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# Columnar self-assembly of luminescent bent-shaped hexacatenars with a central pyridine core connected with substituted 1,3,4oxadiazole and thiadiazoles

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Abstract: Bent-shaped molecules with a central pyridine core flanked with substituted 1,3,4-oxadiazole and thiadiazole derivatives with a variation in the number and the length of terminal tails were synthesized. Thiadiazole based compounds exhibited higher mesophase range in comparison to oxadiazole derivatives, while the oxadiazole derivatives exhibited higher gelation tendency. All hexacatenars exhibited supergelation in hydrocarbon solvents along with an ability to form self-standing, moldable gel at higher concentration. Thiadiazole based compounds exhibited bathochromic absorption and emission in comparison to oxadiazole derivatives but a lower quantum yield. Two of the gelators investigated exhibited aggregation induced enhanced emission in gel and thin film state. This study shows that in addition to  $\pi$ - $\pi$ interactions, nanoseggregation of incompatible molecular subunits like flexible tails play a major role in gelation and liquid crystalline self-assembly. Microscopic studies and X-ray diffraction studies revealed a fibrillar network of several micrometer lengths with long range molecular self-assembly. They showed the ability to sense the acid with an emission quenching/shifting mechanism, that makes it possible to detect the acids by naked eye. Considering the dearth of solid-state organic blue light emitters that are pivotal to realize the white light emission, these polycatenars are promising due to their wide-range Col phase and aggregation induced blue emission. Further the introduction of pyridine central unit enhanced the mesophase stability and an acid sensing functionality in comparison to simple benzene-based bent-shaped polycatenars.

# Introduction

The molecules possessing an anisotropic shape along with incompatible molecular segments exhibit the ability to self-assemble into different liquid crystalline (LC) phases. This self-assembly is mainly driven by the nano-seggregation of incompatible molecular subunits and the tendency of the molecules to align with long-range orientational order or/and positional order.<sup>1</sup> This exceptional amalgamation of order and mobility present in LC materials gives rise to a plethora of properties that is being exploited in several applications.<sup>2</sup> Several non-conventional molecular designs that deviate from the conventional rod (calamitic) and disc-like (discotic) systems have been prepared over the years in quest of novel mesophases and to understand the

impact of different anisometric shapes and noncovalent interactions on the selfassembly.<sup>1,3</sup> Polycatenar liquid crystals (LCs), are one such nonconventional LCs, which have a combination of central elongated rod like and terminal hemi disc shaped units.<sup>4</sup> The hemi discs may contain four to six flexible alkyl chains that provide the necessary fluidity. As they possess the structural characters of both calamitic and discotic LCs, they display various mesophases that are common to these classes of LCs. This depends on the number of outer flexible tails. The columnar self-assembly of such molecules resulting in the one-dimensional (1D) columnar (Col) phases with a large  $\pi$ -overlap are interesting, as they resemble 'molecular wires' with an nonconductive external casing of alkyl tails.<sup>5</sup> This self-assembly shows anisotropic conductivity and optical properties and thus holds promise in the development of several optoelectronic devices.<sup>6</sup> Polycatenar molecular design provides a seamless synthetic flexibility in tuning the transition temperatures, optical and charge transport behavior by proper molecular design, which is a definite advantage in comparison to traditional discotics. Most of the polycatenars reported are known to have a central linear rod-like structure, while very few are known to have a bent structure.<sup>7</sup> The polycatenars with central bent structure have shown lower transition temperature and enhanced mesophase range.<sup>8</sup> There is a growing interest in the research community, in the incorporation of heterocycles in the LC design, as they help in varying the overall lateral and/or longitudinal dipole moment of the molecule, along with the variations in their molecular shape.<sup>9,10</sup> These changes affect the molecular selfassembly and the macroscopic properties of such molecules, and therefore can be effectively utilized to modify the material properties. 1,3,4-oxadiazole and thiadiazoles are preferential candidates among the heterocycles because of their high luminescence, high thermal and photochemical stability.<sup>10</sup> Incorporation of the heterocyclic moieties has shown enhanced mesophase stability due to the increased intermolecular interactions. Col LCs that exhibit high luminescence are of significant importance as this combination features the 1D conductivity and luminescence in a single material, which has a potential to be utilized as an emissive layer of OLEDs along with good conductivity.<sup>11</sup> Such molecular materials will be promising in comparison to inorganic semiconductors (which are hazardous and expensive) and polymers (which have got processability and conductivity issues). Col LCs are known to have high intermolecular order, solution processability and self-healing ability of structural defects. Some of our and other group's recent works on luminescent Col

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LCs based on heterocyclic moieties exhibited their potential as active emissive layers in OLEDs.<sup>12</sup> Efficient  $\pi$ -conjugated and coplanar molecular structure is a major requirement to achieve reduced band gaps in organic semiconductors with high charge carrier mobility and an electro-optical response. Recently, donor-acceptor (D-A) molecular structures have been investigated to attain low-band gap characteristics.<sup>13</sup> 1.3,4-Oxadiazole and thiadiazole moieties can be good electron acceptor molecular components, because of the presence of electronegative atoms. Their presence creates stronger polar induction and reduced molecular symmetry that affects the optical and electronic behaviors.<sup>9</sup> Such molecular structures also promote the ordered self-assembly in bulk as well as in the presence of solvents.<sup>14</sup> Recently we have reported such D-A-D structures that stabilized liquid crystal phases over a long range and also showed supergelation in hydrocarbon solvents due to the enhanced  $\pi$ - $\pi$ interactions.<sup>8c-e,10f</sup>It is always interesting to see if such organogelators show aggregation induced enhanced emission (AIEE) effect, specially in the case of  $\pi$ gelators. This is because the molecules are prepared with a view to utilize them in organic light emitting diodes (OLEDs), where both charge carrier mobility as well as emission in aggregated state is equally important. In most of the cases, such aggregated systems exhibit low luminescence due to the aggregation induced quenching (ACQ). Thus columnar self-assembly and AIEE contradict each other. However, over the years several polycatenars, including bent ones showed AIEE behavior.<sup>14b,8d,e,10f</sup> Further, utilization of 2,6-substituted pyridine will provide an additional functionality for acid sensing due to the presence of an sp<sup>2</sup> hybridized nitrogen atom.<sup>8e</sup> In addition, only a few number of pyridine based bent polycatenars were reported in the literature, prompted us to work on this area.<sup>7c,d,g,h,8e</sup>

As a part of our efforts to synthesize luminescent liquid crystals toward the application in OLEDs, we have synthesized and characterized two series of bent-shaped polycatenars with a central pyridine unit flanked with unsymmetrically substituted oxadiazole or thiadiazole unit (Fig.1). We were curious to compare the optical, photophysical and gelation properties of polycatenars based on 1,3,4-oxadiazole derivatives to their thiadiazole counterparts considering the alternate arrangement of donor and acceptor moieties in the molecular system. We visualized that the incorporation of oxadiazole or thiadiazole in the polycatenar structure impacting the self-assembly and related macroscopic properties. The number of flexible chains and their length were modified to understand the impact on the LC

behavior and gelation. These molecules exhibit low temperature  $Col_r$  and/or high temperature  $Col_h$  phases over a wide thermal range. Most importantly five of the polycatenars were able to gelate in different hydrocarbon solvents. Some of these compounds exhibited aggregation-induced enhancement in emission (AIEE) in thin film and gel state.

#### Synthesis and characterization

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The target molecules **1a-d** and **2a-d** (Fig.1) and their precursors were synthesized as presented in Scheme 1. Syntheses of ethyl mono/di/trihydroxy

Scheme 1. Synthesis of oxadiazole and thiadiazole-based polycatenars.



**Reagents and conditions (yield)** (i) *n*-Bromoalkanes, anhydrous  $K_2CO_3$ , DMF, 80 °C, 24 h (70-80%); (ii) NH<sub>2</sub>NH<sub>2</sub>.H<sub>2</sub>O, Ethanol or butanol, reflux, 48 h (70-80%); (iii) Pyridine-2,6-diacid chloride, THF, Et<sub>3</sub>N, 12 h, reflux; (iv) POCl<sub>3</sub>, reflux, 17 h (60-72%); (v) Lawesson's reagent, toluene, reflux, 17 h (55-60%).

benzoates (6-8) are carried out as reported earlier.<sup>10e</sup> Compounds 5a-d were prepared of corresponding ethyl hydroxyl benzoates following the Williamson's ether synthesis protocol. These alkoxy esters (5a-d) were utilized to prepare the by the *O*-alkylation corresponding hydrazides (4a-d).<sup>10e</sup> These hydrazides on refluxing with 2,6-pyridine dicarboxylic acid chloride in the presence of triethylamine base provided 2,6-di-*N*-pyridinebenzohydrazides (3a-d).<sup>8e</sup> POCl<sub>3</sub> mediated dehydrocyclization provided dioxadiazole derivatives (1a-d). Corresponding dithiadiazole derivatives (2a-d) were prepared by refluxing the compounds 3a-d in presence of Lawesson's reagent in toluene.



Figure 1. Bargraph summarizing the thermal behavior of bent-shaped molecules 1a-d and 2a-d (considering the first cooling cycle).



Figure 2. Overlay of the expanded portion of the  ${}^{1}$ H NMR spectra (CDCl<sub>3</sub>, 600 MHz) of 2c and 1c.

The molecular structures of the final compounds and their precursors were confirmed by various analytical techniques such as <sup>1</sup>H NMR, <sup>13</sup>C NMR, IR spectroscopy, and HRMS or MALDI-TOF (see ESI for details). The electron withdrawing nature of oxadiazole ring is more in comparison to its thiadiazole counterpart due to more electronegative nature of oxygen than sulphur, which is reflected by the <sup>1</sup>H NMR signals. For illustration, <sup>1</sup>H NMR of compound **1c** with two oxadiazole units showed the down field signal for proton H<sub>b</sub> ( $\delta$  = 8.46 ppm) and in comparison to the proton H<sub>b</sub> of compound **2c** ( $\delta$  = 8.42 ppm) with two thiadiazole units (Fig. 2). Similarly the proton H<sub>a</sub> of compound **2c** ( $\delta$  = 8.13 ppm) appeared at low field in comparison, to that of compound **1c** ( $\delta$  = 8.04 ppm). On the other hand, <sup>13</sup>C NMR of compound **1c** exhibited low field signals for the heterocyclic ring carbons of the 1,3,4-oxadiazole at 171 ppm and 169 ppm in comparison to the heterocyclic ring carbons of the 1,3,4thiadiazole (signals at 169 ppm and 167 ppm) of compound **2c**. (See the SI).

# **Thermal behavior**

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The preliminary confirmation for the occurrence of thermotropic liquid crystallinity was the appearance of strong birefringence along with the fluidity on gradual heating of the sample, under the polarizing optical microscopy (POM) observations. Transition temperatures and the enthalpy changes corresponding to these phase transitions were obtained by differential scanning calorimetry (DSC) thermograms. Further, the mesophase assignment was carried out by performing X-ray diffraction (XRD) measurements at different temperature intervals. The phase transitions and the corresponding enthalpy changes are tabulated in table 1 and represented in Fig.1. In comparison to normal carbocyclic LCs, heterocyclic derivatives are expected to show higher enthalpy changes associated with phase transitions, which may be due to the attractive hetero atom interactions and intermolecular hydrogen bonding interactions.<sup>8,10,15</sup>

Compound **1a** and **2a** with the two terminal *n*-hexadecyloxy tails and compound **1b** with the four terminal *n*-hexadecyloxy tails attached to the 3 and 4 positions of the terminal benzene rings turned out to be crystalline (Fig.S25-26). The POM images and XRD patterns confirmed their crystalline nature (Fig.S40). Hexacatenar **1c** with six *n*-hexadecyloxy tails observed as a birefringent fluidic mass under POM observation, which at 66 °C showed a transition in DSC thermogram with

Entry	Phase sequence						
	2 <sup>nd</sup> Heating	1 <sup>st</sup> Cooling					
1a	Cr <sub>1</sub> 131.1 (24.6) Cr <sub>2</sub> 196.6 (54) I	I 191.5 (55.7) Cr <sub>2</sub> 128.7 (23.5) Cr <sub>1</sub>					
1b	Cr <sub>1</sub> 48.4 (9) Cr <sub>2</sub> 133.1 (15.5) I	I 122 (20.1) Cr <sub>2</sub> 44.1 (5.9) Cr <sub>1</sub>					
1c	Col <sub>r1</sub> 66 (107.8) Col <sub>r2</sub> 82.1 (2.8) I	I 75.8 (3) Col <sub>r2</sub> 45.3 (103.8) Col <sub>r1</sub> <sup>b</sup>					
1d	Cr 60.8 (18.1) Col <sub>h</sub> 96.2 (0.9) I	I 92.2 (0.2) Col <sub>h</sub> 42.1 (14.5) Cr					
2a	Cr <sub>1</sub> 127.9 (14.3) Cr <sub>2</sub> 213.9 (22.8) I	I 208.2 (27.4) Cr <sub>2</sub> 124.7 (16.6) Cr <sub>1</sub>					
2b	Cr 119.8 (27.2) Col <sub>r</sub> 129.2 (2) I	I 126.7 (2.5) Col <sub>r</sub> 99.1 (32.7) Cr					
2c	Col <sub>r2</sub> 52.4 (2.2) Col <sub>r1</sub> 87 (9.7) Col <sub>h</sub>	I 95.6 (1.3) Col <sub>h</sub> 70 (8.84) Col <sub>r1</sub> 43.6 (0.6)					
	101 (11.1) I	$\operatorname{Col}_{r2}^{b}$					
2d	Col <sub>r</sub> 61.6 (9) Col <sub>r</sub> 95.2 (16.6) Col <sub>r</sub>	I 119.7 (3.1) Col <sub>r</sub> 73 (13.2) Col <sub>r1</sub> 57.3 (6)					
	121.6 (3.1) I Col <sup>b</sup>						
<sup>a</sup> Peak temperatures in the DSC thermograms obtained during the first cooling and second							
heating c	heating cycles at 5 °C min <sup>-1</sup> ; <sup>b</sup> Crystallization was not observed till -20 °C; Cr = crystal;						
$Col_h = cc$	olumnar hexagonal phase; Col <sub>r</sub> = columnar	ar rectangular phase; I = isotropic liquid.					

**Table 1**. Phase transition temperatures<sup>a</sup> (<sup>o</sup>C) and corresponding enthalpies (kJ mol<sup>-1</sup>) of the oxadiazole and thiadiazole derivatives



**Figure 3.** POM images obtained for compound **1c** at 70 °C (a); at room temperature (b); DSC thermogram of compound **1c** in the second heating (red trace) and first cooling (blue trace) at a scan rate of 5 °C/min (b); Intensity *vs*  $2\theta$  profiles obtained from the SAXS patterns for compound **1c** at 65 °C for Col<sub>r2</sub> phase (d); from the XRD patterns at 40 °C for Col<sub>r1</sub> phase (e) and at 25 °C (f) for Col<sub>r1</sub> phase. (inset shows the expanded portion in the middle angle region and the image pattern)

an enthalpy change of 107.8 kJ/mol. This mesophase was converted into an isotropic liquid at around 82 °C ( $\Delta H = 2.8$  kJ/mol) (Fig.3c). In the cooling cycle, the isotropic liquid showed the growth of mosaic pattern at around 76 °C (Fig.3a). Further cooling showed a transition in DSC at 45 °C ( $\Delta H = 103.8$  kJ/mol), but the texture did not

show much difference (Fig.3b). X-ray diffractogram obtained at 65 °C shown a sharp low angle peak along with two diffused wide angle peaks (Fig.S39). The first diffused peak with a *d*-spacing of 4.96 Å corresponds to the packing of alkyl tails, while the second one at a *d*-spacing of 4.19 Å corresponds to the core-core stacking. As it was difficult to identify the organization of columns in a 2D-lattice with a single peak at low angle, we decided to investigate through small angle x-ray scattering (SAXS) studies. Intensity *vs* 2*θ* profiles obtained from the SAXS patterns for compound **1c** at 65 °C (Fig.3c), showed peaks corresponding to *d*-spacings of 36.11 Å, 19.2 Å, 14.48 Å which can be indexed to Miller indices 01, 11, 12 of a rectangular lattice. From these values, the lattice parameters were calculated and found to be a = 22.67 Å, b =36.11 Å. The unit cell area (*S*) was found to be 818.6 Å<sup>2</sup> and cell volume (V) was found to be 3430 Å<sup>3</sup>. The number of molecules (Z) in the unit rectangular cell was found to be 1.1.

**Table 2.** Results of the (*hkl*) indexation of the XRD profiles of the compounds at a given temperature (T) of the mesophases.<sup>a</sup>

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Compounds	Phase	$d_{\rm obs}({\rm \AA})$	$d_{\rm cal}$	Miller	Lattice parameters (Å), Lattice			
$(D/\text{\AA})$	$(T/^{\circ}C)$		(Å)	indices	area S (Å <sup>2</sup> ), Molecular volume			
				hk	$V(Å^3)$			
1c	Col <sub>r2</sub>	36.11	36.11	01	a = 22.67, b = 36.11, S = 818.6,			
(59.95)	(65)	19.2	19.20	11	V = 3430, Z = 1.1			
		14.48	14.12	12				
		$4.96(h_a)$						
		$4.19(h_{\rm c})$						
		45.62	45.62	01	a = 21.05, b = 45.62,			
		21.05	21.05	10	S = 960.3, V = 4369.37,			
	Col <sub>r1</sub>	15.73	15.47	12	Z = 1.45			
	(40)	12.73	12.33	13				
		7.69	7.73	24				
		$4.55(h_a)$						
		45.55	45.55	01	a = 20.96, b = 45.55,			
		20.96	20.96	10	S = 954.73, V = 4315.37,			
		15.69	15.42	12	Z = 1.44			
	Col <sub>r1</sub>	12.59	12.30	13				
	(25)	10.45	10.48	20				
		8.85	8.62	23				
		7.75	7.71	24				
		$4.52(h_a)$						
1d	Col <sub>h</sub>	35.03	35.03	10	a = 40.45, S = 1417,			
(49.77)	(65)	17.47	17.52	20	V = 5653.8, Z = 2.3			
		$4.86(h_a)$						
		$3.99(h_c)$						
<sup>a</sup> The diameter	(D) of the dis	sk (estimated	l from Che	m 3D Pro 8.	0 molecular model software from			
Combailes C								

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; *c* is height of the unit cell). 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*.

The XRD pattern obtained at lower temperatures (i.e. at 40 °C and room temperature), which is below the transition temperature 45 °C in cooling cycle (Fig.3e-f). The XRD pattern obtained at 40 °C showed five peaks at low angle corresponding to the *d*-spacings of 45.62 Å, 21.05 Å, 15.73 Å, 12.73 Å, 7.69 Å along with a relatively sharp peak at 4.55 Å (in comparison to the XRD pattern at 65  $^{\circ}$ C). The peaks at low angle can be indexed into Miller indices 01, 10, 12, 13 and 24 of a rectangular lattice. Thus the transition observed at 45  $^{\circ}$ C is from one Col<sub>r</sub> to another Col<sub>r</sub> phase. For the sake of identification we have named the higher temperature Col phase as Col<sub>r2</sub> and the low temperature one as Col<sub>r1</sub> phase. The rectangular lattice parameters were calculated and from that the total number of molecules (Z) present in a unit cell was found to be 1.5. The relatively sharp peak at the wide angle corresponds to the enhanced columnar order. Since the texture remained same even at room temperature we were curious to know whether the phase structure remains same or different. The XRD pattern obtained at room temperature showed several peaks in low to mid angle region along with a relatively sharp peak in the wide-angle region, which can be fit in to a rectangular lattice. Thus the Col<sub>r</sub> phase remains unchanged at room temperature. Compound 1d, the dodecyloxy version of compound 1c exhibited a Col<sub>b</sub> phase, which was confirmed by POM images, DSC and XRD studies (Fig.4 and Table 2). Here again the low angle showed a single peak, which prevented us from the unambiguous assignment to a particular mesophase. Thus the SAXS measurements were carried out at this temperature and the *d*-spacings obtained at low angle were closely fitting into a hexagonal lattice (Table 2 and Fig.4c). POM texture (Fig.4a) with large homeotropic domains supports the uniaxial nature of the  $Col_h$ phase.



**Figure 4.** POM image obtained for the Col<sub>h</sub> phase of compound **1d** at 55 °C (a); DSC thermogram of compound **1d** in the second heating (red trace) and first cooling (blue trace) at a scan rate of 5 °C/min (b); Intensity *vs* 2 $\theta$  profiles obtained from the SAXS pattern for compound **1d** at 65 °C for Col<sub>h</sub> phase (c). (inset shows the expanded portion in the middle angle region)



**Figure 5.** POM image obtained for the Col<sub>r</sub> phase of compound **2b** at 110 °C (a); DSC thermogram of compound **2b** in the second heating (red trace) and first cooling (blue trace) at a scan rate of 5 °C/min (b); Intensity *vs*  $2\theta$  profiles obtained from the SAXS pattern for compound **2b** at 110 °C for Col<sub>r</sub> phase (c) (inset shows the expanded portion in the middle angle region)



**Figure 6.** DSC thermogram of compound **2d** in the second heating (red trace) and first cooling (blue trace) at a scan rate of 5 °C/min.



**Figure 7.** POM image obtained for the  $Col_{r1}$  phase of compound **2d** at 110 °C (a); Col<sub>r2</sub> phase of compound **2d** at 69 °C (b); Col<sub>r3</sub> phase of compound **2d** at 40 °C (c); Intensity vs 2 $\theta$  profiles obtained from the XRD patterns for the Col<sub>r1</sub> phase of compound **2d** at 110 °C (d); Col<sub>r2</sub> phase of compound **2d** at 69 °C (b); Col<sub>r3</sub> phase of compound **2d** at 40 °C (c); (inset shows the expanded portion in the middle and wide angle region as well as image patterns)

Compounds ( <i>D</i> /Å)	Phase (T/°C)	$d_{\rm obs}({\rm \AA})$	$d_{\rm cal}({\rm \AA})$	Miller indices hk	Lattice parameters (Å), Lattice area S (Å <sup>2</sup> ), Molecular volume V (Å <sup>3</sup> )
<b>2b</b> (60.0)	Col <sub>r</sub> (110)	40.83 25.60 23.79 16.97 4.98 ( <i>h<sub>a</sub></i> ) 4.02 ( <i>h<sub>c</sub></i> )	40.83 25.60 24.43 16.33	02 10 11 05	a = 25.6, b = 81.7, c = 4.02, S = 2091.5, V = 8407.9, Z = 3.7
	Col <sub>h</sub> (90)	41.48 4.99 ( <i>h</i> <sub>c</sub> )	41.48	10	<i>a</i> = 47.87, <i>c</i> = 4.99, S = 1984.47, V = 9902.51, Z = 3.2
2c (61.06)	Col <sub>r1</sub> (65)	$\begin{array}{c} 45.52 \\ 16.52 \\ 14.25 \\ 7.95 \\ 4.63(h_a) \\ 4.33(h_c) \end{array}$	45.52 16.52 14.21 7.96	03 11 15 25	a = 16.64, b = 136.56, c = 4.33, S = 2272.36, V = 9839.32, Z = 3.2
	Col <sub>r 2</sub> (45)	$\begin{array}{c} 45.52 \\ 15.69 \\ 9.88 \\ 8.09 \\ 4.63 \ (h_a) \\ 4.31 \ (h_c) \end{array}$	45.52 15.69 9.78 8.10	01 22 42 52	a = 43.32, b = 45.52, c = 4.31, S = 1971.93, V = 8499.02, Z = 2.78
	Col <sub>r2</sub> (25)	45.52 16.24 10.21 8.09 4.61 ( <i>h</i> <sub>a</sub> ) 4.35 ( <i>h</i> <sub>c</sub> )	45.52 16.24 10.20 8.09	02 20 33 41	a = 32.48, b = 91.04, c = 4.35, S = 2957, V = 12863, Z = 4.2
<b>2d</b> (50.85)	Col <sub>r1</sub> (100)	$ \begin{array}{r} 37.99\\ 19.39\\ 4.89\ (h_a)\\ 4.00\ (h_c) \end{array} $	37.99 19.39	01 10	a = 19.39, b = 37.99, c = 4.00, S = 736.63, V = 2946.5, Z = 1.2
	Col <sub>r2</sub> (68.5)	41.35 27.88 20.47 13.65 11.33 10.20 8.91 8.20 7.32 6.83 6.23 4.74 (h <sub>a</sub> ) 3.99 (h <sub>c</sub> )	41.35 27.88 20.68 13.78 11.13 10.34 9.07 8.27 7.43 6.91 6.22	01 10 02 03 23 04 24 05 51 35 45	a = 37.75, b = 41.35, c = 3.99, S = 1560.96, V = 6228.24, Z = 2.5
<b>A</b> - 1 - 1	Col <sub>r3</sub> (40)	$\begin{array}{c} \overline{41.35} \\ 23.09 \\ 10.11 \\ 8.11 \\ 4.55 (h_a) \\ 4.00 (h_c) \end{array}$	41.35 23.09 10.08 8.27	01 10 22 05	a = 23.09, b = 41.35, c = 4.00, S = 954.77, V = 3819.09, Z = 1.5

**Table 3.** Results of (hk) indexation of XRD profiles of the compounds **2a-d**, at a given temperature (T) of mesophase<sup>a</sup>

<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; *c* is height of the unit cell). 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*.

Thiadiazole based tetracatenar compound **2b** exhibited enantiotropic  $\text{Col}_r$  phase as evidenced from SAXS studies (Fig.5). Hexacatenar **2c** was polymesomorphic by exhibiting one high temperature  $\text{Col}_h$  phase and two low temperature  $\text{Col}_r$  phases, which was reported earlier.<sup>8e</sup> Interestingly hexacatenar **2d** with six dodecyloxy chains exhibited several phase transitions as evidenced from DSC thermograms (Fig.6). POM images showed a mosaic texture (Fig.7a-c) and the XRD patterns obtained at different temperature intervals showed that there are three different  $\text{Col}_r$  phases (Fig.7d-e, Table 3). The low temperature  $\text{Col}_r$  phase stayed upto room temperature without any signs of crystallization. Such transitions between different  $\text{Col}_r$  phases have been reported earlier.<sup>15b</sup>



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**Figure 8.** Comparison of the thermal behavior of pyridine based bent-shaped molecules **1c-d** and **2c-d** with benzene based bent-shaped molecules reported earlier (**16O**, <sup>8a</sup> **16T** and **12T**<sup>10b</sup>) (considering the first cooling cycle).

It was interesting to compare the thermal behavior of pyridine based bent-shaped molecules **1c-d** and **2c-d** with corresponding benzene based bent-shaped molecules reported earlier (Fig.8). Hexacatenar **1c** with hadecyloxy chains exhibited Col<sub>r</sub> phase over a wide range including room temperature, while the corresponding benzene based hexacatenar **16O** was crystalline at room temperature and exhibited a short-range Col<sub>h</sub> phase.<sup>8a</sup>Similarly, compound **2c** exhibited enhanced mesophase stability by exhibiting Col<sub>r</sub> and Col<sub>h</sub> phases in comparison to the monomesomorphic **16T** which exhibited Col<sub>ob</sub> phase.<sup>10b</sup> Hexacatenar **2d** having shorter alkyl chains exhibited col<sub>ob</sub> phase. In general, the introduction of pyridine as a central core enhanced the

mesophase stability, by lowering the melting temperature. In both cases, whether it is pyridine or benzene; the thiadiazole based hexacatenars exhibited wider mesophase range and higher stability, which was in line with earlier reports.<sup>8c-e,10a-f</sup>

### **Photophysical properties**

Photophysical properties of oxadiazole and thiadiazole based compounds **1a-d** and 2a-d in THF (20 micromolar) solution and annealed thin film state were investigated and the data are summarized in Table 4. It is expected that the presence of two different heterocycles (substituted 1,3,4-oxadiazole and 1,3,4-thiadiazole) may have a distinguishable impact on the photophysical properties.<sup>10</sup> Absorption and emission spectra of the compounds **1a-d** and **2a-d** were measured in micromolar THF solution (Fig. 9a and 10a). These compounds exhibited a red-shifted absorption and emission spectra, in comparison to the benzene-based polycatenars reported earlier.<sup>8a,10b</sup> The solution absorption spectra of compounds 1a-d exhibited a single absorption band at a wavelength of 314 nm whereas compound 2a-d showed red shifted absorption band in range of 337-347 nm. Both the series of compounds **1a-d** and **2a-d** show large value of molar extinction coefficients, which is the inherent property of highly conjugated systems. The single absorption band for these compounds can be attributed to spin allowed  $\pi$ - $\pi$ \* transition of the aromatic system. The values of molar extinction coefficients of oxadiazole derivatives 1a-d ( $\varepsilon$  = 13,000-22,500 M<sup>-1</sup>cm<sup>-1</sup>) were found to be more in comparison to thiadiazole derivatives **2a-d** ( $\epsilon = 4,000-11,000 \text{ M}^{-1}\text{cm}^{-1}$ ). Optical bandgaps of these systems obtained from the absorption onset values shown that the oxadiazoles derivatives **1a-d** 



**Figure 9.** Absorption (solid trace) and emission (dotted trace) spectra of compounds **1a-d** (a); Emission spectra of spin coated thin films (b); photographs taken under the UV light ( $\lambda_{ex} = 365$  nm) in micromolar THF solution and thin films (c)

(3.39-3.46 eV) showed higher band gap in comparison to their thiadiazole counterpart **2a-d** (3.10-3.22 eV). Likewise, emission spectra were obtained by exciting the solutions of these compounds at their absorption maxima exhibited a single emission maximum in the range of 385-465 nm for **1a-d** and a red shifted emission maximum in the range of 421-473 nm for **2a-d** (Table 4, Fig. 9b and 10b) with large Stokes shift. The oxadiazole derivatives **1a-d** showed lower steady state anisotropy values (0.02-0.09) with respect to the thiadiazole derivatives **2a-d** (0.03-0.11). Relative quantum yields of these compounds were measured with respect to standard quinine sulphate solution (0.1 M in H<sub>2</sub>SO<sub>4</sub>), exhibited almost similar quantum yields in the range of 0.48-0.58.



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**Figure 10.** Absorption (solid trace) and emission (dotted trace) spectra of compounds **2a-d** (a); Emission spectra of spin-coated thin films (b); photographs taken under the UV light ( $\lambda_{ex} = 365$  nm) in micromolar THF solution and thin films (c).

fable 4.Photophysical pr	roperties of compounds	<b>1a-d</b> and <b>2a-d</b> in solution <sup>a</sup>	and film state.
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	Solution State								in film State	
Entry	Absorption (nm)	Emission <sup>b</sup> (nm)	Stokes shift (cm <sup>-1</sup> )	$\lambda_{onset}$ (nm)	$\Delta E^{c,d}_{g,opt}$	Steady state anisotropy	Relative Quantum Yield <sup>e</sup>	Absorption (nm)	Emission <sup>b</sup> (nm)	Stokes shift (cm <sup>-1</sup> )
1a	314	385	5873	366	3.39	0.015	0.58	315	416	7708
1b	314	428	8483	367	3.39	0.015	0.48	316	461	9954
1c	314	465	10342	363	3.42	0.088	0.50	311	467	10741
1d	314	452	9723	359	3.46	0.018	0.48	318	479	10570
2a	337	421	5921	386	3.22	0.031	0.55	343	453	7080
2b	341	446	6904	389	3.19	0.027	0.56	345	478	8065
2c	343	473	8013	398	3.12	0.111	0.53	345	473	7844
2d	347	466	7359	401	3.10	0.025	0.48	345	464	7434
<sup>a</sup> micromo wave leng	micromolar solutions in THF; <sup>b</sup> excited at the respective absorption maxima; <sup>c</sup> Band gap determined from the red edge of the longest wave length ( $\lambda_{onsel}$ ) in the UV-vis absorption spectra; <sup>d</sup> In volts (V). <sup>e</sup> Quinine sulfate in 0.1 M H <sub>2</sub> SO <sub>4</sub> solution as the standard.									

The thin films of the compounds on quartz plates were made by the spin coating of the solutions of these compounds in chloroform. As expected, the absorption and

emission bands of these compounds were found to be broad in comparison to their solution spectra. The absorption spectra of the thin films of most of the oxadiazole based compounds **1a-d** as well as thiadiazole based compounds **2a-d** showed a red shift in comparison to the solution spectra, pointing towards the formation of J-type aggregates.<sup>14c</sup> Compound 1c and 2d showed a slight blue shift in the absorption maximum, which may be due to the formation of H-aggregates.<sup>20</sup> Considering the possibility of the several conformational isomers, it is difficult to conclude the type of the aggregates. As the room temperature  $Col_r$  phase of compound 1c and 2c we examined the thin films of the compounds, which were found to be transparent in visible light and remained stable over a long period. The irradiation of these films with UV light of long wavelength exhibited blue emission, which masked the pattern kept behind (Fig.11). The thin film of compound 1c exhibited higher emission intensity (2 folds) in comparison to their micromolar solution in THF, while the emission intensity for compound **2c** was reduced by half (Fig.S31). Both the solutions and thin films of oxadiazole and thiadiazole based compounds exhibited a visually perceivable blue emission under the UV light of long wavelength (Fig.9c and 10c).



**Figure 11.** Thin film of compound **1c** annealed in Col<sub>r</sub> phase placed above a pattern under visible light (a); the same under the UV light ( $\lambda_{ex} = 365$  nm) (b); Thin film of compound **2c** annealed in Col<sub>r</sub> phase placed above a pattern under visible light (c); the same under the UV light ( $\lambda_{ex} = 365$  nm) (d).

# Solvatochromism and acidochromism

We investigated the effect of solvent polarity on the absorption and emission properties of the compounds. The absorption and fluorescence spectra of representative compounds 1c and 2c in different solvents like decane, hexane, tetrachloromethane (CCl<sub>4</sub>), dichloromethane (DCM), chloroform (CHCl<sub>3</sub>), tetrahydrofuran (THF), toluene were recorded and the corresponding photophysical details are summarized in Table 5. Pictures of micromolar solution of compounds 1c

and 2c in different solvents were depicted in Figure S28 and S29. As we know, solvent polarity influences the energy levels of the absorption or emission bands.<sup>16</sup> From the absorption spectra we found that the energy levels of the absorption remain almost unaffected indicating non-polar ground state. In contrast to the absorption band, the emission was red shifted on increasing the solvent polarity from decane to polar solvents like THF (Fig.12). This corresponds to the polar nature of the excited state.<sup>16</sup>

Table 5. Photophysical properties of compound 1c and 2c in different solvents.

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Solvent		1c					
	Absorption (nm)	Emission <sup>b</sup>	Stokes shift (nm)	Absorption (nm)	Emission <sup>b</sup>	Stokes shift(nm)	
Hexane	310	433	123	343	453	110	
Decane	310	428	118	343	449	106	
DCM	310	460	150	343	484	141	
CCl <sub>4</sub>	311	427	116	343	457	114	
Toluene	311	435	124	343	471	128	
CHCl <sub>3</sub>	313	457	144	343	472	129	
THF	314	465	151	343	473	130	
amicromolar	<sup>a</sup> micromolar solutions in different solvents: <sup>b</sup> excited at the respective absorption maxima.						



Figure 12. Normalized emission spectra of compounds 1c (a) and 2c (b) in micromolar concentrations of different solvents



**Figure 13.** Emission spectra obtained for the compound 1c on gradual addition of TFA to the in same (50  $\mu$ M in CHCl<sub>3</sub>) (a); the same obtained for the compound 2c on gradual addition of TFA to the in same (50  $\mu$ M in CHCl<sub>3</sub>).

Considering the presence of an  $sp^2$  hybridized N atom of the pyridine ring, we envisaged that these compounds might act as good proton acceptors. The protonation may change the extent of delocalization and thus affect the optical properties of these compounds, which can be beneficial in the detection of acids. As seen from the Fig.13a and b, the emission intensities of compounds 1c and 2c were reduced by the addition of trifluoroacetic acid (TFA). In the case of compound 1c the gradual addition of TFA led to a blue shifted emission spectra, thus the solution under UV light showed blue light emission, where the difference was not very much detectable visually. However in the case of compound 2c, the gradual addition of TFA led to a red shifted emission spectra, with a visually perceivable green emission under UV light of long wave length (Fig. S32). In both cases the original blue emission was recovered to a certain extent by the addition of an equivalent amount of triethylamine (TEA) (Fig.14 bottom panel). From the <sup>1</sup>H NMR spectra, it was visualized that the protonation of the compounds led to a large downfield shift of the protons on pyridine ring, whereas the neutralization with the triethylamine recovered the signals back to the original in the case of compound 1c or near to the original position in the case of compound 2c (Fig. 14 upper panel).



Figure 14. Expanded region of <sup>1</sup>H NMR spectra of 1c (a) and 2c (b) on subsequent addition of TFA and TEA in CDCl<sub>3</sub> (The bottom panel shows the changes happen on the subsequent addition of TFA and TEA, as seen under daylight and UV light of long wavelength)

# **Gelation studies**

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We were interested in the gelation behavior of these different series of compounds and wanted to study the effect of different heterocycles and the number of peripheral alkoxy tails. Gelation behavior of thiadiazole-based hexacatenar 2c has been reported earlier, and hence we were interested to study the gelation behavior of its oxadiazole counterpart 1c. Further the hexacatenars 1c and 2c stabilized Col phases in bulk, and thus it is interesting to compare their aggregation behavior in presence of solvents (Fig.15). Compounds 1c and 2c were mixed separately in different solvents of varying polarity and proticity. Polar aprotic solvents like chloroform, dichloromethane, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), dimethylformamide (DMF); polar protic solvents like ethanol, n-butanol; nonpolar aromatic solvents like benzene, toluene, *m*-xylene, nonpolar aliphatic solvents like hexane, decane, dodecane and hexadecane were utilized to probe the gelation behavior of these compounds (Table S1). Immediately after mixing, the suspensions were heated to obtain a clear solution. Then, the solutions were allowed to cool to room temperature to form gels. Both the compounds 1c and 2c were found to be soluble in most of the solvents like chloroform, dichloromethane, tetrahydrofuran, toluene, benzene, m-xylene. These compounds were insoluble in DMSO and DMF, and found to precipitate in ethanol and *n*-butanol. In the case of all aliphatic nonpolar solvents, the clear solutions of these compounds became turbid, finally forming a translucent gel. Finally, the formation of the gel was confirmed by "stable to inversion of the glass vial" method (Fig. 15a-d). Further we checked the gelation behavior of other compounds 1a, 1b, 1d, 2a, 2b and 2d in decane (Table 6, Fig.S34). Compounds 1a, 2a and 2b precipitated in decane after dissolving in decane. Among the oxadiazole derivatives

	ation benavior and edges of compound <b>ia a</b> and <b>za a</b> in accune							
Entry	Properties	CGC (wt. %)	$T_{gel}(^{o}C)$					
<b>1</b> a	Р							
1b	G(O)	1.5	53					
1c	G(O)	0.6	56					
1d	G(O)	0.9	52					
2a	Р							
2b	Р							
2c	G(O)	0.5	47					
2d	G(O)	0.7	45					
G = stable gel; $P =$ precipitate; $O =$ opaque. The critical gelation								
concentration (wt.%) is the minimum concentration necessary for gelation.								
$T_{gel}$ (°C) is the	e thermal stability of	f the gels.						

Table 6.	Gelation	behavior and	CGCs of o	compound	1a-d and 2a-d in decane
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**1b-d** showed gelation, while in the case of thiadiazole derivatives, only compounds **2c** and **2d** have shown gelation (Fig.S34-S36). Since we were interested to derive the structure-property relationships we decided to investigate the compounds **1c** and **2c** by extensive photophysical studies, microscopy and XRD studies. Detailed rheological measurements were also carried out on these two representative samples, which are described in a later section. The critical gelation concentration (CGC) and T<sub>gel</sub> of all the gelators were studied in different gelating solvents by 'dropping ball method'<sup>17</sup> and are tabulated in Table 6. Compounds **1c-d** and **2c-d** can be classified as supergelators as their CGC was found to be lesser than 10 mg/mL or 1 wt%.<sup>18</sup> Again, thermal stability of compounds **1c** and **2c** with respect to concentration (Fig. 15e-f) was estimated for both derivatives in decane. The plots showed a steady increase in the thermal stability on increasing concentration. It may be noted that at higher concentration, the gel formed could be casted into any given shape of self-standing gel (Fig. 15g-j), with higher mechanical strength.



**Figure 15.** Solution (a) and gel (b) form of compound 1c and the same for compound 2c (c,d); Plots of  $T_{gel} vs$  concentration for compound 1c (e) and for compound 2c (f) in decane; Images showing the moldability of both the organogels in decane (Concentrations: 1.2 wt% for 1c and 0.8 wt% for 2c) into shapes like cube for 1c (g); trigonal prism for 1c (h); trigonal prism for 2c (j); the same under UV light (365 nm) (k); 2.5 cm long cylinder shaped gel of 2c (i); the same under UV light (365 nm) (l); Images showing response to mechanical forces by 1c and 2c and their recovery (m).

It is interesting to note that, even with the lack of any specific hydrogen bonding moieties, the compounds 1c and 2c were able to form strong gels. The formation of stable gels can be attributed mainly to aromatic  $\pi$ - $\pi$  interaction, dipoledipole interaction and van der Waals interaction of hydrophobic alkyl chains with long chain hydrocarbon solvents. The gel–sol transformation can also be achieved by the appliance of mechanical force (Fig.15m) such as vigorous shaking or sonication, while the solutions reverted back to the original gel state on standing. Interestingly, these organogels have also shown significant self-healing property and can be recovered from any damage imposed on them, on standing (Fig.S35-36).

The microstructures of the representative organogels formed from the compounds 1c and 2c in decane were investigated with field emission scanning microscopy (FESEM) and atomic force microscopy (AFM). The xerogel films of compounds 1c and 2c were prepared by evaporating the spin-coated films of decane solutions ( $5 \times 10^{-6}$  M), followed by their vacuum evaporation for 2-3 h. The AFM images of the xerogels (Fig.16a,b), exhibited dense interwoven network of fibers measuring several micrometers length. For compound 1c, the height of the fiber is around 30-35 nm with a thickness of 0.8 µm. In case of compound 2c, the average length of fibers was 40-60 nm, with a thickness of around 130 nm. These results were again supported through SEM micrographs obtained for the xerogels of 1c and 2c (Fig. 16c,d).

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**Figure 16.** AFM image obtained for the xerogel of compound **1c** obtained from 3.33 mM decane solution (scale bar is 4.0  $\mu$ m) (a); xerogel of compound **2c** (scale bar is 550 nm) (b) (Inset shows the thickness of an individual fiber); SEM images obtained for the xerogel of compound **1c** (scale bar is 2  $\mu$ m) (c); for the xerogel of compound **2c** (scale bar is 200 nm) (d).



**Figure 17.** Intensity *vs*  $2\theta$  profiles obtained from the XRD pattern for the Col<sub>r</sub> phase of the xerogel of compound **1c**.

**Table 7.** Results of (hk) indexation of XRD profiles of the compounds 1c and 2c in the xerogel state at room temperature (RT).

Compounds	Phase/	$d_{\rm obs}({\rm \AA})$	$d_{\rm cal}({\rm \AA})$	Miller	Lattice parameters (Å), Lattice area
(state)	(T/°C)			indices	$S(A^2)$ , Molecular volume V ( $A^3$ )
				hk	
1c	Col <sub>r</sub>	53.05	53.05	01	a = 21.11, b = 53.05, c = 3.77,
Xerogel		21.11	21.11	10	S = 1119.9, V = 4212,
		19.04	19.61	11	Z = 1.4
		15.95	16.52	12	
	(RT)	14.33	13.56	13	
		12.51	13.26	04	
		9.18	9.06	23	
		8.19	8.26	24	
		7.57	7.48	25	
		7.10	7.04	30	
		6.26	6.22	34	
		5.66	5.86	35	
		5.31	5.28	40	
		4.57	4.73	45	
		$4.16(h_a)$			
		$3.77(h_c)$			
2c	Col <sub>r</sub>	47.95	47.95	01	a = 16.60, b = 47.95, c = 3.82,
Xerogel	(RT)	15.69	15.69	11	S = 796, V = 3040.6,
-		9.89	9.72	14	Z = 1
		8.04	8.18	21	
		$4.58(h_a)$			
		$3.82(h_c)$			

Further the arrangement of the molecules in the xerogel state was extensively probed with the help of small angle X-ray diffraction studies. The XRD pattern for xerogel **1c** at room temperature showed several peaks centered at 53.05, 21.11, 19.04, 15.95, 14.33, 12.51, 9.18, 8.19, 7.57, 7.10, 6.26, 5.66, 5.31 and 4.57 Å. These *d*-spacings were quite ideally fitting into a rectangular (Col<sub>r</sub>) lattice structure (Fig.17 and Table 7). In the wide-angle region we have found two diffused reflections centered at 4.16 and 3.77 Å, could be ascribed to the packing of flexible alkyl chains and to the packing of aromatic cores. Similar rectangular arrangement was found in case of the xerogel of compound **2c** as described earlier (Fig.S38).<sup>8e</sup> From the lattice parameters we calculated the number of molecules forming a columnar slice in the case of **1c** and **2c**, which was found to be almost 1. It is interesting to note that these molecules exhibit liquid crystalline behavior and organgelation, while maintaining the same order (Columnar assembly with a rectangular symmetry) over a long range, which is beneficial from the viewpoint of organic electronic devices.<sup>23</sup>

#### Aggregation induced enhanced emission (AIEE) behavior

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The gelation of compounds **1c** and **2c** in decane was followed with the help of fluorescence spectroscopy. They showed a blue-shifted excitation spectra in gel state in comparison to the excitation spectra of solution state (Fig.18a,c). There was a slight red-shifted emission observed in the case of compound **1c**, while the emission was not shifted in the case compound **2c** (Fig.18b,d). We were curious to know the photophysical properties of compound **1c** and **2c** in thin film state. The spin coated thin films on quartz plates showed a blue shifted absorption bands in comparison to



**Figure 18.** Excitation and absorption spectra of compound **1c** (a); **2c** (c) in solution, gel (at CGC) and thin film state; Emission spectra of compound **1c** (b); **2c** (d) in solution, gel (at CGC) and thin film state.

the solution state excitation spectra (Fig.18a,c). This points to the formation of aggregates in the case of thin films and gels in comparison to solution state. The blue

shift in the absorption usually corresponds to the formation of H-aggregates, where the molecules are stacked one above the other in a cofacial or parallel manner. The aggregated states (in thin film and gel) showed several fold enhanced luminescence in comparison to the solution state (Fig.18b,d). Notably, the luminescence was higher in gel state for compound **1c** than in thin film state, while it is higher in thin film state for compound **2c** than in gel state.

To determine the effect of aggregate formation on the luminescence properties as well as organogel formation, decane gels of 1c and 2c were measured at different temperatures and times. Aggregation induced enhanced emission (AIEE) of compound 2c was reported earlier,<sup>8e</sup> which was monitored with respect to temperature and time. In both cases, the intensity of emission increases with the decrease in temperature (Fig. 19a). A bathochromic shift in the emission of 25 nm was observed in the case of 1c in comparison to that of compound 2c (12 nm red shift) (Fig. 19b). In comparison to solution state, a huge increase in the fluorescence intensity in the gel state *i.e.* 10 fold in case of 1c (which is higher than the emission intensity of the thin film), whereas 25 fold in the case of  $2c^{8e}$  (which is lower than the emission intensity of the thin film) was noted (Fig. 19c). Thus even though both the compounds points to the formation of H-aggregates in thin films and gel state, the molecular arrangement is not same in these two different states, which results in different emission behavior.



**Figure 19.** Emission spectra of compound **1c** in decane (3.33 mM) on cooling from 60 °C to 25 °C (a); Normalized emission spectra on cooling from 60 °C to 25 °C (b); Comparison of emission spectra of sol-gel transition (c); Emission spectra obtained as a function of time (d); Plot showing the emission intensity at 415 nm as a function of time (e); Reversible change in the emission intensity at 415 nm by repeated sol-gel transition (f).

Formation of organogel was also confirmed by measuring the emission spectra of the solution as a function of increasing time (Fig.19d). The organogel was formed within 35 minutes in the case of **1c** (Fig.19e), which is little longer in comparison to that of compound 2c (10 minutes in 2c). The reproducibility of gel formation was confirmed after heating and cooling for many cycles as presented in Fig. 19f. The increase in the emission intensity upon aggregation, rather than the emission quenching is due to the ability to overcome aggregation caused quenching (ACQ).<sup>20</sup> In other words the favorable molecular packing in the gel state results in the restricted intramolecular rotations. Thus both bent-shaped oxadiazole and thiadiazole based bent polycatenars 1c and 2c exhibited aggregation-induced enhanced emission (AIEE) effect in the organogel state. Fluorescence life-time measurements carried out for compounds 1c and 2c in decane at 20  $\mu$ M and at their CGC showed the biexponential emission decay with the increase in the life-time of the excited species (Fig.S37 and Table S2). Even though H-aggregates are known to exhibit aggregation caused quenching (ACQ) of luminescence compared to the monomer emission in solution, here completely reverse behavior of the expected was observed.<sup>19</sup> There are very few reports on luminescent H-aggregates,<sup>21</sup> where the luminescence is attributed for the excimer species or due to a small displacement of the two exciton-coupled molecules in the excited state.

# **Rheological properties**

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The viscoelastic properties of the gels formed from compound **1c** and **2c** at concentrations of 0.6 wt. % and 0.5 wt. % were measured with the help of rheological measurements. This involved strain sweep, angular frequency sweep and step strain measurements. For the measurement of rheological responses, a dynamic frequency sweep experiment at constant stress (0.2 kPa) was performed, which can be described by the equation  $G^*(\omega) = G'(\omega) + iG''(\omega)$ , where  $\omega$  is the angular frequency, G' is the storage modulus and G'' is the loss modulus.<sup>22</sup> The value of G' slightly increase and the value of G'' decrease with the frequency from 0.01 to 100 Hz and the value of G' is always higher than that of G'' in the whole range (0.01–100 Hz), signifying that the gels **1c** and **2c** are fairly tolerant to the external force. From Fig. 20a and 20d, it is quite obvious that both **1c** and **2c** gels behave like a solid or viscoelastic like material (i.e. G'> G''). Both G', G'' are feebly dependent on angular frequency at 25 °C using 0.2 mPa stress (Fig.20b and e). As can be observed, these are the two requirements for

a sample to be considered as a gel that is approximately satisfied by both gels 1c and 2c. In order to establish the non-linear viscoelastic regime, which is the characteristic features for dynamics of the sol-gel system, we performed stress dependent nonlinear measurements for compound 1c (0.6 wt.%) and 2c (0.5 wt.%).



**Figure 20**. Angular frequency (rad s<sup>-1</sup>) dependence of G' and G" obtained with small stress amplitudes: (a) 0.6 wt. % of compound **1c** in decane at 25 °C using 0.2 kPa stress; (b) Stress dependence of G' and G" of the same gel **1c** measured at constant frequency (at 25 °C, and frequency at 10 Hz); (c) Thixotropic nature of organogel of **1c** (3.32 mM) in decane at 25 °C (Deformation; stress: 0.2 to 4 kPa, time: 300 s, angular frequency: 10 Hz; Recovery; Stress: 0.2 kPa, time: 300 s; angular frequency: 10 Hz; Angular frequency (rad s<sup>-1</sup>) dependence of G' and G" obtained with small stress amplitudes: (d) 0.5 wt. % of compound **2c** in decane at 25 °C using 0.2 kPa stress; (e) Stress dependence of G' and G" of the same gel **2c** measured at constant frequency (at 25 °C, and frequency at 10 Hz); (f) Thixotropic nature of organogel of **2c** (2.71 mM) in decane at 25 °C (Deformation; stress: 0.2 to 4 kPa, time: 300 s, angular frequency: 10 Hz; Recovery; Stress: 0.2 kPa, time: 300 s; angular frequency (at 25 °C, and frequency at 10 Hz); (f) Thixotropic nature of organogel of **2c** (2.71 mM) in decane at 25 °C (Deformation; stress: 0.2 to 4 kPa, time: 300 s, angular frequency: 10 Hz; Recovery; Stress: 0.2 kPa, time: 300 s; angular frequency: 10 Hz; Recovery; Stress: 0.2 kPa, time: 300 s; angular frequency: 10 Hz; Recovery; Stress: 0.2 kPa, time: 300 s; angular frequency: 10 Hz; Recovery; Stress: 0.2 kPa, time: 300 s; angular frequency: 10 Hz; Recovery; Stress: 0.2 kPa, time: 300 s; angular frequency: 10 Hz; Recovery; Stress: 0.2 kPa, time: 300 s; angular frequency: 10 Hz.)

From Fig. 20b and 20e, we make two observations in case for 1c and 2c separately. Firstly, at low strain amplitudes both G' and G" are nearly constant and G' > G" is steady confirming the solid like behavior and a linear viscoelastic regime. Secondly, both storage modulus and loss modulus became strain dependent above a stress value of 3.27 kPa and 0.8 kPa for 1c and 2c gels respectively. This observation leads to the formation of viscoelastic liquid behavior (G" > G') for both cases at high stress. In order to examine the thixotropic nature of the gels, we have studied the retrieval process of the damaged gels via two continuous processes of deformation and recovery for several times. As observed from Fig. 20c for **1c** and Fig. 20f for **2c**, at a particular angular frequency of 10 Hz for 300 seconds a variable stress of 0.2 to 4 kPa was applied for the deformation process and the value of G' vs time was recorded. It was found that the value of G' decrease in deformation process leading to the formation of viscoelastic liquid at 300 seconds. The same graph was continued in the recovery process where the value of G' starts increasing with time leading to solid like properties at the same angular frequency for a shear stress of 0.2 kPa in both gels. This set of experiment was done five times for the reproducibility of the gel. It can also be concluded that we are dealing with high elastic modulus of consistent physical gels that can be recovered instantly, once eliminating the applied stress.

#### Conclusions

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In this report, we have synthesized several bent-shaped molecules with a central pyridine unit flanked by two unsymmetrically substituted 1,3,4-oxadiazole and thiadiazole moieties. The number and position of the terminal tails were varied. The type of the heterocycle and the number of peripheral tails had a significant impact on the stabilization of the liquid crystalline and organogel self-assembly as well as photophysical properties. Thiadiazole based compounds exhibited higher mesophase stability in comparison to oxadiazole derivatives, while oxadiazole based compounds exhibited higher gelation tendency. In the case of oxadiazole derivatives, tetracatenar and hexacatenars exhibited gelation behavior, while in the case of thiadiazole derivatives only hexacatenars exhibited gelation. The number of peripheral tails also play an important role in stabilizing the gelation in hydrocarbon solvents, which is evident from the fact that all the hexacatenars stabilized supergelation irrespective of the type of heterocycle. The gelation is mainly promoted by attractive  $\pi$ - $\pi$  interactions, which is in contrast to other supergelators that require strong intermolecular hydrogen bonding. The supergelators showed the capability to form self-standing, moldable gel at higher concentration. Thiadiazole based compounds exhibited bathochromically shifted absorption and emission in comparison to oxadiazole derivatives but with a lower quantum yield. In addition these compounds showed the ability to sense the acid with a quenching/shifting in the emission spectrum, which makes it possible to detect acids by naked eye at low concentration. Two of the hexacatenar supergelators

investigated, exhibited aggregation induced enhanced emission with a several fold increase in luminescence intensity in the gel state. The variation in the gelation capability of these molecules shows that although the  $\pi$ - $\pi$  interactions plays a major role in self-assembly, the nanoseggregation of incompatible molecular segments like peripheral flexible tails also contribute in organogelation and LC self-assembly. Scanning probe microscopic studies of the xerogels revealed a fibrillar network of several micrometers corroborating the long range supramolecular self-assembly. Extensive rheological studies proved the viscoelastic and thixotropic nature of the gels. Similar AIEE effect was observed in thin film state too. Stabilization of columnar self-assembly over a long range, along with AIEE behavior is significant from the perspective of emissive solid-state displays. In a nutshell, this study accounts the effect of molecular structural variations on the nature of supramolecular selfassembly and the resultant macroscopic properties, that is of substantial significance to the scientific community working in the broad area of supramolecular chemistry.

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