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Synthesis and characterisation of rod-like metallomesogens of Mn(I) based on Schiff base ligands [1]

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Abstract

Complexation of liquid-crystalline imines to Mn(I) carbonyls led to liquid-crystalline complexes when the ligated imine was sufficiently anisotropic. Thus, all two-ring and some three-ring imine ligands were not mesomorphic when complexed, while some three-ring and all four-ring imines led to mesomorphic complexes. As expected, complexation disturbed the anisotropy of the ligands and led to a lowering of clearing points and a suppression of smectic phase formation. © 1998 Elsevier Science S.A.

Keywords: Synthesis; Metallomesogens; Schiff base ligands

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1. Introduction

The synthesis and characterisation of metal complexes with liquid crystalline properties is now a well established area of materials chemistry and has been the subject of several recent reviews [1–5], including two co-authored by Maitlis [6,7]. Serious UK effort in this area started in 1984 in Sheffield and DWB remembers several early conversations with Peter Maitlis on the subject. The first molecule which Peter drew was pentylcyanobiphenyl, shown in Fig. 1. Materials of this type, discovered by George Gray in the early 1970s at the University of Hull in the UK, led to the widespread commercialisation of liquid crystal displays. Being an organometallic chemist first, foremost and at heart, Peter suggested coordination in an η^6 fashion through one of the rings. Liquid crystals binding $[Cr(CO)_3]$ fragments in this way have since been reported by Ziessel and Deschenaux (Fig. 2) [8]. In fact, it turned out that with these compounds, which are simply substituted benzonitriles, coordination through the nitrile nitrogen was to be preferred; liquid crystals based on palladium and platinum followed (Fig. 1) and the results of these studies were reported in 1986 [9]. He then suggested the synthesis of stilbazoles (Fig. 3)—substituted pyridines [10]. These ligands served the work very well and a variety of effects were demonstrated with them, such as liquid-crystallinity with metals [11,12], liquid-crystallinity through hydrogen bonding to acids [13] and phenols [14], enhanced linear [15] and non-linear polarisabilities [16], Langmuir–Blodgett film formation [17] and pyroelectric response within the L–B films [18]. However, perhaps the most interesting and satisfying results, at least from a pure liquid crystal perspective, were obtained with their complexes to silver(I)—another of Peter's initial suggestions [19–25]. The subject of this paper relates to organometallic *metallomesogens*—a term coined by Peter [6]—and is dedicated to him with much warmth and affection.

An examination of the literature reveals that of all the thermotropic liquid crystalline complexes synthesised thus far, the vast majority contain metals in linear or planar environment and usually with a d^8–d^{10} electronic configurations [26]. Notable exception are the five-coordinated complexes of vanadyl and Fe(III)–Cl moieties [27], both bound in a square-pyramidal fashion, some complexes containing $Fe(CO)_3$ unit [28] and the increasing literature of mesomorphic ferrocene complexes [29]. However, most metal complexes are not derived from metallocenes or from metals in groups

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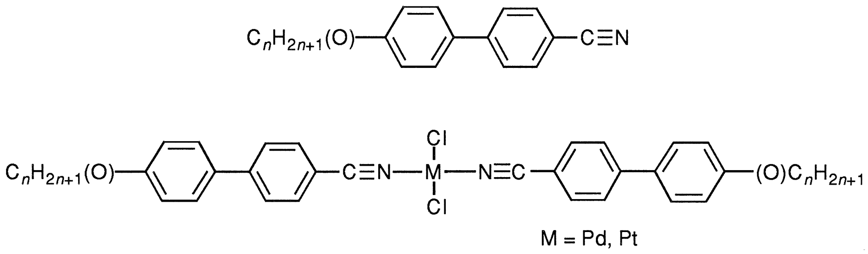


Fig. 1. Cyanobiphenyls and their complexes with Pd(II) and Pt(II).

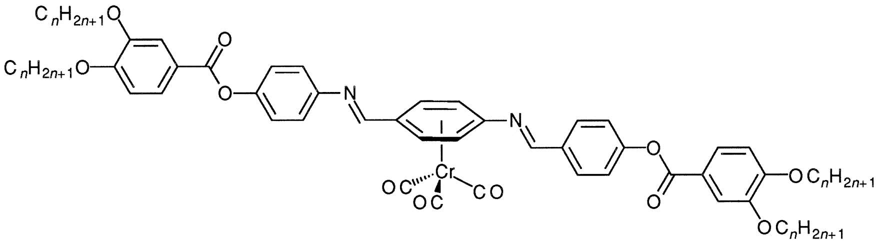


Fig. 2. Organochromium mesogens described by Ziessel and Deschenaux.

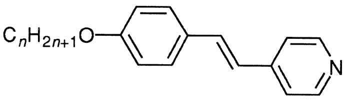


Fig. 3. Structure of 4′-alkoxy-4-stilbazoles.

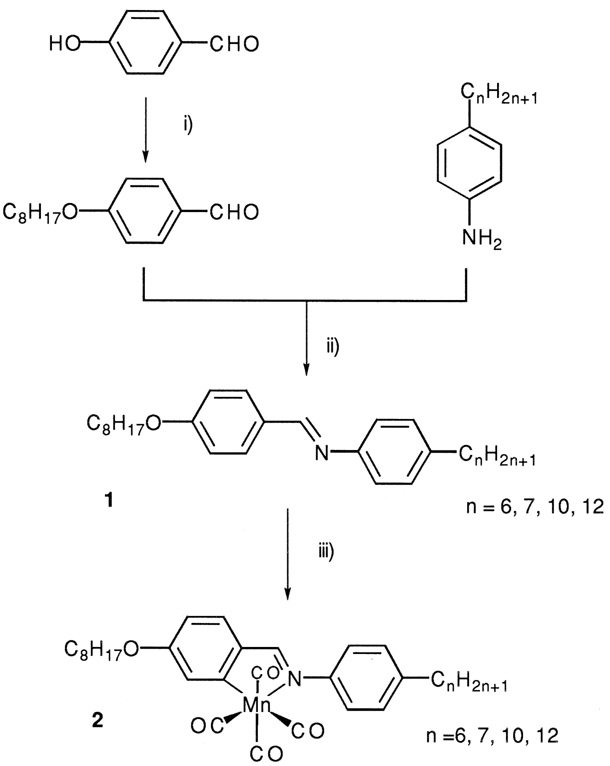


Fig. 4. Synthesis of octahedral Mn(I) complexes of two-ring ligands, *reagents and conditions*: (i) $C_8H_{17}Br$, K_2CO_3/DMF; (ii) toluene/acetic acid (2 drops); (iii) $[MnMe(CO)_5]$/Toluene.

8–12 and so there are whole areas of the periodic table for which calamitic liquid crystalline complexes have not been synthesised.

This is, however, not a straightforward problem, as it is necessary to match the need of liquid crystals to have structural anisotropy with the inevitable disruption which will be caused to such anisotropy by the introduction of high coordinate, and therefore bulky, metal complex fragments. Structurally anisotropic molecules are needed in order to realise liquid crystalline behaviour and hence, planar metal centres represent excellent molecular components as the global anisotropy is unperturbed by their inclusion.

We previously communicated out initial findings that highly anisotropic imines could be bound to $[M(CO)_4]$ fragments (M = Mn, Re) with retention of the liquid crystal properties [30]. We now report these findings in detail and provide further examples of liquid-crystalline manganese complexes.

2. Establishment of a synthetic model

Although mesomorphic manganese complexes were realised with highly anisotropic ligands, it is worth first charting the work which preceded these materials. Thus, in the 1970s, Stone and co-workers had demonstrated that reaction in light petroleum of benzylidene aniline with $[MMe(CO)_5]$ (M = Mn, Re) led to evolution of methane and CO and the generation of the orthometallated complex in yields of about 40%. This was very important as most work on orthometallated complexes had concentrated on group 10 metals. Benzylideneaniline is a very common fragment [31] in organic liquid crystals, and work on it can be traced back to the beginning of the century [32]. Clearly then, a suitable metal/ligand combination was available.

Initially, we began by synthesising simple two-ring imines (Fig. 4; **1**) by reaction of alkoxybenzaldehydes with alkylanilines. These were then complexed on reaction with [MnMe(CO)$_5$].

However, in our hands and with these ligands, we were unable to form the complexes in light petroleum, and changing the solvent to THF only led to trace amounts of product. However, carried out in toluene at reflux, the reaction was complete in 4 h, allowing isolated yields for complexes (**2**) of more than 90%. Several derivatives were made, and their thermal behaviour is now described.

3. Mesomorphism

All of the ligands were known [31] and their mesomorphism is summarised in Table 1. However, none of the complexes was liquid-crystalline, and all simply melted straight into an isotropic (i.e., normal) liquid state at the temperatures indicated in Table 1. Clearly, these ligands were insufficiently anisotropic to tolerate the introduction of the [Mn(CO)$_4$] moiety.

4. Manganese complexes containing three aromatic rings

In order to enhance the structural anisotropy, it was therefore necessary to incorporate additional benzene rings into the ligand. The new ligands (**3**) were synthesised as shown in Fig. 5. Thus, an alkoxybenzoic acid was esterified with 4-hydroxybenzaldehyde using DCC/DMAP to give an alkoxybenzoyloxybenzaldehyde, which was then condensed with a 4-substituted aniline to give the required imine. As before, reaction of the imine with [MnMe(CO)$_5$] in toluene at reflux gave the desired complexes (**4**) in about 70% isolated yield.

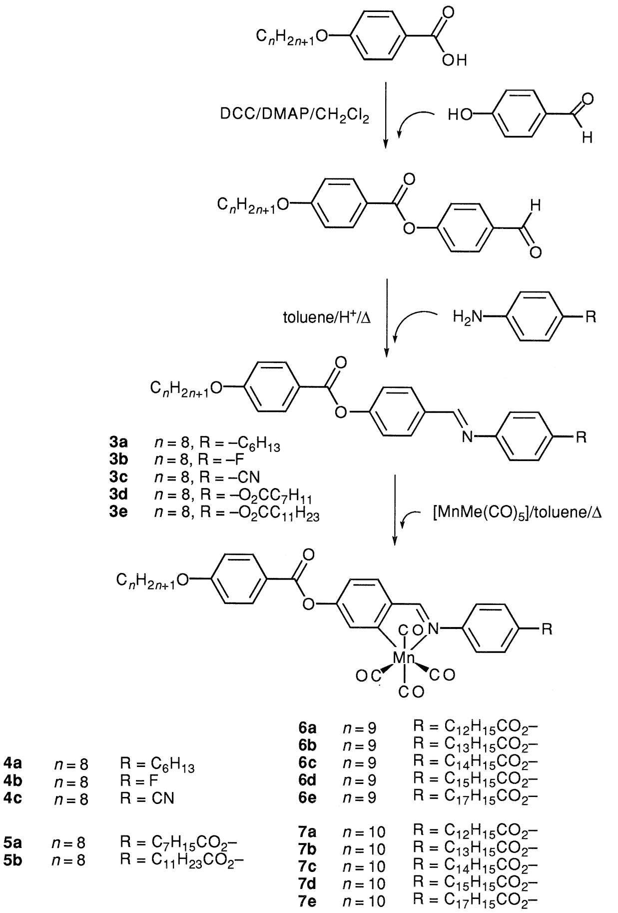


Fig. 5. Synthesis of three-ring ligands (**3**) and related manganese complexes (**4**).

Table 1
Transition temperatures for ligands (**1**) and complexes (**2**)

n		Transition	T/°C	Δ*H*/kJ mol^{-1}	Δ*S*/J K^{-1} mol^{-1}
1	6	Crys-S$_B$	44	37.7	119
		S$_B$-S$_A$	72	3.6	10
		S$_A$-I	84	6.2	17
1	7	Crys-S$_B$	33	24.3	79
		S$_B$-S$_A$	75	3.8	11
		S$_A$-I	87	6.8	19
1	10	Crys-S$_B$	63	57.1	171
		S$_B$-S$_A$	78	4.2	12
		S$_A$-I	87	7.8	22
1	12	Crys-S$_B$	67	58.9	174
		S$_B$-S$_A$	76	3.9	11
		S$_A$-I	84	7.8	22
2	6	Crys-I	40		
2	7	Crys-I	36		
2	10	Crys-I	39		
2	12	Crys-I	57		

5. Mesomorphism

The mesomorphism of the ligands, **3**, was characterised using DSC and polarising optical microscopy, and is summarised in Table 2. The re-entrant behaviour of **3c** has previously been noted by Weissflog [33].

The related Mn(I) complexes (**4a–c**) are non-mesomorphic. The melting point for **4a**, **4b**, and **4c** are 110°C, 124°C and 136°C, respectively, and careful examination of the behaviour on cooling failed to reveal the presence of monotropic (metastable) mesophases. It can be readily seen that the complexes' clearing points are lower than that of their corresponding ligands (ca.

200°C or over) and the more polar the terminal groups, the higher its melting point.

Clearly then, the functionality attached to the core had an important influence on melting point, at least, and so it was decided to see whether other modifications to the three-ring imines could be made which would allow the generation of mesomorphic complexes of manganese(I). The approach taken was to retain the basic motif of the three-ring ligands discussed above, but to introduce one terminal group as an alkanoyloxy function, rather than a simple alkoxy function. The synthetic approach is shown in Fig. 5 and complexes (**5–7**) were synthesised in moderate yield (60–70%) from the ligands via reaction with [MnMe(CO)$_5$] in toluene at reflux.

Two derivatives (**5a–b**) were originally synthesised, and now, the metal complexes did show liquid crystal mesophases, having a monotropic nematic phase. Thermal data for the ligands and their related complexes are collected in Table 3. (Monotropic behaviour means simply that the mesophase is less thermodynamically stable than the crystal phase, and so appears only on supercooling the isotropic melt.) Encouraged by this result, we decided to see whether variation of the chain length in these systems could lead to lower-melting materials which might allow the melting point to fall to a sufficiently low temperature to allow enantiotropic mesomorphism to be seen. To this end, a number of ligands were synthesised based on a nonyloxy or decyloxy group at one end and an alkanoyloxy group at the other. Unfortunately, the ligands were made in rather small quantities and so the ligand mesomorphism has not been characterised. However, there is every reason to assume that it will be similar to that of the two initially prepared ligands.

Table 3
Phase transitions of the mesomorphic three-ring complexes (**6–8**)

Compound	*n*	*m*	Transition	*T* (°C)
5a	7	8	Crys–I	123
			(I–N)	(83)
5b	11	8	Crys–I	93
			(I–N)	(73)
6a	12	9	Crys–I	123
			(I–N)	(83)
6b	13	9	Crys–I	104
			(I–N)	(67)
6c	14	9	Crys–I	99
			(I–N)	(65)
6d	15	9	Crys–I	97
			(I–N)	(65)
6e	17	9	Crys–I	95
			(I–N)	(63)
7a	12	10	Crys–I	102
			(I–N)	(67)
7b	13	10	Crys–I	101
			(I–N)	(66)
7c	14	10	Crys–I	104
			(I–N)	(64)
7d	15	10	Crys–I	102
			(I–N)	(67)
7e	17	10	Crys–I	96
			(I–N)	(64)
8a			Crys–I	124
			(I–N)	(85)
8b			Crys–I	92
			(I–N)	(63)

Table 2
Phase transitions of the three-ring ligands (**3–5**)

Compound	Transition	*T* (°C)	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
3a	Crys–K	69	14.4	42
	K–S_I	74	0.4	1
	S_I–S_C	76	0.9	3
	S_C–N	149	1.3	3
	N–I	193	1.5	3
3b	Crys–S_A	97	26.1	71
	(S_A–E)	(89)	–	–
	S_A–N	181	0.7	2
	N–I	204	0.9	2
3c	Crys–N_{re}[a]	108	–	–
	N_{re}–S_A	152	–	–
	S_A–N	198	–	–
	N–I	255	–	–
3d	Crys–G	72	23.2	67
	G–S_C	94	2.7	7
	S_C–N	148	1.5	4
	N–I	212	1.2	3
3e	Crys–G	76	33.3	96
	G–S_C	100	2.5	7
	S_C–N	172	2.8	6
	N–I	201	1.8	4

[a] Re-entrant nematic phase.

All of these new complexes were mesomorphic, but again, only monotropic phases resulted. Indeed, the melting and (monotropic) clearing points were remarkably independent of chain length as may be seen from

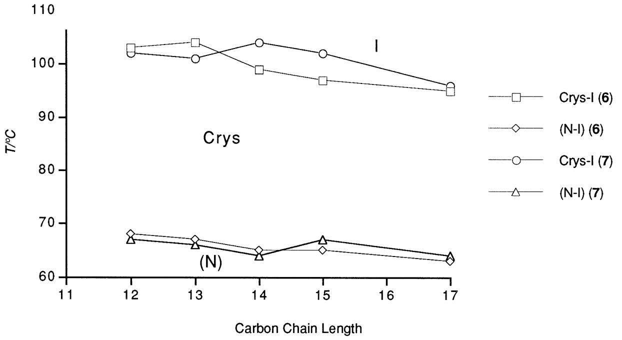


Fig. 6. Phase diagram for complexes **6** and **7**.

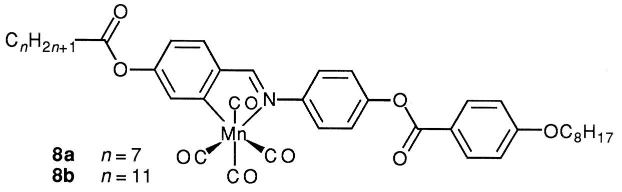


Fig. 7. Isomeric three-ring manganese complexes.

Fig. 6. DSC data were not recorded as it was not always possible to see the monotropic N–I transitions in the DSC experiment, even though they were always observed by optical microscopy.

Finally here, we synthesised two complexes (Fig. 7; **8a** and **8b**) in which the ends of the ligand had been effectively ‘swopped over’; the synthetic approach was exactly analogous to that described for the structurally isomeric ligands. The thermal data are collected in Table 3 alongside their isomers, and the correspondence in transition temperatures is remarkable and is, within experimental error, identical, showing the insensitivity of the complexes to the arrangement of ligand functionalities bound to it.

Thus, while we had generated manganese complexes which were now mesomorphic, which did not decompose and which had relatively low clearing points, the higher melting points led to the observation of only monotropic phases. We therefore decided to press the idea of ligand anisotropy one step further, and undertook the synthesis of some four-ring imine ligands and their complexes with Mn(I).

6. Manganese(I) complexes containing four rings

The ligands (**9**) and complexes (**10**) were synthesised as shown in Fig. 8.

The new ligands were synthesised using the same synthetic steps employed in the smaller ligands, the only extra step being the formation of alkoxybenzoyloxynitrobenzene by a DCC/DMAP coupling of an alkoxybenzoic acid with 4-nitrophenol, followed by its

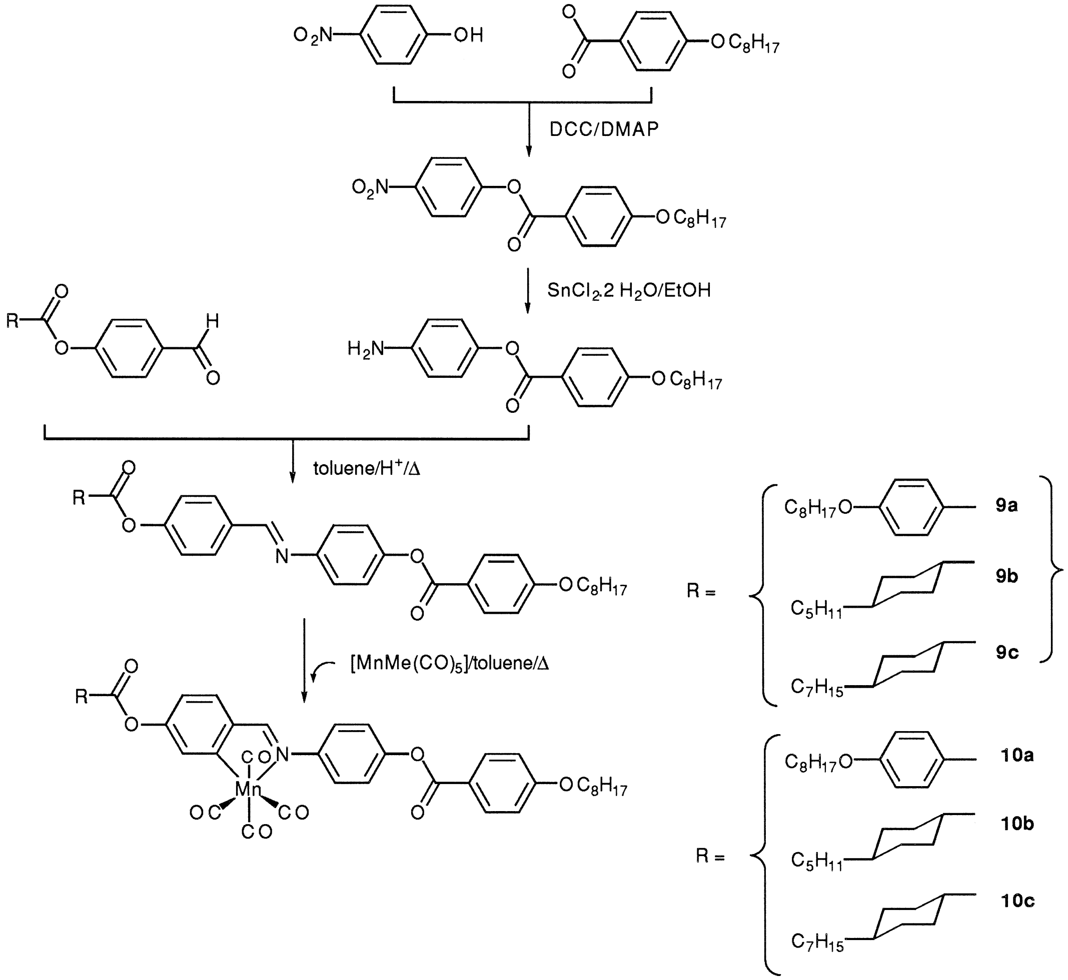
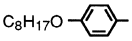
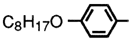


Fig. 8. Synthesis of four-ring ligands and complexes.

Table 4
Mesomorphism of the ligands (**9**) and complexes (**10**) containing four ringsi

R	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
Ligands				
 **9a**	Crys - G	83	27.2	76
	G - S_C	131	3.7	9
	S_C - N	191	0.9	2
	N - I	299	0.9	2
 **9b**	Crys - J	87	33.7	94
	J - S_I	137	0.6	1
	S_I - S_C	143	1.7	4
	S_C - N	216	1.0	2
	N - I	307	1.7	3
 **9c**	Crys - Crys′	63	24.7	73
	Crys′ - G	116	25.2	65
	G - S_C	124	3.8	10
	S_C - N	202	1.9	4
	N - I	298	2.2	4
Complexes				
 **10a**	Crys - N	135	30.8	76
	N - I	184†	–	–
 **10b**	Crys - N	122	37.6	94
	N - I	180†	–	–
 **10c**	Crys - N	154	40.1	94
	N - I	190†	–	–

reduction to alkoxybenzoyloxyaniline using tin(II). The manganese complexes were then prepared in 65% yield by reaction of the ligands with [MnMe(CO)$_5$] in toluene at reflux for 8 h.

7. Mesomorphism

The ligands showed extensive mesomorphism, with all having S_C and nematic phases. Two then showed subsequent formation of a crystal G phase on further cooling of the S_C phase, while for the heptylcyclohexyl derivative, a crystal J and a S_I phase were introduced beneath the S_C phase, as characterised by optical microscopy. As expected with such highly anisotropic ligands, the clearing points were rather high at around 300°C. The thermal data are collected in Table 4.

As now expected, the related complexes were mesomorphic. Thus, **10a**, **10b**, and **10c** melted in a nematic phase at 135, 122 and 154°C, clearing, with decomposition, at 184, 180 and 190°C respectively. Thus, by using the strongly anisotropic, four-ring imines, the perturbation represented by the [Mn(CO)$_4$] group was tolerated and liquid crystal behaviour resulted.

8. Conclusion

By way of conclusion, some useful comparisons between the behaviour of the ligands and their manganese complexes can be made. First, it is noteworthy that the temperature at which the complexes pass into the nematic phase is not much different from the temperature at which the ligands pass into a *fluid* mesophase. The mesomorphism, however, is quite different in that the fluid and ordered smectic phases seen in the ligands have been destabilised so that only nematic phases are seen in the complexes. In many ways, this is expected as the introduction of a bulky lateral substituent would be predicted to reduce that occurrence of smectic phases which require lateral associations. Despite this, we have found that in mesomorphic complexes of 2,2′-bipyridines [34] and of 1,4-diazabutadienes [35] bound the to the [ReBr(CO)$_3$] fragment, smectic C mesophases are seen at certain chain lengths. The origin of this difference in behaviour is, for the present, unclear. The other consequence of the introduction of the lateral [Mn(CO)$_4$] group is to reduce the overall anisotropy and therefore, it is again unsurprising that the clearing point of the complexes is much lower than that of the ligands, in fact by some 100°C, even though the thermal stability was such that the complexes decomposed in the upper reaches of the nematic phase, accelerating on clearing.

Evidently, these are systems of great promise, particularly with respect to the formation of stable, low-melting metallomesogens—one of Peter's great aspirations for the field.

9. Experimental

Apparatus and general techniques of microscopy and calorimetry are as described elsewhere [35].

9.1. 4′-(4-Octyloxybenzoyloxy)benzaldehyde

Dicyclohexylcarbodiimide (5.94 g, 28.8 mmol) and *N*,*N*-dimethylaminopyridine (0.15 g) were added to a stirred solution of 4-octyloxybenzoic acid (6.0 g, 24 mmol) and hydroxybenzaldehyde (3.0 g, 24.0 mmol) in dry dichloromethane (DCM, 100 cm^3). The reaction mixture was stirred at room temperature for 6 h. The dicyclohexylurea was filtered off and the solvent from the filtrate was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, DCM). A colourless product was obtained.

Yield, 7.35 g (87%). m.p. 103°C. ^{1}H NMR(CDCl$_3$) δ: 0.9 (t, 3H, CH$_3$), 1.34–1.85 (m, 12H, 6CH$_2$), 4.05

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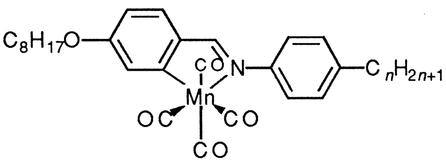
[a] With decomposition.

(t, 2H, $J = 6.5$ Hz, OCH_2), 6.98 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.4 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.12 (d, 2H, $J = 9.0$ Hz, AA′XX′), 10.02 (s, 1H, CHO) ppm.

For the next two aldehydes ($n = 5,7$), the synthesis was performed in an analogous manner—one set of NMR data is given—the other is similar.



^1H NMR (250 MHz, $CDCl_3$, ppm)

9.2. $n = 5$

δ: 0.9 (t, 3H, CH_3), 1.0 (m, 2H, $H_{3ax} - H_{5ax}$), 1.25 (m, 9H, $4CH_2 + H_4$), 1.55 (qd, 2H, $H_{2ax} + H_{6ax}$), 1.85 (dd, 2H, $H_{3eq} + H_{5eq}$), 2.1 (dd, 2H, $H_{2eq} + H_{6eq}$), 2.45 (tt, 1H, H_1), 7.23 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.94 (d, 2H, $J = 9.0$ Hz, AA′XX′), 10.0 (s, 1H, CHO)

9.3. 4′-(4-Octyloxybenzoyloxy)nitrobenzene

DCC (34.61 g, 168 mmol) and DMAP (0.3 g) were added to a stirred solution of 4-octyloxybenzoic acid (35 g, 140 mmol) and hydroxybenzaldehyde (29 g, 210 mmol) in dry DCM (400 cm^3). The reaction mixture was stirred at room temperature for 6 h. The dicyclohexylurea was filtered off and the solvent was removed under reduced pressure. The crude product was crystallized from ethanol to give a colourless solid.

Yield, 46.2 g (89%). ^1H NMR($CDCl_3$) δ: 0.9 (t, 3H, CH_3), 1.25–1.45 (m, 10H, $5CH_2$), 1.8 (qn, 2H, OCH_2CH_2), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.98 (d, 2H, $J = 9$ Hz, AA′XX′), 7.4 (d, 2H, $J = 9$Hz, AA′XX′), 8.1 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.13 (d, 2H, $J = 9$ Hz, AA′XX′) ppm; Elemental analysis (%): Found: C, 68.0; H, 6.8; N, 3.9; $C_{21}H_{25}NO_5$ requires C, 67.9; H, 6.8; N, 3.8.

9.4. 4′-(4-Octyloxybenzoyloxy)aniline

A mixture of 4′-(4-octyloxybenzoyloxy)nitrobenzene (**25**) (5 g, 13 mmol) and 5 equiv. of $SnCl_2 \cdot 2H_2O$ (15.2 g, 65 mmol) was refluxed in ethanol (100 cm^3) for 6 h. After cooling, the mixture was poured into ice and the pH value was adjusted to 7 ~ 8 using sodium hydroxide. The mixture was extracted with ethyl acetate. The ethyl acetate solution was washed three times with brine and was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The brownish solid was purified by column chromatography (silica gel: DCM and 1% triethylamine) and then crystallized from ethanol to give a whitish solid.

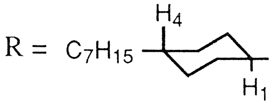
Yield, 3.24 g (70.4%). m.p. 94°C. ^1H NMR($CDCl_3$) δ: 0.9 (t, 3H, CH_3), 1.17 ~ 1.55 (m, 10H, $5CH_2$), 1.82 (qn, 2H, OCH_2CH_2), 3.64 (s, 2H, NH_2), 4.03 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.7 (d, 2H, $J = 9$ Hz. AA′XX′), 6.95 (d, 4H, $J = 9$Hz, 2AA′XX′, overlapped), 8.1 (d, 2H, $J = 9$ Hz, AA′XX′) ppm; Elemental analysis (%): Found: C, 73.6; H, 7.8; N, 4.1; $C_{21}H_{27}NO_3$ requires C, 73.9; H, 8.0; N, 4.1.

9.5. Ligands **1**: (4′-octyloxybenzylidene)-4-hexylaniline

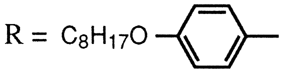
4-Hexylaniline (3.79 g, 19.2 mmol) was dissolved in toluene (25 cm^3) and then acetic acid (2 drops) was added into the solution. 4-Octyloxybenzaldehyde (4.5 g, 19.2 mmol) was added to the solution, and stirred for a few minutes then left unstirred overnight. The crude product was filtered and recrystallized in ethanol to give a colourless crystalline solid.

Yield, 6.45g (85.4%); ^1H NMR($CDCl_3$) δ: 0.9 (m, 6H, $2CH_3$), 1.2–1.6 (m, 18H, $9CH_2$), 1.8 (qn, 2H, OCH2*CH*$_2$), 2.6 (t, 2H, ph-*CH*$_2$), 4.0 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.1 (dd, 2H, $J = 9.0$ Hz, AA′XX′), 7.85 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.4 (s, 1H, CH = N) ppm. Elemental analysis (%): Found: C, 81.9; H, 10.0; N, 3.4; $C_{27}H_{39}NO$ requires C, 82.4; H, 9.9; N, 3.6.

For the homologous Schiff base ligands ($n =$ 7,10,12), the synthesis was performed in an analogous manner; the alkylanilines were commercially available. NMR data were effectively identical and satisfactory analytical data were obtained.



For the ligands **3**, the synthesis was performed in an analogous manner starting from the corresponding alkoxybenzoyloxybenzaldehyde; the aniline derivatives were commercially available.



9.5.1. $R = C_6H^{13}$ (**3a**)

Yield, (67%); ^1H NMR($CDCl_3$) δ: 0.9 (m, 6H, $2CH_3$), 1.2–1.6 (m, 18H, $9CH_2$), 1.85 (qn, 2H, OCH_2CH_2), 2.6 (t, 2H, ph-*CH*$_2$), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.98 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.12 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.18 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.3 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.15 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH = N) ppm. Elemental analysis (%): Found: C, 79.4; H, 8.6; N, 2.6; $C_{34}H_{43}NO_3$ requires C, 79.5; H, 8.4; N, 2.7.

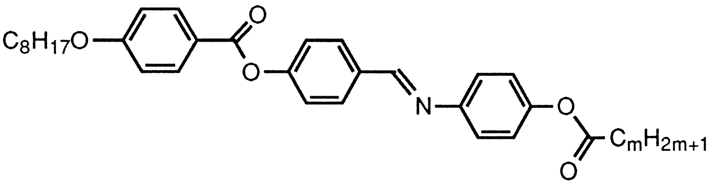
9.5.2. R = F (**3b**)

Yield, (70%); ^{1}H NMR(CDCl$_3$) δ: 0.9 (t, 3H, CH$_3$), 1.28–1.55 (m, 10H, 5CH$_2$), 1.8 (qn, 2H, OCH$_2$CH$_2$), 4.05 (t, 2H, $J = 6.5$ Hz, OCH$_2$), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.05 (dd, 2H, AA′XX′), 7.2 (m, 2H, AA′XX′), 7.3 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.94 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.17 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH = N) ppm. Elemental analysis (%): Found: C, 74.9 H, 6.9; N, 3.0; $C_{28}H_{30}NFO_3$ requires C, 75.1; H, 6.8; N, 3.1.

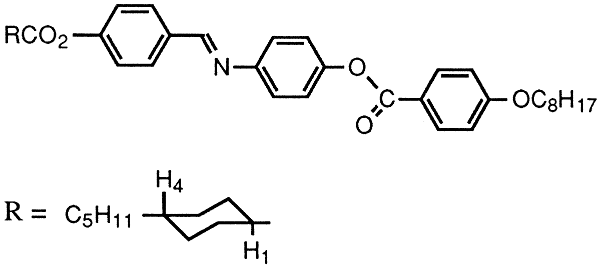
9.5.3. R = CN (**3c**)

Yield, (78%); ^{1}H NMR(CDCl$_3$) δ: 0.9 (t, 3H, CH$_3$), 1.17–1.55 (m, 10H, 5CH$_2$), 1.8 (qn, 2H, OCH$_2$*CH$_2$*), 4.0 (t, 2H, $J = 6.5$ Hz, OCH$_2$), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.15 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.3 (d, 2H, AA′XX′), 7.6 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.92 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.1 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.35 (s, 1H, CH = N) ppm. Elemental analysis (%): Found: C, 76.3 H, 6.6; N, 6.3; $C_{29}H_{30}N_2O_3$ requires C, 76.6; H, 6.7; N, 6.2.

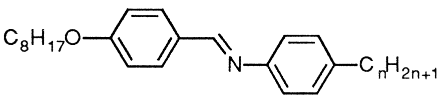
Four-ring imine ligands (**9**) were synthesized similarly to the two-ring imines, **1**, except the final products were purified by crystallization from DCM/methanol.



Yield 81.4%; ^{1}H NMR(CDCl$_3$) δ: 0.85–1.1 (m 8H, 2CH$_3$ + H$_{3ax}$ − H$_{5ax}$), 1.2–1.65 (m, 21H, 9CH2 + H$_4$ + H$_{2ax}$ + H$_{6ax}$), 1.85 (m, 4H, H$_{3eq}$ + H$_{5eq}$ + OCH$_2$*CH$_2$*), 2.15 (dd, 2H, H$_{2eq}$ + H$_{6eq}$), 2.5 (tt, 1H, H$_1$), 4.05 (t, 2H, $J = 6.5$ Hz, OCH$_2$), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.2 (m, 6H, AA′XX′ overlapped), 7.9 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.15 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH = N) ppm. Elemental analysis (%): Found: C, 77.0 H, 8.5; N, 2.3; $C_{40}H_{51}NO_5$ required C, 76.8; H, 8.2; N, 2.2.

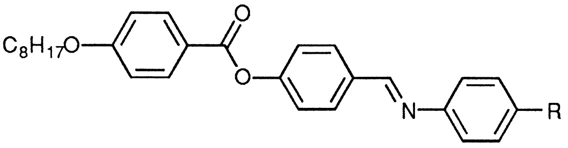


Yield 90%. ^{1}H NMR(CDCl$_3$) δ: 0.85–1.1 (m, 8H, 2CH$_3$ + H$_{3ax}$ − H$_{5ax}$), 1.2–1.65 (m, 25H, 9CH$_2$ + H$_4$ + H$_{2ax}$ + H$_{6ax}$), 1.85 (m, 4H, H$_{3eq}$ + H$_{5eq}$ + OCH$_2$*CH$_2$*), 2.15 (dd, 2H, H$_{2eq}$ + H$_{6eq}$), 2.5 (tt, 1H, H$_1$), 4.05 (t, 2H, $J = 6.5$ Hz, OCH$_2$), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.2 (m, 6H, AA′XX′, overlapped), 7.9 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.15 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH = N) ppm. Elemental analysis (%): Found: C, 76.9; H, 8.5; N, 2.1; $C_{42}H_{55}NO_5$ required C, 77.1; H, 8.5; N, 2.1.



Yield 86.3%; ^{1}H NMR(CDCl$_3$) δ: 0.9 (t, 6H, 2CH$_3$), 1.25–1.5 (m, 22H, 11CH$_2$), 1.85 (m, 4H, OCH$_2$CH$_2$), 4.05 (t, 4H, $J = 9.0$ Hz, 2OCH$_2$), 6.95 (d, 4H, $J = 9.0$ Hz, AA′XX′), 7.2–7.35 (m, 6H, AA′XX′), 7.9 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.15 (d, 4H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH = N) ppm. ^{13}C{^{1}H}NMR(250 MHz CDCl$_3$): δ: 14.11, 22.66, 25.99, 29.11, 29.23, 29.33, 31.8, 68.36, 114.3, 114.4, 121.2, 121.5, 121.8, 122.2, 122.4, 130.0, 132.3, 132.4, 133.7, 149.3, 149.4, 153.6, 159.3, 163.6, 163.7, 164.6, 165.0 ppm; Elemental analysis (%): Found: C, 75.9; H, 7.7; N, 2.0; $C_{43}H_{51}NO_6$ required C, 76.2; H, 7.6; N, 2.1.

Three ring Schiff base ligands which have alkanoyloxy terminal groups were synthesised as described below. Analytical and NMR data are given for one example, all the others gave similar, satisfactory results.



9.5.4. m = 7 (**5a**)

DCC (0.33 g, 1.6 mmol) and DMAP (0.05 g) were added to a stirred solution of octanoic acid (0.2 g, 1.3 mmol) and compound **33** (0.6 g, 1.3 mmol) in dry DCM (30 cm^3). The reaction mixture was stirred at room temperature for 12 h. The dicyclohexylurea was filtered and the solvent was removed under reduced pressure. The crude product was crystallized from DCM/methanol to give a colourless solid.

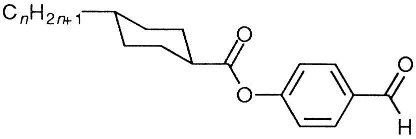
Yield 0.54 g, 69%; ^{1}H NMR(CDCl$_3$) δ: 0.9 (6H, 2CH$_3$, two overlapped triplets), 1.25–1.5 (m, 18H, 9CH$_2$), 1.8 (m, 4H, *CH$_2$*CH$_2$CO$_2$ + OCH$_2$*CH$_2$*), 2.55

(t, 2H, CH_2CO_2), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.1 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.2 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.33 (d, 2H, $J = 9.0$ Hz, AA′XX′), 7.95 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.15 (d, 2H, $J = 9.0$ Hz, AA′XX′), 8.45 (s, 1H, CH = N) ppm. Elemental analysis (%): Found: C, 75.4; H, 7.7; N, 2.4; $C_{36}H_{45}NO_5$ required C, 75.7; H, 7.9; N, 2.5.

9.6. Mn complexes

All Mn(I) complexes were synthesized in an analogous manner by using the method now described. When the number of rings in the ligands were increased from two to four, the reaction time was increased from 4 to 8 h.

Under a nitrogen atmosphere, an equimolar amount of the Schiff base and $[MnMe(CO)_5]$ were dissolved in dry toluene and heated at reflux for between 4 and 8 h. depending on the ligand. The solvent was removed in vacuo and passed through a column of neutral alumina eluting with DCM. The yellow band from the column gave, on removal of the solvent, a yellow solid which was crystallized from DCM/methanol to give the product.



Details are given for $n = 6$. All other complexes gave satisfactory elemental analyses, and related NMR and infrared data.

9.6.1. n = 6

Yield 91.2%; m.p. 38–40°C; IR(DCM solution) ν_{co} cm^{-1}: 2073(w), 1986(vs), 1938(s). ^1H NMR(CD_2Cl_2) δ: 0.9 (6H, $2CH_3$, two overlapped triplets), 1.2–1.6 (m, 18H, $9CH_2$), 1.8 (qn, 2H, OCH_2CH_2), 2.6 (t, 2H, Ph-CH_2), 4.05 (t, 2H, $J = 6.5$ Hz, OCH_2), 6.63 (dd, 1H, $J = 8.4$, 2.4 Hz), 7.12 (d, 2H, $J = 8.4$ Hz, AA′XX′), 7.23 (d, 2H, $J = 8.4$ Hz, AA′XX′), 7.52 (d, 1H, $J = 2.4$ Hz), 7.62 (d, 1H, $J = 8.4$ Hz), 8.17 (s, 1H, CH = N) ppm. Elemental analysis (%): Found: C, 66.4; H, 6.4; N, 2.4; $C_{31}H_{38}NO_5Mn$ requires C, 66.5; H, 6.8; N, 2.5.

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References

[1] D.W. Bruce, in: D.W. Bruce, D. O'Hare (Eds.), Inorganic Materials 2nd edn. Wiley, Chichester, 1996.
[2] J.L. Serrano (Ed.), Metallomesogens. VCH, Weinheim, 1996.
[3] D.W. Bruce, J. Chem. Soc., Dalton Trans., (1993) 2983.
[4] P. Espinet, J.L. Serrano, L.A. Oro, M.A. Esteruelas, Coord. Chem. Rev. 117 (1992) 215.
[5] A.P. Polishchuk, T.V. Timofeeva, Russ. Chem. Rev. 62 (1993) 291.
[6] P.M. Maitlis, A.-M. Giroud-Godquin, Angew. Chem. Int. Ed. Engl. 30 (1991) 402.
[7] S.A. Hudson, P.M. Maitlis, Chem. Rev. 93 (1993) 861.
[8] E. Campillos, R. Deschenaux, A.-M. Levelut, R. Ziessel, J. Chem. Soc., Dalton Trans., (1996) 2533.
[9] D.W. Bruce, E. Lalinde, P. Styring, D.A. Dunmur, P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1986) 581.
[10] D.W. Bruce, D.A. Dunmur, E. Lalinde, P.M. Maitlis, P. Styring, Liq. Cryst. 3 (1988) 385.
[11] J.P. Rourke, F.P. Fanizzi, N.J.S. Salt, D.W. Bruce, D.A. Dunmur, P.M. Maitlis, J. Soc., Chem. Commun., 1990, 229.
[12] D.W. Bruce, D.A. Dunmur, M.A. Esteruelas, S.E. Hunt, R. Le Lagadec, P.M. Maitlis, J.R. Marsden, E. Sola, J.M. Stacey, J. Mater. Chem. 1 (1991) 251.
[13] K. Willis, J.E. Luckhurst, D.J. Price, J.M.J. Fréchet, T. Kato, G. Ungar, D.W. Bruce, Liq. Cryst. 21 (1996) 585.
[14] D.J. Price, K. Willis, T. Richardson, G. Ungar, D.W. Bruce, J. Mater. Chem. 7 (1997) 883.
[15] C. Bertram, D.W. Bruce, D.A. Dunmur, S.E. Hunt, P.M. Maitlis, M. McCann, J. Chem. Soc., Chem. Commun., 1991, 69.
[16] D.W. Bruce, A. Thornton, Mol. Cryst., Liq. Cryst. 231 (1993) 253.
[17] T. Richardson, A. Topaçli, W.H. Abd Majid, M.B. Greenwood, D.W. Bruce, A. Thornton, J.R. Marsden, Adv. Mater. Opt. Electron. 4 (1994) 243.
[18] A. Topaçli, T. Richardson, W.H. Abd Majid, A. Thornton, D.W. Bruce, J.R. Marsden, Int. J. Elec. 77 (1994) 951.
[19] D.W. Bruce, D.A. Dunmur, E. Lalinde, P.M. Maitlis, P. Styring, Nature (London) 323 (1986) 791.
[20] D.W. Bruce, D.A. Dunmur, P.M. Maitlis, P. Styring, M.A. Esteruelas, L.A. Oro, M.B. Ros, J.L. Serrano, E. Sola, Chem. Mater. 1 (1989) 479.
[21] D.W. Bruce, D.A. Dunmur, S.A. Hudson, E. Lalinde, P.M. Maitlis, M.P. McDonald, R. Orr, P. Styring, A.S. Cherodian, R.M. Richardson, J.L. Feijoo, G. Ungar, Mol. Cryst., Liq. Cryst. 206 (1991) 79.
[22] D.W. Bruce, S.C. Davis, D.A. Dunmur, S.A. Hudson, P.M. Maitlis, P. Styring, Mol. Cryst., Liq. Cryst. 215 (1992) 1.
[23] D.W. Bruce, D.A. Dunmur, S.A. Hudson, P.M. Maitlis, P. Styring, Adv. Mater. Opt. Electron. 1 (1992) 37.
[24] H. Adams, N.A. Bailey, D.W. Bruce, S.C. Davis, D.A. Dunmur, S.A. Hudson, S.J. Thorpe, J. Mater. Chem. 2 (1992) 395.
[25] D.W. Bruce, B. Donnio, S.A. Hudson, A.-M. Levelut, S. Megtert, D. Petermann, M. Veber, J. Phys. II France 5 (1995) 289.
[26] D.W. Bruce, Adv. Mater. 6 (1994) 699.
[27] Yu.G. Galyametdinov, G.I. Ivanova, I.V. Ovchinnikov, Izv. Akad. Nauk. SSSR Ser. Khim., 1989, 1931.

[28] L. Ziminski, J. Malthête, J. Chem. Soc., Chem. Commun., 1990, 1495.
[29] R. Deschenaux, J.W. Goodby, in: A. Togni, T. Hayashi (Eds.) Ferrocenes, Vol. Chap. 9, VCH Verlagsgesellschaft, Weinheim, 1994, p. 471.
[30] D.W. Bruce, X.-H. Liu, J. Chem. Soc., Chem. Commun., 1994, 729.
[31] V. Vill, LiqCryst Database 2.1, LCI Publishing, Hamburg.
[32] D.W. Bruce, V. Vill, Liq. Cryst., 1997, in press.
[33] W. Weissiflog, G. Pelzl, D. Demus, Mol. Cryst., Liq. Cryst. 76 (1981) 261.
[34] K.E. Rowe, D.W. Bruce, J. Chem. Soc., Dalton Trans., 1996, 3913.
[35] S. Morrone, D. Guillon, D.W. Bruce, Inorg. Chem. 35 (1996) 7041.