### Chapter-3

Synthesis and Mesomorphism of anthraquinone based bolaamphiphiles

#### Abstract

In this chapter, we have reported the synthesis of anthraquinone derivatives containing both alkoxy as well as ethyleneoxy tails. We have studied the structure-property relationship by changing both the length of hydrophilic i.e. ethyleneoxy chains and the hydrophobic chains i.e alkoxy chains. It was found that all the compounds show columnar phase as typical of discotic compounds. The lyotropic behavior of these compounds with respect to water has also been studied.



Publications based on this work Manuscript under Preparation

# **3.1 Introduction:**

The term "bolaamphiphile" is originally derived from the word "bola", which refers to a weapon made up of a long cord or chain with heavy metal balls attached at either end, often found it useful for throwing at and entangling animals. Bolamphiphiles (**Figure 1**) are the compounds which contain two hydrophilic heads separated by hydrophobic unit<sup>1</sup>. They have been shown great potential in forming diverse self-assembled structures both at interfaces and in solutions. The hierarchical structures shown by bolaamphiphiles has been explored for gene delivery and drug delivery applications<sup>2</sup>.



Figure 1: Schematic of bolaamphiphile<sup>1</sup>

## 3.2 Literature review on ethyleneoxy chains functionalized discotic liquid crystals:

In a liquid crystalline molecule, the flexible periphery plays a vital role in inducing mesogenic behavior. The non-rigid nature of these chains favor conformational disorder which gives entropic contribution favoring the mesomorphic order. The nature of peripheral chains provide amphiphilicity in the materials. Among the various kinds of chains reported, (alkyl, perfluoroalkyl, siIoxane) ethyleneoxy (EG) chains alone have the ability to induce polar interactions. The polar interactions of these tails are generally governed by parameters such as polarity, polarizability, flexibility, shape, and size<sup>3</sup>.

Oligoethylene glycol ethers are one of the widely explored surfactants for their lyotropic mesomorphism in the presence of protic solvents. The mesomorphism of these ethers is sensitive to the hydrophobic part when they are functionalized either with rigid units or flexible tails. The lower molar mass ethers with rigid hydrophobic motif generally organize in lamellar fashion. The

bolaamphiphile with oligo ethylene glycol head-group with rigid nonpolar parts have also been reported to form lamellar mesophases<sup>4</sup>.

The thermotropic properties of supramolecular complexes involving tetra pyridine functionalized pentaerythritol with dimeric benzoic acids with tetra ethylene glycol as a spacer (**Figure 2**) was found to be columnar in nature<sup>5</sup>.



Figure 2: pentaerythritol based columnar mesogen<sup>5</sup>

Phosphazenes have been reported to form columnar phases under appropriate substitutions<sup>6</sup>. The cyclotrisphosphazene with diethylenoxy spacer has been found to be nematic whereas the higher spacers were not (**Figure 3**). Similar observations were reported for benzene based tri substituted ethyleneoxy (EG) chains<sup>7</sup>. It has been proposed that the substitution of the terminal hydroxyl of EG chains with bulky substituents will decrease the tendency to form lyomesophases as the coordination ability of ether oxygens with water reduces.



Disc-shaped amphiphiles generally constitute a hydrophobic core with the lateral decoration of hydrophilic chains. These disc-shaped amphiphiles were found to be exclusively forming both hexagonal and nematic phases<sup>8</sup>. The balance between hydrophilic and hydrophobic parts of the molecule has to be kept in mind to induce mesomorphism. In the case of hexaalkoxy triphenylene with ethyleneoxy chains (**Figure 4**), the lower homolog is not mesomorphic which can be understood by the presence of lesser hydrophilic moieties. In the case of triethyleneoxy ether derivatives, there was no evidence of mesophase as it became water-soluble. But the presence of appropriate functionalization of both hydrophilic as well as hydrophobic environment induces mesomorphism in triphenylenes<sup>9,10</sup>.

TPEO2M (triphenylene hexadiethyleneoxy ether) is one of the widely explored nonionic chromonic systems for the appearance of both nematic and hexagonal phases at low and high weight percentage respectively. Some of the reported amphotropic triphenylenes are given in the figure 4.



Figure 4: Triphenylene based amphiphilic derivatives<sup>11</sup>



**Figure 5: TBC and CTV** based amphiphilic derivatives<sup>12</sup>

Tetrabenzocyclododecane (TBC) was found to show amphotrophy on substitution with hydrophilic groups. In fact, the diethyleneoxy and triethylenoxy derivatives of TBC were the first discotic amphotropic material reported<sup>12</sup>. Cyclotrivaeratrylene (CTV) based ethylenoxy derivatives showed signs of aggregation and complexation behavior with alkali metal ions but not much explored (**Figure 5**).

Phthalocyanines known for their light-harvesting properties have been explored for amphotropic behavior on substitution with ethyleneoxy chains. There are good amount of reports on EG derivatives of phthalocyanines forming thermotropic LCs but not lyotropic<sup>13</sup> (**Figure 6**). Statistical mixture of regioisomers of phthalocyanines with EG side chains found to form the Hexagonal columnar phase in case of tri ethylene glycol derivative<sup>14</sup>. The octaethyleenoxy derivative showed both hexagonal and nematic phases at different weight percentages<sup>15</sup>.



# Figure 6: Phthalocyanine based amphiphilic derivatives<sup>13</sup>

The EG derivatives of porphyrins (**Figure 7**) were reported to form columnar aggregates in the presence of water. The corresponding monolayers of these amphiphilic derivatives were found to be arranged in perpendicular fashion at air solid interface. Whereas, the phthalocyanine multipolar derivative prefers flat arrangement on the aqueous surface<sup>16</sup>.



Figure 7: Porphyrin based amphiphilic derivatives<sup>16</sup>

Phthalocyanines with alkyl chains and ethylenoxy chain in the periphery were found to show both rectangular and hexagonal columnar mesophase. On increasing the number of ethyleneoxy chains hexagonal and lyotropic nematic phase was observed at higher water compositions. Phthalocyanine with smaller hydrophilic chains was assembled in nematic manner<sup>14</sup> (**Figure 8**).



Figure 8: Phthalocyanine based amphiphilic derivatives<sup>14</sup>

Bushby et al. have reported the diethylene glycol functionalized tricycloquinazolines which formed a hexagonal columnar phase<sup>17</sup>. Further, it was observed that there is an enhancement of conductivity of the compounds on doping with potassium ions. Even the photoconductivity studies revealed that there is the presence of both hole and electron transient photocurrent. The mobility values were comparable with some of the best discotic LCs in their columnar phases (**Figure 9**).



Figure 9: Tricycloquinazoline based amphiphilic derivatives<sup>17</sup>

Mullen et al. have reported star-shaped hexabenzocoronene(HBC) with eighteen EG chains in the periphery. They were mesomorphic at room temperature. Further, they showed a drastic decrease in clearing temperature as compared to their alkoxy counterparts. The compounds showed an excellent scope for aggregation in the presence of protic polar solvents <sup>18</sup>. They further used the water-soluble HBCs to make mesoporous silica with columnar structure (**Figure 10**).



# Figure 10: Star-shaped HBC amphiphile<sup>18</sup>

Seo et al. have prepared shape persistent macrocycle with hydrophilic ethyleneoxy chains. They showed great potential for mesomorphism <sup>19</sup> (**Figure 11**).



Figure 11: Macrocyclic phenyl ethynylene based amphiphilic derivatives<sup>19</sup>

Shimura et al. have reported a macrocycle containing both intra- and extra annular chains. The interplay of intraannular diethylene glycol moieties and glutamate-tethered bis(dialkoxybenzyl) units ensured nanosegregation leading to the columnar phase at ambient temperature<sup>20</sup> (**Figure 12**).



Figure 12: Phenylethynylene based amphiphiles <sup>20</sup>

Kohomoto et al has demonstrated the formation of nematic to columnar transition on complexation involving alkali metal salts and triphenylene based benzoates with ethylenoxy tails. The nematic phase was found to be due to steric and electronic repulsion among EG tails (**Figure13**)<sup>21</sup>.



Figure 13: Amphiphilic Triphenylene Benzoates <sup>21</sup>

Kato et al. have synthesized the monomer and dimer with ethyleneoxy space functionalized with alkoxy triphenylene <sup>22</sup>. The introduction of ethylene oxide chains into TP lowered the melting and isotropization temperatures. In case of dimer, the LC property was found to be dependent on the length of the EG spacer. The lithium salt complexes of these molecules were mesomorphic too (**Figure14**).



**Figure 14: Amphiphilic triphenylene dimer**<sup>22</sup>

Aida et al. used the amphiphilic design concept to make bicontinuous donor-acceptor arrays in LC materials<sup>23</sup>. This strategy has the site-specific modification of donor-acceptor dyads with hydrophilic EG chains and paraffinic hydrophobic chains hinder donor-acceptor interactions leading to charge carriers trapping which provides conducting pathways in the materials (**Figure 15**).



Figure 15: Amphiphilic Donor-Acceptor array<sup>23</sup>

Aida et al. have extended the amphiphilic approach by synthesising triply fused copperporphyrin dimer, where periphery is site-specifically modified with hydrophilic and hydrophobic wedges. The amphiphile was found to be mesomorphic over a wide temperature range.(-17°C-99°C) (**Figure16**).



Figure 16: Amphiphilic Triply fused porphyrin dimer<sup>24</sup>

Moreover, the amphiphile was found to show high mobility due to enhancement in  $\pi$ -stacking <sup>24</sup>. Mullen et al. have reported helical behavior in the columnar structure of perylene dimides with triethylenoxy tails<sup>25</sup>(Figure 17).



**Figure 17: Amphiphilic Perylenes forming helical fibers**<sup>25</sup>

Aida et al. have adopted an amphiphilic strategy to non-covalent functionalization of proteins (**Figure 18**). The glue design involves the presence of guanidinium ions which is connected via ethyleneoxy chains to dendronized benzene. The compound was found to have chemotherapeutic potential as it stabilizes the microtubules<sup>26</sup>.



Figure 18: Amphiphilic strategy for protein functionalization<sup>26</sup>

Aida et al. have proposed the formation of graphitic nanotubes from the HBC appended amphiphile in coordination with the platinum complex<sup>27</sup>. The platinum bridge which was found to contain two HBC unitsself-assemble into nanotubes. He extended this approach for thiophenefused coronenes too  $^{28}$  (**Figure 19**).



Figure 19: Graphitic nanotubes from HBC amphiphile<sup>27,28</sup>

Aida et al. have successfully made p-n junction via the co-assembly of HBC based amphiphile with  $C_{60}$  which showed ambipolar character<sup>29</sup> (Figure 20).



Figure 20: Ambipolar HBC-amphiphile-C60 coassembly<sup>29</sup>



Wurthner et al. have adopted amphiphilic strategy to fabricate a nanocapsule system involving a perylene based dye molecule composed of enclosed energy-donor molecules and a bilayer dye membrane as an energy acceptor. The fluorescence color of the dye was found to be sensitive to  $p^{H}$ . Further, the pH-dependent fluorescence color changes covering the whole visible light range, with a white light emission observed at  $p^{H}$  9.0 (**Figure 21**) <sup>30</sup>. Wurthner et al. have explored the influence of swallowtail ethylenoxy tails with perylene in their mesomorphic behavior. Further, the swallowtail substituents were found to be insensitive to the bandgap (**Figure 22**) <sup>31</sup>.

R2 = -CH2CH2(OCH2CH2)3OCH3



Type I: symmetrically N-substituted PBIs (2 x swallowtail)

### Figure 22: Amphiphilic Perylenes with Swallowtails functionalization<sup>31</sup>

11: R1 = -C11H23

Bolaamphiphilic fluorene-based oligomers self-assemble in water to form fluorescent nanoparticles with tunable emission colors covering the entire visible range, even including white. Wurthner et al. have shown the Flourene based bolaamphiphiles self-assembled into nanoparticles in presence of water with emission spanning the whole visible range  ${}^{32}$ (**Figure 23**).



Figure 23: Amphiphilic flourenes<sup>32</sup>

Meijer et al. have adopted amphiphilic strategy to carry out the photodimerization between two oligo phenylene vinylene (OPV) bolamphiphiles. They formed vesicles in the presence of water in which OPV was organized in helical manner<sup>33</sup> (**Figure 24**).



Figure 24: OPV based Bolamphiphiles<sup>33</sup>

HBC derivatives with paraffinic side chains with ester–ether terminal showed hexagonal columnar liquid-crystalline (LC) mesophase for a wide range (0–300 °C). They showed excellent photoconductive behavior<sup>34</sup> (**Figure 25**).



Figure 25: Amphiphilic HBC derivatives <sup>34</sup>

Wurthner et al. have created P-n heterojunction in a highly precise manner using an amphiphilic strategy involving perylene and thiophene based donor and acceptor respectively. The self-assembled amphiphilic fibers were found to have good photoconductivity<sup>35</sup> (**Figure 26**).



Figure 26: p-n Heterojunction through the amphiphilic assembly<sup>35</sup>

George et al. have synthesized naphthalene based bolas which was found to self-assemble into green fluorescent particles used for sensing. George et al. further exploited amphiphilic strategy to naphthalene imide where they showed vapor chromism <sup>36,37</sup> (**Figure 27**).



Figure 27: Amphiphilic Naphthalene diimides<sup>36,37</sup>

Thiebaut et al. showed photovoltaic behavior of face-on oriented bilayer of two discotic columnar liquid crystals, i.e. the water-soluble perylene-tetracarboxylic tetra(ethylene glycol) ester and the heptane-soluble pyrene-tetracarboxylic tetraester<sup>38</sup> (**Figure28**).



Figure 28: Amphiphilic p-n heterojunction bilayer <sup>38</sup>

Lintang et al. synthesized triangular trinuclear gold(I) –pyrazolate complexes which arrange in columnar lamellar phase induced by metallophilic interactions (**Figure 29**)<sup>39</sup>.



Figure 29: Amphiphilic gold-pyrazolate complexes<sup>39</sup>

Yeh et al. provided XRD evidence for 2D hexagonal superlattice formation when studying unsymmetrical dibenzo[*a*,*c*]phenazines with triethylene glycol chains. The charge carrier mobility studies revealed that maximum transient mobilities along the perpendicular and parallel directions to the substrate surface was  $1.0 \times 10^{-4}$  and  $2.7 \times 10^{-5}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> respectively(**Figure 30**)<sup>40</sup>.



Figure 30: Amphiphilic dibenzophenazines 40

Meijer et al. have reported discotic molecule based on benzene triamide with asymmetrical distribution of ethylene glycol chains which was found to self-assemble into fibers in the presence of water (**Figure 31**).<sup>41</sup>



Figure 31: Benzenetriamide based amphiphile<sup>41</sup>

Wurthner et al. have reported the role of a specific hydrophobic effect in the self-assembly of a bolaamphiphilic perylene bisimide (PBI) dye bearing oligo ethylene glycol (OEG) chains resulting entropically driven self-assembly(**Figure 32**)<sup>42</sup>.



Figure 32: Perylene based bolaamphiphile 42

Mullen et al. have reported discotics based on hexabenzocoronene (HBC) substituted with six poly(ethylene glycol) (PEG) chains and further doped with Lithium triflate saltdiffernt ratios. The material was found to show hexagonal phase with nanophase segregation between the HBC column and PEG chains. The PEG functinalised HBCs were explored for their electrolytic behaviour as they show excellent conductivity (**Figure 33**)<sup>43</sup>.

![](_page_20_Figure_2.jpeg)

Figure 33: Polyethyleenglycol functionalized HBC<sup>43</sup>

Wurthner et al. have reported the lyotropic behavior of perylene diimides with tri ethylene glycol, dendron resulting the columnar phase in water (**Figure 34**)  $^{44}$ .

![](_page_20_Figure_5.jpeg)

Figure 34: Amphiphilic perylenes 44

### 3.3 Results and Discussion:

#### 3.3.1 Synthesis:

The bolaamphiphiles were synthesized following the synthetic pathway shown in the scheme (**Figure 35**). Gallic acid was commercially obtained from SD fine chemicals and used without further purification. Rufigallol was synthesized by acid-catalyzed condensation of gallic acid as reported by Grimshaw et al <sup>45</sup> The obtained red solid was used as such for further steps. Rufigallol was alkylated at hydroxyl groups of 2,3,7,6 positions. The tetra alkylated product was confirmed by NMR and elemental analysis. The tetra alkylated anthraquinones(AQ) derivatives were alkylated at hydroxyl position of 1, 5 with ethyleneoxy based tosylates through Williamson etherification. All compounds were purified by column chromatography on silica gel (100-200 mesh) followed by repeated crystallization using suitable analytical grade solvents.

![](_page_21_Figure_4.jpeg)

Figure 35: Synthetic scheme for bolaamphiphiles

The structures of final compounds were confirmed through NMR, elemental analysis. TGA thermogram suggest that all the compounds have good thermal stability (**Figure 36**).

![](_page_22_Figure_2.jpeg)

Figure 36 : TGA thermograms of complexes

## 3.3.2 Mesomorphic characteristics:

Mesomorphic properties of all the compounds were analyzed using POM, DSC and SAXS. POM images of compounds display a mosaic texture which is a typical of columnar phase (**Figure 37**). DSC thermogram too suggests the presence of mesomorphism in these compounds (**Figure 38**). Except compound 4a-1 all the others were room temperature liquid crystals. The hexaalkoxy rufigallols (both symmetric and asymmetric) are one of the widely explored mesomorphic materials. Some of them were room temperature liquid crystalline (RTAQ). RTAQ is one of the widely used columnar liquid crystal for various applications<sup>46</sup>. The thermal behavior of all the compounds is given in the table 1. All the compounds were confirmed to exhibit enantiotropic mesomorphic behavior.

![](_page_23_Picture_1.jpeg)

Figure 37: POM images of A. 4a at RT; B. 4b at RT; C. 4c at RT; D. 4d at RT; E. 4e at RT; F. 4f at RT

![](_page_23_Figure_3.jpeg)

Figure 38. DSC thermograms of compounds 4a-1-4, 4b-4, 4c-4

The structure of the columnar phase was further elucidated through SAXS. The peaks in smallangle regions can be indexed into a hexagonal lattice (they showed peaks with d spacing in the ratio of  $1:1/\sqrt{3}$ , 1/2 which is typical of the hexagonal phase (**Figure 39**). The lattice parameters, area and volume are given in the table. By taking the results, it was found that there is one molecule occupying the single slice of a column (Table 2).

# Table 1: Thermal behavior of compounds

Table 1. <sup>*a*</sup> Phase transition temperatures (°C) and the corresponding energy changes (kJmol<sup>-1</sup>)

Compd.	Phase sequence				
	Heating	Cooling			
4a-1	Col <sub>hp</sub> 40.22 (1.347)I	I 25.78(-1.665)Colhp			
4a-2	Col <sub>h</sub> 67.62(6.16)I	I 63.22(-6.143) Col <sub>h</sub>			
4a-3	Cr 36.23(67.536)Col <sub>h</sub> 72.87(9.27)I	I 70.51 (-8.67) Col <sub>h</sub>			
4a-4	Col <sub>h</sub> 39.82(6.27)I	I 36.04(-5.89)Col <sub>h</sub>			
4b-4	Col <sub>h</sub> 50.35(7.186)I	I 48.61(-7.027)Colh			
4c-4	Cr 35.12(51.18) Col <sub>h</sub> 45.85 (6.72)I	I 43.62(-6.60) Col <sub>h</sub> 14.53(-59.74)Cr			

Compounds 4a-1 showed the columnar hexagonal plastic phase. The confirmation of the plastic phase was done by indexing the two sharp diffraction peaks in the wide-angle region around 3.4 Å, 3.3Å respectively which is a typical signature of plastic phase.

All of them except **4a-1** exhibited room temperature liquid crystalline behavior. Gaussian studies of all the compounds were performed. The optimized structures and the bandgap details have been described in figures. The detailed indexation of the plastic phase is given in table 2.

From the thermal behavior, we can see that as the length of ethyleneoxy chains increases the melting transition disappears. When we increase the hydrophobic chain length the melting

transition reappears. By considering all the above-mentioned results, we propose the following model for these compounds in their mesomorphic state (**Figure 40**).

![](_page_25_Figure_2.jpeg)

Figure 39 X-ray diffractograms of compounds 4a-1, 4a-2, 4a-3, 4a-4, 4b-4, 4c-4.

![](_page_25_Figure_4.jpeg)

Figure 40 Proposed packing of molecules in the columnar phase

COMPOUND	Phase	Spacing (Å)			Lattice parameters
	(temperature			Index	
	in °C)	d obs	d cal		
		17.07	17.07	100	a = 19.71Å ;c=6.88
<b>4a-1</b>	Col <sub>hp</sub> (40)	9.46	9.85	110	Å
		6.87	6.45	210	$A = 336.437 \text{\AA}^2$
		3.44	3.44	002	$V = 1143.886 Å^3$
		3.37	3.39	102	Z=1.013
4a-2	Col <sub>h</sub> (RT)	17.40	17.40	10	a= 20.092Å;
		10.11	10.04	11	$A = 349.604 \text{\AA}^2$
		4.40			V=1206.135Å <sup>3</sup>
		3.45			Z=1.03
4a-3	Col <sub>h</sub> (RT)	18.66	18.66	10	a=21.54 Å;
		10.73	10.72	11	A=401.811Å <sup>2</sup>
		4.33			$V = 1422.411 \text{\AA}^3$
		3.54			Z=1.06
<u>/9-/</u>	Col. ( <b>P</b> T)	10.22	10.22	10	a−22 10Å·
7a-7		11.22	11.22	10	$\Delta = 426 \ A27 \ \text{\AA}^2$
		A 25	11.27	11	$V = 1530 874 Å^3$
		3 59			7-1.08
		5.57			Z-1.00
4 <b>h</b> -4	Col.(RT)	20.76	20.76	10	a−23.97Å·
U		11 98	11.92	11	$\Delta = 497584 \text{\AA}^2$
		10.36	10.5	20	$V = 1756 472 Å^3$
		4 32	10.5	20	7=1.05
		3 53			2-1.00
		5.55			
<b>4c-4</b>	Col <sub>h</sub> (RT)	21.99	21.99	10	a=25.39Å
		12.75	12.8	11	$A = 558.285 \text{\AA}^2$
		11.02	11.20	20	V=1988.660Å <sup>3</sup>
		4.30			Z=1.07
		3.58			

# Table 2: d-spacingsof compounds

**Table 2:** Layer spacing obtained from XRD for **4a-1**, **4a-2**, **4a-3**, **4a-4**, **4b-4** and **4c-4**. (**a** = lattice parameter =  $\sqrt{(4/3)} * d_{10}$ ; lattice area  $S_h = a^2 \sin 60^\circ$ ; lattice volume  $V_h = a^2 \sin 60^\circ * h_c$  ( $h_a$  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;  $\rho$ =Density in Kg/m<sup>3</sup>; **a**=lattice parameter; hc=core core peak ( $h_a$  if core core is not observed); M=molecular weight in Kg/m<sup>3</sup>)

![](_page_27_Figure_1.jpeg)

Figure 41 Optimised structures of compounds 4a-1-4, 4b-4,4c-4

![](_page_27_Figure_3.jpeg)

Figure 42: HOMO-LUMO orbitals of compounds 4a-1-4, 4b-4,4c-4

The optimized structures of all compounds were obtained by GAUSSIAN (**Figure 41**). The structures suggest that all of them are planar. Further, the details of predicted HOMO, LUMO and bandgap of all the compounds are given in figure 42.

### 3.3.3 Lyotropic Behaviour:

The compound contains both hydrophobic alkyl tails and hydrophilic ethylenoxy tails around the core. This prompted us to look for lyotropic behavior in these compounds. From the literature, we have seen some of the ethylenoxy substituted discotics exhibit chromonic phase in the presence of water. There are many reports on these kinds of bolamphiphiles forming supramolecular structures in the presence of different solvents <sup>28</sup>. The liquid crystallinity in those structures was not much explored. Moreover, the chromonic phase of discotics has been reported only in presence of ethyleneoxy tails . This is the first report on the exploration of mesomorphic order of the compounds containing both alkyl as well as ethyleneoxy tails.

The compounds are mixed with water (5wt%) and heated to 60 °C and kept it for incubation for three weeks. After three weeks we noticed birefringence under POM as typical of chromonic M phase. The POM and X ray diffractograms and corresponding d- spacings are given in figure 43 & 44. Compound 4a-1 showed phase segregation on mixing with water suggest nonmesomorphic behavior probably due to lack of enough hydrophilic moieties for enabling water to induce the mesophase. There is not much difference in the spacings observed for the water mixed samples with the virgin ones. The number of hydrophilic moieties present in the structure can take water to some extent only. Beyond that, there was phase segregation (**Figure 43 & Figure 44**).

![](_page_29_Figure_1.jpeg)

Figure 43: POM images of A. 4a-2(5wt%)in water at RT; B. 4a-3(5wt%)in water at RT; C. 4a-4(5wt%)in water at RT; D. 4a-4(5wt%)in water at 25°C; E. 4b-4(5wt%)in water at RT; F. 4c-4(5wt%)in water at RT.

![](_page_29_Figure_3.jpeg)

Figure 44 X-ray diffractograms of compounds 4a-1-4, 4b-4, 4c-4(5wt%) in water

COMPOUND	Phase	Spacing			Lattice parameters
	(temperat	_		Index	_
	ure in °C)	d obs	d cal		
4a-	RT	17.46	17.46	10	a =20.16Å
2(5wt%)+water		10.06	10.08	11	$A = 352.011 \text{ Å}^2$
		8.77	8.73	20	V= 1210.918 Å <sup>3</sup>
		4.26			Z= 1.02
		3.44			
					<u>^</u>
4a-	RT	18.46	18.46	10	a =21.31 Å
3(5wt%)+water		10.70	10.68	11	$A = 393.382 \text{ Å}^2$
		9.28	9.34	20	V= 1384.70 Å <sup>3</sup>
		7.02	7.14	21	Z= 1.04
		4.31			
		3.52			
		10.00	10.00	10	
4a-	RT	18.82	18.82	10	a = 21.73  A
4(5wt%)+water		10.88	10.86	11	$A = 408.9586 A^2$
		9.44	9.41	20	$V = 1611.2969 A^3$
		3.94			Z=1.1
4b-	рт	20.41	20.41	10	а— 23 56 Å
10- A(5wt%)⊥wetor	NI	11 81	11 78	10	$\Delta = 481.022$ Å <sup>2</sup>
+(Swi /0)+water		10.22	10.20	20	$V = 1924 0.01 Å^3$
		4 18	10.20	20	7-1.04
		1.10			
4c-	RT	22.13	22.13	10	a= 25.55 Å
4(5wt%)+water		12.82	12.77	11	$A = 565.326 \text{ Å}^2$
		11.10	11.065	20	V= 2436.55 Å <sup>3</sup>
		4.31			Z=1.13

# Table3: d-spacings of lyotropic systems:

(**a** = lattice parameter =  $\sqrt{(4/3)} * d_{10}$ ; lattice area  $S_h = a^2 \sin 60^\circ$ ; lattice volume  $V_h = a^2 \sin 60^\circ * h_c$  ( $h_a$  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;  $\rho$ =Density in Kg/m<sup>3</sup>; **a**=lattice parameter;  $h_c$ =core core peak ( $h_a$  if core core is not observed); M=molecular weight in Kg/m<sup>3</sup>)

# **3.4 Conclusion:**

The ethyleneoxy functionalization to tetraalkoxy rufigallols has shown to be mesomorphic in nature. They have been found to be assembling into the columnar hexagonal structure. The hexagonal morphology was confirmed through X-ray diffraction. Further they were analyzed for their lyotropic behavior with respect to water. They were found to form a chromonic M phase which has hexagonal order.

## **3.5 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. <sup>1</sup>H NMR and <sup>13</sup>C NMR (Nuclear magnetic resonance spectroscopy) were recorded by Bruker 500MHz instrument using CDCl<sub>3</sub> as solvent and trimethyl silane as an internal standard. Chemical shift values are given in ppm and the solvent CDCl<sub>3</sub> peaks appear at <sup>1</sup>H NMR:  $\delta = 7.23$  ppm and <sup>13</sup>C NMR  $\delta = 77.0$  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 polarizing 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 KJmol<sup>-1</sup>. Panalytical (Empyrean) Cu-Ka (1.54Å) Xray diffractometer was used to further confirm the mesophase structure of all compounds. The thermal stability of all the compounds was studied using TGA 4000 thermogravimetric analysis instrument.

## General procedure for tosylation of ethylene glycols: (compound 1(n=1, 2, 3, 4)

Oligo ethylene glycol monomethyl ether (1eq) and 50 ml of THF were charged to a 500 mL round bottom flask with a magnetic stirrer. This reaction mixture was cooled to 0°C and 6 M NaOH (5eq) was added, followed by a dropwise addition of tosyl chloride (2eq) in 80 ml THF under N<sub>2</sub>. After stirring for 1 h at 0°C, the reaction mixture was allowed to reach room temperature and stirred for another 1 h. The resulting mixture was extracted with  $Et_2O$  (400 ml) and the organic layer was washed with 1 M NaOH and water. After drying over MgSO<sub>4</sub>, the solution was evaporated under vacuum. The product was purified by column chromatography (n=1, n=2, n=3, n=4) as a colorless liquid. **EGMME 1 (n=1) :** Ethylene glycol monomethyl ether (10g, 131.42mmol, 1eq), NaOH(5eq, 110ml, 6M); 50mL TsCl (50.11g, 262.8mmol, 2eq), Yield: 90% ; M.P. 45 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.44 (s, 3H), 3.30 (s, 3H), 3.57(d, *J* = 4 Hz, 2H), 4.15 (d, *J* = 3.5 Hz, 2H), 7.34 (d, *J* = 7.50 Hz, 2H), 7.79 (d, *J* = 7.50 Hz, 2H) ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm =21.61, 58.93, 69.16, 69.87, 127.92, 129.85, 132.91, 144.90; Elemental analysis: C, 52.16; H, 6.13 Calculated (%): C, 52.07; H, 6.05 (expt. %).

**DEGMME 1 (n=2) :** Diethylene glycol monomethyl ether (10g, 83.22mmol, 1eq), NaOH (5eq, 69.35ml, 6M), 50ml ; TsCl (31.73g, 166.45mmol, 2eq), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.44 (s, 3H), 3.35 (s, 3H), 3.48 (bs, 2H), 3.57 (bs, 2H), 3.69 – 3.70(m, 2H), 4.17 (bs, 2H), 7.33 (d, *J* = 7.50 Hz, 2H), 7.79 (d, *J* = 7.00 Hz, 2H) ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm =21.59, 56.22, 58.96, 58.97, 67.02, 68.63, 69.26, 70.55, 70.56, 71.75, 127.93, 129.82, 132.89, 144.85 ; Elemental analysis: C, 52.54; H, 6.61 Calculated (%): C, 52.42; H, 6.82 (expt. %).

**TEGMME 1 (n=3) :** Triethylene glycol monomethyl ether (10g, 60.90 mmol, 1eq), NaOH (51ml, 6M, 5 eq ), 50ml; TsCl (23.22g, 121.8 mmol, 2eq), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.44 (s, 3H), 3.37 (s, 3H), 3.53 (bs, 2H), 3.59 (bs, 6H), 3.68 (bs, 2H), 4.15 (m, 2H) , 7.34 (d, *J* = 7.50 Hz , 2H) ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm = 21.60, 58.97, 68.61, 69.28, 70.48, 70.49, 70.67, 71.85, 127.93, 129.84, 132.93, 144.83 ; Elemental analysis: C, 52.81; H, 6.96 Calculated (%): C, 52.08; H, 6.70 (expt. %).

**TETRAEGMME 1 (n=4) :** Tetra Ethylene glycol monomethyl ether (10g, 48.01 mmol, 1eq), NaOH(40ml, 6M, 5eq) ; TsCl (18.31g, 544.95mmol, 2eq), <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 2.44 (s, 3H), 3.37 (s, 3H), 3.54 (bs, 2H), 3.58 (bs, 4H), 3.63 (bs, 6H), 3.68 (bs, 2H), 4.15 (bs, 2H), 7.34 (d, *J* = 7.00 Hz, 2H), 7.79 (d, *J* = 7.50 Hz, 2H) ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm = 21.67, 58.97, 68.62, 69.28, 70.45, 70.46, 70.53, 70.54, 70.67, 71.88, 127.93, 129.83, 132.94, 144.81; Elemental analysis: C, 80.65; H, 12.18 calculated (%): C, 53.02; H, 7.23 (expt. %). Calculated (%): C, 52.68; H, 6.88 (expt. %).

### General procedure for compounds 3a-c:

In a typical reaction, to a stirred solution of NaOH (4 eq.) in dry DMSO (50 ml) added crude Rufigallol 2 (1 eq), 1-bromoalkane (4.4 eq.), and the mixture was heated to 70 °C and held at the

same temperature under  $N_2$  for 18h. The reaction mixture was cooled, diluted with aq. HCl and extracted with chloroform. The combined organic layer was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Product was crystallized from EtOH: CHCl<sub>3</sub> (4:6).

**Compound 3a :** compound **2** (10g, 32.87 mmol), 1-bromohexane (23.87g, 144.63 mmol, 4.4eq), NaOH (5.25 g ,131.4 mmol, 4eq) Yield: 45% ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): 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, 71.65; H, 8.53 Calculated (%): C, 71.22; H, 8.81 (expt. %).

**Compound 3b :** compound 2 (10g, 32.87 mmol), 1-bromo octane (27.93 g, 144.63 mmol, 4.4eq), NaOH (5.25g ,131.4 mmol, 4eq) Yield:  $45\%_{-}^{1}$ H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  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, 73.10; H, 9.34 Calculated (%): C, 73.37; H, 9.64 (expt. %).

**Compound 3c:** compound 2 (10g, 32.87 mmol), 1-bromo decane (31.99g, 144.63 mmol), NaOH (5.25g, 131.40mmol), Yield: 45%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (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); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  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, 74.50; H, 9.85 Calculated (%): C, 74.96; H, 10.25 (expt. %).

## General procedure for compounds 4a-1 to 4a-4, 4b-4 &4c-4:

To compound **3a-c** (1eq), tosylates (**1**) (4 eq),  $K_2CO_3$  (~20 eq) in DMF was heated overnight at 120°C. Then the hot solution was poured into crushed ice. The precipitate was filtered and washed with water. The precipitate was dissolved in dichloromethane and washed with dilute HCl 2 times

followed by brine. The resulted solution was dried using sodium sulfate and concentrated. The concentrated extract was purified by column chromatography.

**Compound 4a-1 :** compound **3a** (0.5g, 0.78 mmol,1eq), MEGMME tosylate (0.717g, 3.12 mmol, 4eq), K<sub>2</sub>CO<sub>3</sub> (2g, 14 mmol, 20eq), Yield: 60%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 0.91 – 0.92 (m, 12H), 1.34 - 1.36 (m, 16H), 1.49 (bs, 8H) , 1.77 - 1.87 (m, 8H), 3.48 (s, 6H), 3.86 (m, 4H), 4.09 (bs, 4H), 4.15 (bs, 4H), 4.24 (bs, 4H) , 7.60 (s, 2H) ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm = 14.02, 14.07, 22.60, 22.66, 25.67, 25.70, 29.03, 30.27, 31.51, 31.69, 59.05, 69.18, 72.01, 72.77, 74.18, 107.25, 120.35, 132.50, 146.91, 153.38, 157.41, 181.10; Elemental analysis: C, 69.62; H, 8.72 Calculated (%): C, 69.81; H, 9.05 (expt. %).

**Compound 4a-2 :** compound **3a** (0.5g, 0.78 mmol,1eq), DEGMME tosylate (0.855g , 3.12 mmol, 4eq),  $K_2CO_3(2g, 14 \text{ mmol}, 20eq)$ , Yield: 60%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 0.91 – 0.92 (m, 12H), 1.33 - 1.36 (m, 16H), 1.50 (bs, 8H) , 1.78 (bs, 4H), 1.87 (bs,4H), 3.37 (s, 4H), 3.57 (bs , 3H), 3.74 (bs, 3H), 3.97 (bs, 4H), 4.09 (bs, 4H) , 4.16 (bs, 4H), 4.26 (bs, 3H), 7.58 (s, 2H), ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm = 14.02, 14.08, 22.60, 22.66, 25.66, 25.70, 25.71, 29.03, 29.04, 30.27, 31.51, 31.62, 31.70, 59.05, 61.47, 69.13, 69.16, 70.46, 70.59, 72.01, 73.01, 74.12, 74.17, 107.08, 120.20, 120.27, 132.41, 132.49, 132.54, 146.85, 146.87, 146.92, 153.45, 153.50, 154.51, 157.39, 157.52, 181.04, 181.08, 181.32 ; Elemental analysis: C, 67.98; H, 8.72 Calculated (%): C, 68.22; H, 9.06 (expt. %).

**Compound 4a-3 :** compound **3a** (0.5g, 0.78 mmol, 1eq), TRIGMME tosylate (0.99g, 3.12 mmol, 4eq), K<sub>2</sub>CO<sub>3</sub> (2g, 14 mmol, 20eq), Yield: 60%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) = 0.91 – 0.92 (m, 12H), 1.33 - 1.36 (m, 16H), 1.47 - 1.50 (m, 8H) , 1.76 - 1.77 (m, 4H), 1.86 – 1.87 (m, 4H), 3.37 (s, 6H), 3.54 (bs , 4H), 3.64 - 3.68 (m, 8H), 3.76 (bs,4H), 3.96 (bs, 4H), 4.09 (bs, 4H) , 4.15 (bs, 4H), 4.24 (bs, 4H), 7.58 (s, 2H), ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ ppm = 14.02, 14.08, 22.60, 22.66, 25.66, 25.71, 29.04, 30.27, 31.51, 31.69, 59.03, 69.15, 70.57, 70.67, 71.96, 72.99, 74.14, 107.08, 120.25, 132.47, 146.84, 153.46, 157.39, 181.04, ; Elemental analysis: C, 66.58; H, 8.78 Calculated (%): C, 66.93; H, 9.07 (expt. %).

**Compound 4a-4 :**compound **3a** (0.5g, 0.78 mmol, 1eq), TETRAEGMME tosylate (1.13 g, 3.12 mmol, 4eq), K<sub>2</sub>CO<sub>3</sub> (2 g, 14 mmol, 20eq), Yield: 60% ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 0.90 – 0.92 (d, 12H), 1.33 - 1.36 (m, 16H), 1.47 – 1.50 (m, 8H) , 1.76 - 1.78 (m, 4H), 1.86 -1.88 (m, 4H), 3.37 (s, 6H), 3.57 (bs , 4H), 3.64 - 3.66 (m, 16H), 3.75 (bs , 4H), 3.96 (bs , 4H), 4.09 (m, 4H) , 4.15 (m, 4H), 4.24 (bs, 3H), 7.57 (s, 2H), ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm = 14.02, 14.08, 22.59, 22.66, 25.66, 25.71, 29.04, 30.26, 31.51, 31.69, 59.01, 69.16, 70.51, 70.53, 70.55, 70.62, 71.93, 72.99, 74.15, 107.10, 120.24, 132.47, 146.84, 153.44, 157.40, 181.05, ; Elemental analysis: C, 65.45; H, 8.67 Calculated (%): C, 65.86; H, 9.08 (expt. %).

**Compound 4b-4:** compound **3b** (0.5g, 0.66mmol, 1eq), TETRAEGMME tosylate (0.95g, 2.64 mmol, and 4eq), K<sub>2</sub>CO<sub>3</sub> (1.83g, 13.27 mmol, 20eq), Yield: 60%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 0.89 (s, 12H), 1.30 (m, 34H), 1.46 – 1.50 (m, 8H) , 1.77 (bs , 4H), 1.87 (bs , 4H), 3.37 (s, 6H), 3.54 (bs , 4H), 3.64 - 3.66 (m, 16H), 3.74 (bs, 4H), 3.97 (bs, 4H), 4.08 (bs, 4H) , 4.15 (bs, 4H), 4.24 (bs, 4H), 7.57 (s, 2H), ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm = 14.11, 22.67, 22.68, 26.01, 26.05, 29.09, 29.26, 29.32, 29.35, 29.48, 30.32 , 31.82, 31.88, 59.03, 69.16, 70.53, 70.56, 70.63, 71.94, 72.98, 74.15, 107.08, 120.24, 132.47, 146.84, 153.44, 157.39, 181.05, ; Elemental analysis: C, 67.81; H, 9.60 Calculated (%): C, 67.45; H, 9.24 (expt. %).

**Compound 4c-4** :compound **3c** (0.5g, 0.577 mmol, 1eq), TETRAEGMME tosylate (0.85g, 2.31 mmol, 4eq), K<sub>2</sub>CO<sub>3</sub>(1.59g, 5.84 mmol, 10eq), Yield: 60%; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 0.88 (s, 12H), 1.27 (m, 50H), 1.46 – 1.49 (m, 8H) , 1.75-1.77 (m, 4H), 1.87 (bs , 4H), 3.37 (s, 6H), 3.54 (bs , 4H), 3.63 - 3.66 (m, 16H), 3.74 (bs, 4H), 3.95 (bs, 4H), 4.08 (bs, 4H) , 4.15 (bs, 4H), 4.24 (bs, 4H), 7.57 (s, 2H), ; <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  ppm = 14.13, 22.70, 26.02, 26.06, 29.09, 29.35, 29.38, 29.54, 29.59, 29.62, 29.66, 29.71, 30.32 , 31.92, 31.93, 59.02 , 69.16, 70.53, 70.55, 70.63, 71.93, 72.98, 74.16, 107.09, 120.23, 132.46, 146.84, 153.44, 157.40, 181.05, ; Elemental analysis: C, 69.20; H, 9.80 Calculated (%): C, 69.42; H, 10.03 (expt. %)

![](_page_37_Figure_1.jpeg)

![](_page_37_Figure_2.jpeg)

![](_page_38_Figure_0.jpeg)

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![](_page_39_Figure_1.jpeg)

Figure 47: <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of TRIEGMME: n = 3

![](_page_40_Figure_0.jpeg)

Synthesis and Mesomorphism of anthraquinone based bolaamphiphiles

Figure 48: <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of TETRAEGMME: n = 4

![](_page_41_Figure_1.jpeg)

Figure 49: <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of 3a

![](_page_42_Figure_1.jpeg)

Figure 50 : <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of 3b

![](_page_43_Figure_1.jpeg)

Figure 51 : <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of 3c

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Chapter3

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Figure 53: <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of 4a-2

![](_page_46_Figure_0.jpeg)

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Chapter3

![](_page_47_Figure_1.jpeg)

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![](_page_49_Figure_0.jpeg)

Figure 57 : <sup>1</sup>H (top) and <sup>13</sup>C-NMR (bottom) spectra of 4c-4

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