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Recent developments in the chemistry of triphenylene-based discotic liquid crystals

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Invited Article

Recent developments in the chemistry of triphenylene-based discotic liquid crystals

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Triphenylene-based discotic liquid crystals, which have already been used commercially in phase compensation films to improve the viewing angle of liquid crystal display devices, also have application potential as one-dimensional charge carrier systems useful in electrical conduction, photoconduction, electroluminescence, photovoltaic solar cells, gas sensing, optical data storage and other devices. Over the past 25 years, more than 500 triphenylene derivatives have been synthesized to explore these possibilities. Cammidge and Bushby reviewed the chemistry and physical properties of about 100 triphenylene-based discotic liquid crystals prepared up to 1995. This review summarizes advances in the chemistry of triphenylene-based discotic liquid crystals since late 1995.

1. Introduction

Discotic liquid crystals (DLCs) are unique nanostructures with remarkable electronic and optoelectronic properties. The history of these fascinating materials goes back to 1977 when Chandrasekhar and his colleagues reported that not only rod-like molecules, but also compounds with disc-like molecular shapes are able to form mesophases [1]. Over the past twenty-five years, the field of DLCs has grown rapidly and to date about 3 300 compounds falling into this category are known [2]. Generally these compounds have flat or nearly flat cores surrounded by more than three aliphatic chains [2, 3]. Mesophases formed by disc-shaped molecules are of primarily two types: nematic and columnar. A few discotic molecules are also reported to form a discotic lamellar mesophase [4, 5]. In the discotic nematic phase, there is an orientationally ordered arrangement of discs with no long-range translational order (figure 1 (*a*)); while, in the columnar phase, the discs are stacked one on top of another to form columns (figure 1 (*b*)).

Attractive intermolecular interactions are most probably the main factors responsible for the observation of mesogenic properties. The intermolecular interaction between discotic mesogens may be approximated as the sum of two major contributions: namely, a core–core attraction (e.g. dispersion forces) and a hydrophobic interaction between the aliphatic chains. The relative importance of these is, however, difficult to quantify [6].

Rapid development in the field of DLCs occurred after the realization of their potential uses in various device applications. The negative birefringence film formed by polymerized nematic DLCs was the first successful commercial application of DLCs. The Fuji Photo Film Company of Japan recently developed a phase compensation film from polymerized triphenylene-based discotic nematic liquid crystals which is used to improve the viewing angle of commonly used LCDs [7, 8]. Very recently it has been demonstrated that monomeric discotic nematic liquid crystals can be utilized instead of calamitic nematic liquid crystals to overcome the narrow and non-uniform viewing cone problem of classical twisted nematic LCs. The liquid crystal display prepared using hexalkynylbenzene-based discotic nematic liquid crystal shows a wide and symmetrical viewing angle and no reversal of contrast ratio in any direction [9].

The majority of DLCs form columnar mesophases

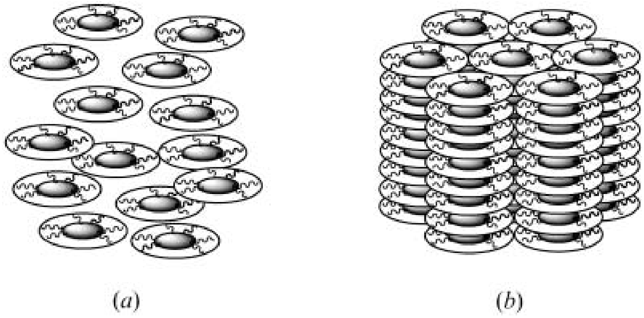

Figure 1. Schematic representations of (*a*) the discotic nematic and (*b*) the columnar phase.

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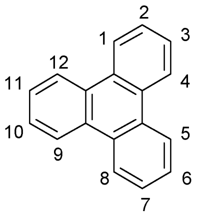
probably due to the strong π–π interactions between the polyaromatic cores. The core–core separation in a columnar mesophase is usually of the order of 3.5 Å so that there is considerable overlap of π-orbitals. As flexible long aliphatic chains surround the core, the intercolumnar distance is usually 20–40 Å, depending on the lateral chain length. Therefore, interactions between neighbouring molecules within the same column would be much stronger than interactions between those in neighbouring columns. Consequently, charge migration in these materials is expected to be quasi-one-dimensional. Conductivity along the columns in columnar mesophases has been reported to be several orders of magnitude greater than in the perpendicular direction [10, 11]. Thus the columns may be described as molecular wires. Charge carrier mobilities up to $0.71\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ along the columns have recently been observed [12]. These supramolecular assemblies are of fundamental importance, not only as models for the study of the energy and charge migration in organized systems, but also as functional materials for device applications such as one-dimensional conductors, photoconductors, light-emitting diodes, photovoltaic solar cells, and gas sensors [13].

2. Triphenylene as a core for discotic liquid crystals

The symmetrical fused aromatic hydrocarbon 'triphenylene' (**1**) has been known in the chemical literature for more than a century. Schultz isolated this compound from the pyrolytic products of benzene and gave it the name triphenylene [14]. In the early twentieth century, it was synthesized from cyclohexanone and its various physical properties were studied [14]. Electrophilic aromatic substitution in unsubstituted triphenylene is directed by steric and electronic effects. Substitution at the β- or 2-position is favoured over that at the α- or 1-position, presumably due to a steric hindrance effect [14].

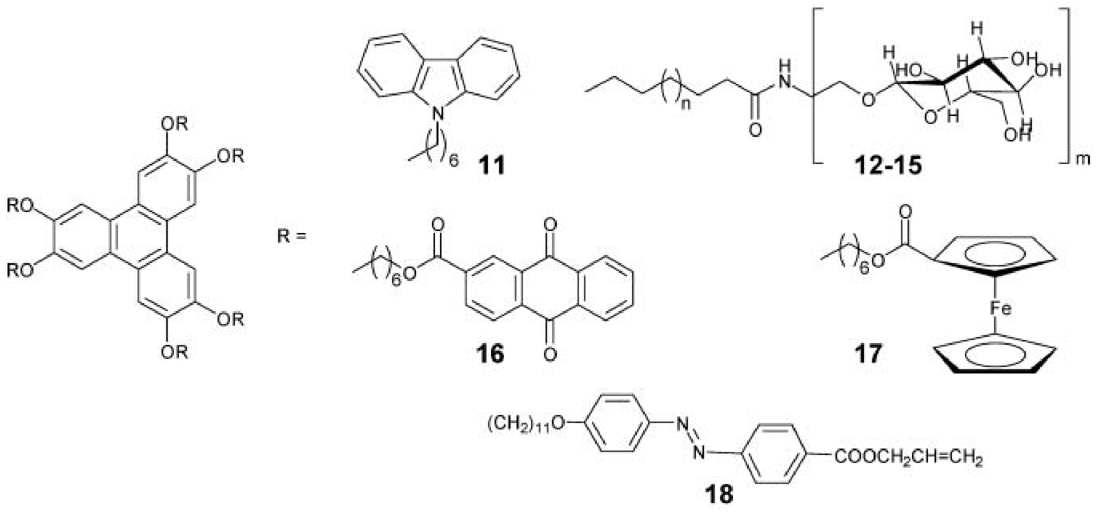


1

The potential of triphenylene as a novel core for DLCs was recognized in 1978 [15] and just a few months after the discovery of mesomorphism in disc-shaped molecules. Ever since, triphenylene has remained the focus of considerable attention of liquid crystal scientists around the world for a number of reasons: thus, its derivatives are thermally and chemically stable, their chemistry is fairly accessible, they show a variety of mesophases and their one-dimensional charge and energy migration properties offer tremendous potential applications. This stimulated numerous synthetic efforts to prepare a variety of triphenylene-based DLCs [16–108]. These materials have been extensively studied for various physical properties such as one-dimensional charge migration [109], one-dimensional energy migration [110], electroluminescence [111], ferroelectric switching [112], alignment and self-assembling behaviour on surfaces [113] and other properties. At present about 500 discotic liquid crystals based on a triphenylene core are known in the literature. The excellent article by Cammidge and Bushby covered the chemistry and physical properties of about 100 triphenylene derivatives prepared up to 1995 [16]. In the present review, advances in the chemistry of triphenylene-based DLCs since late 1995 are summarized. Thus, this article presents the chemistry and physical properties of about 300 monomeric triphenylene derivatives. The chemistry of triphenylene-based discotic dimers, trimers, oligomers and polymers will be the subject of a future publication.

The thermal behaviour of the triphenylene derivatives (structures **2**–**295**) prepared since late 1995 is summarized in 17 tables. Tables 1 and 2 present the thermal behaviour of symmetrical hexaalkoxy- and hexaalkanoyloxy-triphenylene derivatives, respectively. Table 3 covers the thermal behaviour of hexasubstituted triphenylenes having five identical alkoxy tails and one different substitution. In table 4 triphenylene derivatives in which the differing substituent is connected to the core via an ester linkage are collected. The thermal behaviour of hexa-substituted triphenylenes having four identical alkoxy tails at the 6,7,10 and 11 positions and two identical substituents at 2 and 3 positions is listed in table 5. In table 6, while the four alkoxy chains are identical, the remaining two groups at the 2- and 3-positions are of a different nature. Compounds in which two non-identical substituents are at the 2,6- or at 2,11-positions are summarized in tables 7 and 8, respectively. Four compounds in which the three phenyl rings of the triphenylene core each have differing sizes of alkoxy chains are shown in table 9. Symmetrical and unsymmetrical mixed tail hexasubstituted triphenylenes having three alkoxy chains and three other identical groups are listed in tables 10 and 11. Tables 12–14 show the thermal behaviour of heptasubstituted triphenylenes. Trisubstituted triphenylenes are given in table 15, and liquid crystalline octa-substituted triphenylenes in table 16. The physical properties of polyphenylated

Table 1. Thermal behaviour (°C) of the symmetrical hexa-substituted triphenylene ethers.



St.	*R*	Phase transition	Ref.
2	$CH_2COOC_2H_5$	Cr 122 Col_h 172 I	[17]
3	$CH_2COOC_2H_4C_6F_{13}$	Cr 30 Col_h 210 dec	[17]
4	$CH_2COOC_2H_4C_8F_{17}$	Cr 47 Col_h 217 dec	[17]
5	$CH_2COOC_2H_4C_{10}F_{21}$	Cr 115 $Col_?$ 215 dec	[17]
6	$(CH_2)_3CF_3$	Cr 132 Col_h 171 I	[98]
7	$(CH_2)_3C_4F_9$	Cr 116 Col_h 157 I	[98]
8	$(CH_2)_3(CF_2)_5CF_3$	Cr 89 Col_h 183 I	[100]
9	$CH_2CONHC_4H_9$	?	[97]
10	$CH_2CONHC_{12}H_{25}$	?	[97]
11		Cr 89 I	[75]
12	$n=1$; $m=1$	g 74 Col_h 127 I	[89]
13	$n=6$; $m=1$	g 51 Col_r 127 I	[89]
14	$n=1$; $m=3$	g 130 ?	[89]
15	$n=6$; $m=3$	g 104 Col_h 225 I	[89]
16		Cr 70 Cr 98 ?	[69]
17		?	[70]
18		Cr 81.1 Col 104.6 I	[91]

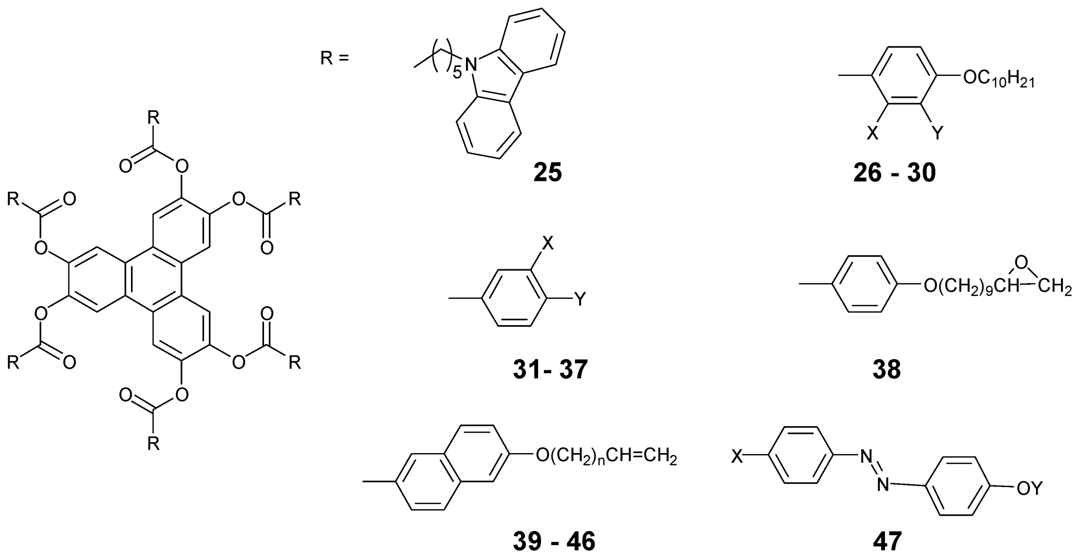
triphenylenes are shown in the final table, table 17. It should be noted that in all the tables, in the large part only liquid crystalline triphenylene derivatives have been tabulated. The thermal behaviour of a few relevant non-liquid crystalline final molecules, however, have also been given, but on the whole non-liquid crystalline intermediates have not been covered. In the tables St. stands for structure, Cr = crystal, Col = columnar phase, Col_h = hexagonal columnar phase, Col_{ho} = hexagonal ordered columnar phase, Col_r = rectangular columnar phase, Col_x = unidentified columnar phase, Col_p = columnar plastic phase, N_D = nematic discotic phase, N* = chiral nematic, BP = blue phase, g = glass transition, M_x and X = unknown mesophase, I = isotropic phase and dec indicates decomposition.

3. Synthesis

3.1. *Symmetrical hexasubstituted triphenylene derivatives*

The symmetrically 2,3,6,7,10,11-hexasubstituted derivatives of triphenylene are the most commonly studied DLCs. A number of hexaethers, thioethers, selenoethers, esters (including benzoates and cyclohexanoates) and hexaalkynes were prepared in the first decade of triphenylene DLC research [16]. In recent years, research has focused primarily on improving the synthesis of triphenylene ethers, as these materials were reported to have interesting conducting and photoconducting properties. Traditionally these molecules were prepared by the alkylation of 2,3,6,7,10,11-hexahydroxytriphenylene, which in turn was

Table 2. Thermal behaviour (°C) of the symmetrical hexa-substituted triphenylene esters.

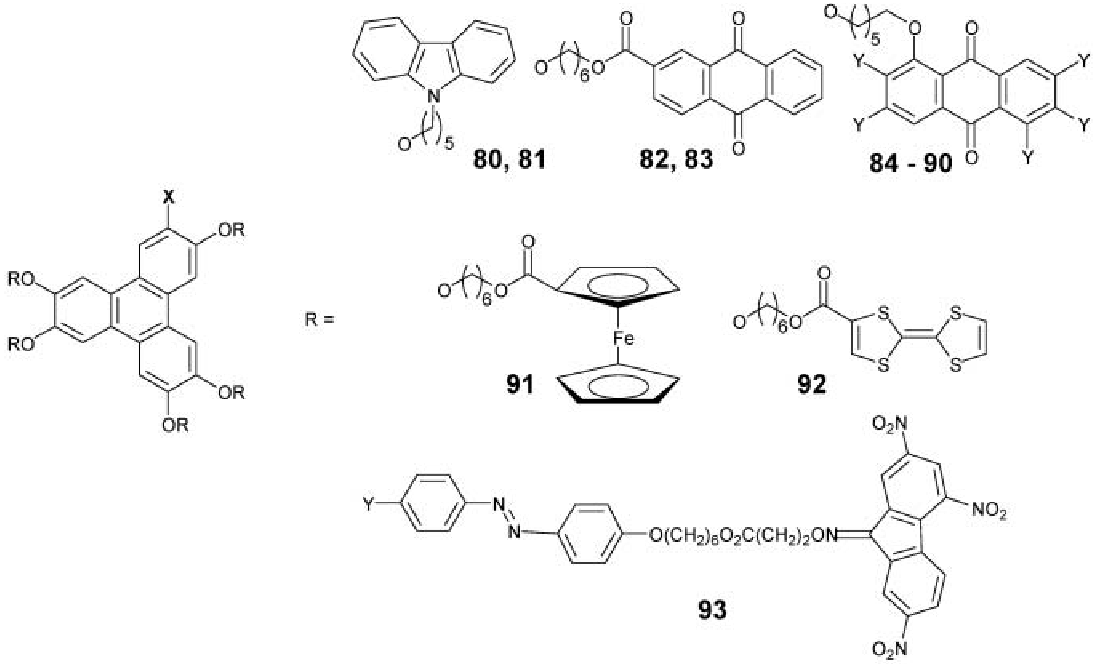


St.	*R*	Phase transition	Ref.
19	$CH(CH_3)OC_7H_{15}$	Cr 49 Col 90 I	[22]
20	$CH(Cl)CH_2CH(CH_3)_2$	Cr (266.8) Col 268 I	[40]
21	$CH(Cl)CH(CH_3)C_2H_5$	Cr (243.7) Col 264.1 I	[40]
22	$(CH_2)_2CH(CH_3)(CH_2)_2CH(CH_3)_2$	Col 112.1 I	[40]
23	$(CH_2)_7CH=CH_2$	Cr 55 Col_r 88 I	[89]
24	$(CH_2)_9Si(CH_3)_2OSi(CH_3)_3$	Col_h 125 I	[89]
25		Cr 290 dec	[74]
26	$X=H$; $Y=C_2H_5$	Cr 129 N_D 206 I	[18]
27	$X=H$; $Y=CH(CH_3)_2$	Cr 161 N_D 202 I	[18]
28	$X=H$; $Y=C(CH_3)_3$	Cr 194 N_D 225 I	[18]
29	$X=C_2H_5$; $Y=H$	Cr 117 N_D 131 I	[18]
30	$X=CH(CH_3)_2$; $Y=H$	Cr [70] N_D 93 I	[18]
31	$X=Cl$; $Y=OC_{10}H_{21}$	Col $>$ 300 I	[61]
32	$X=NO_2$; $Y=OC_{10}H_{21}$	Col $>$ 300 I	[61]
33	$X=OCH_3$; $Y=OC_{10}H_{21}$	Col 265 I	[61]
34	$X=OC_{10}H_{21}$; $Y=OC_{10}H_{21}$	Cr 79 I	[61]
35	$X=Cl$; $Y=OC^*H(CH_3)C_6H_{13}$	Col $>$ 300 I	[61]
36	$X=OCH_3$; $Y=OC^*H(CH_3)C_6H_{13}$	Cr 120 Col 237 I	[61]
37	$X=H$; $Y=OC^*H(CH_3)C_6H_{13}$	Cr 161 Col 213 N* 216 BP 220 I	[61]
38		Cr 104 N_D 180 I	[88]
39	$n=2$	Col_{rd} 249.9 N_D 330.1 I	[75]
40	$n=3$	Col_{rd} 227.4 N_D 327.5 I	[75]
41	$n=4$	Col_{rd} 227.4 N_D 288.8 I	[75]
42	$n=5$	Col_{rd} 222.0 N_D 286.5 I	[75]
43	$n=6$	Col_{rd} 198.2 N_D 273.1 I	[75]
44	$n=7$	Col_{rd} 174.2 N_D 235.7 I	[75]
45	$n=8$	Col_{rd} 174.2 N_D 224.9 I	[75]
46	$n=9$	Col_{rd} 155.5 N_D 217.6 I	[75]
47	$X=CO(CH_2)_3$; $Y=(CH_2)_9CH_3$	Cr (200.2) Col_h 207.5 I	[101]

prepared by demethylation of hexamethoxytriphenylene (scheme 1).

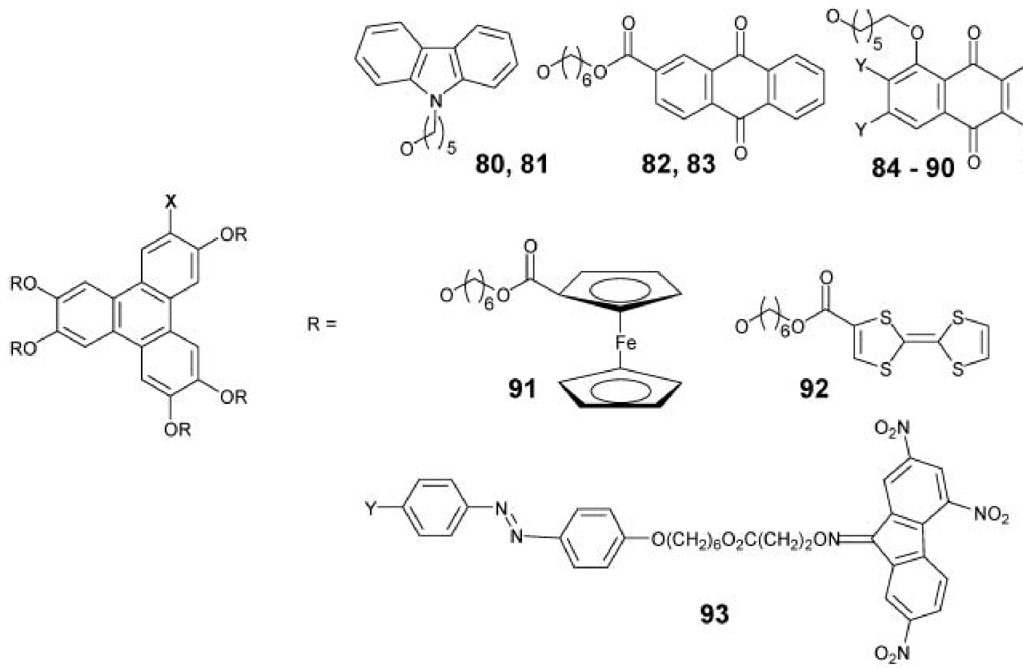
The trimerization of dialkoxybenzene to hexaalkoxytriphenylene involves three consecutive Scholl reactions [114]. Triphenylene derivatives show mesomorphism only when the six peripheral alkoxy chains have a minimum of three carbon atoms, i.e. propyloxy chains. It should be noted that this compound was described earlier to be non-liquid crystalline. Only very recently was its mesomorphic nature reported by Bushby *et al.*

Table 3. Thermal behaviour (°C) of monofunctionalized triphenylene pentaethers.



St.	*X*	*R*	Phase transition	Ref.
48	OSO2CF2	C_5H_{11}	Cr 54 Col$_X$ 85 Col$_h$ 188 I Col$_P$ 87 Col$_{ho}$ 181 I	[19] [30]
49	$O(CH_2)_{11}(CF_2)_7CF_3$	C_5H_{11}	Cr 55 I	[17]
50	$O(CH_2)_{10}Br$	C_4H_9	Cr 56.5 I	[59]
51	$O(CH_2)_{10}Br$	C_5H_{11}	Cr 25 I	[20]
52	$O(CH_2)_{11}Br$	C_6H_{13}	Cr 46 I	[48]
53	$O(CH_2)_5SH$	C_6H_{13}	Cr 94 Col 105 I	[60]
54	$O(CH_2)_{10}SH$	C_5H_{11}	?	[26]
55	$O(CH_2)_2O(CH_2)_2SCOCH_3$	C_6H_{13}	Cr 60.4 Col 74.7 I	[35]
56	$O(CH_2)_2O(CH_2)_2SH$	C_6H_{13}	Cr 75 Col 90.4 I	[35]
57	Br	C_5H_{11}	Col$_x$ 19 Col$_h$ 165 I	[19]
58	Br	C_6H_{13}	Cr 54 Col 142 I	[50]
59	CN	C_5H_{11}	Cr 51 Col$_X$ 85 Col$_h$ 226 I	[23]
60	CN	C_6H_{13}	Cr 75 Cr 93 Col 214 I	[50]
61	$C{\equiv}CSiMe_3$	C_5H_{11}	g −50 Col$_h$ 184 I	[23]
62	$C{\equiv}CMe_2OH$	C_5H_{11}	Cr 58 Col$_h$ 180 I	[23]
63	$C{\equiv}CC_4H_9$	C_5H_{11}	Cr 44 Col$_h$ 155 I	[23]
64	$C{\equiv}CH$	C_5H_{11}	g ? Col$_h$ 146 I	[23]
65	C_6H_{13}	C_5H_{11}	Cr 81 I	[23]
66	$COCH_3$	OC_5H_{11}	Cr 58 Cr 76 Col$_h$ 169 I	[23]
67	$O(CH_2)_2OCOCH{=}CH_2$	C_4H_9	Cr 64 Col$_h$ 116 I	[31]
68	$O(CH_2)_3OCOCH{=}CH_2$	C_4H_9	Cr 63 Cr 83 X 89 Col$_h$ 102 I	[31]
69	$O(CH_2)_2OCOCH{=}CH_2$	C_5H_{11}	Cr 65 X 68 Col$_h$ 97 I	[31]
70	$O(CH_2)_4OCOCH{=}CH_2$	C_5H_{11}	Cr 44 Col$_h$ 84 I	[31]
71	$O(CH_2)_6OCOCH{=}CH_2$	C_5H_{11}	Cr 46 Col$_h$ 54 I	[31]
72	$O(CH_2)_6OCOCH{=}CH_2$	C_6H_{13}	Cr 46 I	[41]
73	$O(CH_2)_6OCOC(CH_3){=}CH_2$	C_6H_{13}	Cr 48 I	[41]
74	$O(CH_2)_{11}OCOC(CH_3){=}CH_2$	C_6H_{13}	Cr 35 I	[48]
75	$O(CH_2CH_2O)_2COCH{=}CH_2$	C_6H_{13}	Cr 48 Col 64 I	[41]
76	$O(CH_2CH_2O)_2COC(CH_3){=}CH_2$	C_6H_{13}	Cr 45 Col 56 I	[41]
77	$O(CH_2CH_2O)_2CH_3$	C_6H_{13}	Cr 55.4 Col$_h$ 69.3 I	[76]
78	$O(CH_2)_6OH$	C_6H_{13}	Cr 62 Col 67 I	[41]
79	$O(CH_2)_2O(CH_2)_2OH$	C_6H_{13}	Cr 60 Col 66 Col 78 I	[41]
80		C_5H_{11}	Cr 106 I	[74]
81		C_5H_{11}	Cr 72 I	[74]

Table 3. (*Continued*)



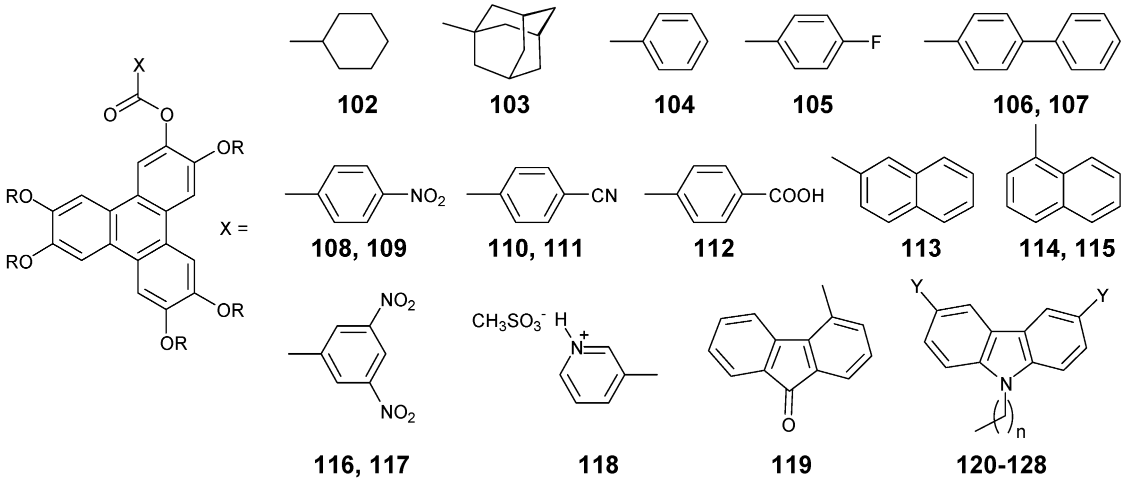
St.	*X*	*R*	Phase transition	Ref.
82		C_5H_{11}	Cr 52–55 I	[69]
83		C_6H_{13}	Cr 53–57 I	[69]
84	$Y = H$	C_5H_{11}	Cr 43 M_x 67 I	[68]
85	$Y = H$	C_6H_{13}	Cr 52 M_x 61 I	[68]
86	$Y = H$	C_7H_{15}	Cr 38 ?	[68]
87	$Y = H$	C_8H_{17}	Cr 40 M_x 53 I	[68]
88	$Y = H$	C_9H_{19}	Cr 21 Cr 31 M_x 44 I	[68]
89	$Y = H$	$C_{10}H_{21}$	Cr 37 Cr 49 M_x 63 I	[68]
90	$Y = C_6H_{13}$	C_6H_{13}	g 40 Col 96.9 I	[96]
91		C_6H_{13}	Cr 52–54 I	[70]
92		C_6H_{13}	Cr 42–44 I	[70]
93			g 19.4 Col 56.3 I	[71]

[102]. The trimerization using chloranil is limited to the preparation of hexamethoxytriphenylene; with higher homologues such as 1,2-dihexyloxybenzene it gives only a poor yield of hexahexyloxytriphenylene with many side products. Therefore, to prepare these long-chain derivatives, the methyl groups of hexamethoxytriphenylene are dealkylated with boron tribromide or HBr, and the resulting hexaphenol is then alkylated with an appropriate alkyl halide to obtain different hexaalkoxy triphenylene discotics [15].

A very clean synthesis of hexalkoxytriphenylenes in moderate yield is the cyclic anodic trimerization of dialkoxybenzene followed by a chemical or electrochemical reductive work-up [115], but this slow reaction is only applicable to a very small scale, and thus limited in its use. However, this provided a clue that a chemical reductive work-up in the oxidative trimerization process may improve the yield of hexaalkoxytriphenylenes. A dramatic advancement in the synthesis of triphenylene hexaethers was achieved by the Leeds group who used only a catalytic amount of H_2SO_4 (0.3%) in dichloromethane followed by a reductive work-up. Preparation of different alkoxytriphenylenes in 55–86% yields was reported using this method [16].

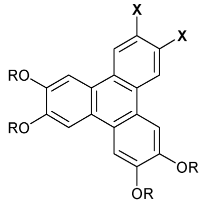
Recently two novel reagents, molybdenum pentachloride [36] and vanadium oxytrichloride [78], were reported to be highly efficient for the preparation of triphenylene ethers. It is observed that even the catalytic amount of H_2SO_4 is not required for this trimerization. Unlike $FeCl_3$ and $MoCl_5$, $VOCl_3$ is a liquid oxidizing reagent and miscible with various organic solvents. This may be a reason for the almost spontaneous trimerization of dialkoxybenzenes into hexaalkoxytriphenylenes using $VOCl_3$. Dichloromethane

Table 4. Thermal behaviour (°C) of unsymmetrical hexasubstituted triphenylene derivatives having one ester and five alkoxy substitutions.



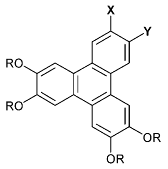
St.	*X*	*R*	Phase transition	Ref.
94	CH_3	C_6H_{13}	Cr 66 Col_h 136 I	[85]
95	C_5H_{11}	C_6H_{13}	Cr 49 Col_h 154 I	[85]
96	$(CH_2)_4(CF_2)_3CF_3$	C_5H_{11}	Cr 38 Col_h 98 I	[17]
97	$C(CH_3)_3$	C_5H_{11}	Col_p 65 Col_h 178 I	[30]
98	$CH(Cl)CH_2CH(CH_3)_2$	C_4H_9	Col 200.7 I	[40]
99	$CH(Cl)CH(CH_3)C_2H_5$	C_4H_9	Col 192.7 I	[40]
100	$CH(Cl)CH_2CH(CH_3)_2$	C_5H_{11}	Col 191.1 I	[40]
101	$CH_2CH_2CH{=}CH_2$	C_4H_9	g −43 Col_p 78 Col_{ho} 188 I	[62]
102		C_5H_{11}	g −43 Col_{ho} 190 I	[32]
103		C_5H_{11}	Col_p 135 Col_{ho} 186 I	[30]
104		C_5H_{11}	Col_h 193 I	[51]
105		C_6H_{13}	Cr<0 Col_h 182 I	[85]
106		C_5H_{11}	Cr 94 Col_h 135 I	[51]
107		C_6H_{13}	Cr 55 Col_h 147 I	[85]
108		C_5H_{11}	Cr 74 Col_h 190 I	[51]
109		C_6H_{13}	Cr 59 Col_h 175 I	[85]
110		C_5H_{11}	g 0 Col_{ho} 186 I	[32]
111		C_6H_{13}	Cr 59 Col_h 175 I	[85]
112		C_5H_{11}	Cr 203 Col_h ? I	[51]
113		C_6H_{13}	Cr 162 I	[85]
114		C_5H_{11}	Cr 103 Col_h 158 I	[51]
115		C_6H_{13}	Cr<0 Col_h 121 I	[85]
116		C_5H_{11}	Cr 131 Col_h 201 I	[51]
117		C_6H_{13}	Cr 110 Col_h 192 I	[85]
118		C_5H_{11}	Cr (168) Col_h 199 I	[51]
119		C_5H_{11}	Cr (124) Col_h 147 I	[51]
120	$Y{=}H$; $n{=}3$	C_5H_{11}	Cr 77 I	[74]
121	$Y{=}H$; $n{=}5$	C_5H_{11}	Cr 99 I	[74]
122	$Y{=}H$; $n{=}7$	C_5H_{11}	Cr 78 I	[74]
123	$Y{=}COC_4H_9$; $n{=}5$	C_5H_{11}	Cr 58 I	[105]
124	$Y{=}COC_4H_9$; $n{=}10$	C_5H_{11}	Cr 58 I	[105]
125	$Y{=}COC_{14}H_{29}$; $n{=}4$	C_5H_{11}	Cr 58 I	[105]
126	$Y{=}COC_4H_9$; $n{=}5$	C_6H_{13}	Cr 58 I	[105]
127	$Y{=}COC_4H_9$; $n{=}5$	C_7H_{15}	Cr 58 I	[105]
128	$Y{=}C_6H_{13}$; $n{=}5$	C_4H_9	Cr 58 I	[105]

Table 5. Thermal behaviour (°C) of unsymmetrical hexasubstituted triphenylene derivatives of the following structure.



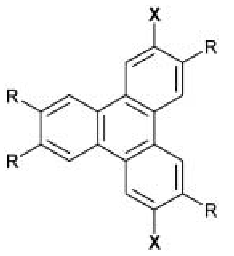
St.	*X*	*R*	Phase transition	Ref.
129	Br	C_6H_{13}	Cr 130 Col 141 I	[42]
130	SC_6H_{13}	C_6H_{13}	Cr (81) Col$_h$ 86 I	[77]
131	$O(CH_2)_2CH(CH_3)(CH_2)_3CH(CH_3)_2$	C_5H_{11}	Col$_h$ 63 I	[78]
132	$O(CH_2)_3COOH$	C_6H_{13}	Cr (117) Col$_h$ 130 I	[79]
133	$O(CH_2)_4COOH$	C_6H_{13}	Cr 94 Col 102 Col$_h$ 105.3 I	[79]
134	$O(CH_2)_5COOH$	C_6H_{13}	Cr (78) Col$_h$ 103.8 I	[79]
135	$O(CH_2)_6COOH$	C_6H_{13}	Cr (68) Col$_h$ 106.1 I	[79]
136	$O(CH_2)_7COOH$	C_6H_{13}	Cr 95.4 I	[79]
137	$O(CH_2)_{10}COOH$	C_6H_{13}	Cr 69.1 I	[79]
138	$O(CH_2)_5SH$	C_6H_{13}	Cr 67 Col$_h$ 79 I	[60]
139	OCH_3	C_5H_{11}	Cr 80 I	[43]
140	OC_9H_{19}	C_5H_{11}	Cr 54 Col$_h$ 74 I	[43]
141	$OC_{10}H_{21}$	C_5H_{11}	Cr (56) Col$_h$ 57 I	[43]
142	$OC_{11}H_{23}$	C_5H_{11}	Cr 61 I	[43]
143	OC_4H_9	C_6H_{13}	Cr 59 Col$_h$ 90 I	[43]
144	OC_8H_{17}	C_6H_{13}	Cr 47 Col$_h$ 84 I	[43]
145	$OC_{10}H_{21}$	C_6H_{13}	Cr 58 Col$_h$ 74 I	[43]
146	$OC_{12}H_{25}$	C_6H_{13}	Cr 64 I	[43]
147	OC_4H_9	C_8H_{17}	Cr 60 Col$_h$ 67 I	[43]
148	OC_6H_{13}	C_8H_{17}	Cr 46 Col$_h$ 84 I	[43]
149	$OC_{10}H_{21}$	C_8H_{17}	Cr 48 Col$_h$ 73 I	[43]
150	$OC_{12}H_{25}$	C_8H_{17}	Cr 51 Col$_h$ 61 I	[43]
151	OC_4H_9	$C_{10}H_{21}$	Cr 65 Col$_h$ 76 I	[43]
152	OC_5H_{11}	$C_{10}H_{21}$	Cr 61 Col$_h$ 63 I	[43]
153	OC_6H_{13}	$C_{10}H_{21}$	Cr 44 Col$_h$ 72 I	[43]
154	OC_8H_{17}	$C_{10}H_{21}$	Cr 60 Col$_h$ 86 I	[43]
155	$OC_{12}H_{25}$	$C_{10}H_{21}$	Cr 41 Col$_h$ 62 I	[43]
156	C_7H_{15}	C_6H_{13}	Cr 164 I	[105]

Table 6. Thermal behaviour (°C) of unsymmetrical hexasubstituted triphenylene derivatives of the following structure.



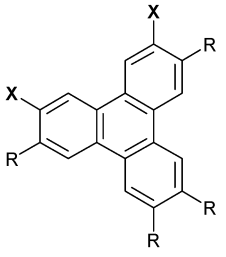
St.	*X*	*Y*	*R*	Phase transition	Ref.
157	OCH_3	OC_5H_{11}	C_4H_9	Cr 86.9 Col$_h$ 110.4 I	[78]
158	Br	CN	C_6H_{13}	Cr 170 Col 190 I	[42]
159	Br	SC_5H_{11}	C_5H_{11}	Cr 75.6 Col$_h$ 144.8 I	[92]
160	CN	SC_5H_{11}	C_5H_{11}	Cr 121 Col$_h$ 193.8 I	[92]
161	$C\equiv CMe_2OH$	SC_5H_{11}	C_5H_{11}	Cr 81.8 Col$_h$ 167.8 I	[92]
162	$C\equiv CH$	SC_5H_{11}	C_5H_{11}	Cr 57.7 Col$_h$ 125.4 I	[92]
163	OCH_3	St. 84	C_5H_{11}	Cr 33 Cr 66 ?	[69]
164	OCH_3	St. 85	C_6H_{13}	Cr 59 Cr 89 Col 102 I	[69]
165	OCH_3	St. 91	C_6H_{13}	Cr 42–44 I	[70]
166	OCH_3	St. 92	C_6H_{13}	Cr 76–78 I	[70]

Table 7. Thermal behaviour (°C) of unsymmetrical hexasubstituted triphenylene derivatives of the following structural type.



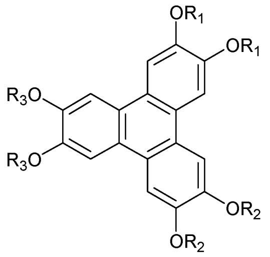
St.	*X*	*R*	Phase transition	Ref.
167	$O(CH_2)_6CH{=}CH_2$	OC_5H_{11}	Cr 55 Col_h 73 I	[21]
168	$O(CH_2CH_2O)_2CH_3$	OC_6H_{13}	Cr 44 I	[76]
169	Br	OC_6H_{13}	Cr 40 Col_h 179 I	[77]
170	SC_6H_{13}	OC_6H_{13}	Cr 24 Col_h 102 I	[77]
171	OC_6H_{13}	SC_6H_{13}	Cr 54 Col_h 100.5 I	[77]
172	St. **25**	OC_5H_{11}	Cr 114 I	[74]
173	St. **11**	OC_5H_{11}	Cr 147 I	[74]
174	$OCH_2COO\ C_2H_5$	OC_6H_{13}	Cr 88.5 Col_h 129.2 I	[104]
175	C_7H_{15}	OC_6H_{13}	Cr 170 I	[105]
176	OC_6H_{13}	C_7H_{15}	Cr 157 I	[105]

Table 8. Thermal behaviour (°C) of unsymmetrical hexasubstituted triphenylene derivatives of the following structure.



St.	*X*	*R*	Phase transition	Ref.
177	Br	OC_6H_{13}	Cr 63 Col_h 179 I	[77]
178	SC_6H_{13}	OC_6H_{13}	Cr 45 Col_h 123 I	[77]
179	OC_6H_{13}	SC_6H_{13}	Cr 72 Col_h 111 I	[77]
180	C_7H_{15}	OC_6H_{13}	Cr 175 I	[105]
181	OC_6H_{13}	C_7H_{15}	Cr 155 I	[105]

Table 9. Thermal behaviour (°C) of unsymmetrical hexasubstituted triphenylene derivatives with three different types of alkoxy chains. All data from ref. [43].



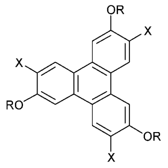
St.	R_1	R_2	R_3	Phase transition
182	C_4H_9	C_6H_{13}	C_8H_{17}	Cr 48 Col_h 72 I
183	$C_{10}H_{21}$	C_6H_{13}	C_8H_{17}	Cr 47 Col_h 75 I
184	$C_{12}H_{25}$	C_6H_{13}	C_8H_{17}	Cr 39 Col_h 75 I
185	$C_{12}H_{25}$	C_8H_{17}	$C_{10}H_{21}$	Cr 47 Col_h 65 I

was found to be the only solvent that gives a good yield of the trimerization product [78]. The reason for the poor performance of the reaction in various other solvents is still not clear. Although $MoCl_5$ and $VOCl_3$ are reported to give better yields, they are expensive and very sensitive to moisture. Therefore, the $FeCl_3$ method is perhaps the best method for preparing symmetrical hexaalkoxytriphenylenes in large amounts. However, as $MoCl_5$ and $VOCl_3$ allow milder reaction conditions, giving fewer purification problems and better yields in trimerization as well as in phenyl–biphenyl coupling reactions, they may be better choices for small-scale laboratory preparations. Hexaesters of triphenylene are still prepared from hexahydroxytriphenylene. An improved synthesis of this polyphenol has recently been reported by Bechgaard and co-workers [37].

3.2. *Hydroxy-functionalized hexa-substituted triphenylene derivatives*

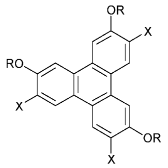
The hydroxy-functionalized triphenylenes are very valuable precursors for the synthesis of dimers, oligomers, polymers, networks, mixed tails, lower and higher degree substituted derivatives. Seven different types of alkoxy-hydroxytriphenylene derivatives, **296** (monohydroxy), **297** (2,3-dihydroxy), **298** (2,6-dihydroxy),

Table 10. Thermal behaviour (°C) of symmetrical mixed tail hexasubstituted triphenylenes.



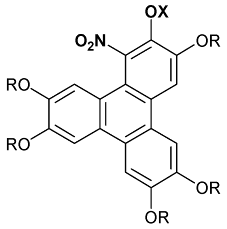
St.	*R*	*X*	Phase transition	Ref.
186	C_5H_{11}	Br	Cr 187 Col$_h$ 216 I	[24]
187	C_5H_{11}	$COCH_3$	g? Col$_X$ 194 Col$_h$ 250 I	[24]
188	C_5H_{11}	COC_5H_{11}	g? Col$_h$ 274 I	[24]
189	C_5H_{11}	SC_5H_{11}	Cr 27 Col$_h$ 127 I	[24]
190	C_5H_{11}	$C{\equiv}CSiMe_3$	Cr 213 Col$_X$ 236 I	[24]
191	C_5H_{11}	$C{\equiv}CMe_2OH$	Cr 118 Col$_h$ 250 dec	[24]
192	C_5H_{11}	$C{\equiv}CC_4H_9$	Cr 17 Col$_X$ 33 Col$_h$ 165 I	[24]
193	C_5H_{11}	$OCOCH(Cl)CH(CH_3)C_2H_5$	Cr 200.9 I	[40]
194	C_5H_{11}	$OCOCH_3$	Cr 185 I	[52]
195	C_5H_{11}	$OCOC_3H_7$	Cr 132.7 Col$_h$ 253.9 I	[52]
196	C_5H_{11}	$OCOC_4H_9$	Cr 130.6 Col$_h$ 244.6 I	[52]
197	C_5H_{11}	$OCOC_5H_{11}$	Cr 109.9 Col$_h$ 218.4 I	[52]
198	C_5H_{11}	$OCOC_7H_{15}$	Cr 61.8 Col$_h$ 168.3 I	[52]
199	C_5H_{11}	$OCOC_8H_{17}$	Cr 31.5 I	[52]
200	C_5H_{11}	OC_3H_7	Cr ? Col$_h$ 105 I	[63]
201	C_5H_{11}	OC_4H_9	Cr ? Col$_h$ 129 I	[63]
202	C_5H_{11}	OC_6H_{13}	Cr ? Col$_h$ 106 I	[63]
203	C_5H_{11}	OC_7H_{15}	Cr ? Col$_h$ 91 I	[63]
204	C_5H_{11}	OC_8H_{17}	Cr ? Col$_h$ 68 I	[63]
205	C_5H_{11}	OC_9H_{19}	Cr ? Col$_h$ 59 I	[63]
206	C_6H_{13}	OC_4H_9	Cr ? Col$_h$ 96 I	[63]
207	$(CH_2)_5SH$	OC_6H_{13}	Col$_h$ 44.1 I	[60]
208	C_5H_{11}	St. **11**	Cr 132 I	[74]
209	C_5H_{11}	St. **25**	Cr 106 I	[74]
210	C_5H_{11}	St. **121**; $Y{=}C_6H_{13}$	?	[106]
211	C_5H_{11}	St. **121**; Y–COC_5H_{11}	Cr 92 I	[106]

Table 11. Thermal behaviour (°C) of unsymmetrical mixed tail hexasubstituted triphenylenes.



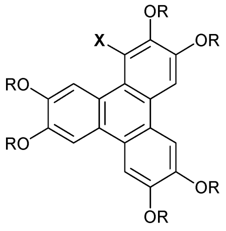
St.	*R*	*X*	Phase transition	Ref.
212	C_5H_{11}	Br	Cr 104 Col$_h$ 195 I	[24]
213	C_5H_{11}	$C{\equiv}CSiMe_3$	Cr 117 Col$_X$ 217 I	[24]
214	C_5H_{11}	$OCOCH_3$	Cr 146.5 I	[52]
215	C_5H_{11}	$OCOC_3H_7$	Cr 61.7 Col$_h$ 230.2 I	[52]
216	C_5H_{11}	$OCOC_4H_9$	Cr 82.5 Col$_h$ 227.6 I	[52]
217	C_5H_{11}	$OCOC_5H_{11}$	Cr 69.2 Col$_h$ 203.3 I	[52]
218	C_5H_{11}	$OCOC_7H_{15}$	Cr 61.9 Col$_h$ 155.3 I	[52]
219	C_5H_{11}	$OCOC_8H_{17}$	Cr 56.5 Col$_h$ 126.7 I	[52]
220	C_6H_{13}	$O(CH_2CH_2O)_2CH_3$	Cr 36 I	[76]
221	C_5H_{11}	St. **11**	Cr 122 I	[74]
222	C_5H_{11}	St. **25**	Cr 104 I	[74]
223	C_5H_{11}	St. **121**; $Y{=}C_6H_{13}$	?	[106]
224	C_5H_{11}	St. **121**; $Y{=}COC_5H_{11}$	Cr 78 I	[106]

Table 12. Thermal behaviour (°C) of α-nitro-triphenylene derivatives.



St.	*R*	*X*	Phase transition	Ref.
225	C_2H_5	C_2H_5	Cr 179 I	[102]
226	C_3H_7	C_3H_7	Cr 131.6 Col 147.5 I	[102]
227	C_4H_9	C_4H_9	Cr 61.2 Col_h 141.3 I	[44]
			Cr 53 Col 143.3 I	[102]
228	C_5H_{11}	C_5H_{11}	Col_h 141.4 I	[53]
			Cr < −20 Col 141.4 I	[102]
229	C_6H_{13}	C_6H_{13}	Cr 42.9 Col_h 137.3 I	[33]
			Cr < −20 Col 137 I	[102]
230	C_7H_{15}	C_7H_{15}	Col_h 129.8 I	[33]
			Cr < −20 Col 129.3 I	[102]
231	C_8H_{17}	C_8H_{17}	Cr < −20 Col 128.4 I	[102]
232	C_9H_{19}	C_9H_{19}	Cr 0 Col 127 I	[102]
233	$C_{10}H_{21}$	$C_{10}H_{21}$	Cr 7.1 Col 118.4 I	[102]
234	$C_{11}H_{23}$	$C_{11}H_{23}$	Cr 27 Cr 37.3 Col 116 I	[102]
235	$C_{12}H_{25}$	$C_{12}H_{25}$	Cr 31 Cr 39.8 Col 107.7 I	[102]
236	$C_{14}H_{29}$	$C_{14}H_{29}$	Cr 40.6 Cr 52 Col 97 I	[102]
237	$C_{16}H_{33}$	$C_{16}H_{33}$	Cr 37.5 Cr 63.9 Col 86.1 I	[102]
238	C_4H_9	H	Cr 106 dec	[53]
239	C_5H_{11}	H	Cr 105 dec	[53]
240	C_4H_9	$COCH_3$	Cr 155 I	[53]
241	C_5H_{11}	$COCH_3$	Cr 72.8 Cr 129.8 Col_h 141 I	[53]
242	C_4H_9	CH_2CH_2OH	Col_x 127.8 Col_h 144.4 I	[53]
243	C_5H_{11}	CH_2CH_2OH	Cr 95.6 Col_h 130.3 I	[53]
244	C_5H_{11}	$(CH_2CH_2O)_2COCH{=}CH_2$	Cr 68 Col_h 141 I	[95]

Table 13. Thermal behaviour (°C) of heptasubstituted triphenylene derivatives.



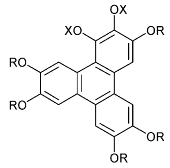
St.	*R*	*X*	Phase transition	Ref.
245	C_4H_9	NH_2	Cr 102 I	[44]
246	C_6H_{13}	NH_2	Cr 53.6 Col_h 69.1 I	[33]
			Cr 35 Col 77 I	[16]
247	C_4H_9	$NHCOCH_3$	Cr 132.9 Col_h 172.1 I	[44]
248	C_6H_{13}	Cl	Cr 31.1 Col_h 96.1 I	[33]
			Cr 37 Col 98 I	[16]
249	C_4H_9	Cl	Cr 55 Col 96 Col_h 112.2 I	[78]
250	C_6H_{13}	Br	Cr 37 Col_h 83 I	[33]
251	C_6H_{13}	F	Cr 39 Col_h 116 I	[34]
			Cr 43.8 Col_h 123.1 I	[80]

299 (2,7-dihydroxy), **300** (2,11-dihydroxy), **301** (2,6,10-trihydroxy) and **302** (2,6,11-trihydroxy), have been prepared using selective or non-selective chemical methods.

To prepare side chain and main chain polymers, the Ringsdorf group prepared mono- and di-acetyltriphenylenes by partial alkylation of hexaacetoxytriphenylene in low yields [116]. These acetyltriphenylenes can be hydrolysed to hydroxytriphenylenes. Later, they reported the synthesis of various hydroxytriphenylenes by a non-selctive cleavage of alkoxy chains of a hexaalkoxytriphenylene using 9-Br-BBN [117]. This reagent under optimized conditions affords two isomeric trialkoxy-trihydroxytriphenylenes in high yield [38].

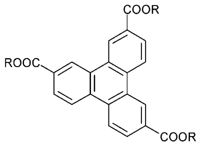
It is evident from the literature that an arylmethyl ether can be selectively cleaved in the presence of other arylalkyl ethers. This strategy was utilized to develop a rational synthesis of various mono- and di-hydroxytriphenylenes [118]. Monomethoxypentaalkoxy- and dimethoxytetraalkoxy-triphenylenes can be prepared

Table 14. Thermal behaviour (°C) of heptasubstituted triphenylene derivatives of the following structure. All data from ref. [64].



St.	*R*	*X*	Phase transition
252	C_3H_7	C_3H_7	Cr 92.3 I
253	C_4H_9	C_4H_9	Cr 65.7 Col 70.1 I
254	C_5H_{11}	C_5H_{11}	Cr 45.7 Col$_h$ 75.0 I
255	C_6H_{13}	C_6H_{13}	Cr 44.6 Col$_h$ 69.5 I
256	C_7H_{15}	C_7H_{15}	Cr 46.6 Col$_h$ 71.8 I
257	C_8H_{17}	C_8H_{17}	Cr 44.3 Col$_h$ 68.7 I
258	C_3H_7	$C_{12}H_{25}$	Cr 50.3 I
259	C_4H_9	C_3H_7	Cr 74.3 I
260	C_4H_9	C_5H_{11}	Cr 58.7 Col$_h$ 69.3 I
261	C_4H_9	C_6H_{13}	Cr 56.2 Col$_h$ 59.1 I
262	C_4H_9	C_7H_{15}	Col$_h$ 47.6 I
263	C_5H_{11}	C_4H_9	Cr 47.9 Col$_h$ 70.5 I
264	C_5H_{11}	C_6H_{13}	Cr 47.6 Col$_h$ 68.6 I
265	C_8H_{17}	$C_{10}H_{21}$	Col$_h$ 63.9 I
266	C_3H_7	$COCH_3$	Cr 152.0 I
267	C_4H_9	$COCH_3$	Cr 122.3 I
268	C_5H_{11}	$COCH_3$	Cr 88.1 Col$_h$ 105.7 I
269	C_6H_{13}	$COCH_3$	Cr 85.6 Col$_h$ 90.0 I
270	C_7H_{15}	$COCH_3$	Cr 72.9 Col$_h$ 90.6 I
271	C_8H_{17}	$COCH_3$	Cr 57.8 Col$_h$ 88.7 I
272	C_4H_9	COC_3H_7	Col$_x$ 97.4 Col$_h$ 121.1 I
273	C_5H_{11}	COC_4H_9	Col$_h$ 129.1 I
274	C_8H_{17}	COC_7H_{15}	Cr 55.5 Col$_h$ 121.7 I

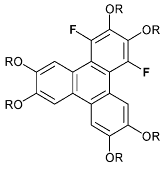
Table 15. Thermal behaviour (°C) of trisubstituted triphenylene derivatives. All data from ref. [87].



St.	*R*	Phase transition
275	CH_3	Cr 258 I
276	C_2H_5	Cr (135) Col 161 I
277	C_3H_7	Cr (82) N$_D$ 137 I
278	C_4H_9	Cr (59) N$_D$ 86 I
279	C_5H_{11}	Cr 111 I
280	C_6H_{13}	Cr 101 I
281	C_8H_{17}	Cr 77 I
282	$CH_2CH(C_2H_5)C_4H_9$	Cr 111 Col 124 I

by the so-called biphenyl route [118]. This multi-step synthesis provides well-defined final products in moderate yields. Scheme 2 shows the synthesis of 2,7-dihydroxy-3,6,8,9-tetralkoxytriphenylene using this method [104].

Table 16. Thermal behaviour (°C) of octatasubstituted triphenylene derivatives.



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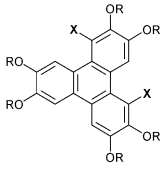
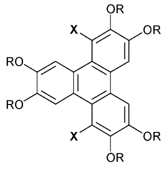


284 - 286



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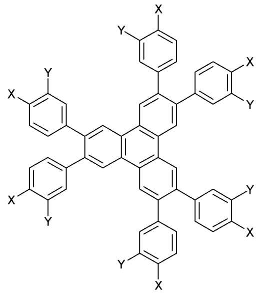
St.	*R*	*X*	Phase transition	Ref.
283	C_6H_{13}		Col 121.2 I	[80]
284	C_4H_9	NO_2	Cr 109 I	[53]
285	C_5H_{11}	NO_2	Cr 60.6 Col$_h$ 96 I	[53]
286	C_7H_{15}	NO_2	Col$_h$ 80–85 I	[53]
287	C_6H_{13}	CN	Col$_h$ 236.9 I	[50]

Bushby and Lu very recently demonstrated the use of an isopropoxy masking group in a biphenyl-phenyl oxidative coupling route for the preparation of mono- and di-hydroxy-substituted triphenylenes [82]. An efficient synthetic procedure for the preparation of mono-, di- and trifunctionalized triphenylenes starting from the readily available hexaalkoxytriphenylene by aryl-ether cleavage with B-bromocatecholborane (2-bromo-1,3,2-benzodioxaboroles) was reported recently [46]. This reagent was particularly found to be very effective for the preparation of mono- and tri-hydroxytriphenylene derivatives. However, it should be noted that the separation of the monohydroxypentaalkoxytriphenylene from unreacted hexaalkoxytriphenylene is tedious and needs highly efficient column chromatography.

3.3. *Unsymmetrical and mixed tail hexa-substituted triphenylene derivatives*

Unsymmetrical peripheral substitution has a large effect on the thermal behaviour of liquid crystalline materials. The breaking of symmetry in a hexaalkoxytriphenylene can be achieved in different ways, for example, by changing the length of some of the side chains, by changing the nature of one or more of the side chains or by using lower or higher degrees of substitution. The last few years have witnessed a tremendous growth in the synthesis of unsymmetrical triphenylene discotics as evident from the synthesis of more than 200 new unsymmetrical triphenylene derivatives in just the past eight years. Traditionally, these materials have been prepared by oxidative trimerization of a mixture of two different 1,2-dialkoxybenzene derivatives [119] or by partial alkylation of hexaacetoxytriphenylene followed by alkylation [116]. More efficient methods have now been developed to prepare these materials. One of the most important methods is

Table 17. Thermal behaviour (°C) of polyphenylated triphenylene derivatives.



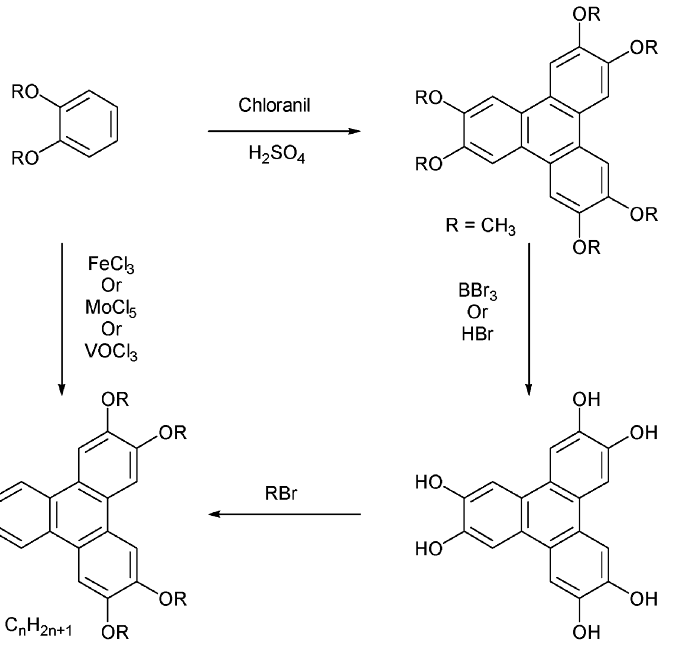
St.	*X*	*Y*	Phase transition	Ref.
288	OC_6H_{13}	OC_6H_{13}	Cr 111 Col_h 126 I	[67]
			Cr 65 Col_h 135 I	[66]
289	OC_8H_{17}	OC_8H_{17}	Cr 85 Col_h 104 I	[67]
290	$OC_{10}H_{21}$	$OC_{10}H_{21}$	Cr 74 Col_h 103 I	[67]
291	$OC_{12}H_{25}$	$OC_{12}H_{25}$	Cr 47 Col_h 101 I	[67]
292	C_9H_{19}	H	Cr 59 I	[83]
293	$C_{12}H_{25}$	H	Cr 36 I	[83]
294	OC_6H_{13}	H	Cr 153 I	[83]
295	$OC_{11}H_{23}$	H	Cr 66 I	[83]

the biphenyl–phenyl oxidative coupling [118] as shown in scheme 2. The hydroxyalkoxytriphenylenes **296**–**302**, described already, have been extensively used to prepare a number of unsymmetrical and mixed tail triphenylene DLCs using classical chemistry.

In a novel approach, a series of functionalized triphenylene DLCs were synthesized by reductive removal of hydroxy group(s) followed by electrophilic aromatic substitution at the exposed β-site (scheme 3). Thus a variety of functional groups can be introduced in the triphenylene nucleus. Such unsymmetrical and low degree-substituted triphenylenes can also be prepared using highly efficient but sophisticated organometallic chemistry [120]. Bromination of the non-liquid crystalline pentaalkoxytriphenylene **303** gives the liquid crystalline monobromo derivative **306**. It is interesting to note that the precursor molecules, monomethoxytriphenylene, monohydroxytriphenylene and pentaalkoxytriphenylene are not liquid crystalline. Dipolar interactions and/or extension of the core due to the bulky bromine atom may be the driving force for the induction of a mesophase. Compound **306** can also be prepared by a direct coupling of a tetraalkoxybiphenyl with 1-bromo-2-alkoxybenzene [50]. Several derivatives, such as cyano, and alkynes, can be prepared by replacing the bromine atom [23]. Interestingly and somewhat surprisingly, the classical nitration of **303** occurs preferentially in the sterically hindered 1-position indicating that electronic effects dominate in the nitration of alkoxytriphenylenes [23].

3.4. *Hepta-substituted triphenylene derivatives*

In order to enhance the mesophase stability in triphenylene discotics, earlier efforts focused mainly on the modification of the aliphatic tails. Recently the functionalization of the triphenylene nucleus by classical electrophilic aromatic substitution reactions was found to be useful in manipulating the physical



Scheme 1. Synthesis of hexaalkoxytriphenylenes.

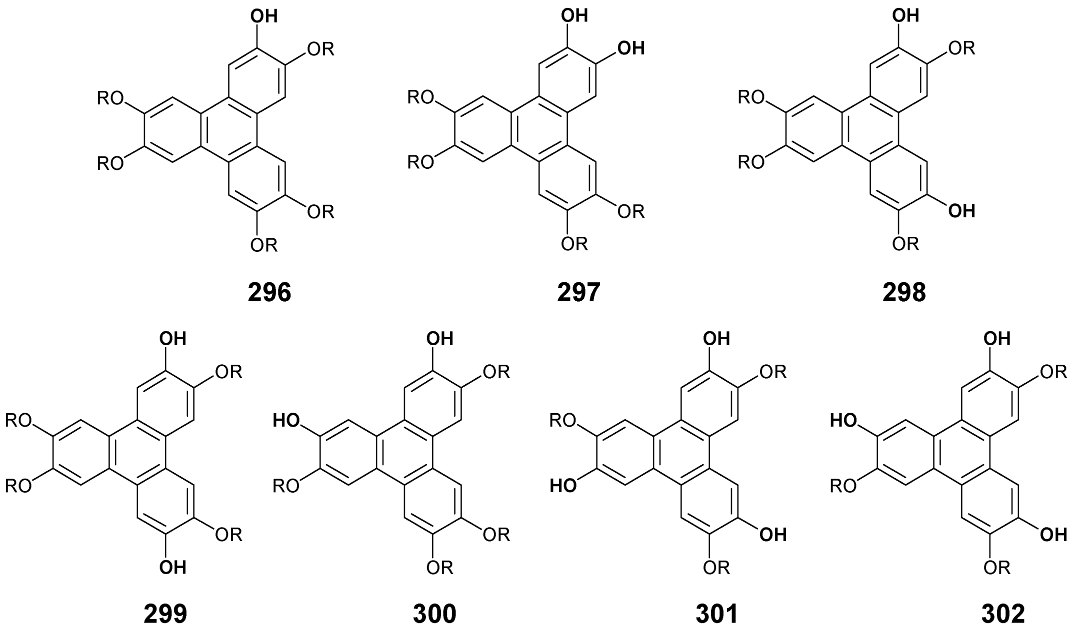
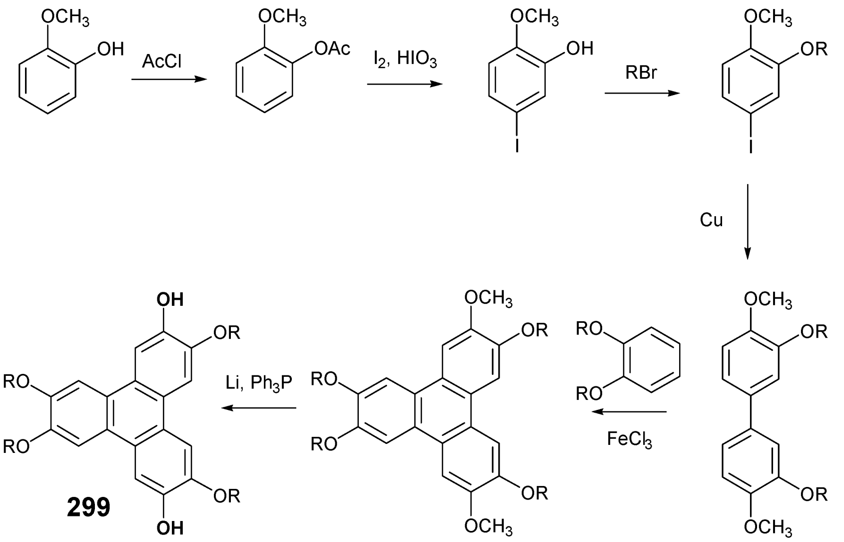


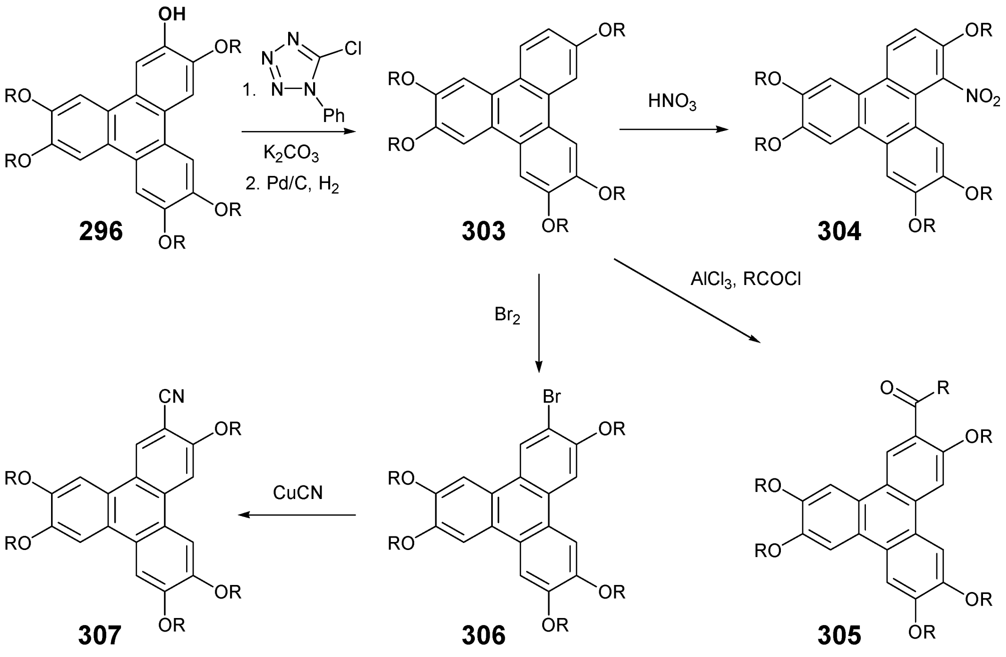
Figure 2. Chemical structures of different hydroxyalkoxytriphenylenes.

properties of these materials. A number of α-nitro, halo and cyano derivatives of hexaalkoxytriphenylene have been prepared. The functionalization of the nucleus at the α-position is important not only to induce colour, a molecular dipole, enhanced liquid crystalline properties and a chemically reactive site but also to helically deform the normally planar triphenylene core. This has recently been verified by single crystal X-ray analysis of 2,3,5,6,10,11-hexaethoxy-1-nitrotriphenylene [102].

There are three methods to prepare hepta-substituted triphenylenes. Firstly, direct electrophilic aromatic substitution in hexaalkoxytriphenylenes (scheme 4): Nitration of the parent hydrocarbon triphenylene is reported to yield a trinitro derivative, but under controlled conditions a mixture of 1-nitro- and 2-nitro-triphenylenes is formed [14]. In a pentaalkoxy-triphenylene, while classical electrophilic aromatic substitution reactions such as Friedel–Crafts acylation and halogenation give only β-substitution, nitration, as mentioned already, gives primarily the α-nitro product. In hexaalkoxytriphenylenes, only the α-positions, ('bay regions', 1, 4, 5, 8, 9 and 12 positions) are free for



Scheme 2. Synthesis of 2,7-dihydroxy-3,6,8,9-tetraalkoxytriphenylene.

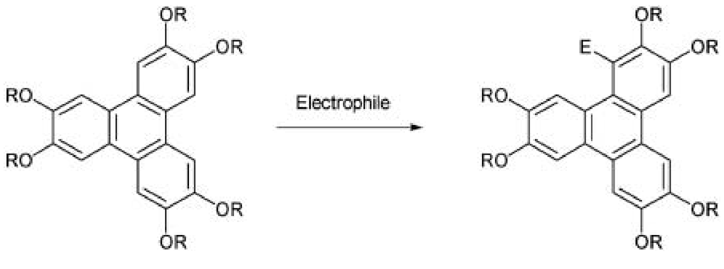


Scheme 3. Synthesis of core-functionalized hexasubstituted triphenylenes.

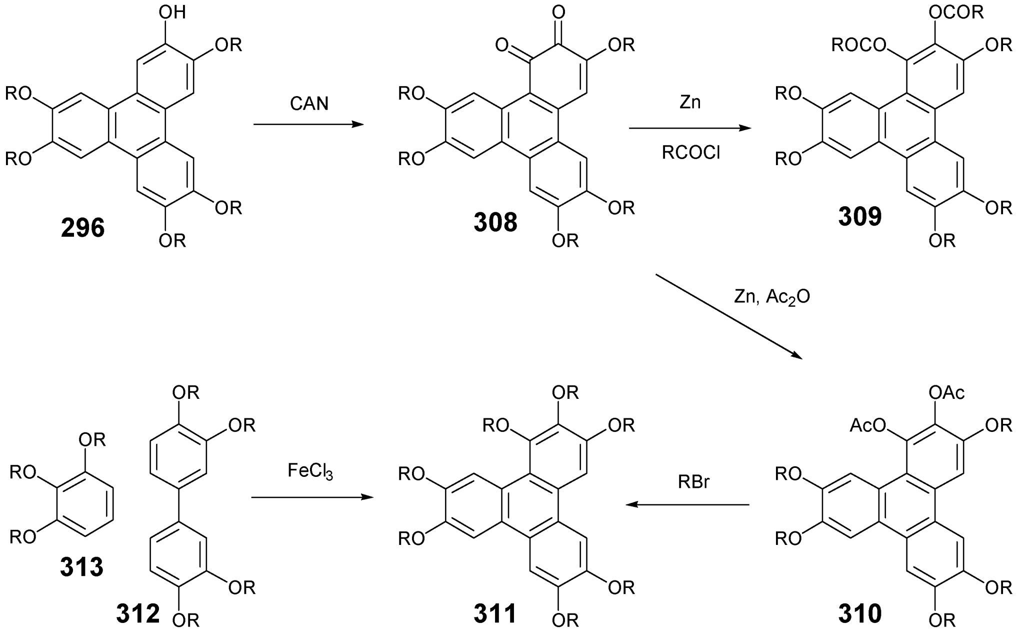
further substitution. Nitration of 2,3,6,7,10,11-hexaalkoxytriphenylenes provides the α-nitro product in very high yields. Solvents play an important role in the nitration of hexaalkoxytriphenylenes. In a mixture of ether–acetic acid, almost exclusively the α-nitro product is formed [16]. Even under exhaustive conditions, in this solvent system, only a small amount of trinitrohexaalkoxytriphenylene forms. Changing the solvent system from ether–acetic acid to dichloromethane–nitromethane imparts a dramatic effect and all three rings of triphenylene can be successively nitrated under very mild conditions. The trinitration proceeds with high regioselectivity to give exclusively one isomer having *C*3 symmetry, i.e. 1,5,9-trinitro-2,3,6,7,10,11-hexaalkoxytriphenylene. The monohydroxypentaalkoxytriphenylenes can also be nitrated at the α-position but this reaction is complicated and often only the oxidized products, the 3,6,7,10,11-pentaalkoxytriphenylene-1,2-diones, can be isolated. Alkoxynitrotriphenylenes are valuable precursors to several other derivatives, such as amino, mono- and di-alkylamino, acylamino and azo derivatives, and thus a number of new triphenylene derivatives can be prepared.

Chlorination of 2,3,6,7,10,11-hexahexyloxytriphenylene (HAT6) with iodine monochloride gives a mixture of 1-chloro-, 1,8-dichloro- and 1,5-dichloro-HAT6. Under exhaustive conditions it gives 1,4,5,9-tetrachloro-HAT6 [34]. Praefcke *et al* have also reported the synthesis of 1-chloro-HAT6 and 1-bromo-HAT6 by the chlorination of HAT6 with aluminium trichloride/sulphuryl chloride and bromination of HAT6 with bromine in carbon tetrachloride [33]. While the α-bromo atom could not be replaced by alkylthiolates, it can be easily replaced with a cyano nucleophile [33].

The second route to hepta-substituted triphenylenes, particularly heptaalkoxytriphenylenes, is the *o*-quinone route (scheme 5). Oxidation of the 2-hydroxy-3,6,7,10,11-pentaalkoxytriphenylenes **296** with various oxidizing agents such as chromium trioxide, nitric acid and ceric ammonium nitrate yields the ring-oxidized



Scheme 4. Synthesis of α-substituted hexaalkoxytriphenylenes.



Scheme 5. Synthesis of heptaalkoxy- and dialkanoyloxy-pentaalkoxytriphenylenes.

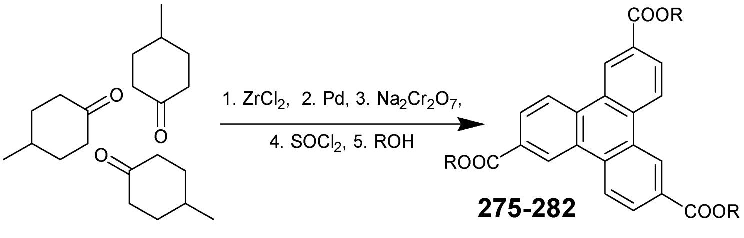
products, the 3,6,7,10,11-pentaalkoxytriphenylene-1,2-diones **308**. Reductive acetylation of these *o*-quinones with zinc and acetic anhydride in triethylamine results in the formation of diacetates **309**. Reductive esterification of the *o*-diquinone with various acid chlorides yields 1,2-dialkanoyloxy-3,6,7,10,11-pentaalkoxytriphenylenes **310**. These diacetates can be directly alkylated with various alkyl halides to produce symmetrical (having all seven chains identical) or unsymmetrical (two peripheral chains are different) heptaalkoxytriphenylenes **311** in very high yield [64].

Hepta-substituted triphenylenes can also be prepared by a biphenyl–phenyl oxidative coupling route (scheme 5). Thus, when tetraalkoxybiphenyls **312** were reacted with trialkoxybenzenes **313** under oxidative coupling conditions using either $MoCl_5$, $VOCl_3$ or $FeCl_3$, heptaalkoxytriphenylenes were formed in moderate yields. Similarly, unsymmetrical hepta-alkoxytriphenylenes can also be prepared using tetraalkoxybiphenyl and trialkoxybenzene derivatives having different chains. It should be noted that the unsymmetrical heptaalkoxytriphenylenes prepared from these two routes are different. The *o*-quinone route gives an unsymmetrical heptaalkoxytriphenylene where two out of seven chains are different, while the biphenyl route gives a product in which three out of seven chains are different. Moreover, mixed esters–ethers **309** can be achieved only via the *o*-quinone route as the phenyl–biphenyl coupling usually works only with highly electron-rich precursors [64].

3.5. *Other lower and higher substituted triphenylene derivatives*

Usually triphenylenes with less than six peripheral substitutions are not liquid crystalline. Exceptionally, a few alkyl esters of triphenylene 2,6,10-tricarboxylic acid have recently been claimed to be liquid crystalline [87]. These were prepared by the dehydrating cyclotrimerization of 4-methylcyclohexanone with $ZrCl_2$ as shown in scheme 6. The thermal behaviour of these derivatives is presented in table 15.

A few octasubstituted triphenylenes have also been



Scheme 6. Synthesis of triphenylene triesters.

found to be liquid crystalline (table 16). To date, no triphenylene derivative with more than eight substituents has been reported to be liquid crystalline.

3.6. *Extended triphenylenes*

It has been demonstrated that the degree of order determines charge mobility in columnar liquid crystalline materials [121]. It is expected that an increase in the orbital overlap area will lead to a higher charge mobility. Van de Craats has recently observed a positive effect of increasing the macrocyclic core size on the intracolumnar charge carrier mobility. Hexabenzocoronenes show remarkably high charge carrier mobilities (up to $0.38\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) in the liquid crystalline phase [122]. Another aim in extending the triphenylene core was to prepare novel board-like molecules between calamitic and discotic systems with the hope of finding the biaxial nematic phase [123]. Efforts have been made to extend the triphenylene core either by fusing-on phenyl rings in compounds such as benzo[b]triphenylene (**314**) [124], dibenzo[g,p]chrysene (**315**) [125], dibenzo[fg,op]naphthacene (**316**) [126], tetrabenzo[a,c,h,j]anthracene (**317**) [123], coronene (**318**) [127], hexabenzotrinaphthalene (**319**) [83]; or by attaching phenyl rings to the β-positions (table 17). The triphenylene core was also extended by attaching it to hetrocyclic systemes such as phenenthrophenazines (**320**, **321**) [58, 73], triphenylenophthalocyanine (**322**) [94] (figure 3). The physical properties of only polyphenylated triphenylenes are shown in table 17, as all other derivatives may be classified as new discotic cores. These materials have been prepared by palladium-catalysed cross-coupling between hexabromotriphenylene and an excess of arylboronic acids. It is noteworthy that although the solubility of hexabromotriphenylene is very poor in most organic solvents, aryl–aryl cross-coupling or nucleophilic displacement of the bromine atom works very well.

4. Physical properties

The concept of mesophase stabilization by the introduction of semifluorinated alkyl chains, well studied in calamitic systems, has been extended to triphenylene-based DLCs (**3–8**, **49**, **96**). The nature of the mesophase structure does not usually change with the introduction of fluorinated chains but the thermal behaviour is strongly affected [17]. In the case of butyloxy chains, the hexagonal plastic phase was converted to a disordered columnar phase upon terminal fluorination [100]. It has been reported recently that triphenylene discotics with such terminal fluoroalkylated chains show a strong tendency towards homeotropic alignment of the columnar phase [99].

Compounds **9** and **10** prepared from hexahydroxytriphenylene and 2-bromo-*N*-alkylacetamides were found to be efficient gelators of some hydrocarbon solvents. Formation of the hexagonal columnar phase and rectangular columnar phase in the cyclohexane gels of **9** and **10**, respectively, was observed by X-ray diffraction studies. Such organogelators have recently been reported to be useful as photo- and electrochemical materials [98].

Carbazole derivatives are well known for their photoconducting properties. Incorporation of the carbazole moiety in the supramolecular structure of triphenylene discotics may enhance their physical properties. To investigate this possibility, a number of triphenylene derivatives such as **11** and **25** (with hexapendent carbazole groups), **80**, **81**, **120–128** (with one pendent carbazole group), **172**, **173** (with two pendent carbazole groups) and **208–211**, **221–225** (with three pendent carbazole groups) were prepared but none of them show mesomorphic properties in the pure state. However, upon doping with the electron-acceptor trinitrofluorenone (TNF), the induction of a columnar phase due to charge-transfer (CT) complex formation was observed [74, 106].

CT interactions have a profound effect on the induction and stabilization of mesophases [128]. An interesting example is the creation of a columnar nematic and columnar hexagonal phase by mixing non-liquid crystalline multiynes with TNF [129, 130]. Computer simulation studies by Bates and Luckhurst indicate that the quadrupolar interaction may be responsible for the formation of such chemically induced liquid crystalline phases [130]. Recently, several examples of triphenylene derivatives were reported in which an electron acceptor such as TNF (**93**) or anthraquinone (**16**, **82–90**) was covalently connected to the electron-rich donor. While in some cases an intermolecular CT interaction between the electron deficient moiety and the triphenylene nucleus was observed [69], in many cases no additional CT band in the UV spectrum was detected [68]. In most of the discotic donor-σ-acceptor architectures the electron deficient moiety has been limited to non-liquid crystalline molecules, but recently in an interesting example, a liquid crystalline electron deficient unit was connected to the liquid crystalline electron rich triphenylene derivative [97]. Compound **90** displays a columnar mesophase over a wide temperature range, and it may be possible that the discotic liquid crystalline donor and acceptor subunits are segregated in different columns. However, further studies are required to confirm the detailed structure.

The conducting properties of tetrathiafulvalene and ferrocene derivatives have been well established, and an

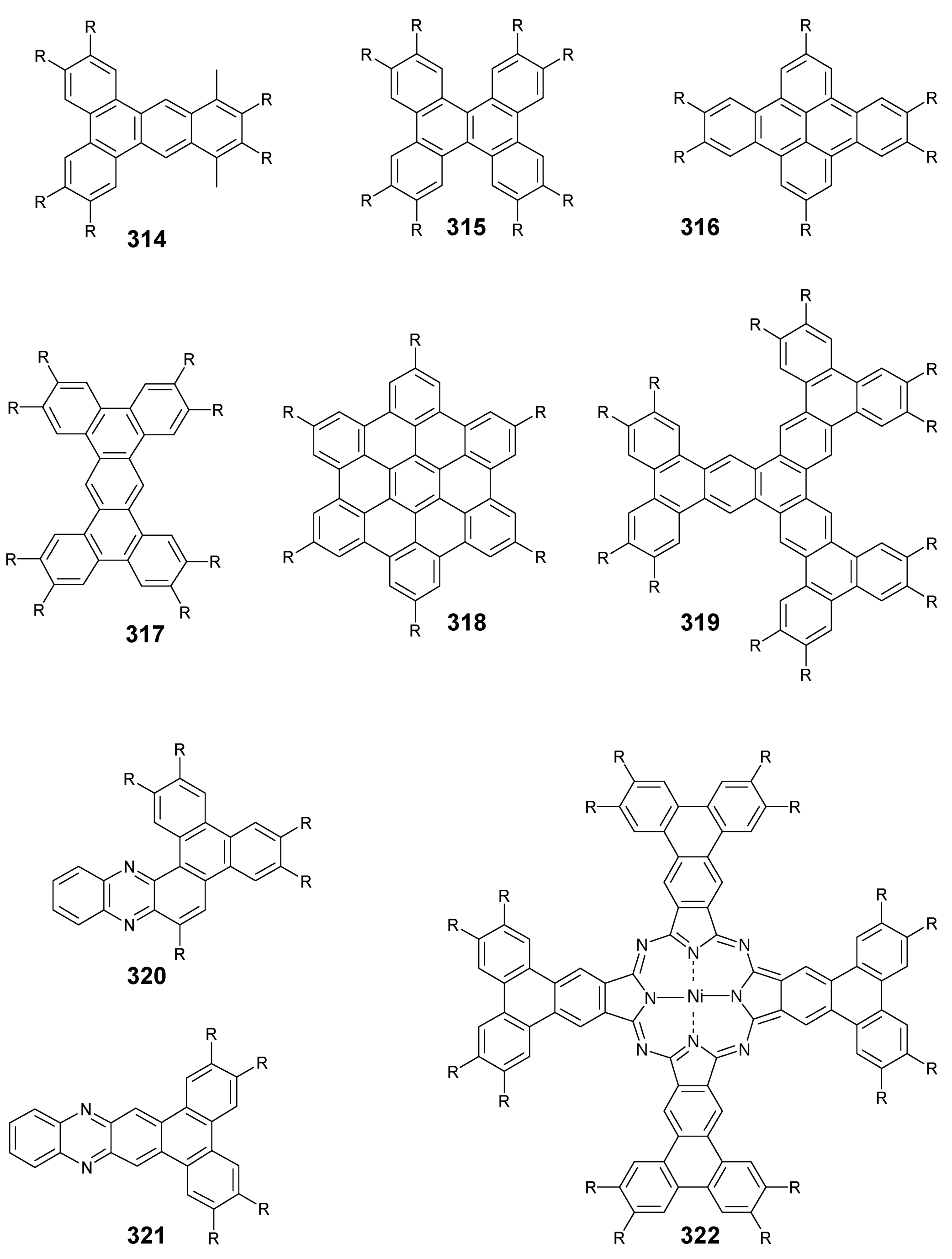


Figure 3. Chemical structures of some extended triphenylenes.

enormous effort has been directed towards the production of highly organized single crystals of these materials. In an approach to create a highly ordered supramolecular system, these moieties have been incorporated into triphenylene-based discotic molecules (**17**, **91**, **92**, **165**, **166**) but not one has shown mesomorphic properties.

Sugar-coated triphenylene-based discotic liquid crystals have been reported by the Stoddart group [89]. In compounds **12**–**15** bulky carbohydrate units are attached to the ends of the alkyl chains. These amphiphilic materials, having a central hydrophobic part and peripheral hydrophilic units, exhibit both thermotropic and lyotropic mesophase behaviour.

Two triphenylene mesogens (**18** and **47**) with peripheral azobenzene units were recently reported

[91, 101]. While compound **47** was found to show kinetically controlled monotropic bimesomorphism, with a metastable smectic and a stable hexagonal columnar phase, compound **18** exhibits an enantiotropic columnar phase.

The attachment of a flexible siloxane part to a calamitic or discotic core is known to suppress crystallization due to the bulkiness of these groups. These molecules show a strong tendency to freeze-in the mesophase on cooling and thus an increase in the mesophase range. A tetramethylcyclosiloxane-based triphenylene tetramer exhibits a glass transition at −48°C and clearing temperature 141°C. It shows no sign of crystallization on storage for a long time at room temperature [25]. Compound **24** is a new example in this group. The polymerizable olifinic precursor **23** is also liquid crystalline.

Among the hexaesters of triphenylene, hexabenzoates have received much attention as they display a nematic phase. It is interesting to note that only triphenylene benzoates and radial multiynes form the discotic nematic mesophase. This could be because of the relatively weak interactions between the imperfectly planar super-discs. Most of the triphenylene benzoates show the nematic phase at very high temperatures, limiting their use. In order to reduce their transition temperatures, lateral substitution in the inner and outer sides of the peripheral phenyl groups **26**–**37** was systematically investigated [18]. Lateral substitution, in general, suppresses columnar phases but the stability of the nematic phase remains relatively unaffected. While lateral alkyl group substitution does not change the nature of the mesophase, lateral polar group substitution significantly suppresses the nematic phase [61]. One of the chiral alkoxy chain-substituted hexabenzoates **37** is reported to exhibit a discotic blue phase [61]. A number of hexanaphthoates, **39**–**46**, were also found to display the discotic nematic phase at elevated temperatures in addition to a columnar rectangular phase [75].

The replacement of one of the alkoxy chains of a hexaalkoxytriphenylene by an ester group, **94**–**128**, results in a large effect on the nature and stability of the mesophase. Usually these monoalkanoyloxypentaalkoxytriphenylenes show a broader mesophase range than the parent hexaalkoxy or hexaalkanoyloxytriphenylene. When the ester group is bulky in nature, such as adamantanoate **103** or pivaloate **97**, a suppression of the crystallization and a stabilization of the mesophase was observed. In addition, these compounds also exhibit a more ordered plastic columnar phase at lower temperature [30]. Monoesters with a strongly polar group generally show higher melting points, and increasing the size of the ester group often decreases the mesophase range [85].

Replacing one of the alkoxy chains by a polar group such as Br or CN in a hexaalkoxytriphenylene (**57**–**60**) greatly stabilizes the columnar phase, and its range is enhanced. The presence of a more ordered mesophase and the enhancement of fluorescence was also reported in some of these polar monofunctionalized triphenylene discotics [23]. The replacement of a vicinal alkoxy chain by another Br atom (**129**) increases the melting point significantly, and consequently the columnar phase range decreases [42, 77]. On the other hand, the replacement of the alkoxy chain at other positions gives compounds such as 2,4-dibromo- (**169**) and 2,11-dibromo-tetraalkoxytriphenylene (**177**) with better mesophase ranges [77]. Both symmetrical and unsymmetrical tribromotrialkoxytriphenylenes (**186**, **212**) show very high melting and clearing temperatures [24]. Replacement of the β-halogen by the more polar cyano group increases the stability of columnar phase significantly [23, 50]. This effect is also observed when only one of the two halogens is converted to a cyano group [42]. The β-halogen(s) can be displaced by thioalkoxy group(s) to give a series of mixed alkoxy-thioalkoxy triphenylenes. The mesophase behaviour of these compounds is dependent on the position and relative number of substituents. Most of the compounds in this mixed alkylthio-alkoxy series show only the hexagonal columnar phase, but one compound, namely 3,6-bis(hexyloxy)-2,7,10,11-tetrakis(hexylthio)-triphenylene, is claimed to exhibit a highly ordered helical phase that has so far been observed only in hexahexylthiotriphenylene [77].

In mixed hexaalkoxytriphenylenes, unsymmetrical substitution generally reduces the clearing temperature. In most cases the maximum clearing temperature is found when all six alkoxy chains have an equal number of carbon atoms [43]. Compounds with shorter and longer alkyl chains connected to the core alternatively also show clearing temperatures lower than that of shorter-chain hexaalkoxytriphenylenes [63]. Interdigitation of chains is reported in such molecules. The mesophase range of mixed tail symmetrical and unsymmetrical triphenylenes having three alkoxy and three alkanoyloxy substitutions was reported to be much higher when compared with hexaether or hexaester derivatives of triphenylene [52]. Again, symmetrical mixed ether-ester derivatives are thermally more stable than unsymmetrical alkoxy-alkanoyloxytriphenylene derivatives. While mixed alkoxy, alkoxy-thioalkyl, alkoxy-alkanoyloxy, alkoxy-alkenyl, alkoxy-ketoalkyl compounds are generally liquid crystalline, mixed alkoxy-alkyl derivatives of triphenylene do not show mesomorphism.

Dispite the non-planarity of the nucleus, many of the α-substituted hexaalkoxytriphenylenes (**225–251**) exhibit, quite surprisingly, much larger mesophase ranges. Within an α-substituted halogen series, the stability of the mesophase decreases on increasing the size of the halogen atom. Replacement of the halogen atoms by cyano groups, as in the case of β-substitution, significantly increases the stability of the columnar phase. Most of the α-nitrohexaalkoxytriphenylenes display wider mesophase ranges than the parent hexaalkoxytriphenylenes. Induction of a columnar phase in some non-liquid crystalline hexaalkoxytriphenylenes was also observed upon α-nitration [102]. While the dinitrohexabutyloxytriphenylene is not liquid crystalline, its two higher homologues are mesogenic. All the trinitrohexaalkoxytriphenylenes are non-liquid crystalline [53].

α-Alkoxy substitution (**252–265**) reduces both the melting and clearing temperatures compared with the hexaalkoxytriphenylenes. This may be due to the presence of the additional alkoxy chain and the steric hindrance caused by it. In the heptaalkoxytriphenylene series, the melting and clearing temperatures do not change significantly. In all the compounds, mesophases supercool to room temperature. No members of the series show any sign of crystallization upon storing at room temperature for long periods. Mixed ether-ester hepta-substituted triphenylenes (**272–274**) show relatively higher isotropization temperatures. The presence of an unidentified high ordered mesophase in the lower homologue of this series was also reported. These mixed ether-ester derivatives have smaller core–core separations and higher correlation lengths than heptaalkoxytriphenylenes and, therefore, are better candidates for charge transport studies [64].

In polyphenylated triphenylenes **292–295**, a single alkyl or alkoxy chain per phenyl ring is insufficient to induce mesomorphism. This may be because of the unfilled space around the large core. Dodecaalkoxy-substituted polyphenylated triphenylenes **288–291** are liquid crystalline. These large core liquid crystalline as well as non-liquid crystalline triphenylenes have recently been mixed with several hexaalkoxytriphenylenes to enhance their mesophase range. It is reported that complimentary polytropic interactions (CPI) are responsible for the stabilizing effect [66, 76, 80, 85].

5. Summary and outlook

Within 25 years of their discovery, the first commercial application of triphenylene-based DLCs has already been realized and a number of practical devices based on columnar phases have been envisaged. The most promising applications of columnar triphenylene discotics are in the fields of environmental sensing, electroluminescence and photoconductivity. Although a large number of DLCs have been synthesized and our understanding of their properties has advanced significantly, there is still much to be understood. The synthesis, characterization and structure–property relationships of a variety of DLCs are necessary for exploration of the full technological potential of these materials. In view of the considerable efforts devoted by researchers working in the field, there is a good possibility that a triphenylene-based semiconducting device will soon be a reality. It is hoped that the present review in conjunction with the earlier review [16] will help researchers working in this field to achieve their goals.

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