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Rufigallol-based self-assembled supramolecular architectures

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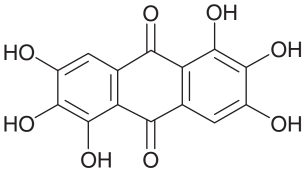
Discotic liquid crystals have been attracting growing interest not only because of the fundamental importance as model systems for the study of charge and energy transport but also due to their potential application in organic electronic devices. The 1,2,3,5,6,7-hexahydroxy-9,10-anthraquinone, commonly known as rufigallol, is one of the earliest systems reported to form columnar mesophases. Over the past 25 years, more than 100 discotic liquid crystals based on this core have been realized and studied for various physical properties. This review summarizes synthesis and thermal behaviour of all these materials. A brief summary of various physical studies on these materials has also been given.

Keywords: Discotic liquid crystals; Rufigallol; Hexahydroxyanthraquinone; Columnar phase

1. Introduction

Rufigallol (**1**) is a molecule of both biological and materials science interest. It has been known in the chemical literature for more than a century [1]. Recently, rufigallol has been reported as a novel oxidant drug [2, 3]. A remarkable synergistic antimalarial interaction between rufigallol and the structurally similar compound exifone has been described [4]. It is believed that rufigallol acts in a pro-oxidant fashion to produce oxygen radicals inside parasitized erythrocytes [4]. It should be noted that malaria remains a global health problem. More than 40% of the world's population is at risk from malaria. A number of hydroxyanthraquinones including rufigallol have recently been identified as active antimalarial compounds [2–4]. Rufigallol has also been recognized for its vitamin K activity [5].



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On the other hand, rufigallol has been found to function as the core fragment for a remarkable family of discotic liquid crystals (DLCs). Discotic liquid crystals have been attracting growing interest not only because of the fundamental importance as model systems for the study of charge and energy transport but also as functional materials for organic electronic device applications [6–13]. In a columnar mesophase, the core-core separation is usually of the order 0.35 nm so that there is considerable overlap of π-orbitals. The intercolumnar distance is usually 2–4 nm, depending on the lateral chain length. Therefore, interactions between neighbouring molecules within the same column would be much stronger than interactions between neighbouring columns. Consequently, charge migration in these materials is expected to be quasi-one-dimensional. DLCs can be aligned on a surface either face-on (homeotropic alignment) or edge-on (planar alignment) as shown in figure 1. Recently, several methods have been developed to align discotic molecules either face-on or edge-on [14–27]. The homeotropic alignment generally occurs during mesophase formation from the isotropic phase while special techniques are required to achieve a planar alignment. The homeotropic alignment with a face-on orientation of the discs and the director perpendicular to the substrate is beneficial for devices like light emitting diodes, photovoltaic solar cells, etc. On the other hand, planar alignment with edge-on orientation of the discs and the director parallel to the substrate is important to construct thin-film transistors.

1,2,3,5,6,7-hexahydroxyanthraquinone derivatives are one of the earliest systems reported to form columnar mesophases. They are interesting materials as these molecules have an elongated core with a 2-fold symmetry axis, are coloured and exhibit an important polymorphism, the core is electron-deficient in nature, they are thermally stable and their chemistry is fairly easy. Billard and co-workers reported the first discotic liquid crystalline hexaesters of rufigallol in 1980 [28] and since then about 100 different discotic liquid crystalline derivatives of this molecule have been prepared and studied for various physical properties [29–61]. This review covers synthesis and thermal behaviour of all these materials (tables 1–10). In the tables that follow, as well as in the text, transition temperatures are given in °C, Cr = crystal, Col = columnar phase, $\mathrm{Col_h}$ = hexagonal columnar phase, $\mathrm{Col_b}$ = biaxial columnar phase, M = unidentified mesophase, $\mathrm{Col_r}$ = rectangular columnar phase, g = glass transition, and I = isotropic phase.

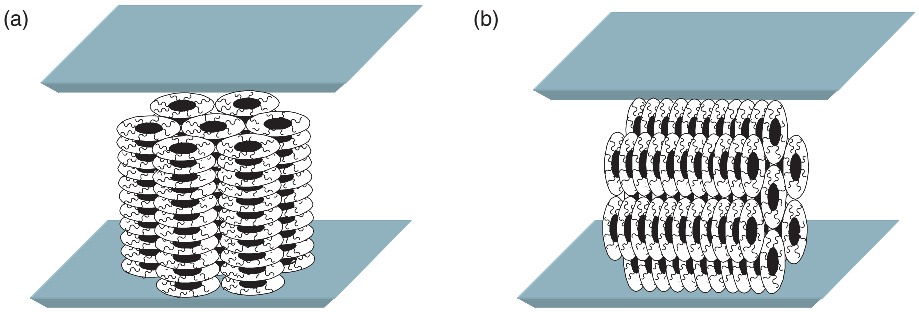


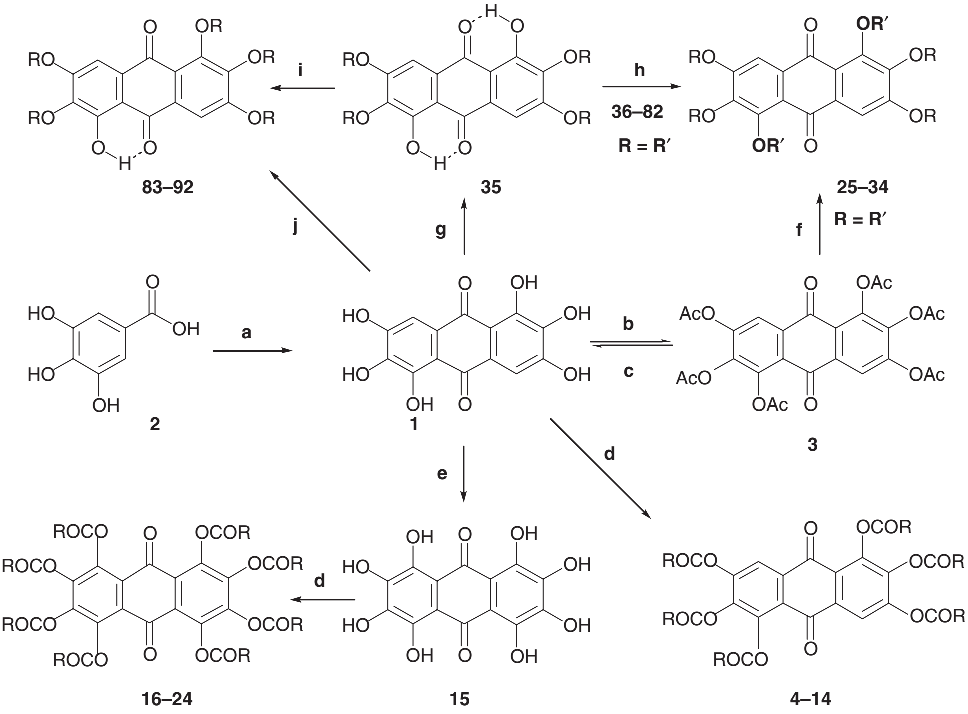
Figure 1. Schematic representation of (a) homeotropic and (b) planar alignment of discotic liquid crystals.

2. Synthesis and physical properties

2.1. *Synthesis of rufigallol*

The synthesis of rufigallol by the action of sulphuric acid on gallic acid was reported as early as in 1836 (scheme 1) [1]. Thus, heating gallic acid (**2**) in 98% H_2SO_4 at 100°C gives rufigallol (**1**) in about 20% yield. The crude product is difficult to filter as it clogs badly. Purification of rufigallol can be achieved by centrifuging the crude product followed by acetylation of the dried product in acidic conditions [1]. The hexaacetate (**3**) separates as yellow plates and can be recrystallized from acetic anhydride.

Though a large number of DLCs have been derived from rufigallol, it is surprising that no new efficient method to prepare rufigallol has been developed. Very recently we have observed that the self-condensation of gallic acid in the presence of sulphuric acid can be achieved, in high yield, in about one minute, by using microwave heating [60]. Thus, irradiation of gallic acid (2.0 g) in 6.0 mL of concentrated H_2SO_4 under microwaves (360 W) for 90 s yielded 1.4 g (84%) of rufigallol. The product was isolated simply by adding water to the reaction mixture followed by filtration of the solid product. This was converted to its hexaacetate by the treatment with acetic anhydride in 60% yield. Hydrolysis of the pure hexaacetate furnished pure rufigallol. The overall yield of the pure rufigallol from gallic acid was about 50%.



Scheme 1. (a) H_2SO_4, heat; (b) Ac_2O, H_2SO_4; (c) Aq NaOH; (d) Py-acetone, RCOCl; (e) H_3BO_3, HgO, H_2SO_4; (f) DMF, Na_2CO_3, RBr, 160°C; (g) DMSO, NaOH, RBr, TBAB, 80°C; (h) DMF, K_2CO_3, RBr, TBAB, ~100°C; (i) DMF, Cs_2CO_3, RBr; (j) ROH, TPP, DEAD.

Table 1. A list of known rufigallol-hexaesters and their thermal behaviour.

St.	R	Phase transition	Ref.
4	C_3H_7	Cr 216 I	[30]
5	C_4H_9	Cr 170 I	[30]
6	C_5H_{11}	Cr 152 I	[30]
7	C_6H_{13}	Cr 112 Col (108) Col 134 I	[30]
		Cr 98 Col 108 Col 127 I	[33]
		Cr 104 Col 133 I	[33]
8	C_7H_{15}	Cr 110 Col 133 I	[30]
		Cr 108 Col (99) Col 128 I	[33]
		Cr 106 Col 126 I	[33]
9	C_8H_{17}	Cr 91 Col (83) Col 128 I	[30]
		Cr 80 Col 106 Col 123 I	[33]
10	C_9H_{19}	Cr 109 Col 128 I	[30]
		Cr 106 Col 128 I	[33]
11	$C_{10}H_{21}$	Cr 92 Col 126 I	[30]
12	$C_{11}H_{23}$	Cr 99 Col 124 I	[30]
		Cr 91 Col 106 I	[33]
13	$C_{12}H_{25}$	Cr 96 Col 120 I	[30]
14	$C_{13}H_{27}$	Cr 103 Col 117 I	[30]

Table 2. Thermal behaviour of octa-alkanoyloxy-9,10-anthraquinones. All data from ref. [33].

St.	R	Phase transition
16	C_8H_{17}	Cr 85.5 Col_b 150.1 I
17	C_9H_{19}	Cr 86.5 Col_b 148.0 I
18	$C_{10}H_{21}$	Cr 98.7 Col_b 147.2 I
19	$C_{11}H_{23}$	Cr 102.0 Col_b 143.4 I
20	$C_{12}H_{25}$	Cr 101.0 Col 104.6 Col_b 140.1 I
21	$C_{13}H_{27}$	Cr 99.2 Col 104.5 Col_b 138 I
22	$C_{14}H_{29}$	Cr 104.0 Col 110.1 Col_b 134.6 Col_h 135.9 I
23	$C_{15}H_{31}$	Cr 102.5 Col 109.5 Col_b 121.9 Col_h 132.3 I
24	$C_{16}H_{33}$	Cr 107.3 Col 113.0 Col_b 121.2 Col_h 131.1 I

Table 3. A list of known symmetrical rufigallol-hexaethers and their thermal behaviour.

S.N.	R	Phase transition	Ref.
25	C_4H_9	Cr 105 Col_h 131 I	[31]
		Cr (122.5) Col_h 123.7 I	[36]
26	C_5H_{11}	Cr 83 Col_h 117 I	[31]
27	C_6H_{13}	Cr 53 Col_h 105 I	[31]
		Cr 20 Col_r 49 Col_h 106 I	[58]
28	C_7H_{15}	Cr 49 Col_h 102 I	[31]
29	C_8H_{17}	Cr 37 Col_h 96 I	[31]
		Cr 7 M 22 M 35 Col_h 97 I	[43]
		Cr 2 Cr 19 M 31 Col_h 96 I	[53]
30	C_9H_{19}	Cr 32 Col_h 92 I	[31]
		Cr 41 Col_h 92 I	[58]
31	$C_{10}H_{21}$	Cr 48 Col_h 87 I	[31]
32	$C_{11}H_{23}$	Cr 26 Col_h 84 I	[31]
33	$C_{12}H_{25}$	Cr 37 Col_h 79 I	[31]
34	$C_{13}H_{27}$	Cr 62 Col_h 72 I	[31]

Table 4. A list of known unsymmetrical rufigallol-hexaethers (figure 2(a), structures **36–57**) and their thermal behaviour.

St.	R	R′	Phase transition	Ref.
36	C_4H_9	C_3H_7	Cr 133.4 I	[36]
37	C_4H_9	C_5H_{11}	Cr 105.5 D_h 123.2 I	[36]
38	C_4H_9	C_6H_{13}	Cr 84 D_h 118.7 I	[36]
39	C_4H_9	C_7H_{15}	Cr 82.8 D_h 108 I	[36]
40	C_4H_9	C_8H_{17}	Cr 77.2 D_h 92.1 I	[36]
41	C_4H_9	C_9H_{19}	Cr 77.3 D_h 79.5 I	[36]
42	C_4H_9	$C_{10}H_{21}$	Cr (38.6) D_h 59.8 I	[36]
43	C_4H_9	$C_{11}H_{23}$	Cr 34.1 I	[36]
44	C_4H_9	$C_{12}H_{25}$	Cr 39 I	[36]
45	C_8H_{17}	C_3H_7	Cr 80.2 I	[36]
46	C_8H_{17}	C_4H_9	Cr 80.7 I	[36]
47	C_8H_{17}	C_5H_{11}	Cr 55.4 D_h 73.9 I	[36]
48	C_8H_{17}	C_6H_{13}	Cr 53.9 D_h 86.5 I	[36]
49	C_8H_{17}	C_7H_{15}	Cr 39.9 D_h 91.4 I	[36]
			Cr –8.6 M 44.8 D_h 93.4 I	[43]
50	C_8H_{17}	C_9H_{19}	Cr 51.1 D_h 83.4 I	[36]
			Cr 53.9 D_h 96.6 I	[43]
51	C_8H_{17}	$C_{10}H_{21}$	Cr 32.2 D_h 57.9 I	[36]
			Cr 48.5 D_h 95.3 I	[43]
52	C_8H_{17}	$C_{11}H_{23}$	Cr 38.2 D_h 56.5 I	[36]
			Cr 22.2 D_h 91.9 I	[43]
53	C_8H_{17}	$C_{12}H_{25}$	Cr 50 D_h 70.1 I	[36]
54	C_6H_{13}	$CH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)_2$	Col_h 77.7 I	[60]
55	C_7H_{15}	$CH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)_2$	Col_h 78.7 I	[60]
56	C_8H_{17}	$CH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)_2$	Col_h 72.3 I	[60]
57	C_9H_{19}	$CH_2CH_2CH(CH_3)(CH_2)_3CH(CH_3)_2$	Col_h 67.4 I	[60]

Table 5. Thermal behaviour of mixed tail rufigallol-hexaethers (figure 2(b), structures **58–63**). All data from ref. [42].

St.	R	Phase transition
58	C_5H_{11}	Cr 171.9 I
59	C_6H_{13}	Col 135.8 Col_h 151 I
60	C_7H_{15}	Cr 77 Col 128.9 Col_h 143.5 I
61	C_8H_{17}	Col 121.4 Col_h 137 I
62	C_9H_{19}	Cr 84.2 Col 104.8 Col_h 132.1 I
63	$C_{10}H_{21}$	Col 92.8 Col_h 129.6 I

2.2. *Rufigallol-hexa-n-alkanoates*

Esterification of rufigallol with an excess of appropriate acid chloride in acetone-pyridine or toluene-pyridine at elevated temperature yields hexaesters **4–14** in low (23%) yield (scheme 1, route d) [28]. No further effort has been made to improve the synthesis of these materials. Eleven members of the hexa-*n*-alkanoyloxy-9,10-antraquinone series have been prepared. Their thermal behaviour is presented in table 1.

While lower homologues (up to hexanoate) of the series do not show liquid crystallinity, all the higher members of the series display an enantiotropic mesophase. Moreover, three members (heptanoloxy- to decanoyloxy-) also exhibit monotropic

Table 6. Thermal behaviour of mixed tail rufigallol-hexaethers (figure 2(c), structures **64**–**75**). All data from ref. [44].

St.	R	R′	Phase transition
64	C_4H_9	H	Cr 162 I
65	C_6H_{13}	H	Cr 140 I
66	C_8H_{17}	H	Cr 72.5 Col 130.5 I
67	$C_{10}H_{21}$	H	Cr 82 Col 107.7 Col 122.5 I
68	C_3H_7	THP	Cr 126 I
69	C_4H_9	THP	Cr 103 (93 Col_h) I
70	C_5H_{11}	THP	Cr 79.5 Col_h 101.5 I
71	C_6H_{13}	THP	Cr 83.5 Col_h 91 I
72	C_7H_{15}	THP	Cr 80.5 Col_h 85.5 I
73	C_8H_{17}	THP	Cr 64 Col_h 76 I
74	C_9H_{19}	THP	Cr 58.5 Col_h 70 I
75	$C_{10}H_{21}$	THP	Cr 52 Col_h 62.5 I

Table 7. Thermal behaviour of mixed tail rufigallol-hexaethers (figure 2(d), structures **76**–**82**). All data from ref. [46].

St.	R	Phase transition
76	C_5H_{11}	Cr 138 Cr 167.5 I
77	C_6H_{13}	Cr 147.5 Cr 158.5 (140 Col_h) I
78	C_7H_{15}	Cr 124.5 Cr 156.5 (141 Col_h) I
79	C_8H_{17}	Cr 126.5 Cr 143.5 (134.5 Col_h) I
80	C_9H_{19}	Cr 108.5 Cr 132.5 (128 Col_h) I
81	$C_{10}H_{21}$	Cr 118.5 (115.5 Col_h) I
82	$C_{10}H_{21}$	Cr 120 I

Table 8. A list of known monohydroxy-pentaalkoxy-rufigallols and their thermal behaviour.

St.	R	R′	Phase transition	Ref.
83	C_3H_7	C_3H_7	Cr 68.4 Col 106.6 I	[56]
84	C_4H_9	C_4H_9	Cr 57.7 Col 127.6 I	[56]
85	C_5H_{11}	C_5H_{11}	Cr 32.4 Col 125.3 I	[56]
86	C_6H_{13}	C_6H_{13}	Col 113 I	[56]
87	C_7H_{15}	C_7H_{15}	Col 104.8 I	[56]
88	C_8H_{17}	C_8H_{17}	Col 90.4 I	[56]
89	C_9H_{19}	C_9H_{19}	Col 86.4 I	[56]
90	$C_{10}H_{21}$	$C_{10}H_{21}$	Col 80.6 I	[56]
91	$C_{12}H_{25}$	$C_{12}H_{25}$	Col 67.5 I	[56]
92	C_5H_{11}	CH_2PhNO_2	M_1 71.9 Col 171.6 I	[41]

columnar phase. X-ray diffraction studies indicate that both the phases are columnar rectangular. They differ only in the size of lattice and molecular orientations in the columns.

Corvazier and Zhao investigated the confinement effect on the phase behaviour of rufigallol-hexa-*n*-octanoate [40]. Millipore membranes of various pore sizes were taken as the confining media. The suppression of the monotropic phase inside the

Table 9. Thermal behaviour of rufigallol main-chain polymers. All data from ref. [37].

St.	R	*n*	MW	Phase transition
99	C_4H_9	6	6800	g 72 Col_r 164 Col_r 175 I
100	C_4H_9	8	17,000	g 72 Col_h 164 Col_h 176 I
101	C_4H_9	10	6400	Col_h 133 Col_h 144 I
102	C_4H_9	12	5400	Col_h 138 I
103	C_8H_{17}	6	7400	Col_r 132 I
104	C_8H_{17}	8	14,500	g 54 Col_r 96 I
105	C_8H_{17}	10	8800	Col_r 108 I
106	C_8H_{17}	12	7600	Col_r 127 I

Table 10. Thermal behaviour of rufigallol-based metallomesogens. All data from ref. [50].

St.	R	Metal	Phase transition
107	C_4H_9	Cu	Cr 184 I
108	C_5H_{11}	Cu	Cr 175 I
109	C_6H_{13}	Cu	Cr 170 I
110	C_7H_{15}	Cu	Col 136 (5.5) I
111	C_8H_{17}	Cu	Cr 152 (12) Col 162 (6) I
112	C_9H_{19}	Cu	Cr 140 (12.6) Col 161 (4.8) I
113	$C_{12}H_{25}$	Cu	Cr 72 (42) Col 121 (1.5) Col 146 (5) I
114	C_4H_9	Pd	Cr 202 I (d)
115	C_5H_{11}	Pd	Cr 187 I (d)
116	C_7H_{15}	Pd	Cr Col 179 (7.3) Col 191 (12.3) I (d)
117	C_8H_{17}	Pd	Cr 168 (7.9) Col 192 (10.3) I (d)
118	C_9H_{19}	Pd	Cr Col 160 (3.9) Col 180 (7.4) I (d)
119	$C_{10}H_{21}$	Pd	Cr 59 (13.5) Col 161 (6.2) I (d)
120	$C_{12}H_{25}$	Pd	Cr 70 (39) Col 171 (6) I (d)

membrane of smaller pore size was observed. However, the confinement does not impart any effect on the overall crystallization mechanism. This material was also dispersed in different polymers like, polystyrene, poly(methyl methacrylate) and poly(ethyl methacrylate). It is reported that orientation of discotic molecules can be achieved by the stretching of polymer dispersed discotic liquid crystal films [39].

2.3. *Octa-alkanoyloxy-9,10-anthraquinones*

Oxidation of 1,2,3,5,6,7-hexahydroxyanthraquinone yields octahydroxyanthraquinone **15** (scheme 1, route e). Thus heating rufigallol with boric acid and mercuric acid in concentrated H_2SO_4 at 250°C furnished 1,2,3,4,5,6,7,8-octahydroxy-9,10-anthraquinone in about 35% yield. Esterification of this octahydroxy-9,10-anthraquinone with alkanoyl chlorides provides octa-alkanoyloxyanthraquinone discotics **16–24** in about 60% yield (scheme 1) [33]. Nine members of the series ranging from octa-*n*-octanoyloxy- to octa-*n*-hexadecanoyloxy-9,10-anthraquinone have been prepared and all are reported to be liquid crystalline. Their thermal behaviour is presented in table 2.

The first four members of the series display only a single optically biaxial columnar phase, while higher members exhibit two or three columnar mesophases.

Compared with the hexaalkanoyloxy-9,10-anthraquinone, the octa-alkanoyloxy-anthraquinone posses larger mesomorphic range and the higher homologues exhibit a uniaxial columnar phase which was absent in the hexa-substituted derivatives. Though, a variety of novel mesogens can be derived from octahydroxy-9,10-anthraquinone, surprisingly, no further work has been carried out on this molecule.

2.4. *Hexa-n-alkoxyrufigallols*

Ten aliphatic ethers of rufigallol **25–34** having identical peripheral chains have been prepared by Carfagna *et al.* [31]. These rufigallol-ethers were prepared directly from rufigallol-hexaacetate. Thus, alkylation of hexaacetoxy-rufigallol with an excess of appropriate alkyl halide in DMF at reflux temperature afforded 1,2,3,5,6,7-hexaalkoxy-9,10-anthraquinones (scheme 1, route f). Recently, it has been observed that alkylation of rufigallol under microwave heating produced these ethers in a few minutes [60]. However, the reaction can be carried out only on a small scale.

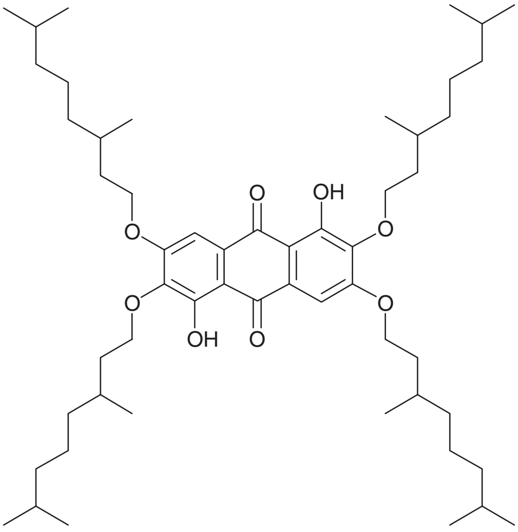
The thermal data for rufigallol hexaethers with identical peripheral chains (**25–34**) are listed in table 3. Following the general trend in LCs, the temperature for the mesophase to the isotropic phase decreases smoothly with increasing length of the alkyl chains. On the other hand, the melting transitions do not follow a regular pattern. It was also observed that solution-crystallized and melt-crystallized samples display different phase behaviour [58]. X-ray diffraction studies indicate the formation of hexagonal columnar phase in all the hexaalkoxy-rufigallols. A few members also exhibit rectangular columnar phase at lower temperature [31, 33, 58].

Maeda *et al.* studied the phase behaviour of three hexaalkoxy-rufigallols under hydrostatic pressure using a high pressure differential thermal analyzer [58]. Under pressure, on one hand, induction of $\mathrm{Col_r}$ phase in hexaoctyloxy-rufigallol was observed. On the other hand, the stable $\mathrm{Col_r}$ phase of hexahexyloxy-rufigallol has a decreased temperature range with increasing pressure and then the $\mathrm{Col_r}$ phase disappears under higher pressure. The temperature dependent dielectric spectroscopy of four homologous hexaalkoxy-rufigallols in the frequency range of 10 Hz to 10 MHz has recently been carried out by Gupta *et al.* [59]. The dielectric anisotropy ($\Delta\varepsilon\prime = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$) has been found to be positive throughout the entire range of the $\mathrm{Col_h}$ phase for all of the four compounds of this series. No relaxation phenomenon is found in the frequency range of the measurement i.e., 10 Hz to 10 MHz. They have also measured the DC conductivity of these compounds found in the range 10^{-10} to $10^{-11}\,\mathrm{S\,m^{-1}}$. Chandrasekhar *et al.* measured AC conductivity of hexapentyloxy-rufigallol doped with a small amount of an electron donor anthracene [47]. The conductivity was found to be nearly seven orders of magnitude higher in the columnar phase relative to that in the isotropic phase, as well as that in the columnar phase in the undoped state. Thermoelectric power studies confirmed the nature of the charge carrier as electrons in anthracene-doped hexapentyloxy-rufigallol.

2.5. *Mixed tail hexaalkoxyrufigallols*

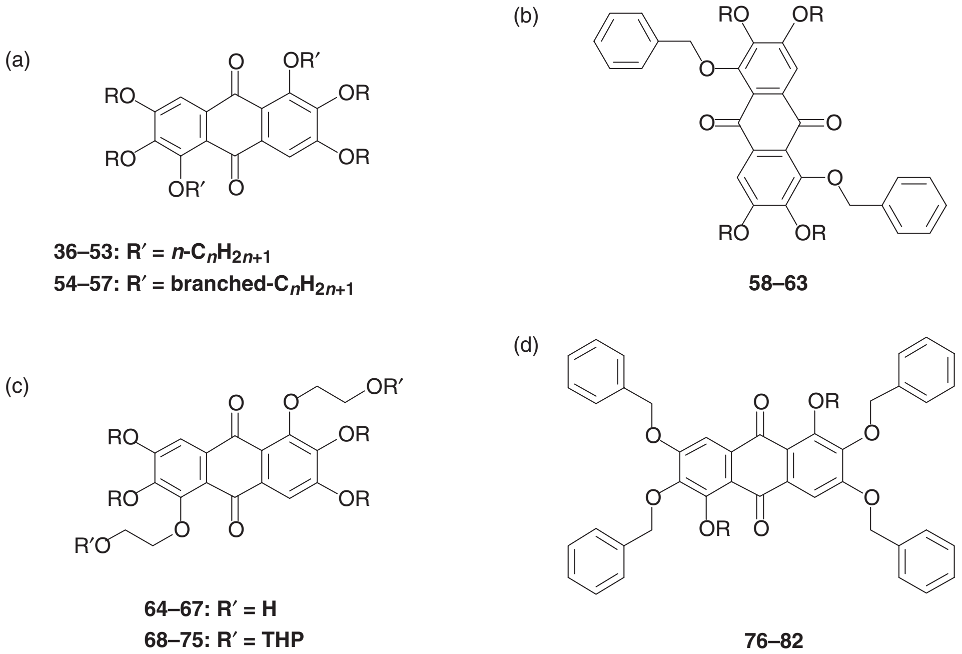
The nature of aliphatic chains around the periphery of the core plays an important role in deciding the thermal behaviour of DLCs. The topic has been well-studied in the case of triphenylene-based DLCs [6–8]. Generally, an introduction of dissymmetric side-chains does not affect the nature of the mesophase but results in the reduction of mesophase stability (lower clearing temperature). As melting temperature decreases significantly, often the mesophase range increases in dissymmetric DLCs.

In the hexahydroxy-rufigallol, the hydroxyl groups at 1- and 5-positions are hydrogen bonded and, therefore, are less reactive. Under milder etherification conditions, the hydrogen bonded 1- and 5-positions do not get alkylated and thus 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone **35** forms (scheme 1, route g). All the 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinones having normal alkyl chains were reported to be nonliquid crystalline, however, very recently it has been observed that a branched-chain substituted tetraalkoxy derivative **35a** displays a broad room-temperature mesophase [60]. This could be because the branched chains fill the necessary space around the core to induce mesomorphism. Further substitution on this compound at 1- and 5-positions may lead to many new DLCs.



35a: Col$_h$ 115.7 I

The unequal reactivity of hydroxyl groups leads to the preparation of several unsymmetrical rufigallol derivatives **36–82**. These unsymmetrical rufigallols can be subdivided in to four groups (figure 2): (a) compounds having two different *n*-alkyl or branched alkyl chains at 1- and 5-positions (Structures **36–57**); (b) compounds in which the two H-bonded positions were substituted by benzyl groups (Structures **58–63**); (c) compounds in which the two H-bonded positions were substituted by hydroxyethyl or THP-protected hydroxyethyl groups (Structures **64–75**); and (d) compounds in which the two H-bonded positions are having *n*-alkyl chains but the other four positions are bearing benzyl groups (Structures **76–82**). Thermal data of all these materials are listed in tables 4–7. Most of these materials exhibit hexagonal columnar phase. Their thermal behaviour largely depends on the number and nature of substitutions. An important observation is that the introduction of two branched alkyl chains (**54–57**) reduces the melting point significantly and these mixed tail derivatives display very wide temperature range columnar phase which is stable



(a) **36–53: R′ = *n*-C_nH_{2n+1}**
54–57: R′ = branched-C_nH_{2n+1}

(b) **58–63**

(c) **64–67: R′ = H**
68–75: R′ = THP

(d) **76–82**

Figure 2. Structural types of mixed tail rufigallol discotics.

at room temperature [60]. While rufigallols with two or four branched alkyl chains are room-temperature liquid crystals, substitution of all the six alkyl chains by branched alkyl chains destroys the mesomorphism completely [60].

2.6. *Mono-hydroxy-pentaalkoxyrufigallols*

Monofunctionalized discotics are extremely valuable precursors for the preparation of discotic dimers, oligomers, and polymers. The importance of monofunctionalized discotics may be realized by looking at the large number of DLCs derived from monofunctionalized triphenylenes [6–8]. Consequently, several methods have been developed to prepare monohydroxy-pentaalkoxytriphenylenes. However, these efforts have been limited to triphenylene moiety only and methods to prepare monofunctionalized derivatives of other discotic cores are scarce.

As mentioned in the previous section, it is very easy to prepare difunctionalized rufigallol as the H-bonded hydroxyl groups at 1- and 5-positions do not get alkylated under milder conditions. In principle, monoalkylation of 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone should give the monohydroxy-pentaalkoxy-rufigallol easily but, in practice, alkylation of rufigallol-tetraethers under different reaction conditions results in the formation of a mixture of unreacted (tetraalkylated), pentaalkylated and hexaalkylated products. All efforts to isolate pure monohydroxy-pentaalkoxyanthraquinone were futile. However, the problem was solved by acetylating the crude product as R_f values of the tetraalkoxydiacetoxyrufigallol, pentaalkoxymonoacetoxyrufigallol and hexaalkoxyrufigallol were significantly different on a chromatographic column and thus all three products could be separated readily by column chromatography.

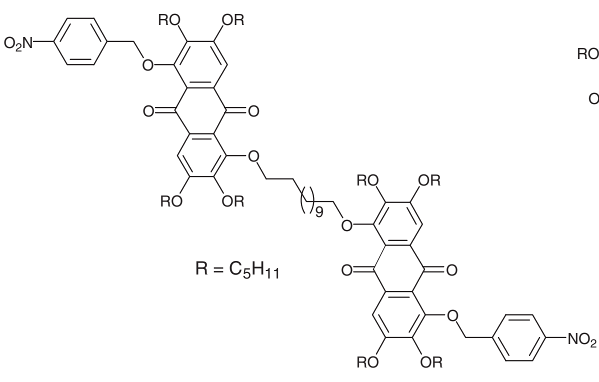
Pure monoacetoxy-pentaalkoxyrufigallol on hydrolysis afforded the desired monofunctionalized anthraquinone derivatives. We have recently observed that alkylation of rufigallol with aliphatic alcohol under Mitsunobu's conditions predominantly produces monohydroxy-pentaalkoxyrufigallol in good yield [61]. All the monohydroxy-pentaalkoxyrufigallols **83–92** (scheme 1) display hexagonal columnar phase over a wide temperature range. Their thermal data are summarized in table 8.

2.7. *Rufigallol-based discotic-calamitic hybrids*

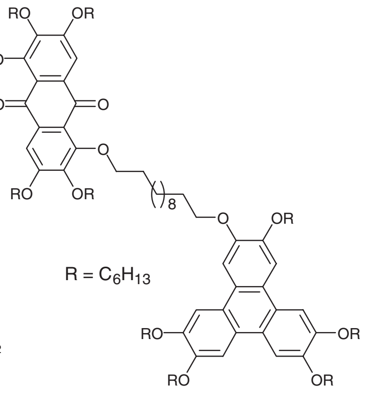
Recently Pal and Kumar prepared a number of alkoxycyanobiphenyl-substituted rufigallols **93–96** by systematically replacing one, two, four, and five alkyl chains by cyanobiphenyl-tethered alkoxy chains (figure 3). Most of these hybrid materials display a nematic phase. Their full characterization is in progress [61].

2.8. *Rufigallol-based discotic dimers*

Connecting two conventional mesogens via a spacer resulted in the formation of a dimer. Generally, these materials show quite different behaviour to conventional low molar mass liquid crystals and in particular their transitional behaviour exhibits a dramatic dependence on the length and parity of the flexible spacer. Dimers represent ideal model compounds for polymers or networks due to their ease of purification and characterization and the possibility of freezing, in their mesophase, to a glassy state. A number of discotic dimers based on different cores like benzene, triphenylene, phalocyanine, etc., have been synthesized and studied for various properties [6–8]. However, probably because of difficulties in obtaining monofunctionalized anthraquinone, only two rufigallol-based discotic dimers **97** and **98** have so far been reported. The *bis*[1-(4-nitrobenzyloxy)-2,3,6,7-tetrapentyloxy-9,10-anthraquinone-5-oxo]dodecane (**97**) was prepared from its corresponding monomer **92** by alkylating with 1,12-dibromododecane [45]. The monomer **92** was easily prepared and purified due to the polar nature of nitrobenzyl group attached at the 1-position.



97: Col 180 I



98: Col 96 I

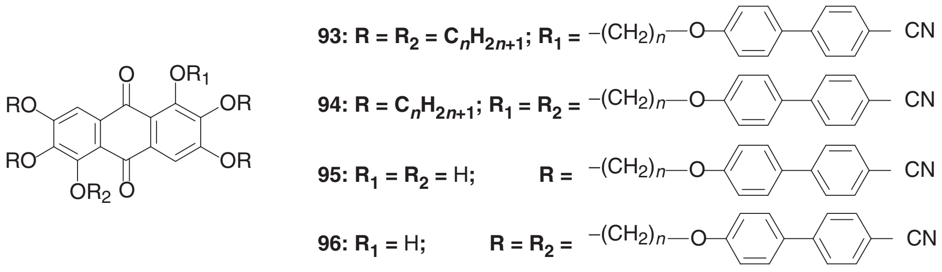
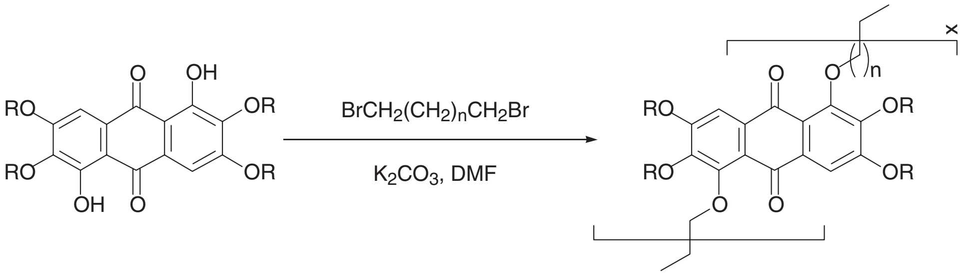


Figure 3. Chemical structures of rufigallol–cyanobiphenyl hybrids.



35

99-106

Scheme 2. Synthesis of rufigallol-based main chain polymers.

The donor–σ–acceptor dimer **98** is perhaps the only example of discotic dimers where an electron-rich triphenylene discotic was connected to an electron-deficient anthraquinone discotic via an alkyl chain spacer [57]. Though several examples of dimers were reported in which an electron acceptor like TNF or anthraquinone was co-valently connected to the electron-rich donor [7, 8], in all the reported examples the electron-deficient moiety has been limited to the nonliquid crystalline molecules. The compound **98** exhibits a wide-range columnar phase. The possibility of segregated donor and acceptor columns in the columnar phase has been proposed. Such dimers having segregated donor and acceptor columns could be of great importance in devices like photovoltaic solar cells.

2.9. *Rufigallol-based discotic main chain polymers*

The precursors for the synthesis of discotic main chain polymers are difunctionalized discotic derivatives. The functional groups are often hydroxyl moieties which can be easily converted to ethers or esters. It is usually very difficult to get well-defined difunctional discotic molecules and this could be one of the reasons that only a few discotic main chain polymers are known. Contrary to that, as mentioned above, it is very easy to prepare dihydroxy-functionalized rufigallols. Raja *et al.* utilized these synthons to prepare two series of main chain discotic polymers [36]. Thus, polyalkylation of 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone with various α,ω-dibromoalkanes afforded polymers **99–106** (scheme 2). These polymers do not show melting transition but directly transform from glassy state to columnar mesophase which, on further heating, converted to the isotropic phase. It was

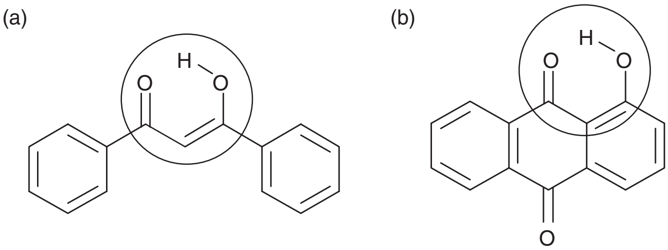


Figure 4. Molecular structures showing similarity between (a) β-diketone (keto-enol form) and (b) 1-hydroxyanthraquinone systems.

observed that polymers with spacer length more than double the peripheral alkyl chain length display $\mathrm{Col_h}$ phase while the polymers with spacer length equal or smaller than double the peripheral alkyl chain length display $\mathrm{Col_r}$ phase. The thermal data of these polymers are listed in table 9.

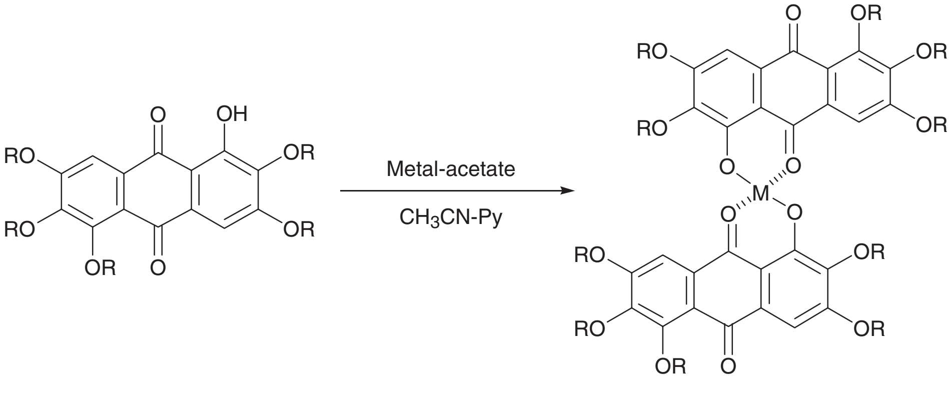
2.10. *Rufigallol-based discotic metallomesogens*

Metallomesogens are metal complexes which exhibit liquid-crystalline properties. The incorporation of metal into liquid crystalline compounds is of great interest because such materials are expected to have properties associated with metal atoms such as magnetism, electron-rich nature, colour, etc., in conjunction with liquid crystalline properties such as fluidity, processability, supramolecular order, etc. The introduction of metal into mesogenic molecules has brought about a considerable expansion in the field of discotic liquid crystals because the coordination geometry of many metals (particularly square-planar) causes the molecule to adopt an approximately planar structure.

β-Diketonates were the first disc-like complexes reported to exhibit mesomorphism in the pure state. They are amongst the most widely synthesized and studied metallomesogens [62–65]. They exhibit either calamitic or discotic mesomorphism, depending on subtle differences in the molecular structure. A number of β-diketone derivatives are known to show nematic, smectic, columnar, and lamellar mesophases. β-Diketone complexes having both calamitic and discotic features are also known.

A comparison of the structure of β-diketone molecule (figure 4a), with that of a 1-hydroxyanthraquinone derivative (figure 4b) clearly demonstrate a similarity between the two systems. Therefore, similar to β-diketone system, a large number of metallomesogens can be prepared from monofunctionalized rufigallols.

Refluxing monohydroxy-pentaalkoxy-rufigallols with metal acetate in acetonitrile-pyridine easily furnished metal-bridged rufigallol dimers (scheme 3). Two series of complexes; one with copper and other with Pd were prepared in this way [48–50]. While the Pd complexes were found to be thermally unstable at higher temperature, the Cu complexes of the same ligand were stable. The thermal data of these discotic metallomesogens are listed in table 10. The higher homologues of both the series form columnar phase but the exact nature of the columnar phase has not been revealed. Lower members of both the series are not liquid crystalline but columnar mesophase and can be induced by doping them with an electron acceptor, trinitrofluorenone [48–50]. As all the Pd complexes start decomposing on heating,



84–91 **107–120**

Scheme 3. Synthesis of rufigallol-based metallomesogens.

their thermal data are not reproducible and, consequently, these materials are of little practical interest.

3. Summary and outlook

Discotic molecules are of interest for their intriguing supramolecular architectures. Their strong π–π interactions within a column lead to high electronic mobilities, a property that is essential in the development of eco-friendly organic electronic devices. Like organic materials, there are two types of discotic liquid crystalline semiconductors; *p*-type, in which the majority of charge carriers are holes and *n*-type, where the majority of charge carriers are electrons. Both *p*-type and *n*-type organic semiconductors are required for various device applications such as photovoltaic solar cells, light emitting diodes, etc. Most of the discotic liquid crystals are electron rich (*p*-type) systems and only a few electron deficient (*n*-type) discotics are known. Rufigallol is an attractive electron-deficient discotic core as it possesses C_2 symmetry, its derivatives are coloured, they are thermally and chemically stable, and their chemistry is simple. As described in this article, a variety of discotic liquid crystals having a very wide mesophase range and room temperature stability have already been derived from this core and it can be expected that many more new materials like side chain polymers, oligomers, donor–acceptor–donor or acceptor–donor–acceptor triads, discotic–calamitic hybrids, etc., should be realized in the future. Unfortunately, Physicists have not given much attention to these materials and few physical studies have been carried out. Efforts have to be made to utilize rufigallol-based DLCs in fabricating devices like photovoltaic cells, TFTs, LEDs, etc., to uncover the full potential of these materials.

References

[1] J. Grimshaw and R.D. Haworth, J. Chem. Soc. **56** 4225 (1956).

[2] M.V. Ignatushchenko, R.W. Winter and M. Riscoe, Am. J. Trop. Med. Hyg. **62** 77 (2000).

[3] J. Ziegler, R. Linck and D.W. Wright, Current Med. Chem. **8** 171 (2001).

[4] R.W. Winter, K.A. Cornell, L.L. Johnson, *et al*., Antimicrob. Agents Chemother. **40** 1408 (1996).

[5] G.J. Martin and C.F. Lischer, J. Biol. Chem. **137** 169 (1941).

[6] S. Kumar, Chem. Soc. Rev. **35** 83 (2006).

[7] S. Kumar, Liq. Cryst. **32** 1089 (2005).

[8] S. Kumar, Liq. Cryst. **31** 1037 (2004).

[9] B. Donnio, D. Guillon, R. Deschenaux, *et al*., Comprehensive Coordination Chemistry **7** 357 (2003).

[10] R.J. Bushby and O.R. Lozman, Current Opinion in Colloid & Interface Sci. **7** 343 (2002).

[11] C. Tschierske, Annu. Rep. Prog. Chem., Sect. C **97** 191 (2001).

[12] D. Demus, J. Goodby, G.W. Gray, *et al.* (Editors), in *Handbook of Liquid Crystals*, Vol. 2B (Wiley-VCH, Weinheim, 1998).

[13] S. Chandrasekhar and S. Kumar, Sci. Spectra 66 (1997).

[14] J.C. Wittmann and C. Smith, Nature **352** 414 (1991).

[15] N.C. Maliszewskyj, P.A. Heiney, J.Y. Josefowicz, *et al*., Science **264** 77 (1994).

[16] H. Schonheer, F.J.B. Kremer, S. Kumar, *et al*., J. Am. Chem. Soc. **118** 13051 (1996).

[17] F. Charra and J. Cousty, Phys. Rev. Lett. **80** 1682 (1998).

[18] T. Bjornholm, T. Hassenkam and N. Reitzel, J. Mater. Chem. **9** 1975 (1999).

[19] P. Smolenyak, R. Peterson, K. Nebesny, *et al*., J. Am. Chem. Soc. **121,** 8628 (1999).

[20] E. Eichhorn, J. Porphyrins Phthalocyanines **4** 88 (2000).

[21] C.Y. Liu and A.J. Bard, Chem. Mater. **12** 2353 (2000).

[22] T. Parova, S. Tsvetkov, J. Vij, *et al*., Mol. Cryst. Liq. Cryst. **351** 95 (2000).

[23] T. Parova, J. Vij and A. Kocot, Adva. in Liq. Cryst. **113** 341 (2000).

[24] R.J. Bushby, S.D. Evans, O.R. Lozman, *et al*., J. Mater. Chem. **11** 1982 (2001).

[25] P. Samori, X.M. Yin, N. Tchebotareva, *et al*., J. Am. Chem. Soc. **126** 3567 (2004).

[26] X. Crispin, J. Cornil, R. Friedlein, *et al*., J. Am. Chem. Soc. **126** 11889 (2004).

[27] M. Palma, J. Levin, V. Lemaur, *et al*., Adv. Mater. **18** 3313 (2006).

[28] A. Queguiner, A. Zann, J.C. Dubois, *et al*., in *Liquid Crystals*, edited by S. Chandrasekhar (Heyden, London, 1980), pp. 35–40.

[29] J. Billard, J.C. Dubois, C. Vaucher, *et al*., Mol. Cryst. Liq. Cryst. **66** 115 (1981).

[30] C. Carfagna, A. Roviello and A. Sirigu, Mol. Cryst. Liq. Cryst. **122** 151 (1985).

[31] C. Carfagna, P. Iannelli, A. Roviello, *et al*., Liq. Cryst. **2** 611 (1987).

[32] M. Werth, J. Leisen, C. Boeffel, *et al*., J. Phys. II France **3** 53 (1993).

[33] J. Billard, Z. Luz, R. Poupko, *et al*., Liq. Cryst. **16** 333 (1994).

[34] A. Hollander, J. Hommels, K.O. Prins, *et al*., J. Phys. II France **6** 1727 (1996).

[35] Z. He, Y. Zhao and A. Caille, Liq. Cryst. **23** 317 (1997).

[36] K.S. Raja, S. Ramakrishnan and V.A. Raghunathan, Chem. Mater. **9** 1630 (1997).

[37] K.S. Raja, V.A. Raghunathan and S. Ramakrishnan, Macromolecule **31** 3807 (1998).

[38] R.Y. Dong and C.R. Morcombe, Liq. Cryst. **27** 897 (2000).

[39] Y. Chenard, N. Paiement and Y. Zhao, Liq. Cryst. **27** 459 (2000).

[40] L. Corvazier and Y. Zhao, Liq. Cryst. **27** 137 (2000).

[41] K. Krishnan and V.S.K. Balagurusamy, Liq. Cryst. **27** 991 (2000).

[42] V. Prasad, K. Krishnan and V.S.K. Balagurusamy, Liq. Cryst. **27** 1075 (2000).

[43] K. Krishnan and V.S.K. Balagurusamy, Mol. Cryst. Liq. Cryst. **350** 1 (2000).

[44] V. Prasad and D.S. Shankar Rao, Mol. Cryst. Liq. Cryst. **350** 51 (2000).

[45] K. Krishnan and V.S.K. Balagurusamy, Liq. Cryst. **28** 321 (2001).

[46] V. Prasad, Liq. Cryst. **28** 647 (2001).

[47] S. Chandrasekhar and V.S.K. Balagurusamy, Proc. R. Soc. Lond. A **458** 1783 (2002).

[48] S. Kumar and J.J. Naidu, Mol. Cryst. Liq. Cryst. **378** 123 (2002).

[49] S. Kumar and J.J. Naidu, Liq. Cryst. **29** 1369 (2002).

[50] J.J. Naidu and S. Kumar, Mol. Cryst. Liq. Cryst. **397** 17/[317] (2003).

[51] S.V. Dvinskikh, H. Zimmermann, A. Maliniak, *et al*., J. Magn. Reson. **163** 46 (2003).

[52] S.V. Dvinskikh, H. Zimmermann, A. Maliniak, *et al*., J. Magn. Reson. **164** 165 (2003).

[53] S.V. Dvinskikh, Z. Luz, H. Zimmermann, *et al*., J. Phys. Chem. B. **107** 1969 (2003).

[54] S.V. Dvinskikh, D. Sandstrom, Z. Luz, *et al*., J. Chem. Phys. **119** 413 (2003).

[55] R.Y. Dong and R. Shearer, Chem. Phys. Lett. **375** 463 (2003).
[56] S. Kumar, J.J. Naidu and S.K. Varshney, Liq. Cryst. **30** 319 (2003).
[57] S. Kumar, J.J. Naidu and S.K. Varshney, Mol. Cryst. Liq. Cryst. **411** 355 (2004).
[58] Y. Maeda, H. Yokoyama and S. Kumar, Liq. Cryst. **32** 833 (2005).
[59] M. Gupta, R. Dhar, V.K. Agrawal, *et al.*, in *Proceedings of the 16th Conference on Liquid Crystals*, edited by J. Zielinski (ISBN: 978-83-89399-47-2) (2007), pp. 109–116.
[60] H.K. Bisoyi and S. Kumar, Tet. Lett. **48** 4399 (2007).
[61] S.K. Pal and S. Kumar, to be communicated.
[62] J.L. Serrano (Editor), in *Metallomesogens* (VCH Verlagsgesellschaft, Weinheim, 1996).
[63] A.M. Giroud-Godquin, in *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess and V. Vill, Vol. 2B (Wiley-VCH, Weinheim, 1998), Chapter XIV, pp. 901–932.
[64] S.A. Hudson and P.M. Maitlis, Chem. Rev. **93** 861 (1993).
[65] B. Donnio and D.W. Bruce, Structure and Bonding **95** 193 (1999).