Chapter-5

Synthesis and characterization of amphiphilic anthraquinones with glycerol head groups

Abstract

This chapter contains compounds involving glycerol functionalization in anthraquinone scaffold. The compounds were found to show columnar rectangular phase. It was further noticed that the pre-final compounds were also mesomorphic showing hexagonal phase. All the compounds were found to have good thermal stability. The final compounds were analyzed for lyotropic behavior with respect to water and formamide. Only chiral compounds with formamide were found to be mesomorphic.



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5.1 Introduction:

Amphiphilic diols can be thought of analogous to carbohydrates in terms of their structure. They constitute a large class of amphotropic mesogens¹. The mesomorphism in these system can be induced by the possibility of hydrogen-bond formation between the neighbors. The lyotropic behavior of all the diols were purely based on the degree of hydration of diol groups present in the system. Only 2 or 3 water molecules have been taken by these diols through hydrogen bonding. The typical phase diagram of a diol based head group with alkyl chain hydrophobic group is given in figure 1^2 .



Figure 1: Phase diagram of diol-water system²

5.2 Mesomorphic diols:

The mesomorphic character in diols are induced by hydrogen bonding ability of polar moieties of molecules. In addition to hydrogen bonding, there is phase segregation between the rigid aromatic rings and flexible chains around the compound which enhances the aggregate formation. The aggregates that formed further self-assembled into diverse liquid crystalline phases. The phase sequence looks analogous to a typical lyotropic system ³. The structure of mesophases was found

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to be dependent on the relative size of hydrophobic groups with respect to hydrophilic moieties ⁴ which constitute the molecule. Further, the mesophase formation can be fine-tuned with the help of number of alkyl chains attached to the aromatic ring and attached number of polar groups ^{5–7}. In polyols systems, the mesophases was induced by both hydrogen bonds and other intermolecular interactions. The substituents such as perflouro, carboxy siloxanes were found to impart greater stability to mesophases. In conclusion in polyols system, the higher probability of columnar phase formation results when there is more compact and larger polar component in a molecule ⁷.

In binary amphiphiles composed of two incompatible segments, the LC behavior depends on the relative volume of the two incompatible segments. Smectic phases result in molecules with a comparable cross-section area of the incompatible motif. On the increasing size of one of the incompatible units, increase curvature which leads to the formation of columnar and cubic mesophases (**Figure 2**). Similar behavior can be found in mesomorphic amphiphilic systems, surfactant-water systems and binary block copolymer systems.

5.2.1 Literature review on liquid crystals with glycerol-based head groups:

Amphiphilic diols with longer alkyl chains have been found to show amphotrophy⁸. They were found to show L_{α} , L_{β} , and H_{II} (inverse hexagonal) phases. The temperature range



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Figure 2: Mesomorphic glycerol functionalized rigid systems⁹



Figure 3: Structure and mesomorphic behaviour of varied end functionalised diols⁸

corresponding to H_{II} was found to be increasing with the chain length (**Figure 3**). The mesomorphic behavior is summarized in the figure3. Further, the mesomorphic behavior was fund to be sensitive to the polarity of the terminal group. From the table, we can see that when the terminal group was functionalized with the carboxylates group (more polar), the mesophase was lost. This observation can be accounted for as follows. When you increase the polarity of terminal groups on the hydrophobic moiety of the diols leads to loss of distinct orientation of molecules in the smectic layers. The terminal polar moiety serve as hydrogen acceptors which leads to disruption of the H-bonding network.

Bolaamphiphiles with terminal chain functionalized with hydroxyl group stabilization of LC phases were observed. Depending on the hydrophobic spacer either L_{β} or both L_{α} , L_{β} phases were observed. The stabilization was expected because hydroxyl groups are known for both their H-bonding donating and accepting nature, they tend to stabilize the hydrogen bonding network and

in turn the lamellar organization. In the case of bolaamphiphiles, the length of polymethylene spacer was found to influence the presence of both L_{α} , L_{β} , and only L_{β} phase^{10,11} (**Figure 4**).



Figure 4: Structure and mesomorphic behaviour of Bolaamphiphilic multiols¹⁰

5.2.2 Bolamphiphiles connected rigid hydrophobic rings:

The rigid units (cyclohexane, benzene) connecting the diols were found to show the potential for amphotropic behavior. The mesophase stability was highly influenced by the elongation of the rigid hydrophobic group separating the two diol groups (**Figure 5**) (**Figure 6**) $^{12-15}$.





	Transition temperatures		
	Water-free	Water-saturated	
C ₇ H ₁₅ -OHOH	or 109 (SB 99) SA 249 is	not determined	
С ₆ H ₁₃ ОН	cr 160 SA 194 is	not determined	
$C_6H_{13} - \underbrace{ \begin{array}{c} \\ \\ \\ \\ \\ \end{array} }^N - \underbrace{ \begin{array}{c} \\ \\ \\ \\ \\ \\ \end{array} }^{-OH} OH$	cr 113 is	cr 88 SA 92 is	
C ₇ H ₁₅ N-N OH	cr109 is	cr 64 SA 131 is	

Figure 6: Mesomorphism of diols with heterocyclic rings¹⁷

This observation was very much illustrated by the phenyl benzoate based amphiphile. The introduction of diol instead of alkyl chains was found to be stabilizing further the nematic phase was replaced by smectic in nature (**Figure 7**).





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When the diol groups and the aromatic rings were separated by alkyl spacer the clearing temperature decreases with odd-even effect. The clearing temperatures were found to be sensitive to the polarity of the rigid core as many of heterocyclic spacer derivatives lack mesomorphism (**Figure 8**). The polarity of heterocyclic core was found to be minimized by the elongation of alkyl tails in the hydrophobic part. ^{15,18}



n	Water-free	Transition temperatures Water-saturated
7	cr 109 is	cr 64 S 131 is
11	cr 109 (S _C 108) S _A 134 is	cr 73 S 178 is
15	cr 110 (S _C 115) S _A 148 is	cr 76 \$ 193 is

Figure 8: Influence of heterocyclic ring on mesomorphism of diols²

Cyanobiphenyl (CB) derivatives, one of the widely explored calamitic systems, was used for diols functionalization. One of the notable observations was that the diol functionalized CB systems exhibit nematic phase rather than smectic phase as observed in the above-mentioned systems. The nematic nature of these CB derivatives was attributed to competing H-bonding interactions involving cyano group with the H-bonding interactions among the diols which was responsible for the smectic nature of diols based bolaamphiphiles. The CB derivatives showed smectic behavior in the presence of water, as the water molecules incorporated in the network of intermolecular H bonds between the diols¹⁹.

Phenyl and naphthyl derivatives connecting diols were showing smectic A phase. In the case of large rigid units, additional smectic phases were formed. In the case of cyclohexane and bicyclooctane smectic B was seen. In the case of heteroaromatic spacer smectic C was observed. The smectic nature was attributed to hydrogen bonding between diols which hinders the longitudinal movement of individual molecules. The smectic behavior of diols was retained when there is the introduction of OH group near the head group in the CB systems. The glucose functionalized CB system was smectic in nature. The presence of a cyano group in the hydrophobic part of bolaamphiphile was found to disrupt the smectic phase leading to a nematic or non-mesomorphic character ²⁰(**Figure 9**).



Figure 9: Cyanobiphenyls functionalised with amphiphiles¹⁹

The heterocyclic ring spacer was found to show similar behavior as carbocyclic systems (**Figure 10**). Pyrimidine system shown in figure 10 showed nematic, smectic A and smectic C phases as the water content increases ²¹.





An introduction of hydrophilic groups connecting the diol head with aromatic groups found to show cubic phase in water. They showed mesophase in formamide, glycerol and ethylene glycol too (**Figure 11**).



Figure 11: 1, 2, 4-thiadiazole functionalised with amphiphiles

It was found that the bolamphiphilic diols (**Figure 12**) separated by biphenyl show greater stability ²³



Figure 12: Bolaamphiphilic diols¹⁰

As mentioned above when hydrogen bond acceptor was added as one of the head group the disruption of smectic nature was observed as mentioned in the figure 13, all the tetraols are smectic in nature 24 (Figure 13).



Figure 13: Comparison with diols with other substituents¹⁰

Giesselmaan et al. have reported formation of lyotropic phase of 2-D correlated tilted fluid structures in phenyl pyrimidine based amphiphilic diols with water. Further these diols were reported to show lyotropic phase sequence as typical of lyotropic systems ²⁵ (**Figure 14**).



Figure 14: Structure and mesophases of pyrimidine functionalised chiral diol²⁵

Giesselmann et al. reported photoresponsive amphotropic liquid crystalline system constituting azobenzenes derivatives with ethyleneglycol spacer and glycerol heads. Thes compounds with single alkyl chain were smectic in nature. The compound with one OH group was found to show Sm C phase. In diols here SmC as well as SmA was observed in protic solvents. Compounds with multiol alkyl

chains were found to show hexagonal phase and protic solvents were found to stabilize the hexagonal order²⁶(Figure15).



Figure 15: Photoresponsive amphotropic diol ²⁶

Giesselmaan et al. have reported phenylpyrimidine based amphiphilic sytem showing amphotropic behaviour. The compounds showed monotropic chiral nematic phase for a small temperature range. But in presence of water the system exhibited enantiotropic chiral nematic, and two columnar phases. They showed smA * phase for large range of compositions. One of the interesting report was that the above 20wt% the system showed lyotropic Sm C* phase which was found to have electrooptical behaviour as typical of thermotropic system. This is the first report on electrooptically switching of Sm C* phase in lyotropic systems. The smectic C* and two columnar phases (col 1 & col 2) were retained but they appeared only on cooling when the compound was mixed with formamide²² (**Figure 16**).



Figure 16: Lyotropic smectic C* phase of phenylpyrimidine functionalised with diol ²²

Giesselmann et al. extended the amphiphilic diols using calamitic systems by replacing phenylpyrimidine systems to flourenone systems. They too were found to show lyotropic SmC* phase ²⁷ (**Figure 17**).



Figure 17: Structure of flourenone functionalised chiral diol²⁷

In the rod-like system the bulkiness of lateral substituents leads to loss of long-range positional ordering which was reflected in replacement of smectic behavior with nematic or sometimes nonmesomorphic behavior. But it was noticed that the LC behavior can be retained if there is an incompatibility between lateral and terminal chains. The incompatibility induced stabilization of mesophases in calamitic systems through competition between polyphilicity and shape anisotropy facilitated the formation of new mesomorphic structures with complex morphologies. The formation of complex morphological liquid crystalline phases can be accounted as follows when either lateral or terminal substituents contributes cohesive energy density by hydrogen bonding or being ionic in nature²⁸. By taking this incompatibility induced stabilization of mesophase into consideration, two different amphiphilic systems were designed and studied extensively for their mesophase behavior (**Figure 18**).

- a. T shaped bolapolyphiles
- b. X shaped bolapolyphiles



Figure 18: Schematic of T-shaped and X-shaped bolapolyphiles ²⁹

5.2.3 T- Shaped bolaamphiphiles:²⁹

T shaped poyphiles composed of three units which are incompatible to each other

- 1. Central core(oligo 1,4 phenylenes, oligo 2,5 thiophenes, oligo (1,4-phenylene ethynylenes)
- 2. Polar terminal groups (Glycerol head groups)
- 3. Lateral chains (linear alkyl chains, branched alkyl chains, siloxanes, carbosianes, semiperfluorinated chains)

General representation of the structure of T shaped bolpolyphile is shown in figure 18.

When semiperflourinated chains are used as lateral chains, which brings significant amount of incompatibility with the polar groups and aromatic units, the stability of mesophase gets enhanced .Semiperflourinated chains have been found to have larger volumes compared to alkyl chains of similar length which plays a vital role in mesophase stabilisation.

The following are the diverse phases shown by these T- shaped bolapolyphiles

1. Polygonal honeycombs

2. Giant honeycombs

3. Smectic A

T shaped bolaamphiphiles show smectic mesophase as mentioned above in the absence of lateral chains with higher transition temperatures. The smectic layering is done by having the rod like cores and glycerol heads are organised in alternating layers. Shorter lateral chains aggregate into domains with a shorter correlation which was confirmed by the broad peaks in SAXS. On further extending the length of lateral chains the smectic domains were found to fuse into columns arranged parallel to layer planes and lead to the formation of long-range 2D lattice. The formation of the 2D lattice was found to be of honeycomb-like structure adjacent to the Smectic phase. This structure often has rectangular lattice with a c2mm space group. Further elongation of lateral chains induces honeycombs with different cross-sections of cylinders.

One of the main points about self-organization of these T- shaped bolapolyphiles is that the π conjugated core arranges themselves in perpendicular direction to the columnar axis forming walls connected at the seams by glycerol groups through H-bonding. The ratio of volume of the chains to the length of rod like cores forms cells with morphology ranging from rhombic, triangular, square, pentagonal, hexagonal etc.

The columnar phase shown by these polyphiles are not similar to columnar phase of discotics where the π - conjugated core constitutes the individual columns which arrange in 2D lattice in alkyl chain continuum. In this scenario the columns rigid aromatic core forms continuous frame work of cylinders fused to polygonal honeycomb structure around fluid columns of alkyl tails. The polygonal cylinders structure goes to higher end as lateral chain length increase.

The hydrogen bonded glycerol heads forms network along the columns which connect the bolamphiphilic cores and fuse them into nets which leads to honeycomb like structures (**Figure 19**). The morphologies formed were found to be dependent on nature of lateral chains³⁰ (**Figure 20**).



Figure 19: Mesophases of T-Shaped bolaamphiphiles ²⁸



Figure 20: Examples of T-shaped bolaamphiphilic compounds⁹

5.2.4 X- Shaped bolaamphiphiles: ³¹

X -shaped polyphiles contains rigid core with polar head groups on periphery with attaching two or more lateral chains at opposite sides to each other. The incorporation of additional lateral chain

was found to have significant impact on polygonal honeycombs. The influence of lateral chain was shown in case of terphenyl and bi thiophene systems (**Figure 21 & Figure 22**).

Square columnar phase was observed for tetrathiophene base bolapolyphiles. The isomeric compounds which had varied connection of lateral chains formed nematic mesophase apart from square phase. The nematic phase formed was found to be cybotactic in nature. In case of sexithiophene rigid system square phase was retained on attaching four lateral chains. The branching of lateral chains in the above mentioned system was found to form a hexagonal lattice.



Figure 21: Examples of X-shaped bolaamphiphiles ²⁸



Figure 22: X-shaped bolapolyphiles ²⁸

5.3 Results and discussion:

5.3.1 Synthesis:

Commercially available solketal was taken and tosylated using standard conditions. The tosyalted solketal was used for functionalizing the free OH group of anthraquinone through Williamson etherification. The obtained product was isolated and characterized using NMR. The deprotection of isopropylidene group was done by refluxing in presence of acid in THF yielded



Figure 23: Synthetic scheme of glycerol based bolaamphiphiles

the deprotected solketal i.e glycerol heads groups (**Figure 23**). All compounds were purified by column chromatography on silica gel (100-200 mesh) followed by repeated crystallization using suitable analytical grade solvents. The structure of final compounds was confirmed through NMR, and elemental analysis. The TGA thermogram of both the series of compounds (**4a-e &5a-e**) suggests good thermal stability (**Figure 24**).



Figure 24: TGA thermograms of cmpounds 4a-e & 5a-e

5.3.2 Mesomorphic properties of compounds 4a-e:

The solketal derivatized tetraalkoxy anthraquinones were explored for their mesomorphic behavior. The mesomorphic properties of the compounds were analysed using POM, DSC, and XRD. All the compounds were mesomorphic. POM images of all the compounds suggest the presence of columnar phase (**Figure 25**). DSC thermograms further validate the POM observation (**Figure 26**). The thermal behavior of all the solketal functionalized anthraquinones is given in the table1.

Small-angle diffraction patterns confirm the hexagonal order of columns as the small angle peaks can be indexed into a hexagonal lattice (**Figure 27**). The detailed indexation of diffraction peaks and lattice parameters of all the compounds are given in the table 2. From the diffraction

data, the number of molecules occupying a single slice of the column was found to be 1 (**Figure 28**)



Figure 25: POM images of 4a (70 °C); 4b (85°C); 4c (80°C); 4d (82°C); 4e (68°C)



Figure 26: DSC thermograms of 4a-e

Compd.	Phase sequence					
	Heating	Cooling				
4 a	Col _h 134.42(16.55) I	I 131.45 (-14.19) Col _h				
4 b	Cr 72.29 (4.38) Col _h 120.46 (13.86) I	I 117.98 (-12.09)Col _h				
4 c	Cr 74.21(3.37)Col _h 121.47 (11.62) I	I 118.87 (-10.32)Col _h 52.92 (-0.84) Cr				
4d	Col _h 106.53 (7.06)I	I 104.05 (-7.08)Col _h				
4 e	$Cr 66.70(48.12)Col_h 95.69(8.73)I$	I 93.97 (-8.41)Col _h				

Table 1. ^a Phase transition temperatures (°C) and the corresponding energy changes (kJmol⁻¹)



Figure 27: X_ray diffractograms of compounds 4a-e in Hexagonal phase

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COMPOUND	Phase	Spacing			Lattice parameters
	(temperature in °C)	d obs	dcal(Å)	Index	
		(Å)			
4a	130	17.53 8.76 6.61 4.60 3.59	17.53 8.76 6.62 4.60 3.59	10 20 21	$\begin{array}{c} a{=}20.24 \text{ \AA} \\ S{=}354.397 \text{ \AA}^2 \\ V{=}1240.391 \text{ \AA}^3 \\ Z{=}1.02 \end{array}$
4b(R)	95	18.46 9.26 4.60 3.68	18.46 9.12 4.60 3.68	10 20	a=21.31 Å S= 393.382 Å ² V=1447.64 Å Z= 1.04
4c(S)	110	18.46 10.71 9.23 4.57 3.70	18.46 10.65 9.23 4.7 3.70	10 11 20	a=21.31 Å S= 393.382 Å ² V=1447.64 Å Z= 1.04
4d	80	19.33 11.18 4.63 3.64	19.33 11.16 4.63 3.64	10 11	a=22.28 Å S= 429.88 Å ² V=1564.766 Å Z= 1.06
4e	80	20.65 11.8 4.60 3.65	2065 11.92 4.60 3.65	10 11	a=23.84 Å S= 429.88 Å ² V=1564.766 Å Z= 1.06

Table 2: Layer spacing obtained from XRD for 4a-e.

Table1: Layer spacing obtained from XRD for **4a**, **4b**, **4c**, **4d** and **4e**. (a = lattice parameter = $\sqrt{(4/3) * d_{10}}$; lattice area S_h = a²sin60°; lattice volume V_h = a²sin60°*h_c (h_a if h_c is not observed); No of molecules per slice of column (**Z**)= ($\sqrt{3*N_a*P*a^{2*}h}$)/2M; N_a=Avogadro number; P=Density in Kg/m³; a=lattice parameter; hc=core core peak (h_a if core core is not observed); M=molecular weight in Kg/m³)



Figure 28: Proposed model for packing of compounds 4a-e in hexagonal phase



Figure 29: POM images of 5a (125°C); 5b (100°C); 5c (110°C); 5d (115°C); 5e(88°C)



Figure 30: DSC thermograms of 5a-e

Table 3. ^a Phase transition temperatures	(\mathcal{C}) and the	corresponding energ	y changes (kJmoľ	·1)
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Compd.	Phase sequence					
	Heating	Cooling				
5a	Cr 85.5(69.59) Col _r 149.69 (30.10)I	I 132.85 (-25.27) Col _r 76.39 (-6.61) Cr				
5b	Cr 75.13 (2.41) Col _r 122.20(9.30)I	I 119.12 (-9.18) Colr 68.68 (-1.65)Cr				
5c	Cr 75.57 (1.61) Col _r 124.89 (8.18)I	I 122.18 (-8.96)Colr 72.40 (-1.33) Cr I				
5d	Cr 65.96 (46.1)Col _r 134.82(8.42) I	I 114.98 (6.94)Col _r				
5e	$Cr 73.65 (24.65)Col_r 106.71(14.30)I$	I 103.27(14)Colr 84.2(28.3)Cr				



Figure 31: X_ray diffractograms of compounds 5a-e in Rectangular phase

5.3.3 Mesomorphic properties of compounds 5a-e:

The glycerols **5a-e** were explored for their mesomorphic behavior. The mesomorphic properties of the compounds were analyzed using POM, DSC, and XRD. All the compounds were mesomorphic. POM images of all the compounds suggest the presence of columnar phase (**Figure 29**). DSC thermograms further validate the POM observation (**Figure 30**). The thermal behavior of all the glycerols derivatives is given in the table 3.

Small-angle diffraction patterns (**Figure 31**) confirm the rectangular morphology of columns as the small angle peaks can be indexed into a rectangular lattice (Table 4). The detailed indexation of diffraction peaks and lattice parameters of all the compounds are given in the table. From the diffraction data, the number of molecules occupying a single slice of the column was found to be 2 (**Figure 32**).



Figure 32: Proposed model for packing of compounds 5a-e in rectangular phase

5.3.4 Lyotropic properties of compounds 5a-e:

The compounds 5a-e were analyzed for lyotropic behavior with respect to water. They were found to be non-mesomorphic. They were not birefringent. They were tested for their liquid crystalline behaviour with respect to formamide. The 5wt% formamide system was equilibrated for two weeks. The compound 5a which is functionalized with racemic glycerol was not mesomorphic whereas the compound **5b** and **5c** containing the enantiomeric glycerols were found to show columnar phase. The POM images and diffraction patterns are given in the figure 33&34 (Table 5)

COMPOUND	Phase	Spacing			Lattice parameters
	(temperature			Index	
	in °C)	d obs	d cal		
		(Å)			
			<u> (Å) </u>		
5a		21.03	21.03	20	a=42.06 Å
	80	14.23	14.23	11	b=15.12 Å
		10.51	10.50	40	$S = 635.947 Å^2$
		4.28			V=2225.8152 Å ³
		3.56			Z=1.699
5b(R)		22.80	22.84	20	a=44.16 Å
	85	14.19	14.23	11	b=14.98 Å
		11.38	11.43	40	$S = 659.24 \text{\AA}^2$
		4.60	4.48		V=2399.6504Å ³
		3.64	3.63		Z=1.83
5c(S)	70	23.19	23.19	20	a=46.38 Å
		14.51	14.51	11	b=15.27 Å
		11.64	11.59	40	$S = 708.540 \text{\AA}^2$
		4.24	4.24		V=2508.2345 Å ³
		3.54	3.54		Z=1.911
5d		30.53	30.53	10	a=30.536 Å
		20.37	20.37	11	b=27.42 Å
	60	15.24	15.26	20	S=837.1326Å ²
		12.17	12.50	12	V=2996.9347 Å ³
		10.63	10.20	22	Z= 2.002
		10.18	10.17	30	
		7.63	7.84	23	
		4.34	4.34		
		3.51	3.51		
5	00	22.27	22.27	10	2_ 27 Å
36	90	20.46	20.46	10	a = 32.27 A b = 26.45 Å
		16.22	20.40	20	$S = 853.787 \text{ Å}^2$
		11.85	12.23	12	$V = 2971 \ 1800 \ \text{\AA}^3$
		10.85	10.75	$\frac{12}{30}$	7-1765
		10.03	10.75	22	2-1.703
		8.08	8.34	$\frac{22}{32}$	
		6.60	6.81	33	
		4.32	4.32		
		4.11	4.11		
		3.48	3.48		

Table 4: Layer spacing obtained from XRD for 5a-e.

Table 2 : Layer spacing obtained from XRD for **5a**, **5b**, **5c**, **5d** and **5e** lattice area S_h = a*b; lattice volume V_h = a*b*h_c (h_a if h_c is not observed); No of molecules per slice of column (**Z**)= (N_a*p*a*b*h)/ M; N_a=Avogadro number; p=Density in Kg/m³; **a**=lattice parameter; h_c=core core peak (h_a if core core is not observed); M=molecular weight in Kg/m³



Figure 33: POM images of 5a (5wt %) in formamide at RT; 5b (5wt %) in formamide at RT; 5c (5wt %) in formamide at RT



Figure 34: X-ray diffractograms of compounds 5b&5c 5wt% in formamide

COMPOUND	Phase	Spa	cing		Lattice parameters
	(temperature in °C)	d obs (Å)	d cal	Index	
			(A)		,
5b(5wt%)+formamide		23.51	23.51	20	a=47.02 A
	RT	14.35	14.35	11	b=15.06 Å
					$S = 708.54 \text{\AA}^2$
5c(5wt%)+formamide	RT	23.66	23.66	20	a=46.38 Å
		14.45	14.45	11	b=15.27 Å
					$S = 708.540 \text{\AA}^2$

Table 5: Layer spacing obtained from XRD for 5b, 5c (5wt %) in formamide

5.4 Conclusion:

We have synthesised glycerol based bola amphiphilic anthraquinones and studied their liquid crystalline behaviour. The results suggest that the solketal functionalised anthraquinones were found to be assembling in hexagonal columnar phase. The glycerol compounds 5a-e were assembling in rectangular phase. The chiral derivatives of glycerols 5b & 5c in formamide were found to be mesomorphic.

5.5 Experimental section:

All the chemicals and reagents are purchased from Sigma Aldrich and used directly. The solvents are AR grade and they were distilled and dried using corresponding protocols before usage. The crude products were subjected to column chromatography using silica gel (100-200 mesh) and recrystallized using suitable solvents. All the intermediates and final products structure were confirmed by NMR, Mass, Elemental analysis. ¹H NMR and ¹³C NMR (Nuclear magnetic resonance spectroscopy) were recorded by Bruker 500MHz instrument using CDCl₃ as solvent and trimethyl silane as internal standard. Chemical shift values are given in ppm and the solvent CDCl₃ peaks appear at ¹H NMR: δ = 7.23 ppm and ¹³C NMR δ = 77.0 ppm. Peak multiplicity is given as s = singlet, d = doublet, t = triplet, m = multiplet, b = broad peak. Elemental analysis was done by using Elementar Vario MICRO Select instrument. Samples were placed between the glass slides and kept inside Mettler FP82HT hot stage which is controlled by Mettler FP90 central processor and the liquid crystal textures were recorded using Olympus BX51 polarising optical microscope (Olympus, Tokyo, Japan). Mettler Toledo DSC instrument was used to record the phase transition temperatures of all the compounds. The peak temperatures are given in °C and corresponding enthalpy values are given in KJ mol⁻¹. Panalytical (Empyrean) Cu-Kα (1.54Å) Xray diffractometer was used to further confirm the mesophase structure of all compounds. Thermal stability of all the compounds was studied using TGA 4000 thermo gravimetric analysis instrument.

The general procedure of tosylation of solketals;

To a solution of solketal (1eq) in THF (120 mL), a solution of NaOH (5N) was added. The contents were immersed in an ice bath and tosyl chloride (1.5eq) in THF (100 mL) was added drop wise. The mixture was stirred overnight, concentrated, mixed with water, and extracted with ether. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated to give a low melting solid in quantitative yield (31 g, 98%)

Compound 1a : solketal (5g, 37 mmol, 1eq), THF(100ml), TsCl (10.80g, 56.66 mmol, 6eq), NaOH(5N, 20ml) Yield: 90% ; M.P. 45 °C; ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 1.31 (s, 3H), 1.34 (s, 3H), 2.45 (s, 3H), 3.76 – 3.77 (m, 1H), 3.96 – 4.03 (m, 3H), 4.27 (bs, 1H), 7.35 (d, *J*= 7.5Hz, 2H), 7.80 (d, *J*= 7.5Hz, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 21.65, 25.14, 26.63,

66.16, 69.50, 72.91, 110.05, 127.99, 129.93, 132.63, 145.09; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %).

Compound 1b : R-solketal (3g, 22.6mmol, 1eq), THF(100ml), TsCl (6.5g, 34mmol, 6eq), NaOH(5N, 12 ml) Yield: 90%; M.P. 45 °C ^{.1}H NMR (500 MHz, CDCl₃): δ (ppm) = 1.31 (s, 3H), 1.34 (s, 3H), 2.45 (s, 3H), 3.75– 3.78 (m, 1H), 3.96 – 4.05 (m, 3H), 4.25 – 4.29 (m, 1H), 7.35 (d, *J*= 8Hz, 2H), 7.79(d, *J*= 8Hz, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 21.66, 25.16, 26.64, 66.22, 69.49, 72.93, 110.07, 128.02, 129.92, 132.72, 145.07; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %).

Compound 1c: s-solketal (3g, 22.6 mmol, 1eq), THF (100ml), TsCl (6.5g, 34 mmol, 6eq), NaOH (5N, 12ml) Yield: 90%; M.P. 45 °C. ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 1.31 (s, 3H), 1.34 (s, 3H), 2.45 (s, 3H), 3.74 – 3.77 (m, 1H), 3.96 – 4.05 (m, 3H), 4.25 – 4.29 (m, 1H), 7.35 (d, *J*= 8Hz, 2H), 7.79 (d, *J*= 8 Hz, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 21.62, 25.12, 26.60, 66.10, 69.55, 72.91, 110.01, 127.96, 129.93, 132.61, 145.09; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %).

General procedure for the synthesis of compounds 3a, 3d & 3e:

In a typical reaction, to a stirred solution of NaOH (4 eq.) in dry DMSO (50 ml) added crude rufigallol **2** (5 g, 0.164 mmol, 1 eq) and 1-bromoalkane (4.4 eq.), and the mixture was heated to 70 °C and held at the same temperature under N₂ for 18h. The reaction mixture was cooled, diluted with aq. HCl and extracted with chloroform (80 ml X 5). The combined chloroform extracts were washed with water and dried over anhydrous Na2SO4. Product was crystallized from EtOH: CHCl3 (4:6). Yield 45 % (yellow solid).

Compound 3a : ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 0.91 – 0.92 (m, 12H), 1.33 - 1.39 (m, 25H), 1.50 - 1.52 (m, 9H), 1.80 - 1.89 (m, 8H), 4.17 - 4.19 (m, 8H), 7.43 (s, 2H), 12.80 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ ppm = 14.05, 14.07, 22.59, 22.62, 25.85, 25.93, 28.98, 29.10, 29.13, 30.27, 31.76, 31.84, 69.41, 73.75; 104.79, 111.84, 128.89, 141.20, 157.26, 158.05, 186.48; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %).

Compound 3d : ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 0.89 (s, 12H), 1.29 (bs, 33H), 1.49 - 1.50 (m, 8H) , 1.78 - 1.79 (bs, 4H), 1.87 (bs, 4H), 4.16 (t, *J* = 5.0 Hz, 8H) , 7.40 (s, 2H), 12.77 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ ppm = 14.11, 22.67, 22.68, 25.90, 25.99, 29.09, 29.26, 29.30, 29.31, 29.45, 30.27, 31.81, 31.87, 69.39, 73.75, 104.74, 111.80, 128.86, 141.13, 157.23, 158.04, 186.44; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %).

Compound 3e ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 0.88 (s, 12H), 1.27 (bs, 50 H), 1.48 - 1.49 (m, 12H) , 1.79 - 1.87 (m, 8H), 4.16 (t, *J* = 5.0 Hz, 8H) , 7.41 (s, 2H), 12.78 (s, 2H); ¹³C NMR (125 MHz, CDCl₃): δ ppm = 14.05, 14.07, 22.59, 22.62, 25.85, 25.93, 28.98, 29.10, 29.13, 30.27, 31.76, 31.84, 69.41, 73.75; 104.79, 111.84, 128.89, 141.20, 157.26, 158.05, 186.48; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %).

General procedure for preparation of Solketals:

A mixture of compound 3 (1eq), tosylate 1a-c (3eq) and K₂CO₃ (10eq) in DMF (20 mL) was stirred at 90 °C under an atmosphere of nitrogen for 24 h. The volatiles were removed in vacuo. The residue was mixed with water (100 mL), then extracted with CH₂Cl₂ (3 ¥ 80 mL). The combined organic extracts was dried over anhydrous MgSO4 and then evaporated to dryness under reduced pressure. The residue was chromatographed on a silica gel column using EtoAc-pet ether (10:90 v/v) as the eluent. The product was obtained as a white solid (5.02 g, 79%

Compound 4a: compound 3a&1a

¹H NMR (500 MHz, CDCl₃): δ (ppm) = 0.91 – 0.93 (m, 12H) , 1.30 – 1.40 (m, 23H), 1.44 – 1.54 (m, 15H), 1.58 – 1.59 (m, 4H), 1.76 – 1.85 (m, 4H), 1.86 – 1.90 (m, 4H), 4.00 – 4.26 (m, 16H), 4.62 – 4.64 (m, 2H), 7.58 (s, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ ppm =14.01, 14.05, 22.59, 22.64, 25.40, 25.66, 25.71, 26.91, 29.05, 30.25, 31.51, 31.68, 67.40, 69.26, 74.25, 74.42, 107.30, 109.33, 120.05, 132.48, 146.76, 153.08, 157.47, 180.90; Elemental analysis: C, 69.15; H, 8.78 calculated (%): C, 69.21; H, 8.71 (expt. %)

R solketal Compound 4b :compound 3a & 1b ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 0.87 – 0.92 (m, 12H) , 1.25 – 1.40 (m, 32H), 1.44 – 1.53 (m, 15H), 1.57 (s, 6H), 1.76 – 1.81 (m, 4H),

1.85 – 1.90 (m, 4H), 4.00 – 4.26 (m, 16H), 4.60 – 4.65 (m, 2H), 7.58 (s, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ ppm =, 14.09, 22.61, 22.65, 25.39, 25.95, 26.00, 26.90, 29.02, 29.08, 29.17, 30.29, 31.78, 31.85, 67.38, 69.24, 74.25, 74.40, 74.57, 107.27, 109.33, 120.02, 132.46, 146.73, 153.06, 157.46, 180.91; Elemental analysis: C, 69.10; H, 8.81 calculated (%): C, 69.30; H, 8.72 (expt. %)

S solketal Compound 4c : compound 3a & 1c ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 0.87 – 0.92 (m, 12H) , 1.26 – 1.40 (m, 33H), 1.44 – 1.53 (m, 15H), 1.56 (s, 13H), 1.76 – 1.81 (m, 4H), 1.85 – 1.90 (m, 4H), 4.00 – 4.26 (m, 16H), 4.60 – 4.65 (m, 2H), 7.58 (s, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ ppm =, 14.09, 14.10, 22.61, 22.65, 25.39, 25.95, 26.00, 26.90, 29.02, 29.08, 29.17, 30.29, 31.78, 31.85, 67.37, 69.24, 74.25, 74.39, 74.57, 107.26, 109.33, 120.02, 132.46, 146.72, 153.06, 157.46, 180.91; Elemental analysis: C, 69.30; H, 9.18 calculated (%): C, 69.50; H, 8.8 (expt. %)

C8 solketal Compound 4d : compound 3d & 1a ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 0.87 – 0.91 (m, 12H), 1.25 – 1.40(m, 43H), 1.44 – 1.53(m, 15H), 1.59 (s, 3H), 1.76 – 1.81 (m, 4H), 1.85 – 1.90 (m, 4H), 4.08 – 4.26 (m, 17H), 4.61 – 4.64 (m, 2H), 7.58 (s, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ ppm = 14.10, 22.68, 25.41, 26.02, 26.06, 26.92, 29.10, 29.27, 29.32, 29.48, 30.31, 31.82, 31.88, 67.40, 69.26, 74.26, 74.43, 74.60, 107.31, 109.33, 120.07, 132.49, 146.77, 153.09, 157.48, 180.91 ; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %)

C10 solketal Compound 4e : compound 3e & 1a ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 0.86 – 0.89 (m, 12H), 1.27 – 1.40 (m, 54H), 1.44 – 1.52 (m, 14H), 1.56 (s, 6H), 1.75 – 1.80 (m, 4H), 1.86 – 1.89 (m, 4H), 4.08 – 4.26 (m, 16H), 4.61 – 4.64 (m, 2H), 7.58 (s, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ ppm = 14.11, 22.70, 25.41, 26.03, 26.07, 26.92, 29.10, 29.36, 29.37, 29.53, 29.59, 29.62, 29.64, 29.69, 30.31, 31.93, 67.40, 69.26, 74.25, 74.43, 74.59, 107.29, 109.33, 120.06, 132.48, 146.76, 153.08, 157.48, 180.90 ; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %)

Glycerols:

General procedure for synthesis of compounds 5a-e:

The solketals **4a-e** were dissolved in THF (10 mL). To the solution, 2 M HCl (2.5 mL) solutions were added and the reaction mixture stirred at 70 °C for overnight. The mixture was cooled, concentrated, and precipitated from the excess amount of hexane. The compound was purified by dissolving in the minimum amount of DCM, added excess hexane, and centrifuged. The solid was then filtered and dried.

C6 glycerol Compound 5a : compound **4a** (0.5g , 0.57 mmol, 1eq), THF 50ml, HCl (2M)solution (10ml) Yield: $90\%_{1}^{1}H$ NMR (500 MHz, CDCl₃): δ (ppm): 0.89 – 0.94 (m, 12H), 1.32 -1.39 (m,16H), 1.45 – 1.53 (m,8H), 1.58 (s,5H), 1.75 – 1.81 (m, 4H), 1.85 – 1.90 (m, 4H), 2.51 (bs, 2H), 4.06 – 4.08 (m, 6H), 4.16 – 4.20 (m, 6H), 4.45 – 4.48 (m, 2H), 5.16 (t, *J*=5.0 Hz ,2H), 7.62 (s, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ ppm = 14.00, 14.04, 22.59, 22.62, 25.64, 25.71, 29.03, 30.21, 31.49, 31.60, 63.51, 69.43, 70.40, 70.43, 74.17, 76.32, 76.36, 107.80, 118.95, 132.39, 146.45, 153.53, 157.80, 181.70; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %)

C6 R glycerol Compound 5b: compound **4b** (0.5g, 0.57 mmol, 1eq), THF 50ml, HCl (2M) solution (10ml) Yield: 90%. ¹H NMR (500 MHz, CDCl₃): δ (ppm): 0.88 – 0.92 (m, 12H), 1.25 – 1.52 (m,36H), 1.64 (bs, 2H), 1.75 – 1.81 (m, 4H), 1.85 – 1.91 (m, 4H), 2.62 – 2.64 (m, 2H), 3.79 – 3.86 (m, 4H), 4.05 – 4.09 (m, 6H), 4.13 – 4.20 (m, 6H), 4.46 – 4.49 (m, 2H), 5.20- 5.21 (m, 2H), 7.59 (s, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ ppm = 14.00, 14.03, 22.58, 22.62, 25.63, 25.70, 29.02, 30.20, 31.48, 31.60, 63.50, 69.46, 70.35, 70.43, 74.21, 107.88, 118.98, 132.46, 146.47, 153.57, 157.83, 181.81; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %)

C6 S glycerol Compound 5c : compound **4c** (0.5g , 0.57 mmol, 1eq), THF 50ml, HCl (2M)solution (10ml) Yield: 90% ; ¹H NMR (500 MHz, CDCl₃): δ (ppm): 0.90 – 0.92 (m, 12H), 1.25 - 1.43 (m,26H), 1.44 – 1.53 (m, 9H), 1.61 (bs, 2H), 1.75 – 1.81 (m, 4H), 1.85 – 1.91 (m, 4H), 2.59 (bs, 2H), 3.74 – 3.85 (m, 4H), 4.05 – 4.09 (m, 6H), 4.13 – 4.20 (m, 6H), 4.46 – 4.49 (m, 2H), 5.19- 5.20 (m, 2H), 7.60 (s, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ ppm = 14.08, 22.61, 22.63, 25.94, 26.00, 29.01, 29.07, 29.10, 30.25, 31.78, 31.82, 63.49, 69.44, 70.38, 74.19, 76.44, 107.84, 118.95, 132.43, 146.45, 153.55, 157.81, 181.78; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %)

C8 glycerol Compound 5d: compound **4d** (0.5g, 0.50 mmol, 1eq), THF 50ml, HCl (2M) solution (10ml) Yield: 90%; ¹H NMR (500 MHz, CDCl₃): δ (ppm): ¹³C NMR (125 MHz, CDCl₃): δ ppm; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %)

C10 glycerol Compound 5e : compound **4e** (0.5g , 0.46 mmol, 1eq), THF (50ml), HCl (2M)solution (10ml) Yield: 90% ; ¹H NMR (500 MHz, CDCl₃): δ (ppm): 0.90 – 0.92 (m, 12H), 1.25 - 1.43 (m,26H), 1.44 – 1.53 (m, 9H), 1.61 (bs, 2H), 1.75 – 1.81 (m, 4H), 1.85 – 1.91 (m, 4H), 2.59 (bs, 2H), 3.74 – 3.85 (m, 4H), 4.05 – 4.09 (m, 6H), 4.13 – 4.20 (m, 6H), 4.46 – 4.49 (m, 2H), 5.19- 5.20 (m, 2H), 7.60 (s, 2H) ; ¹³C NMR (125 MHz, CDCl₃): δ ppm = 14.08, 22.61, 22.63, 25.94, 26.00, 29.01, 29.07, 29.10, 30.25, 31.78, 31.82, 63.49, 69.44, 70.38, 74.19, 76.44, 107.84, 118.95, 132.43, 146.45, 153.55, 157.81, 181.78; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 80.46; H, 12.64 (expt. %)

5.6 Spectra of compounds:



Figure 35: ¹H (top) and ¹³C-NMR (bottom) spectra of 1a



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Figure 36: ¹H (top) and ¹³C-NMR (bottom) spectra of 1b



Figure 37: ¹H (top) and ¹³C-NMR (bottom) spectra of 1c



Figure 38: ¹H (top) and ¹³C-NMR (bottom) spectra of 3a



Figure 39: ¹H (top) and ¹³C-NMR (bottom) spectra of 3d



Figure 40: ¹H (top) and ¹³C-NMR (bottom) spectra of 3e



Figure 41: ¹H (top) and ¹³C-NMR (bottom) spectra of 4a



Figure 42: ¹H (top) and ¹³C-NMR (bottom) spectra of 4b



Figure 43: ¹H (top) and ¹³C-NMR (bottom) spectra of 4c



Figure 44: ¹H (top) and ¹³C-NMR (bottom) spectra of 4d



Figure 45: ¹H (top) and ¹³C-NMR (bottom) spectra of 4e



Figure 46: ¹H (top) and ¹³C-NMR (bottom) spectra of 5a



Figure 47: ¹H (top) and ¹³C-NMR (bottom) spectra of **5b**



Figure 48: ¹H (top) and ¹³C-NMR (bottom) spectra of 5c



Figure 49: ¹H (top) and ¹³C-NMR (bottom) spectra of 5d



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Figure 50 : ¹H (top) and ¹³C-NMR (bottom) spectra of **5**e

5.7 References and Notes:

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