### Accepted Manuscript

Synthesis and self-assembly of aroylhydrazone based polycatenars: A structure-property correlation



Hemant Kumar Singh, Ravindra Kumar Gupta, Sachin Kumar Singh, D.S. Shankar Rao, S. Krishna Prasad, Ammathnadu S. Achalkumar, Bachcha Singh

PII:	80167-7322(18)32904-0
DOI:	https://doi.org/10.1016/j.molliq.2019.04.003
Reference:	MOLLIQ 10726
To appear in:	Journal of Molecular Liquids
Received date:	4 June 2018
Revised date:	29 March 2019
Accepted date:	1 April 2019

Please cite this article as: H.K. Singh, R.K. Gupta, S.K. Singh, et al., Synthesis and self-assembly of aroylhydrazone based polycatenars: A structure-property correlation, Journal of Molecular Liquids, https://doi.org/10.1016/j.molliq.2019.04.003

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Synthesis and self-assembly of aroylhydrazone based polycatenars: a structure-property correlation

Hemant Kumar Singh<sup>a,b</sup>, Ravindra Kumar Gupta<sup>b</sup>, Sachin Kumar Singh<sup>a,b</sup>, D. S. Shankar Rao<sup>c</sup>, S. Krishna Prasad<sup>c</sup>, Ammathnadu S. Achalkumar<sup>\*b</sup> and Bachcha Singh<sup>\*a</sup>

<sup>a</sup> Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi-221005, India.
<sup>b</sup> Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, India.
<sup>c</sup> Centre for Nano and Soft Matter Sciences, Jalahalli, Bangalore-560013, India.
Email: bsinghbhu@rediffmail.com

Abstract. Two series of aroylhydrazone based polycatenars which differ from each other in terms of the linking groups (semi flexible ester or flexible ether linkage) were synthesized. These hexacatenars were mesogenic and also showed gelation in organic solvents at very low concentration, which is assisted by the intermolecular hydrogen bonding. Both the series of hexacatenars were prepared by varying the peripheral chain length from n-hexyloxy to nhexadecyloxy chain. In the case of ester based series on moving from n-decyloxy to ndodecyloxy chain, a transition from columnar rectangular phase to columnar hexagonal phase was noticed. Such behavior was not seen in the case of ether-based hexacatenars, irrespective of the chain length. Representative hexacatenars from each series exhibited gelation at low concentration, but the critical gelation concentration of ester-based hexacatenar was almost half of that observed for ether-based hexacatenar. From these studies we can understand the importance of the linking group, which constitutes very small part of the molecule, but has a significant effect on the type of the self-assembly in bulk as well as in presence of solvents. The presence of semi-flexible ester group provides a bent conformation to the molecule, while the presence of flexible ether group provides a linear shape to the molecule, as evident from the molecular modeling studies. Further the presence of the ester group enhances the extent of intermolecular hydrogen bonding with the solvent that leads to a lowercritical gelation concentration in comparison to the ether-based linking group. Such H-bonded liquid crystals have potential in the preparation of liquid crystalline physical gels and related applications.

#### **1. Introduction**

Aroylhydrazones containing --CO-NH-N=C-- moiety have been identified as one of the versatile class of compounds containing lateral intermolecular hydrogen bonding (Hbonding) [1]. The aroylhydrazone moiety provides certain unique features to the molecule like (i) a trinuclear azomethine group (-C=N-NH-) which provides opportunities to obtain the molecules of diverse structures, (ii) the possibility of configurational isomerisation arising from the inherent nature of the C=N double bond and (iii) amide linkage (-C=O-NH-) that provides the intermolecular hydrogen bonding (C=O---H-N) leading to the stabilization of supramolecular assembly. Due to these structural features, aroylhydrazone based compounds show different physicochemical properties which lead to many applications in various fields ranging from organic synthesis, biological, bactericidal, fungicidal, analytical, industrial, pharmacological, medicinal chemistry and supramolecular chemistry [2-10]. There are a number of reports on aroylhydrazone based compounds and their metal complexes, but research on aroylhydrazone derivatives exhibiting mesomorphic behavior is still in its initial stages except few reports on such mesogens [11-26]. This is largely attributed to the extensive hydrogen bonding between amide linkage in these types of ligands and the high melting point of the corresponding metal complexes. In order to obtain mesogenic aroylhydrazone derivatives, the commonly used approach is the diminution of hydrogen bonding between neighboring layers via (i) coordination of aroylhydrazone derivatives with the metal ions through oxygen and nitrogen donor atoms, so that amidic bond could not be available for intermolecular hydrogen bonding or (ii) using the polycatenar substitution pattern of the alkoxy chains attached to aromatic core or (iii) both approaches in a single molecule [11-15]. The polycatenars, or phasmid-like LCs, are nonconventional LCs with a dumbbell shape, including a central long rod-like aromatic unit connected to two terminal hemi-discs with multiple flexible chains [27-29]. These molecules self-assemble to form various liquid crystalline (LC) phases due to the nanophase segregation of incompatible molecular subunits like central rigidaromatic core and terminal flexible chains. They are very sensitive to small structural variations resulting in the changes of macroscopic self-assembly and hence their mesogenic properties [30-32]. The length of the flexible chains present in the polycatenars and the extent of intermolecular interactions decide the type of the mesophase exhibited by the polycatenars. This hybrid molecular design with the features of both rod-like and disc-like LCs, make them capable of exhibiting mesophases common to both these classes by a systematic structural tuning. Usually the hexacatenars stabilize columnar phase with hexagonal (Col<sub>h</sub> phase), rectangular (Col<sub>r</sub> phase) or an oblique (Col<sub>ob</sub>) symmetry.

Supramolecular gels form a unique class of materials. Such gelators possess specific structural attributes that lead to the immobilization of large volume of solvents during gelation. In spite of the low concentration of organogelators in comparison to the amount of solvent, the organogels are very sensitive to the molecular structure of the gelator [33-36]. There are subtle interactions of gelator-gelator and gelator-solvent molecules in stabilizing the organogels which can be altered by the molecular structure. The organogelation is further assisted by several weak forces like H-bonding,  $\pi$ - $\pi$  interactions, hydrophobic or hydrophilic interactions or van der Waals interactions. This class of materials is promising in a wide range of applications in the areas of optoelectronics, inorganic nanostructure templates, sensors and controlled drug delivery systems [37-47]. Merging of these two different fields has given rise to a new area of 'liquid crystalline physical gels'. This type of gels exhibit enhanced tunable electrooptical, photoresponsive and electronic properties due to the combination of these two different entities which form phase-separated structures [47]. Our recent results on aroylhydrazone based polycatenar LCs, which stabilize gelation at very low concentration (2 wt %), encouraged us to investigate more into structure-property relationship that direct these delicate interactions which stabilize the LC and organogel self-assembly [26]. Thus, we have synthesized hexacatenars containing aroylhydrazone moiety with an overall reduction in the molecular length in comparison to the earlier reported derivatives [26]. We envisaged that such molecules may have potential in the preparation of liquid crystalline physical gels in future.

Two series of hexacatenars were prepared by extending the aroylhydrazone core unit through semi-flexible ester (-C(=O)O-) and flexible ether (-O-CH<sub>2</sub>) linking groups. The mesophase behavior of the ester and ether based compounds was investigated with respect to a variation in chain length and linking group. Mesophase crossover from  $Col_r$  phase to  $Col_h$ phase was found in these derivatives, which was studied in detail with the help of polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and powder X-ray diffraction (XRD) studies.

#### 2. Results and discussion

#### **2.1.** Synthesis and characterization

The synthesis of ester and ether based hexacatenars is provided in Scheme 1. *O*-alkylation of methyl 3,4,5-trihydroxybenzoate with 1-bromoalkane in 2-butanone using anhydrous potassium carbonate leads to the formation of methyl 3,4,5-trialkoxybenzoate. 3,4,5-Trialkoxybenzohydrazide was prepared by reaction of methyl 3,4,5-trialkoxybenzoate with

hydrazine monohydrate in refluxing ethanol. 4-(3,4,5-Tris(tetradecyloxy)benzoyloxy) benzaldehyde and 4-(3,4,5-tris(hexadecyloxy)benzyloxy)benzaldehyde were synthesized according to reported methods [26]. The aroylhydrazone based compounds were obtained by the condensation reaction of 3,4,5-trialkoxybenzohydrazide with appropriate aldehyde in refluxing ethanol. The structures of all the precursors and final compounds were confirmed using <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, IR spectroscopy and CHN analyses (see the Electronic Supporting Information for details).



**Scheme 1.**Reactions and reagents: (a) RBr (n equiv.),  $K_2CO_3$  (4 × n equiv.), KI (catalyst), refluxing in 2butanone, 24-72 h, 70-85% (b) KOH (3 equiv.), refluxing in EtOH, 4 h, 80-90% (c) 4-hydroxybenzaldehyde (1 equiv.), DMAP (1.1 equiv.), DCC (1 equiv.), stirring in dry DCM, 4-6 h, RT, 60-80% (d) LAH (1.2 equiv.), stirring in dry THF at 0°C, 4 h, 88-95% (e) SOCl<sub>2</sub> (3 equiv.), stirring in dry DCM at 0°C, DMF (cat.), 1 h, 75-85% (f) 4-hydroxybenzaldehyde (1 equiv.),  $K_2CO_3$  (3 × n equiv.), refluxing in dry DMF, 6-10 h, 60-70% (g) NH<sub>2</sub>NH<sub>2</sub>.H<sub>2</sub>O(1.5 equiv.), refluxing in absolute EtOH, 12 h, 85-90%. (h) Acetic acid (cat.), refluxing in EtOH, 12 h, 70–80%.

#### 2.2. Mesomorphic behavior

The thermal behavior of the hexacatenars was studied by the use of thermo gravimetric analyses (TGA), DSC, POM and XRD studies (in selected cases). Transition temperatures and their corresponding enthalpy and entropy changes are tabulated in Table 1 and

graphically represented in Fig. 1. The mesomorphic behavior of these hexacatenars containing ester and ether linkages are described in the following sections.

#### 2.2.1.Compounds with ester linkage

From TGA analyses, the degradation temperature of the compound 1 was found to be above 300 °C (ESI). Except the shorter homologues with *n*-hexyloxy chains (1, n=6), all the hexacatenars (1, n = 8, 10, 12, 14, 16) exhibited the Col phase.



Fig. 1. Bar graph showing the thermal behavior of the compounds  $(1/n6 \rightarrow 1/n16)$  with ester linkage (in cooling cycle).

Tuble 11 hased and conceptioning thermodynamic parameters							
	T, °C [ $\Delta$ H, kJ/mol; $\Delta$ S, J/(mol K)]						
Compound	Heating	Cooling					
1/n6	Cr 130.9 (96.1; 237.8) I	I 122.3 (-78.4; -198.2) Cr					
1/n8	Cr 103.7 (61.5; 163.2) Col <sub>r</sub> 122.3 (2.1; 5.3) I	I 120.1 (-1.4; -3.5) Col <sub>r</sub> 52.7 (-11.1; -34.0) Cr					
1/n10	Cr 65.0 (104.5; 309.1) Col <sub>r</sub> 117.2 (2.7; 6.9) I	I 113.2 (-2.3; -5.9) Col <sub>r</sub> 24.4 (-40.3; -135.4) Cr					
	0	17.2 (-14.0; -48.2) Cr'					
1/n12	Cr 63.4 (88.6; 263.3) Col <sub>h</sub> 108.7 (2.8; 7.4) I	I 104.7 (-1.8; -4.8) Col <sub>h</sub> 13.5 (-31.1; -108.5) Cr					
1/n14	Cr 65.3 (118.0; 348.5) Col <sub>h</sub> 106.7 (2.6; 6.9) I	I 102.2 (-2.0; -5.4) Col <sub>h</sub> 30.3 (-33.8; -111.4) Cr					
1/n16	Cr 82.4 (60.4; 169.8) Col <sub>h</sub> 104.9 (2.0; 5.2) I	I 98.6 (-1.8; -4.8) Col <sub>h</sub> 8.1 (-15.0; -53.4) Cr					
2/n6	Cr 58.7 (42.1; 127.0) Col <sub>r</sub> 125.9 (3.9; 9.8) I	I 120.4 (-2.7; -6.9) Col <sub>r</sub> 38.7 (-30.9; -99.1) Cr					
2/n8	Cr 47.0 (38.0; 118.8) Cr' 60.9 (8.6; 25.8) Col <sub>r</sub>	I 116.4 (-2.0; -5.2) Col <sub>r</sub> 24.0 (-29.5; -97.5) Cr					
	119.4 (2.3; 5.9) I						
2/n10	Cr 43.9 (47.2; 148.9) Col <sub>r</sub> 111.6 (1.9; 5.1) I	I 108.3 (-1.7; -4.5) Col <sub>r</sub> 29.2 (-36.4; -120.3) Cr					
2/n12	Cr 48.5 (64.6; 200.8) Col <sub>r</sub> 105.6 (2.0; 5.2) I	I 102.3 (-1.7; -4.5) Col <sub>r</sub> 29.5 (-43.6; -144.2) Cr					
2/n14	Cr 50.1 (32.3; 99.9) Col <sub>r</sub> 104.1 (6.7; 17.8) I	I 102.9 (-5.3; -14.2) Col <sub>r</sub> 30.2 (-44.2; -145.6) Cr					
2/n16	Cr 53.2 (52.4; 160.7) Col <sub>r</sub> 101.6 (2.2; 5.9) I	I 97.9 (-2.1; -5.7) Col <sub>r</sub> 32.7 (-38.9; -127.2) Cr					

**Table 1**. Phase transitions and corresponding thermodynamic parameters

Abbreviations: Cr, Cr' = crystalline state,  $Col_r = rectangular columnarmesophase$ ,  $Col_h = hexagonal columnar$ mesophase, I = isotropic liquid.

All the hexacatenars with *n*-octyloxy to *n*-hexadecyloxy (n= 8–16) carbon chain length exhibited enantiotropic Col phase. Compound **1/n10** showed a mesophase range of 52 °C. The crystalline compound melts at 65 °C ( $\Delta$ H = 104.5 kJ/mol) to enter a mesophase, before converting into an isotropic liquid at 117.2 °C (Fig. 2b). On cooling the isotropic liquid, mesophase appears at 113.2 °C with a typical fan-shaped texture characteristic of Col phase (Fig. 2a). This remains as such up to 24.4 °C with the same texture without any signs of crystallization, as evidenced by the DSC thermogram (Fig. 2b).



**Fig. 2.** (a) POM image for the Col<sub>r</sub> phase of compound 1/n10 at 103 °C; (b) DSC traces obtained for the first cooling and second heating cycles of compound 1/n10; (c) XRD profiles depicting the intensity against the  $2\theta$  obtained for the Col<sub>r</sub> phase of compound 1/n10 at 26 °C.

To confirm the mesophase structure and supramolecular organization of the compound 1/n10, XRD studies were carried out (Fig. 2c). X-ray diffraction patterns for the compound 1/n10 were recorded in the LC phase at different temperature intervals while cooling the isotropic liquid. Indexation of the reflections obtained in the XRD profiles of the compound 1/n10 is tabulated in Table 2. The X-ray profile of compound 1/n10 at 26 °C showed four reflections with *d*-spacings of 31.81, 22.16, 15.97 and 12.12 Å in the small-angle region, corresponding to the Miller indices (10), (12), (20) and (05), respectively. In the wide angle region, two diffuse peaks are found at 4.33 and 4.16 Å, corresponding to the packing of the alkoxy tails and stacking of the molecular cores within the column, respectively. The second diffused peak is stronger than the first indicating the ordered packing of hexacatenars within the column. On indexing *d*-spacings obtained in the small angle region, the diffraction profile showed a two-dimensional rectangular lattice with lattice constants a = 31.8 Å and b = 61.8 Å (Table 2). Thus, this phase was assigned as a Col<sub>r</sub> phase.

This can be schematically represented as below. It is known that two or more hexacatenars combine together to form a disc and such discs self-assemble to form Col phases. From the XRD studies it is evident that in the  $Col_r$  phase of the compound 1/n10, three molecules form a columnar slice, which in turn pack themselves into a column, and

these columns self-organize in a rectangular lattice to stabilize  $\text{Col}_r$  phase (*p2mm* symmetry). The packing of three molecules together is facilitated by the bent structure provided by the ester linking group as shown in the Fig. 3.

Table 2. X-Ray diffraction data of the compounds 1/n10, 1/n12, 2/n8 & 2/n10								
Comp	Mesophase	T/°C	d-spacing/Å	d-spacing/Å	Miller	lattice	Lattice area $S$ (Å <sup>2</sup> ),	
ds.			observed	calculated	indices/hk	spacing/Å	molecular volume V	
						(Å <sup>3</sup> )		
1/n10	$\operatorname{Col}_{r}$	26	31.81	31.81	10	<i>a</i> =31.8	S=1964.8, V=8168.1,	
			22.16	22.06	12	<i>b</i> =61.8 Z=3.4		
			15.97	15.93	20			
			12.12	12.35	05			
			4.33	4.33				
			4.16	4.16				
1/n12	$\operatorname{Col}_h$	26	32.15	32.08	10	<i>a</i> =37.1	<i>S</i> =1193.8,	
			16.15	16.08	20		V=5296.0, Z=2.1	
			12.20	12.15	21			
			4.44	4.44				
2/n8	$\operatorname{Col}_{r}$	26	30.58	30.44	11	<i>a</i> =43.9	S=1871, V=7764,	
			21.31	21.21	02	<i>b</i> =42.6	Z=2.9	
			15.39	15.29	22			
			13.77	13.87	31			
			11.86	11.93	23			
			4.36	4.36				
			4.14	4.14				
2/n10	$\operatorname{Col}_{r}$	50	29.96	29.96	11	a=35.2	S=2005.7,	
			28.45	28.57	02	<i>b</i> =56.9	V=8937.8, Z=3.5	
			17.17	17.02	21			
			4.46	4.46				



Fig. 3. Schematic showing the self-assembly of the compound 1n/10 in Col<sub>r</sub> phase

Interestingly, the compound **1** with longer side chains, n=12, 14 and 16, showed a typical Col<sub>h</sub> phase. For the compound **1/n12** transitions Cr-Col<sub>h</sub>-I in heating cycle, and I-Col<sub>h</sub>-Cr in cooling cycle was observed. From DSC thermograms a typical larger enthalpy for the Cr-Col<sub>h</sub> transition at temperature 63.4 °C and a lower enthalpy for the Col<sub>h</sub>-I transition at temperature

108.7 °C in heating cycle were observed (Fig. 4b). Under the POM, compound **1** (n=12, 14, 16) showed characteristic birefringent fluid phases that are typical of Col phases. The formation of broken fan textures with homeotropic domains has been observed (Fig. 4a). The textures are mobile down to room temperature without any further change in the texture.



**Fig. 4.** (a) POM image for the Col<sub>h</sub> phase of the compound 1/n12 at 100 °C; (b) DSC traces obtained for the first cooling and second heating cycles of the compound 1/n12; (c) XRD profiles depicting the intensity against the  $2\theta$  obtained for the Col<sub>r</sub> phase of the compound 1/n12 at 26 °C.

Variable temperature powder XRD measurements were performed to determine the symmetry of the columnar mesophase formed by the compound 1/n12 at 26 °C (Table 2). The intensity vs 20 plot obtained from the XRD pattern of the Col phase at 26 °C (Fig. 4c) showed a strong reflection corresponding to a *d*-spacing of 32.15 Å in the low angle region, followed by reflections with d-spacings of 16.15 and 12.20 Å. These reflections were corresponding to the Miller indices of (10), (20), and (21) in the ratio 1:  $1/\sqrt{4}$ :  $1/\sqrt{7}$  and therefore, these values confirm the Col<sub>h</sub> phase. In the wide-angle region, a relatively diffused peak with a *d*-spacing of 4.44 Å was observed. The calculated lattice parameter *a* was 37.1 Å. This is approximately 30% less than the diameter obtained from the DFT analysis. It may be due to the folding of flexible chains or the possible interdigitation of flexible chains in the neighboring columns. Polycatenar molecules due to their dumbbell-shape are not big enough to fill the columnar cross-section. Therefore, two or more molecules have to aggregate side by side to generate a columnar slice (disc), which in turn stacks to form the columns. Such molecular association leads to association of the rigid aromatic parts of the molecules in the center, and the periphery with flexible alkoxy chains. The force responsible for this kind of arrangement is driven by the nanophase segregation, due to the incompatibility of these molecular sub units as well as the tendency of the system to minimize the free space during packing [48-54]. There are three and two molecules in columnar cross-section of the column of 1/n10 and 1/n12, respectively. The mesophase crossover from  $Col_r$  to  $Col_h$  arrangements with increasing terminal alkoxy chain length was observed for the hexacatenars on moving

from 1/n10 to 1/n12; *i.e.* with the increasing carbon number the Col<sub>h</sub> phase arrangement predominates over the Col<sub>r</sub> phase. The mesophase crossover from Col<sub>r</sub> to Col<sub>h</sub> was generally attributed to the requirement of greater core-core interaction required for the stabilization of Col<sub>r</sub> phases [55-57]. It is understood that increase in length of terminal alkoxy chains weakens the core-core interaction, that is assisted by the intermolecular H-bond interaction (-C=O<sup>...</sup>H-N-) and thus leads to the formation of Col<sub>h</sub> phase from Col<sub>r</sub> phase in such systems. Thus in the case of compound 1/n12 with six *n*-dodecyl chains, only two molecules associate to form a disc, as evident from XRD studies (Fig. 5, Table 2). This kind of loose packing leads to the stabilization of Col<sub>h</sub> phase. This is also complimented by the reduced core-core interaction with the increase in the chain length. Such behavior is commonly observed in the case of discotic Col phases, where the lower homologues exhibit Col<sub>r</sub> phase, while the higher homologues exhibit Col<sub>h</sub> phase [14].



Fig. 5. Schematic showing the self-assembly of the compound 1n/12 in Col<sub>h</sub> phase

From the bargraph shown in Fig. 1, it is evident that in the case of mesogenic ester compounds, with the increase in chain length ( $n = 8 \rightarrow 16$ ), a significant decrease in melting temperature was observed, while the decrease in the clearing point was very low. This results increase in the thermal range of mesophase in the case of hexacatenars ( $1/n8 \rightarrow 1/n12$ ). This trend of increase in the mesophase range is found to be inconsistent for the compound with the highest chain length (1/n16) and a slight decrease was found in the case of 1/n14. Thus we can infer that for this type of polycatenars, the appropriate peripheral chain length is a significant aspect in deciding the thermal range of the mesophase. Moderate length soft alkoxy tails may be assumed as most appropriate to gain good mesophase stability.

#### 2.2.2. Compounds with ether linkage

The hexacatenars of this series with ether linkage and of varying chain length (2, n= 6, 8, 10, 12, 14, 16), exhibited the Col phases and were characterized by DSC, polarizing optical

microscope and XRD analysis (for n= 8, 10). From TGA analysis, it was found that the hexacatenars 2 were stable at least up to 300 °C. The phase transition temperatures and enthalpies of the compounds (2, n=  $6\rightarrow 16$ ) are given in Table 1. The compounds with *n*-hexyloxy to *n*-hexadecyloxy (n= 6-16) carbon chain length exhibited enantiotropic columnar phase. For example, in the second heating scan of the compound 2/n8, three sharp peaks appear at 47, 69.4 and 119.4 °C which are attributed to crystal to crystal, crystal to mesophase and mesophase to isotropic transition, respectively (Fig. 6b). The DSC thermogram recorded in the cooling scan exhibits two distinct peaks at 116.4 and 24 °C corresponding to isotropic to mesophase and mesophase to crystal phase transitions, respectively. POM observations reveal that on cooling from the isotropic state to 80 °C, fan shaped textures of the columnar mesophase emerged (Fig. 6a). This was also confirmed by XRD studies carried out at 26 °C in cooling cycle, with a characteristic pattern commonly observed for the Col<sub>r</sub> phase (Fig. 6c). Similar type of textural pattern is also shown by the compound 2/n6.



**Fig. 6.** (a) POM image for the Col<sub>h</sub> phase of the compound **2/n8** at 90 °C; (b) DSC traces obtained for the first cooling and second heating cycles of the compound **2/n8**; (c) XRD profiles depicting the intensity against the 2 $\theta$  obtained for the Col<sub>r</sub> phase of the compound **2/n8** at 26 °C.

The supramolecular organization of the compound (2/n8) in the Col phase was studied by XRD technique. The results of indexing of diffraction pattern obtained from the powder 2D pattern (Fig. 6c) of hexacatenar 2/n8 are presented in Table 2. The small angle region showed reflections that can be assigned to a two-dimensional rectangular lattice with lattice constants a = 43.9 Å and b = 42.6 Å (Table 2) and thus the Col phase can be assigned as a Col<sub>r</sub> phase. DSC thermogram of the compound 2/n10 shows two endothermic and two exothermic peaks. Two endothermic transitions were seen in the DSC that are attributed to crystal to mesophase and mesophase to isotropic phase transitions, while exothermic transitions are isotropic to mesophase and mesophase to crystal phase (Fig. 7b). As we move from lower to higher alkoxy chain length (n=8 to 10), we found broken fan textures of the Col phase on cooling in the POM (Fig. 7a). The textures are mobile down to room temperature without further change

in the texture. Similar type of textural patterns is also shown by the compounds 1 (n=12, 14 and 16). In the case of discotic columnar LCs, it is usual to predict a transition from a  $\text{Col}_r$  to a  $\text{Col}_h$  phase with an increase in peripheral chain length, but such a tendency was not observed in this class of polycatenars [30, 48].



**Fig. 7.** (a) POM image for the Col<sub>h</sub> phase of the compound 2/n10 at 50 °C; (b) DSC traces obtained for the first cooling and second heating cycles of the compound 2/n10; (c) XRD profiles depicting the intensity against the 20 obtained for the Col<sub>r</sub> phase of the compound 2/n10 at 50 °C.

In order to identify the type of Col phase, X-ray diffraction pattern (Fig. 7c) of the compound **2/n10** has been obtained. The diffractogram of the compound **2/n10** at 50 °C showed three reflections at a *d*-spacing of 29.96, 28.45 and 17.17 Å in the low angle region (Table 2). These reflections, along with the diffused halo at wide angles, can be indexed to a Col<sub>r</sub> phase with Miller indices of (11), (02) and (21). Diffused peak is observed at *d*-spacing of 4.46 Å, corresponding to the packing of alkoxy chains. For the compounds under study (**2/n8** & **2/n10**) there are three hexacatenars that form a columnar slice. The thermal behavior of the compounds **2** (n=6→16) in cooling cycleis summarized in bar graph (Fig. 8). From the bar graph, we found the significant decrease in melting temperature with the increase in chain length (n=  $8 \rightarrow 16$ ). The mesophase stability is almost similar for the compounds **2** (n=6, 8) and slightly decreases from n=10 to 16.

Thus the two classes of molecules show differences in their thermal behavior based on the linking group. The ester based hexacatenars (1) exhibited a cross-over from  $\text{Col}_r$  phase to  $\text{Col}_h$  phase with an increase in chain length, while the ether based hexacatenars (2) exhibited solely  $\text{Col}_r$  phase irrespective of their chain length. The bent structure provided by the ester linking group allows the molecules to pack with certain restrictions, and due to this, the intermolecular H-bonding interactions are fragile and get perturbed with the increase in the terminal chain length from 1n/10 to 1n/12. However, in the ether series, the methylene linking group is flexible and can orient in any direction, without allowing the dilution of

intermolecular H-bonding interactions, thus the entire series exhibit Col<sub>r</sub> phase irrespective of the chain length (Fig. 9a).



Fig. 8. Bar graph showing the thermal behavior of the compounds  $(2/n6\rightarrow 2/n16)$  with ether linkage in cooling cycle.



Fig. 9. Chemical structure showing the bond rotation of ester and ether based hexacatenars (a); Energy minimized molecular models of hexacatenars 1n/10 and 2n/10 from a molecular mechanics (MM2) method.

#### **2.3.** Photophysical properties

To see the effect of solvent polarity and structural changes on the optical properties of the ester and ether based polycatenars, we have measured the absorption and fluorescence spectra. Due to the little effect on the optical properties by the length of the alkoxy tails, we have chosen compounds 1/n10 and 2/n10 as representatives. The absorption and fluorescence spectra of the compounds 1/n10 and 2/n10 were recorded in micromolar chloroform and butanol solutions. The absorption spectra of the compound 1/n10 showed a single absorption maximum at 308 nm in both the butanol and chloroform solutions, where as the absorption spectra of the compound 2/n10 showed absorption maximum at 317 nm in chloroform solution and 319 nm in butanol (Fig. 10a, c). The ester based polycatenar 1/n10 in chloroform and butanol showed an emission band centered at 397 nm with a Stokes shift of 89 nm. In contrary, the compound 2/n10 exhibited a red shifted emission maximum at 383 nm with a

Stokes shift of 66 nm (Fig. 10b, d). This may be due to the electron donating nature of ether linkage in comparison to the ester linkage.



Fig. 10. Absorption spectra of the compounds 1/n10(a) and 2/n10(b); Emission spectra of the compounds 1/n10(c) and 2/n10(d) (red trace: in butanol; black trace: in chloroform).

#### 2.4. Gelation studies

The gelation property of the compounds 1/n10 and 2/n10 were examined in different organic solvents at different concentrations, the results are listed in Table 3. The organic solvent containing 1/n10 and 2/n10 were heated in a sample vial until the solid was completely dissolved. Then the solution was cooled at room temperature. Gel formation was observed during the cooling process, which was confirmed by the inversion of the glass vial (Fig. 11a). As shown in Table 3, 1/n10 and 2/n10 show good gelation properties in *n*-butanol. Among these compounds, compound 1/n10 showed critical gelation concentration (CGC) of 0.8 wt% in *n*-butanol while 2/n10 showed CGC of 2.1 wt% in *n*-butanol. Gelators which form stable gels at less than 1 wt% concentration are termed as supergelators [58-61]. Strong intermolecular interactions like H-bonding are required for such type of stable gel [62]. 2/n10showed higher CGC possibly due to the flexible ether (-O-CH<sub>2</sub>) linking group in comparison to the semi-flexible ester (-C(=O)O-) group in 1/n10. This is interesting because the ester group in 1n/10 provides an additional site for intermolecular hydrogen bonding with the

solvent (1-butanol), while the same is lacking in the case of 2n/10. Further, the ether-based polycatenars exhibit a linear structure in comparison to the ester-based polycatenar (Fig. 9b). Because of this the CGC observed for 2n/10 is almost double than that of 1/n10.

Table 3.Gelation behavior of 1/n10 and 2/n10							
Entry	Solvent	1/n10			2/n10		
		Properties	CGC (wt.%)	$T_{gel}(^{\circ}C)$	Properties	CGC (wt.%)	$T_{gel}(^{\circ}C)$
1	1-Butanol	G(0)	0.8	48	G(O)	2.1	40
2	Decane	S			S		
3	Dodecane	S			S	<b>-</b>	
4	Hexadecane	S			S		
5	Toluene	S			S		
6	m-Xylene	S			S		
7	DCM	S			S		
8	Chloroform	S			S		
9	Cyclohexane	S			S		
10	DMSO	Р			Р		
11	Methanol	Р			Р		

G = stable gel; P = precipitate; O = opaque; S =Soluble; CGC= Critical gelation concentration (wt. %) is the minimum concentration necessary for gelation.  $T_{gel}$  (°C) is the thermal stability of the gels at CGC.



Fig. 11. Solution and gel forms of the compounds 1/n10 and 2/n10 (a); FESEM image of the xerogel of the compounds1/n10(b) and 2/n10(c).

In order to obtain a visual insight into the morphologies of the molecular aggregation mode, the microstructures of the gel of 1/n10 and 2/n10 were examined with field emission scanning electron microscopy (FESEM), as shown in Fig. 11b, c. The compounds were made soluble in *n*-butanol at their CGC. A small drop of this solution was placed on a glass slide and kept aside to form a very thin layer of stable gel. Later these films were dried in vacuum which kept the structure intact. Complete evaporation of the solvent led to the formation of xerogels, which were characterized by FESEM. The images of the 1/n10 showed the highly entangled network nanofibers of several micrometers length in comparison to the 2/n10 (Fig. 11b, c).

#### 3. Conclusion

Mesomorphic properties of two new classes of mono substituted aroylhydrazones based hexacatenars, which differ from each other with the type of linking unit (ester and ether) have been studied. The length of the alkoxy chain was varied from n-hexyloxy to n-hexadecyloxy. All the hexacatenars stabilized columnar self-assembly. For the ester-based hexacatenars, the lower homologues stabilized a columnar phase with a rectangular symmetry, while the higher homologues exhibited a columnar phase with hexagonal symmetry. Interestingly, one of the ester-based hexacatenar exhibited a room temperature columnar rectangular phase. This mesophase crossover phenomenon with the increase in length of terminal alkoxy chains may be due to the weakened core-core interaction, that is assisted by the intermolecular H-bond interaction (-C=O<sup>...</sup>H-N-), which eventually leads to the formation of Col<sub>h</sub> phase from Col<sub>r</sub> phase in such systems. The bent structure provided by the ester linking group allows the molecules to pack with certain restrictions, and due to this, the intermolecular H-bonding interactions are fragile and get upset with the increase in the terminal chain length. In contrast, ether based hexacatenars solely exhibited a columnar rectangular phase regardless of the chain length. This may be due to the flexibility provided by the methylene linking group that can orient in any direction, without allowing the dilution of intermolecular H-bonding interactions, irrespective of the chain length. The effect of the molecular structure is also witnessed from the critical gelation concentration required for the organogels formed by these two classes. The representative ester based hexacatenar formed a stable gel at lower critical gelation concentration due to the ester linkage, which can take part in hydrogen bonding and a bent structure. The representative ether based hexacatenar formed a stable gel at almost double critical gelation concentration in comparison to the ester based hexacatenar, due to the lack of extra hydrogen bonding site and linear molecular structure. This study thus reveals the minute interplay of the structural characteristics that affect the liquid crystalline and organogels supramolecular self-assemblies. Such H-bonded liquid crystals have potential in the preparation of liquid crystalline physical gels and related applications.

#### Acknowledgements

Hemant Kumar Singh is grateful to DST, SERB for providing fellowship under N-PDF (PDF/2016/001706) scheme. BS is grateful to DRDO, India (Project No. ERIP/ER/1203053/M/01/1542) for providing financial assistance.

### References

[1] X.Su, I.Aprahamian, Hydrazone-based switches, metallo-assemblies and sensors, Chem. Soc. Rev. 43 (2014) 1963-1981.

[2] K. Hruskova, P. Kovarikova, P. Bendova, P. Haskova, E. Mackova, J. Stariat, A. Vavrova, K. Vavrova, T. Simunek, Synthesis and initial in vitro evaluations of novel antioxidant aroylhydrazone iron chelators with increased stability against plasma hydrolysis, Chem. Res. Toxicol. 24(2011) 290-302.

[3] P.V. Bernhardt, J. Mattsson, D.R. Richardson, Complexes of cytotoxic chelators from the dipyridyl ketone isonicotinoyl hydrazone (HPKIH) analogues, Inorg. Chem.45 (2006) 752-760.

[4] S. Adsule, V. Barve, D. Chen, F. Ahmed, Q.P. Dou, S. Padhye, F.H. Sarkar, Novel Schiff base copper complexes of quinoline-2 carboxaldehyde as proteasome inhibitors in human prostate cancer cells, J. Med. Chem.49(2006) 7242-7246.

[5] S.Y. Ebrahimipour, I. Sheikhshoaie, J. Simpson, H. Ebrahimnejad, M. Dusek, N. Kharazmi, V. Eigner, Antimicrobial activity of aroylhydrazone-based oxidovanadium (v) complexes: in vitro and in silico studies, New J. Chem.40 (2016) 2401-2412.

[6] H.H. Monfared, S. Sadighian, M.A. Kamyabi, P. Mayer, Iron (III) aroylhydrazone complexes: Structure, electrochemical studies and catalytic activity in oxidation of olefins, Journal of Molecular Catalysis A: Chemical304(2009)139-146.

[7] B.B. Tang, H. Ma, G.Z. Li, Y.B. Wang, G. Anwar, R. Shi, H. Li, Synthesis, crystal structures and luminescent properties of tetranuclear Zn molecular clusters with aroylhydrazone ligand, Cryst. Eng. Comm. 15(2013) 8069-8073.

[8] L. Zhang, P. Zhang, L. Zhao, J. Wu, M. Guo, J. Tang, Single-molecule magnet behavior in an octanuclear dysprosium (III) aggregate inherited from helical triangular Dy3 SMMbuilding blocks, Dalton Trans. 45(2016) 10556-10562.

[9] D. Patra, N. Biswas, B. Kumari, P. Das, N. Sepay, S. Chatterjee, M.G. Drew, T. Ghosh, Afamily of mixed-ligand oxidovanadium (V) complexes with aroylhydrazone ligands: a combined experimental and computational study on the electronic effects of para substituents of hydrazone ligands on the electronic properties, DNA binding and nuclease activities,RSC Adv.5(2015) 92456-92472.

[10] X. Zhang, H. Mu, H. Li, Y. Zhang, M. An, X. Zhang, J. Yoon, H. Yu, Dual-channel sensing of CO<sub>2</sub>: Reversible solution-gel transition and gelation-induced fluorescence enhancement, Sensors and Actuators B: Chemical255(2018) 2764-2778.

[11] M.N. Abser, M. Bellwood, M.C. Holmes, R.W. McCabe, Aroylhydrazinatonickel (II) and copper (II) complexes; a new class of metallomesogens, J. Chem. Soc., Chem. Commun.(1993) 1062-1063.

[12] M.N. Abser, M. Bellwood, C.M. Buckley, M.C. Holmes, R.W. McCabe, Examination of the structural features necessary for mesophase formation with aroylhydrazinato-nickel (II) and-copper (II) complexes, J. Mater. Chem.4 (1994) 1173-1180.

[13] P. Battistini, M. Carcelli, E. Dalcanale, C. Pelizzi, G. Pelizzi, L. Righini, Nickel (II) complexes of 2, 6-disubstituted pyridine bishydrazones as potential metallomesogens. Suppression of the mesogenic properties induced by dimerization, Mol. Cryst. Liq. Cryst. 309 (1998) 167-188.

[14] C.K. Lai, C.H. Tsai, Y.S. Pang, Discotic metallomesogens: mesophase crossover of columnar rectangular to hexagonal arrangements in bis (hydrazinato) nickel (II) complexes,J. Mater. Chem.8(1998) 1355-1360.

[15] A. Bacchi, M. Carcelli, O. Francescangeli, F. Neve, P. Pelagatti, C. Pelizzi, Correlated columnar phases: aroylhydrazinato nickel (II) complexes as novel discotics,*Inorg. Chem. Commun.*2(1999) 255-257.

[16] C.V. Yelamaggad, R. Prabhu, D.S. Rao, S.K. Prasad, The first examples of supramolecular discotic  $C_3h$  tris(N-salicylideneamine)s featuring inter-and intra-molecular H-bonding: synthesis and characterization, Tet Lett. 51(2010) 4579-4583.

[17] G. Shanker, M. Prehm, C.V. Yelamaggad, C. Tschierske, Benzylidenehydrazine based room temperature columnar liquid crystals, J. Mater. Chem.21(2011) 5307-5311.

[18] S.K. Singh, K. Vikram, B. Singh, Synthesis, characterisation and mesomorphic properties of ester containing aroylhydrazones and their nickel (II) complexes,Liq. Cryst.38(2011) 1117-1129.

[19] S.K. Singh, H.K. Singh, R. Nandi, V. Kumar, N. Tarcea, J. Popp, R.K. Singh, B. Singh, Synthesis, characterization and mesomorphic investigations of ester-substituted aroylhydrazones possessing a lateral hydroxyl group, Polyhedron74(2014) 99-112.

[20] S.K. Singh, V. Kumar, R. Nandi, H.K. Singh, R.K. Singh, B. Singh, Microwave-assisted synthesis and mesomorphic investigations of p-substituted aroylhydrazones and their nickel (II) and copper (II) complexes, Liq. Cryst. 42(2015) 222-232.

[21] S.K. Singh, V. Kumar, H.K. Singh, P. Kanth, B. Singh, Microwave-assisted synthesis, characterisation and mesomorphic investigations of novel disubstituted aroylhydrazones,Liq. Cryst. 42(2015) 1179-1190.

[22] H.K. Singh, S.K. Singh, R. Nandi, M.K. Singh, V. Kumar, R.K. Singh, D.S.S. Rao, S.K. Prasad, B. Singh, Tuning the thermotropic properties of liquid crystalline p-substituted aroylhydrazones, RSC Adv. 5(2015) 44274-44281.

[23] S. Parthasarathi, D.S.S. Rao, H.K. Singh, B. Singh, S.K. Prasad, Anchoring transition driven by short range ordering in Calamitic-discotic composites, Thermochimica Acta 616(2015) 61-68.

[24] H.K. Singh, S.K. Singh, R. Nandi, D.S.S. Rao, S.K. Prasad, R.K. Singh, B. Singh, Observation of exceptional 'de Vries-like' properties in a conventional aroylhydrazone based liquid crystal,RSC Adv. 6(2016) 57799-57802.

[25] R. Nandi, S.K. Singh, H.K. Singh, D.S.S. Rao, S.K. Prasad, B. Singh, R.K. Singh, Molecular approach to phase transitions in a calamitic ester substituted aroylhydrazone liquid crystal, J.Raman Spectrosc. 47 (2016) 1095-1101.

[26] H.K. Singh, B. Pradhan, S.K. Singh, R. Nandi, D.S.S. Rao, S.K. Prasad, A.S. Achalkumar, B. Singh, Substituted Aroylhydrazone Based Polycatenars: Tuning of Liquid Crystalline Self-Assembly, ChemistrySelect3(2018) 4027-4037.

[27] A. Mori, T. Itoh, H. Taya, K. Kubo, S. Ujiie, U. Baumeister, S.Diele, C. Tschierske, Mesomorphic property of 2, 5-dibenzoyloxy-, 5-benzoylamino-2-benzoyloxy-, and 2, 5-dibenzoylamino-tropones with mono-, di-, and tri-alkoxyl groups on the benzoyl groups and their benzenoid derivatives, Liq. Cryst.37(2010) 355-368.

[28] K. Rowe, D. Bruce, The synthesis and mesomorphism of di-, tetra-and hexa-catenar liquid crystals based on 2, 2'-bipyridine,J. Mater. Chem. 8(1998) 331-341.

[29] S.K. Pathak, S. Nath, R.K. Gupta, D.S.S. Rao, S.K. Prasad, A.S. Achalkumar, Effect of regioisomerism on the self-assembly and photophysical behavior of 1, 3, 4-thiadiazole-based polycatenars, J. Mater. Chem. C3 (2015) 8166-8182.

[30] J.Malthête, A. Levelut, N.H. Tinh, Phasmids: a new class of liquid crystals, J. Phys. Lett. 46 (1985) 875-880.

[31] J.Malthête, H.T. Nguyen, C. Destrade, Phasmids and polycatenar mesogens, Liq. Cryst. 13(1993) 171-187.

[32] H.T. Nguyen, C. Destrade, J.Malthête, Phasmids and polycatenar mesogens, Adv. Mater. 9(1997) 375-388.

[33] S. Nath, S.K. Pathak, J. De, S.K. Pal, A.S. Achalkumar, Star-shaped  $\pi$ -gelators based on oxadiazole and thiadiazoles: a structure–property correlation,Mol. Syst. Des. & Eng. 2(2017) 478-489.

[34] B. Pradhan, V.Vaisakh, G.G. Nair, D.S.S. Rao, S.K. Prasad, A.S. Achalkumar, Effect of Atomic-Scale Differences on the Self-Assembly of Thiophene-based Polycatenars in Liquid Crystalline and Organogel States, Chem. Eur. J. 22(2016) 17843-17856.

[35] B. Pradhan, R.K. Gupta, S.K. Pathak, J. De, S.K. Pal, A.S. Achalkumar, Columnar selfassembly of luminescent bent-shaped hexacatenars with a central pyridine core connected with substituted 1, 3, 4-oxadiazole and thiadiazoles, New J. Chem. 42(2018) 3781-3798.

[36] S.K. Pathak, B. Pradhan, M. Gupta, S.K. Pal, A.S. Achalkumar, Liquid-crystalline starshaped supergelator exhibiting aggregation-induced blue light emission, Langmuir 32(2016) 9301-9312.

[37] S.S. Babu, V.K. Praveen, A. Ajayaghosh, Functional  $\pi$ -gelators and their applications, Chem. Rev. 114(2014) 1973-2129.

[38] S.S. Babu, S.Prasanthkumar, A. Ajayaghosh, SelbstorganisierteGelbildnerfür die organischeElektronik,Angew. Chem. 124(2012) 1800-1810.

[39] S.S. Babu, S.Prasanthkumar, A. Ajayaghosh, Self-Assembled Gelators for Organic Electronics. Angew. Chem. Int. Edit. 51(2012) 1766-1776.

[40] S. Diring, F. Camerel, B. Donnio, T. Dintzer, S. Toffanin, R. Capelli, M. Muccini, R. Ziessel, Luminescent ethynyl-pyrene liquid crystals and gels for optoelectronic devices, J. Am. Chem. Soc. 131(2009) 18177-18185.

[41] J.H. Jung, Y. Ono, S. Shinkai, Chirale Silica-Spiralendurch Sol-Gel-Polykondensation von Tetraethoxysilan in einemCholesterin-Organogel-System, Angew. Chem. 112(2000) 1931-1933.

[42] J.H. Jung, Y. Ono, S. Shinkai, Sol–Gel Polycondensation of Tetraethoxysilane in a Cholesterol-Based Organogel System Results in Chiral Spiral Silica, Angew. Chem. Int. Edit. 39(2000)1862-1865.

[43] S. Kobayashi, N. Hamasaki, M. Suzuki, M. Kimura, H.Shirai, K. Hanabusa, Preparation of helical transition-metal oxide tubes using organogelators as structure-directing agents,J. Am. Chem. Soc. 124(2002)6550-6551.

[44] E.D. Sone, E.R. Zubarev, S.I. Stupp, Semiconductor nanohelicestemplated by supramolecular ribbons, Angew. Chem. Int. Edit. 41(2002)1705-1709.

[45] G.Gundiah, S. Mukhopadhyay, U.G. Tumkurkar, A. Govindaraj, U. Maitra, C. Rao, Hydrogel route to nanotubes of metal oxides and sulfates, J. Mater. Chem. 13(2003) 2118-2122.

[46] C. Wang, Q. Chen, F. Sun, D. Zhang, G. Zhang, Y. Huang, R. Zhao, D. Zhu, Multistimuli responsive organogels based on a new gelator featuring tetrathiafulvalene and azobenzene groups: Reversible tuning of the gel-sol transition by redox reactions and light irradiation, J. Am. Chem. Soc., 132(2010)3092-3096.

[47] T. Kato, Y. Hirai, S. Nakaso, M. Moriyama, Liquid-crystalline physical gels, Chem. Soc. Rev. 36(2007) 1857-1867.

[48] M.Gharbia, A. Gharbi, H. Nguyen, J.Malthete, Polycatenar liquid crystals with long rigid aromatic cores: a review of recent works, Curr Opin Colloid Interface Sci. 7(2002) 312-325.

[49] D.Guillon, A. Skoulios, J. Malthete, Columnar mesophases from disklike clusters of rods, Europhys Lett., 3(1987)67.

[50] B. Donnio, B. Heinrich, T.G. Krzywicki, H. Delacroix, D.Guillon, D.W. Bruce, The synthesis, mesomorphism, and characterization by X-ray diffraction and freeze-fracture electron microscopy of polycatenar liquid crystals of silver (I) showing columnar and cubic mesophases, Chem. Mater. 9(1997) 2951-2965.

[51] D. Fazio, C.Mongin, B.Donnio, Y. Galerne, D.Guillon, D.W. Bruce, Bending and shaping: cubics, calamitics and columnars, J. Mater. Chem. 11(2001)2852-2863.

[52] S.J. Yoon, J.H. Kim, K.S. Kim, J.W. Chung, B. Heinrich, F. Mathevet, P. Kim, B.Donnio, A.J. Attias, D. Kim, Mesomorphic Organization and Thermochromic Luminescence of Dicyanodistyrylbenzene-Based Phasmidic Molecular Disks: Uniaxially Aligned Hexagonal Columnar Liquid Crystals at Room Temperature with Enhanced Fluorescence Emission and Semiconductivity, Adv. Funct. Mater. 22(2012)61-69.

[53] J. Tang, R. Huang, H. Gao, X. Cheng, M. Prehm, C. Tschierske, Columnar mesophases of luminescent polycatenar liquid crystals incorporating a 1, 3-substituted benzene ring interconnecting two 1, 3, 4-oxadiazoles,RSC Adv. 2(2012)2842-2847.

[54] E.Y. Elgueta, M.L. Parra, J.Barberá, J.M. Vergara, M.Dahrouch, E.W. Díaz, New polycatenar Schiff bases derived from 1, 3, 4-thiadiazole: synthesis, mesomorphism and luminescence behavior, Liq. Cryst. 43(2016)1649-1658.

[55] S.Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Haegele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, Discotic liquid crystals: from tailor-made synthesis to plastic electronics, Angew. Chem. Int. Edit. 46(2007)4832-4887.

[56] H. Zheng, C.K. Lai, T.M. Swager, Controlling Intermolecular Interactions between Metallomesogens: Side-Chain Effects in Discotic Copper, Palladium, and VanadylBis(beta-Diketonates), Chem Mater. 7(1995)2067-2077.

[57] C. Destrade, P. Foucher, H. Gasparoux, N.H. Tinh, A.Levelut, J. Malthete, Disc-like mesogen polymorphism, Mol. Cryst. Liq. Cryst. 106(1984)121-146.

[58] A. Gopal, R. Varghese, A. Ajayaghosh, Oligo (p-phenylene-ethynylene)-Derived Super- $\pi$ -Gelators with Tunable Emission and Self-Assembled Polymorphic Structures, Chem. Asian J. 7(2012)2061-2067.

[59] Q. Wang, J.L. Mynar, M. Yoshida, E. Lee, M. Lee, K. Okuro, K.Kinbara, T. Aida, High-water-content mouldable hydrogels by mixing clay and a dendritic molecular binder, Nature 463(2010) 339.

[60] S.K. Pathak, B. Pradhan, R.K. Gupta, M. Gupta, S.K. Pal, A.S. Achalkumar, Aromatic  $\pi$ - $\pi$  driven supergelation, aggregation induced emission and columnar self-assembly of star-shaped 1, 2, 4-oxadiazole derivatives, J. Mater. Chem. C4(2016)6546-6561.

[61] A.P. Sivadas, N.S. Kumar, D.D. Prabhu, S. Varghese, S.K. Prasad, D.S.S. Rao, S. Das, Supergelation via Purely Aromatic  $\pi$ - $\pi$  Driven Self-Assembly of Pseudo discotic Oxadiazole Mesogens, J. Am. Chem. Soc. 136(2014)5416-5423.

[62] L.E. Buerkle, S.J. Rowan, Supramolecular gels formed from multi-component low molecular weight species, Chem. Soc. Rev 41(2012)6089-6102.

### **Highlights:**

> Two series of aroylhydrazone based polycatenars were synthesized and their self-assembly and organogelation are reported.

> In ester based series on moving from *n*-decyloxy to *n*-dodecyloxy chain, a transition from  $Col_r$  to  $Col_h$  was noticed.

> The critical gelation concentration of ester-based hexacatenar was almost half of that observed for ether-based hexacatenars.

➢ From these studies we can understand the importance of the linking group on self-assembly in bulk as well as in presence of solvents.

A CER MAN