compounds is summarized in table 1. A comparison between the thermal behaviors of the compounds of the present series is furnished in Fig. 1.

Compound **1a** containing two styrene units with a total of four alkoxy chains and one 3,4-di-*n*-decyloxy benzenecarboxamide connected to the central benzene ring (effectively six peripheral chains) turned out to be crystalline. Compound **1b**, where the benzene carboxamide is derived from 3,4,5-tri-*n*-decyloxy benzene carboxylic acid (seven peripheral chains in total) melts into a fluidic birefringent pattern at  $\approx 89$ °C ( $\Delta H = 65.3$  kJ/mol), after passing through a crystal to crystal transitions (Fig. 2c). This spanned over a temperature range of 14 degrees before transforming into another

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mesophase at  $\approx 102$  °C ( $\Delta H = 10.5$  kJ/mol). This birefringent texture then turns into an isotropic liquid at 126 °C.

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

Phase sequence							
	2 nd Heating	1 st Cooling					
1a	Cr 65 (155.7) I	I 24.7 (168.1) Cr					
1b	Cr ^c 88.6 (65.3) Col _r 102 (10.5)	I 117.1 (43.5) Col _h 93 Col _r 79.1					
	Col _h 126 (39.3) I	$(3.2) \operatorname{Cr}^{d}$					
1c	Col _h 111.9 (22.3) I	I 110.2 (22.5) Col _h ^b					
1d	Col _h 109.1 (52.5) I	I 107 (52) Col _h ^b					
1e	Col _h 77.5 (39.4) I	$I 75 (36.4) Col_h^b$					

^aPeak temperatures in the DSC thermograms obtained during the second heating and cooling cycles at 5 °C/min. ^bThe mesophase is not crystallizing up to -20 °C. Cr = Crystal phase; Col_h = Columnar hexagonal phase; Col_r = Columnar rectangular phase; I = Isotropic phase. ^cThis crystalline state is preceded by the following Cr-Cr transitions at 82.8 (18.7); ^dBelow this temperature there is another Cr-Cr transition at 72.3 (75) Cr.



**Figure 2.** POM photograph of compound **1b** at 95  $^{\circ}$ C (a) and at 90  $^{\circ}$ C (b); DSC scans of first cooling (blue trace) and second heating (red trace) cycles of compound **1b** (c); XRD pattern obtained for compound **1b** at 110  $^{\circ}$ C and 90  $^{\circ}$ C (d).

Compounds Phase (T/°C)		$d_{\rm obs}({\rm \AA})$	$d_{\rm cal}({\rm \AA})$	Miller	Lattice	parameters		
$(D/\text{\AA})^{a}$					indices hkl	(Å)		
1b	)	Col _h (110)	28.7	28.7	100	a = 33.1		
41.	9		$5.1(h_a)$					
		$\operatorname{Col}_{r}(90)$	27.5	27.5	200	<i>a</i> = 55		
		1( )	23.8	23.8	110	b = 26.4		
			19.3	19.1	210			
			$5.10(h_a)$		-			
10	:	Col _h (80)	31.6	31.6	100	<i>a</i> = 36.5		
		/	18.5	18.2	110			
40.	9		15.7	15.8	200			
			$4.9(h_a)$					
		Col _h (28)	32.2	32.2	100	<i>a</i> = 37.1		
		/	18.8	18.6	110			
			16	16.1	200			
			$4.84(h_a)$					
1d		Col _h (80)	31.7	31.7	100	<i>a</i> = 36.5		
			18.2	18.3	110			
(41.	6)		15.7	15.8	200			
			$4.9(h_a)$					
		Col _h (28)	32.7	32.7	100	<i>a</i> = 37.8		
			18.9	18.9	110			
			16.5	16.4	200			
			$4.8(h_a)$					
1e	:	$\operatorname{Col}_{h}(50)$	30.6	30.6	100	<i>a</i> = 35.4		
			17.7	17.7	110			
(41	)		15.4	15.3	200			
			$4.9(h_a)$					
		Col _h (28)	31.6	31.6	100	<i>a</i> = 36.5		
			18.3	18.3	110			
			15.7	15.8	200			
			$4.8(h_a)$					

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

^aThe 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_h phase). The spacings marked  $h_a$  correspond to diffuse reflections in the wide-angle region arising from correlations between the alkyl chains.

Slow cooling of the isotropic liquid shows the emergence of spherulites from the dark field of view and further cooling witnessed the widening and merging of these arms with each other (Fig. 2a) to form a mosaic textures. Such textures are observed for phases with reduced flexibility like smectic or columnar phases. The presence of homeotropic domains points to the uniaxial nature of the mesophase, which is in line with the proposed columnar hexagonal (Col_h) phase as below. Powder XRD studies on the sample was carried out at different temperature intervals on cooling from isotropic liquid to understand the symmetry of the Col phase (Fig. S50). For the sake of explanation we describe here the XRD patterns obtained at 110 °C and 90 °C (Fig.2d and Table 2). The XRD pattern obtained at 110 °C and 90 °C showed a single diffused peak at wide angle ( $19^{\circ} < 2\theta < 26^{\circ}$ ) corresponding to the *d*-spacings of  $\approx 5.1$ 

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Å. This diffused peak corresponds to the packing of flexible peripheral tails in the liquid crystalline phase. Considering the presence of amide linkage which often leads to decreased core-core distance due to intermolecular H-bonding, the absence of core-core stacking reflection is quite surprising.³⁴ The diffraction pattern obtained at 110 °C showed a single sharp reflection at the low angle region ( $2^{\circ} < 2\theta < 7^{\circ}$ ) at a *d*-spacings of 28.7 Å. This can be assigned to 100 reflection of a hexagonal lattice, with a lattice parameter *a* = 33.1 Å. This corresponds to the intercolumnar distance and found to be lesser than the calculated molecular diameter 41.9 Å. This points to an interdigitation of the peripheral alkyl tails or due to the chain melting in liquid crystalline state.

The XRD patterns showed a transition at 93 °C where the 100 peak of Col_h phase splits into 200 and 110 reflections (see the SI). It should be noted that the transition was hard to detect by POM or DSC (Fig.S50 and Fig.2c). For example, the XRD pattern at 90 °C (Fig. 2d) showed *d*-spacings of be 27.51 Å, 23.81 Å and 19.62 Å, which can be fitted into rectangular lattice with Miller indices of 200, 110, 210. The lattice parameters of the rectangular unit cell was found to be a = 55 Å, b = 26.4 Å. The mesophase crystallizes around 80 °C.

Star shaped molecule 1c with two styrene units with a total of six alkoxy chains and one 4-n-decyloxy benzene carboxamide connected to the central benzene ring (effectively seven peripheral chains as in the case of compound **1b**) exhibit a room temperature mesophase, as identified by its fluid birefringent texture, sticky nature of the sample and DSC. The mesophase converts to isotropic liquid at a temperature of  $\approx 112$  °C ( $\Delta H = 22.3$  kJ/mol). Slow cooling of isotropic liquid yields a mosaic texture that is characteristic of  $Col_h$  phase (Fig. 3a). The texture remains unchanged till room temperature (Fig. 3b) and DSC scans did not show the sign of crystallization till -20 °C and also in the subsequent heating cycles (Fig. 3c). Powder XRD patterns obtained at 80 °C and room temperature (Fig. 3d) showed that the symmetry of the Col phase is hexagonal in nature. The low angle region of the XRD pattern obtained at 80 °C showed one intense reflection at a *d*-spacing of 31.6 Å and two weak reflections centered at 18.5 Å and 15.7 Å. There was a diffused peak corresponding to a *d*-spacing of 4.9 Å which arises from the packing of flexible chains. The first three reflections at the low angle region can be indexed into 100, 110 and 200 reflections of a hexagonal lattice and the ratio of these spacing were 1:

 $1/\sqrt{3}$ : $1/\sqrt{2}$ . The hexagonal lattice constant 'a' was 36.5 Å, which is approximately 10% less than the molecular diameter, suggesting an interdigitation of peripheral alkyl tails. The XRD pattern observed at room temperature was similar to the one observed at high temperature with a marginal increase in the value of 'a'. This must be accounted for the stretching of alkyl tails on lowering the temperature. Compounds 1d and 1e with eight and nine alkyl tails respectively stabilized room temperature Col_h phase as evidenced from POM textures (Fig.4), DSC and XRD studies (See Fig. S48, S51, S52 and Table 2).



**Figure 3.** POM photograph of compound **1c** at 104 °C (a) and at 28 °C (b); DSC scans of first cooling (blue trace) and second heating (red trace) cycles of compound **1c** (c); XRD pattern obtained for compound **1c** at 80 °C (red trace) and at 28 °C (black trace), the inset shows the image patterns obtained (d).

A small decrease in the thermal range of the  $Col_h$  phase was seen on moving from 1c to 1d (from seven to eight alkyl chains) but a drastic decrease in the clearing temperature was observed in the case of compound 1e with nine alkyl chains. Thus on comparing the mesomorphic behavior of compounds 1b and 1c, it is evident that even



Figure 4. POM photographs of  $Col_h$  phases of compound 1d at 28 °C (a); and compound 1e at 28 °C (b).

though both the molecules are having same number of alkyl chains, compound **1b** exhibit higher melting and clearing points in comparison to compound **1c**. Further increase in the number of alkyl tails on the benzene carboxamide moiety (for compounds **1d** and **e**) leads to a reduction in clearing temperature, as it may reduce the core-core interaction of the star shaped molecule. It is interesting to note that a minimum of seven flexible tails are necessary to exhibit liquid crystallinity as seen from the thermal behavior of **1a**, **b** and **c**, where compound **1a** with five flexible tails is crystalline, while compounds **1b** and **1c**, both compounds with seven flexible tails turns to be liquid crystalline.

#### Photophysical and electrochemical studies

Photophysical properties of the star shaped stilbene amides **1a-e** in micromolar THF solution are represented in Table 3. Absorption and fluorescence spectra of the compounds **1a-e** were taken in THF (Fig. 5). As can be seen, the absorption spectra for the solutions of hekates **1a-e** showed a small variation in absorption maxima varying from 317-333 nm, which may be due to their substitution pattern. The series of molecules show large values of the molar absorption coefficients, implying that these are highly conjugated systems ( $\varepsilon \ge 39110 \text{ M}^{-1}\text{ cm}^{-1}$ ). The single absorption band of these systems is attributed to  $\pi$ - $\pi$ * transition of the double bond conjugated with aromatic system. Optical bandgaps of these systems were calculated from the red edge of the absorption spectra were in the range of 3.17 – 3.24 eV. Emission spectra obtained by exciting the micromolar solutions of these compounds at their absorption maxima did not show much variation and the emission



**Figure 5.** Normalized absorption (solid line) and emission spectra (dotted line) in micromolar THF solution obtained for **1a-e** (a); Normalized emission spectra of thin films of compounds **1a-e** (excited at the absorption maxima obtained in solution state) (b); Images of the micromolar solutions (Left panel) and thin films (Right panel) of compounds **1a-e** under UV light of long wavelength (365 nm) (c).

Table 3. Photophysical^a and electrochemical ^c properties of star shaped compounds 1a-e

	Absorp	Emission	Stoke's	Quantum	Absorption ⁱ	Emission ⁱ	$\Delta E_{g, opt}$ d, e	E _{10x} ^f	E _{HOMO} ^{d, h}	E _{LUMO}
	(nm)	(IIIII)	(cm ⁻¹ )	yield		(IIII)				
1a	332	406	5489	0.25	339	422	3.19	1.77	-6.11	-2.92
1b	333	407	5460	0.39	339	414	3.23	1.71	-6.05	-2.82
1c	327	407	6011	0.27	334	439	3.17	1.79	-6.13	-2.96
1d	317	407	6976	0.35	337	426	3.24	1.79	-6.13	-2.89
1e	328	412	6216	0.24	332	427	3.20	1.78	-6.12	-2.92
^a Micromolar solutions in THF. ^b Excited at the respective absorption maxima. ^c Experimental conditions: Micromolar DCM solutions, Ag/AgNO ₃ as reference electrode, glassy carbon as working electrode, platinum rod as counter electrode, TBAP (0.1 M) as a supporting electrolyte, room temperature. ^d In electron volts (eV). ^c Band gap was determined from the red edge of the longest wave length in the UV-Vis absorption spectra $E_g$ (eV) = 1240/(wavelength in nm), <b>1a</b> : 389 nm, <b>1b</b> : 385 nm, <b>1c</b> : 392 nm, <b>1d</b> : 383 nm; <b>1e</b> : 388 nm. ^f In volts (V). ^g Estimated from the formula $E_{LUMO} = E_{HOMO} + E_{g, opt}$ . ^h Estimated from the onset reduction peak values by using $E_{HOMO} = -(4.8 - E_{1/2,Fe,Fet} + E_{ox, onset})$ eV. ⁱ in thin film. ^j Relative quantum yield calculated with respect to quinine sulphate solution in 0.1 M H ₂ SO ₄ with a quantum yield of 0.54.										

maxima and was centered around 406-412 nm. We were interested to study the emissive nature of these molecules in solid state. The thin films of the compounds were prepared by annealing the isotropic liquids of the samples sandwiched between the glass cover slips. They showed a red-shifted absorption and emission spectra (Table 3, Fig.5b and Fig.S54), which points to the formation of aggregates. The red-shifted absorption and emission spectra of the annealed thin films in comparison to the respective spectra in micromolar solution state points to the formation of J-aggregates.²⁸ The solution and thin films exhibited a blue emission under the UV light

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of long wavelength ( $\lambda = 365$  nm) (Fig. 5c). Quantum yields of these compounds were measured with respect to quinine sulphate solution (in 0.1 M H₂SO₄, with quantum yield of 0.54) were found to be in the range 0.25 to 0.39 (Table 3, Fig. S56).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. All the compounds exhibited irreversible oxidation and reduction waves (Fig. S57). The optical band gap  $E_{g, opt}$  was estimated from the red edge of the absorption spectra was found to be around 3.2 eV. 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-e** exhibited LUMO levels ranging from -2.82 to -2.96 eV and HOMO levels ranging from -6.05 to -6.13 eV.

**Gelation studies.** The compounds were investigated for their ability to aggregate in solutions of *n*-hexane, *n*-decane, *n*-dodecane, *n*-hexadecane, chloroform, dichloromethane, ethanol, dimethylsulfoxide (DMSO), tetrahydrofuran, benzene, toluene and *m*-xylene. Compound **1a** with six decyloxy chains and **1b** with seven



**Figure 6.** Emission spectra showing an increase in the emission intensity with time on gelation (5 mM, *n*-hexadecane)(a); Normalized emission spectra showing a red shift on gelation (b); Plot showing the change in the emission intensity at  $\lambda_{max}$  with respect to time (c); Images showing the gel formation with respect to time in daylight (d); Images showing the gel formation under the UV light (365 nm) with respect to time (e).

decyloxy chains (where the amide part contains three decyloxy chains), exhibited gelation in *n*-hexadecane, while other compounds in this series did not show gelation. It should be noted that compound **1a** is crystalline, **1b** is liquid crystalline at higher temperature, while other compounds **1c-e** are room temperature liquid crystals, which relates to the delicate balance of rigidity and fluidity required for the gelation. The number and position of the alkoxy chains also matter in this self-assembly process. This can be understood from the fact that compound **1b** with seven decyloxy chains stabilized the gel formation in *n*-hexadecane while compound **1c**, which also possess seven alkyl chains, but at different position was soluble. The gelation of compound **1b** was confirmed by the inversion of the glass vial (Fig. 6d, S58c, Table 2 and 3 in SI). This compound was soluble in chloroform, dichloromethane and tetrahydrofuran, while it precipitated in ethanol and DMSO. Compound **1b** showed a low critical gelation concentration (CGC) of 0.75 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.³⁰⁻³¹ The organogel was formed within 20 minutes after dissolving in *n*-hexadecane (Fig.6c-e). The formation of gel was proved by fluorescence spectroscopy by plotting the fluorescence intensity at  $\lambda_{max}$  against the time taken for gelation in minutes. The emission intensity increases with the time and reaches saturation at 20 minutes (Fig. 6a-c). Visually this change is apparent on irradiating the solution at these time intervals with the UV light of long wavelength ( $\lambda$ = 365 nm) (Fig. 6e). Normalized emission spectra showed a red shift in the emission maxima from 437 nm to 449 nm (a shift of 12 nm, Fig. 6b). Formation of organogel was also confirmed by measuring the emission spectra of the solution on decreasing temperature. The emission intensity increased on decreasing the temperature with a red shift from 435 nm to 456 nm (Fig. S58a-c). In order to have a clear understanding, we have overlapped the emission spectra of compound 1b at 20  $\mu$ M, 5 mM (in solution state) and 5 mM (in gel state) solutions in *n*-hexadecane. This solution at 5 mM concentration, showed a red-shifted emission maximum in comparison to the 20  $\mu$ M solution (See SI, Fig.S53). On gelation, there is a huge increase (six fold) in the luminescence intensity with a red-shifted emission maximum in comparison to the solution state emission (Fig. S58a and Fig. S53). Thus this is a phenomenon of aggregation induced emission, where the increase in concentration leading to aggregation of fluorophores with a desired configuration to prevent the aggregation quenching. The desired configuration could be achieved due to restricted

intramolecular rotation (RIR) or by a favorable packing of molecules as a result of gelation. This can be explained as follows. For the solution in CGC at room temperature (at 5 mM), the molecules are present as aggregates, but with a very little restriction imposed on their intramolecular rotation, which leads to the efficient annihilation process associated with the active intramolecular rotation. Gel formation and the decrease of temperature reinforce the RIR process, enhances the strength of the H-bonding and activate the radiative decay leading to AIE effect.⁴² Other possibility is that, the aggregates formed in the gel state have the molecules arranged in a favorable packing to exhibit this phenomenon. This gel formation was reversible for many cycles of heating and cooling as evidenced by the change in the emission intensity (Fig. S58d).



**Figure 7.** Normalized excitation and emission spectra of compound **1b** in *n*-hexadecane at 5mM (blue trace) and 20  $\mu$ M (black trace) concentration (a); The fluorescence decay of compound **1b** in hexadecane at 5mM (red trace) and 20  $\mu$ M (blue trace) concentrations (black trace is instrument response function;  $\lambda_{exc} = 290$  nm) (b); Dynamic light scattering curve observed for compound **1b** in *n*-hexadecane in micromolar concentration (c); Moldability of organogel of **1b** in *n*-hexadecane (1.5 wt%) into different shapes as seen in day light: trigonal prism (d); cube (e); cylinder (f); the same shapes under UV light ( $\lambda = 365$  nm) (g), (h) and (i); ability to sustain the weight (j); Photograph of gel after standing for 1 month in daylight and under UV light ( $\lambda = 365$  nm) (k); Plots of  $T_{gel}$  vs concentration for compound **1b** in *n*-hexadecane (1).

We were interested to study the emissive nature of compound **1b** in gel state. The solution at this concentration showed a red-shifted excitation and emission

spectra (Fig.7a), in comparison to the respective spectra obtained in micromolar solution state. This points to the formation of J-aggregates where the molecules are arranged in a slip-stacked arrangement.⁴¹ Fluorescence lifetime studies to confirm the presence of different species at these different concentrations (20 µM and 5mM hexadecane solutions) were carried out by monitoring at their emission maxima (407 nm for dilute solution and 450 nm for concentrated solution). The solution with lower concentration showed exponential decay with one excited species  $[T_1 = 3.07 \text{ ns}]$ . Thesolution with higher concentration showed the different excited state species, with a lifetime of  $T_1 = 4.11$  ns (Fig.7b). The species with lower lifetime was a solvated monomer, whereas the species with the higher lifetime is formed due to aggregation. Dynamic light scattering studies at this concentration showed that the solution was containing aggregates of 100-110 nm size (Fig. 7c). We have investigated the thermal stability of the gel with respect to concentration by 'dropping ball' method,⁴³ which showed a gradual increase (Fig.7l) on increasing the concentration. The gel prepared at 1.5 wt% concentration showed higher mechanical strength and found to be moldable into any shape as shown in Fig.7d-i and the luminescence remained unchanged. The gel kept in inverted position over a period of 15 days showed enormous stability without showing any solvent leaching or collapse of architecture. The gel under the UV light of long wavelength showed the blue emission (Fig. 7k).



**Figure 8.** AFM images obtained for compound **1b** at 1mM *n*-hexadecane solution (scale bar is 1  $\mu$ m) (a); at 1 x 10⁻⁵ M (scale bar is 780 nm) (b); Expanded regions of figure 10b and showing the height profiles of the individual fibers (c); Expanded regions of figure 10b and showing the thickness of an individual fiber (d).



Figure 9. POM image of the xerogel obtained for compound 1b (a); XRD pattern obtained for the xerogel of compound 1b (b).



**Figure 10.** Schematic showing the arrangement of compound **1b** in the discotic lamellar phase which is reinforced by intermolecular hydrogen bonding.

Atomic force microscopy (AFM) was carried out to understand the surface morphology revealed that the entangled network of nanofibres with an average height of 60 nm and thickness of 60-100 nm forms the gel (Fig. 8). The polarizing optical image of the organogel showed a birefringent texture (Fig. 9a). This motivated us to characterize its xerogel by powder X-ray diffraction studies to characterize the mode of self-assembly. The thin film of the xerogel was formed by drop casting a 1 mM solution on glass slide. The diffraction pattern in the thin film state did not provide the

data which is helpful for the analysis of the self-assembly of the molecule **1b** in the xerogel state. Thus the film was scratched and the powder obtained was filled in capillary tube and anlysed with XRD studies. XRD pattern of the xerogel (Fig. 9b, Table 2 in SI) showed two small peaks at small angle region  $(2\theta < 3^{\circ})$  corresponding to the *d* spacings of 63.1 Å and 33.3 Å. The ratio of these two peaks is almost near to 1:0.5 and can be fitted into 100 and 200 reflections arising from lamellar (D_L) phase, which is rarely observed.⁴⁴⁻⁴⁷ Further in the middle angle region  $(2\theta \approx 8^{\circ})$  a small peak corresponding to the *d*-spacing of 10.51 Å was observed which can be asigned to 600 reflection from lamellar phase. Additionally a diffused peak at wide-angle region ( $2\theta = 20.3^{\circ}$ ) corresponding to a *d* spacing of 4.38 Å was observed which corresponds to the packing of alkyl tails (Fig. 9b). The *d*-spacing corresponding to the 100 reflection is almost 50 % more than the molecular length (Fig.10). This corresponds to the intercalation of alkyl tails from the neighbouring layers. The molecular arrangement is reinforced by the intermolecular H-bonding as shown in Fig.10.

#### Conclusion

We have reported a new class of star shaped stilbene derivatives containing an amide linkage which vary from each other with the number and position of the flexible tails. This structural variation has showed a tremendous effect on the mode of self-assembly. The compounds formed by the connection of dialkoxy styrene with a benzene at 3 and 5 positions and a single amide linkage at 1 position of the central benzene ring exhibited either a crystalline phase or a columnar phase, which depended on the number of alkoxy tails in the amide unit. The compound with six alkoxy tails (two alkoxy tails on the amide unit) was crystalline, while the compound with seven alkoxy tails (three alkoxy tails on the amide unit) was bimesomorphic showing hexagonal and rectangular columnar phase. These two compounds exhibited gelation at very low concentration in *n*-hexadecane, to qualify them as supergelators. The next set of compounds formed by connecting two trialkoxy styrene units and an amide unit to a central benzene ring showed an improved thermal behavior. All the compounds of this subset exhibited room temperature hexagonal phase, while the increase in the number of flexible chains reduced the clearing temperature. These compounds did not show gelation in hydrocarbon solvents as the first two compounds. All the compounds exhibited blue luminescence in solution and thin film state. Red

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shifted absorption and emission of compounds in thin films suggested the formation of *J*-type aggregates. Similar observation was found in the case of compound with seven alkoxy tails (three alkoxy tails on the amide unit) confirming the presence of *J*aggregates in gel state. The gel formation was reversible for any number of cycles. This compound at higher CGC formed a self-standing gel that can be molded into any shape. More interestingly this compound showed aggregation induced blue light emission.

The microscopic characterization of the gel showed a highly interwoven network of fibers. Polarizing optical microscopy of the xerogel films showed a birefringent texture, which is evidence to the anisotropic nature of self-assembly. From XRD studies, it was found that these molecules self-assembled into a intercalated lamellar phase. Considering the scarcity 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 are promising towards the development of solid state displays.

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#### References

- 1. Terech, P.; Weiss, R. G. Low Molecular Mass Gelators of Organic Liquids and the Properties of Their Gels. *Chem. Rev.* **1997**, *97*, 3133.
- Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A. Liquid crystals of disc-like molecules. *Pramana* 1977, 9, 471.
- 3. O'Neill, M.; Kelly, S. M. Ordered Materials for Organic Electronics and Photonics. *Adv. Mater.* 2011, *23*, 566–584.
- Jones, B. A.; Ahrens, M. J.; Yoon, M.-H.; Facchetti, A.; Marks, T. J.; Wasielewski, M. R. High-Mobility Air-Stable n-Type Semiconductors with Processing Versatility: Dicyanoperylene-3,4:9,10-bis(dicarboximides). *Angew. Chem., Int. Ed.* 2004, *43*, 6363–6366.

- Hesse, H. C.; Weickert, J.; Al-Hussein, M.; Do⁻ssel, L.; Feng, X.; Mullen, K.; Mende, L. S. Discotic materials for organic solar cells: Effects of chemical structure on assembly and performance. *Sol. Energy Mater. Sol. Cells* 2010, *94*, 560–567.
- Li, Q. Self-Organized Semiconductors: From Materials to Device Applications, John Wiley & Sons, New York, 2011.
- Schmidt Mende, L.; Fechtenkotter, A.; Mullen, K.; Moons, E.; Friend, R. H.; Mackenzie, J. D. Self-organized discotic liquid crystals for high-efficiency organic photovoltaics. *Science* 2001, 293, 1119.
- Wöhrle, T.; Wurzbach, I.; Kirres, J.; Kostidou, A.; Kapernaum, N.; Litterscheidt, J.; Haenle, J. C.; Staffeld, P.; Baro, A.; Giesselmann, F.; Laschat, S. Discotic Liquid Crystals, *Chem Rev.* 2016, *116*, 1139–1241.
- 9. Sergeyev, S.; Pisula, W.; Geerts, Y. H. Discotic liquid crystals: a new generation of organic semiconductors *Chem Soc Rev.* 2007, *36*, 1902–1929.
- Detert, H.; Lehmann, M.; Meier, H. Star-Shaped Conjugated Systems. *Materials* 2010, *3*, 3218–3330.
- Lehman, M. Star Mesogens (Hekates)—Tailor-Made Molecules for Programming Supramolecular Functionality. *Chem. Eur. J.* 2009, 15, 3638–3651.
- 12. Lehman, M. Handbook of Liquid Crystals, 2nd ed. Vol. 5, p. 243.
- Wöhrle, T.; Beardsworth, S. J.; Schilling, C.; Baro, A.; Giesselmann, F.; Laschat, S. Columnar propeller-like 1,3,5-triphenylbenzenes: the missing link of shape-persistent hekates, *Soft Matter* 2016, *12*, 3730-3736.
- Percec, V.; Glodde, M.; Bera, T. K.; Miura, Y.; Shiyanovskaya, I.; Singer, K. D.; Balagurusamy, V. S. K.; Heiney, P. A.; Schnell, I.; Rapp, A.; Spiess, H. W.; Hudson, S. D.; Duan, H. Self-organization of supramolecular helical dendrimers into complex electronic materials. *Nature* 2002, *419*, 384–387.
- Babu, S. S.; Praveen, V. K.; Ajayaghosh, A. Functional π-Gelators and Their Applications. *Chem Rev.* 2014, 114, 1973-2129.
- 16. Ghosh, S.; Praveen, V. K.; Ajayaghosh, A. The Chemistry and Applications of π-Gels. *Annu. Rev. Mater. Res.* **2016**, *46*, 235–262.
- Friggeri, A.; Feringa, B. L.; Esch, J. Entrapment and release of quinoline derivatives using a hydrogel of a low molecular weight gelator. *J. Controlled Release* 2004, 97, 241–248.
- 18. Praveen, V. K.; George, S. J.; Varghese, R.; Vijayakumar, C.; Ajayaghosh, A. Self-Assembled  $\pi$ -Nanotapes as Donor Scaffolds for Selective and Thermally Gated Fluorescence Resonance Energy Transfer (FRET). *J. Am. Chem. Soc.* **2006**, *128*, 7542–7550.
- Ajayaghosh, A.; Praveen, V. K.; Vijayakumar, C. Organogels as scaffolds for excitation energy transfer and light harvesting, *Chem Soc Rev.* 2008, 37, 109– 122.
- Basak, S.; Nanda, J.; Banerjee, A. Multi-stimuli responsive self-healing metallo-hydrogels: tuning of the gel recovery property. *Chem. Commun.* 2014, 50, 2356-2359.

#### Langmuir

- 21. Kartha, K. K.; Sandeep, A.; Praveen, V. K.; Ajayaghosh, A. Detection of Nitroaromatic Explosives with Fluorescent Molecular Assemblies and  $\pi$ -Gels, *Chem. Rec.* **2015**, *15*, 252–265.
  - 22. Thirumalai, R.; Mukhopadhyay, R. D.; Praveen, V. K.; Ajayaghosh, A. A slippery molecular assembly allows water as a self-erasable security marker, *Sci. Rep.* **2015**, DOI: 10.1038/srep09842 (1-11).
  - 23. Würthner, F.; Thalacker, C.; Diele, S.; Tschierske, C. Fluorescent *J*-type Aggregates and Thermotropic Columnar Mesophases of Perylene Bisimide Dyes. *Chem. Eur. J.* **2001**, *7*, 2245–2253.
  - 24. Hu, R.; Leung, N. L. C.; Tang, B. Z. AIE macromolecules: syntheses, structures and functionalities. *Chem. Soc. Rev.* 2014, 43, 4494.
  - 25. Praveen, V. K.; Ranjith, C.; Armaroli, N. White-Light-Emitting Supramolecular Gels, *Angew. Chem. Int. Ed.* **2014**, 53, 365–368.
  - 26. Mukherjee, S.; Thilagar, P. Organic white-light emitting materials, *Dyes and Pigments* **2014**, *110*, 2–27.
  - 27. Tonzola, C. J.; Kulkarni, A. P.; Gifford, A. P.; Kaminsky, W.; Jenekhe, S. A. Blue-Light-Emitting Oligoquinolines: Synthesis, Properties, and High-Efficiency Blue-Light-Emitting Diodes. *Adv. Funct. Mater.* **2007**, *17*, 863.
  - Camerel, F.; Ziessel, R.; Donnio, B.; Bourgogne, C.; Guillon, D.; Schmutz, M.; Iacovita, C.; Bucher, J.-P. Formation of Gels and Liquid Crystals Induced by Pt-Pt and π–π* Interactions in Luminescent σ-Alkynyl Platinum(II) Terpyridine Complexes. *Angew. Chem., Int. Ed.* 2007, *46*, 2659–2662.
  - Babu, S. S.; Praveen, V. K.; Kartha, K. K.; Mahesh, S.; Ajayaghosh, A. Effect of the Bulkiness of the End Functional Amide Groups on the Optical, Gelation, and Morphological Properties of Oligo(p-phenylenevinylene) p-Gelators, *Chem. Asian J.* 2014, *9*, 1830–1840.
  - 30. Yoshida, R. Self-Oscillating Gels Driven by the Belousov–Zhabotinsky Reaction as Novel Smart Materials. *Adv. Mater.* **2010**, *22*, 3463–3483.
  - Gopal, A.; Varghese, R.; Ajayaghosh, A. Oligo(p-phenylene-ethynylene)-Derived Super-π-Gelators with Tunable Emission and Self-Assembled Polymorphic Structures *Chem. Asian J.* 2012, *7*, 2061–2067.
  - Ziessel, R.; Pickaert, G.; Camerel, F.; Donnio, B.; Guillon, D.; Cesario, M.; Prange, T. Tuning Organogels and Mesophases with Phenanthroline Ligands and Their Copper Complexes by Inter- to Intramolecular Hydrogen Bonds. *J. Am. Chem. Soc.* 2004, *126*, 12403-12413.
  - Westphal, E.; Prehm, M.; Bechtold, I. H.; Tschierske, C.; Gallardo, H. Room temperature columnar liquid crystalline phases of luminescent non-symmetric star-shaped molecules containing two 1,3,4-oxadiazole units. *J. Mater. Chem. C* 2013, *1*, 8011-8022.
  - Palma, M.; Levin, J.; Lemaur, V.; Liscio, A.; Palermo, V.; Cornil, J.; Geerts, Y.; Lehmann, M.; Samorì, P. Self-Organization and Nanoscale Electronic Properties of Azatriphenylene-Based Architectures: A Scanning Probe Microscopy Study. *Adv. Mater.* 2006, *18*, 3313–3317.

- Miyajima, D.; Araoka, F.; Takezoe, H.; Kim, J.; Kato, K.; Takata, M.; Aida, T. Ferroelectric columnar liquid crystal featuring confined polar groups within core-shell architecture. *Science* 2012, *336*, 209–213.
- 36. Bleier, H. Organic Materials for Photonics, Ed.: G. Zerbi, Elsevier, Amsterdam, 1993, 77-101.
- Coya, C.; de Andrés, A.; Zaldo, C.; Álvarez, A. L.; Arredondo, B.; Gómez, R.; Segura, J. L.; Seoane, C. Full-solution-processed blue organic light emitting device based on a fluorescent 1,3,5-tristyrylbenzene stilbenoid small molecule. *Journal Of Applied Physics* 2009, 105, 044510.
- Lehmann, M.; Fischbach, I.; Spiess, H. W.; Meier, H. Photochemistry and Mobility of Stilbenoid Dendrimers in Their Neat Phases. J. Am. Chem. Soc. 2004, 126, 772-784.
- 39. Achalkumar, A. S.; Yelamaggad, C. V. Light emitting, star-shaped tris(*N*-salicylideneaniline) discotic liquid crystals bearing *trans*-stilbene fluorophores: synthesis and characterization. *Tetrahedron Letters* **2012**, *53*, 7108–7112.
- Achalkumar, A. S.; Veerabhadraswamy, B. N.; Hiremath, U. S.; Rao, D. S. S.; Prasad, S. K.; Yelamaggad, C. V. Photoluminescent discotic liquid crystals derived from tris(N-salicylideneaniline) and stilbene conjugates: Structureproperty correlations. *Dyes and Pigments* 2016, *132*, 291-305.
- 41. Huang, D.; Prehm, M.; Gao, H.; Cheng, X.; Liu, Y.; Tschierske, C.; Synthesis and self-assembly of luminescent hexacatenar molecules incorporating a 4,7-diphenyl-2,1,3-benzothiadiazole core. *RSC Adv.* **2016**, *6*, 21387-21395.
- 42. Hong, Y.; Lama, J. W. Y.; Tang, B. Z. Aggregation-induced emission: phenomenon, mechanism and applications. *Chem. Commun.* **2009**, 4332–4353.
- 43. Takahashi, A.; Sakai, M.; Kato, T. Melting Temperature of Thermally Reversible Gel. VI. Effect of Branching on the Sol–Gel Transition of Polyethylene Gels. *Polym. J.* **1980**, *12*, 335.
- Sakashita, H.; Nishitani, A.; Sumiya, Y.; Terauchi, H.; Ohta, K.; Yamamoto, I. X-Ray Diffraction Study on Discotic Lamellar Phase in Bis(1,3-di(p-nalkoxyphenyl)propane-1,3-dionato)copper(II). *Mol. Cryst. Liq. Cryst. Inc. Nonlinear Opt.* 1988, *163 (1)*, 211–219.
- Mansueto, M.; Sauer, S.; Butschies, M.; Kaller, M.; Baro, A.; Woerner, R.; Hansen, N. H.; Tovar, G.; Pflaum, J.; Laschat, S. Triphenylene Silanes for Direct Surface Anchoring in Binary Mixed Self-Assembled Monolayers. *Langmuir* 2012, 28 (22), 8399–8407.
- 46. Prasad, V.; Roy, A.; Nagaveni, N. G.; Gayathri, K. Anthraquinone-based discotic liquid crystals: new monomers and dimmers. *Liq. Cryst.* **2011**, *38 (10)*, 1301–1314.
- Ong, C. W.; Chan, Y. C.; Yeh, M. -C.; Lin, H. -Y.; Hsu, H.-F. Lamellar organization of discotic dimer enforced by steric manipulation. *RSC Adv.* 2013, 3 (23), 8657–8659.

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