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Mesomorphic di- and tetra-fluorinated imines and their complexes with Re[I]

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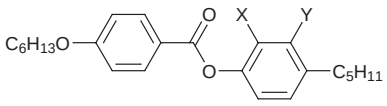
The synthesis of some di- and tetra-fluoro imine mesogens is described and their mesomorphism is compared with that of the parent, unfluorinated materials. The comparison reveals that in the fluorinated compounds, more ordered smectic phases were suppressed and crystal phases were destabilised; nematic phases were uniformly destabilised. The imines were then reacted with $[ReMe(CO)_5]$ to give related orthometallated complexes which were also mesomorphic.

Introduction

In low molar mass liquid crystalline systems, fluoro-substitution has been known since 1925.[1] Fluorine has the smallest van der Waals' radius of any substituent other than hydrogen (F = 1.47 Å, H = 1.2 Å)[2] and it also has highest electronegativity of any element. Fluorine can, therefore, exert appreciable electronic effects and yet, because of its small size, its effect on the close packing of the molecules is less than any other substituent. The effect of fluorination in mesogens has been well documented[3] and several general conclusions can be drawn from investigations carried out on calamitic systems. Lateral fluoro substitution in low molar mass systems has varied effects and critically depends on the position at which the fluoro substituent is introduced.[4] Fig. 1 shows the transition temperatures for a parent compound and also for two of its mono-fluorinated derivatives. It can be seen that the 2-fluoro derivative (fluorine positioned centrally) has reduced nematic character compared with the parent system, while when the fluoro substituent is positioned near the end of core unit (3-fluoro derivative), nematic character has been eliminated and smectic phase stability has been enhanced. Both of the fluorinated compounds have a lower melting point than the parent system.



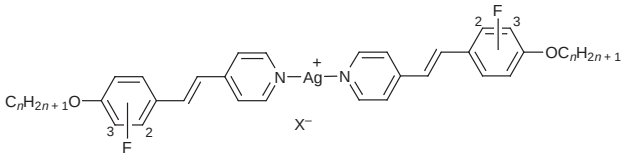
X	Y	
H	H	Crys • 50 • N • 63 • I
F	H	Crys • 28 • N • 37 • I
H	F	Crys • 40 • S_A • 49 • I

Fig. 1 Example of the dependence of transition temperatures on position of fluorination

Predicting the effect which lateral fluoro-substitution will have is, however, difficult because steric factors must be considered in addition to molecular polarizability.[3b,c] In most systems, however, the trends for laterally fluoro-substituted compounds show similar patterns, depending on their number and distribution. Positioned so that they contribute to an 'outboard' dipole, they have the possibility to stabilise smectic phases perhaps at the expense of nematic phases, while positioned to create a net lateral dipole, they can reduce clearing points and promote nematic phases, often at the expense of smectic phases (Fig. 1). Some of these effects are rather beautifully illustrated by the work of the Hull group with substituted terphenyls.[5] From all of these studies, it is clear that a subtle combination of steric and electronic effects acts to determine the resulting mesomorphism.

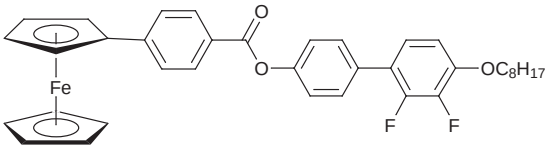
Lateral fluorination has also been studied in low molar mass metallomesogens. For example, the central core of stilbazole silver(I) complexes was modified by introduction of lateral fluoro-substituents into complexes with triflate and dodecyl sulfate counter ions.[6] Depending on the position of the fluoro substituent, the mesomorphic behaviour is affected in a different way. When the fluoro substituents occupy position 3 of the aromatic rings (Fig. 2) nematic phases are formed less frequently or even suppressed totally, melting points are decreased, and smectic C phases are destabilised, resulting in a pronounced widening of the smectic A phases in comparison with their non-substituted stilbazole silver(I) complexes. Further, the cubic phase seen in the parent complexes is now absent. However, when the fluoro substituents occupy position 2, different effects are observed; the clearing points are significantly depressed and melting points are also decreased, but to a lesser extent. The smectic C phase is stabilised at the total expense of the smectic A phase, the nematic phase is promoted and for $X = C_{12}H_{25}OSO_3$, cubic phases are retained. Imrie and coworkers[7] have reported a difluoro-substituted ferrocene metallomesogen (Fig. 3), and here, fluoro substitution led to lower temperature mesogens. Fluorination has also been studied in, for example, complexes of salicylaldimates,[8] salen,[9] dithiobenzoates[10] and β-diketonates.[11]

As part of our studies on calamitic metallomesogens containing octahedral metal centres,[12] we have studied orthometallated



X = OTf, $C_{12}H_{25}OSO_3$

Fig. 2 Laterally fluorinated stilbazole complexes of silver(I)



Crys • 115 • N • 129 • I

Fig. 3 Mesomorphic difluoro-substituted ferrocene

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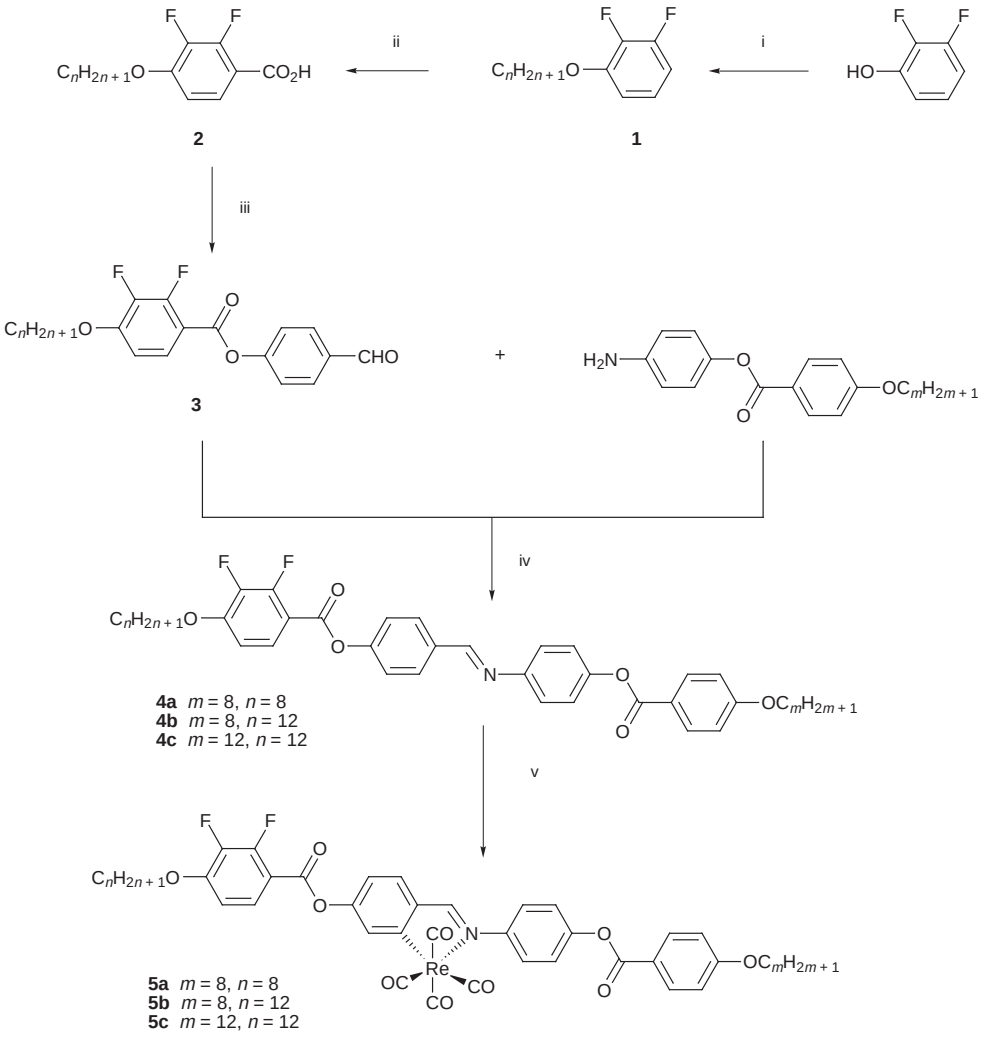
manganese and rhenium complexes of extended imines.[13] In these systems we typically found that a four-ring imine (*e.g.* **10**) with a clearing point of around 300 °C and more than one smectic phase, could be reacted with $[MMe(CO)_5]$ (M = Mn, Re) to give the orthometallated, tetracarbonyl derivative (*e.g.* **13**) of the ligand which would clear at more than 100 °C lower than the free ligand and would show only a nematic phase. We were then able to show[13c] that by using shorter, three-ring imines it was possible to realise materials with (monotropic) clearing points as low as about 70 °C. We were therefore keen to look at other strategies which might lead to lower melting points and, therefore, we undertook a study of fluorinated derivatives of the ligands and their metal complexes. Three, four-ringed imines were chosen and both di- and tetra-fluorinated derivatives, and their complexes with rhenium, were obtained.

Results and Discussion

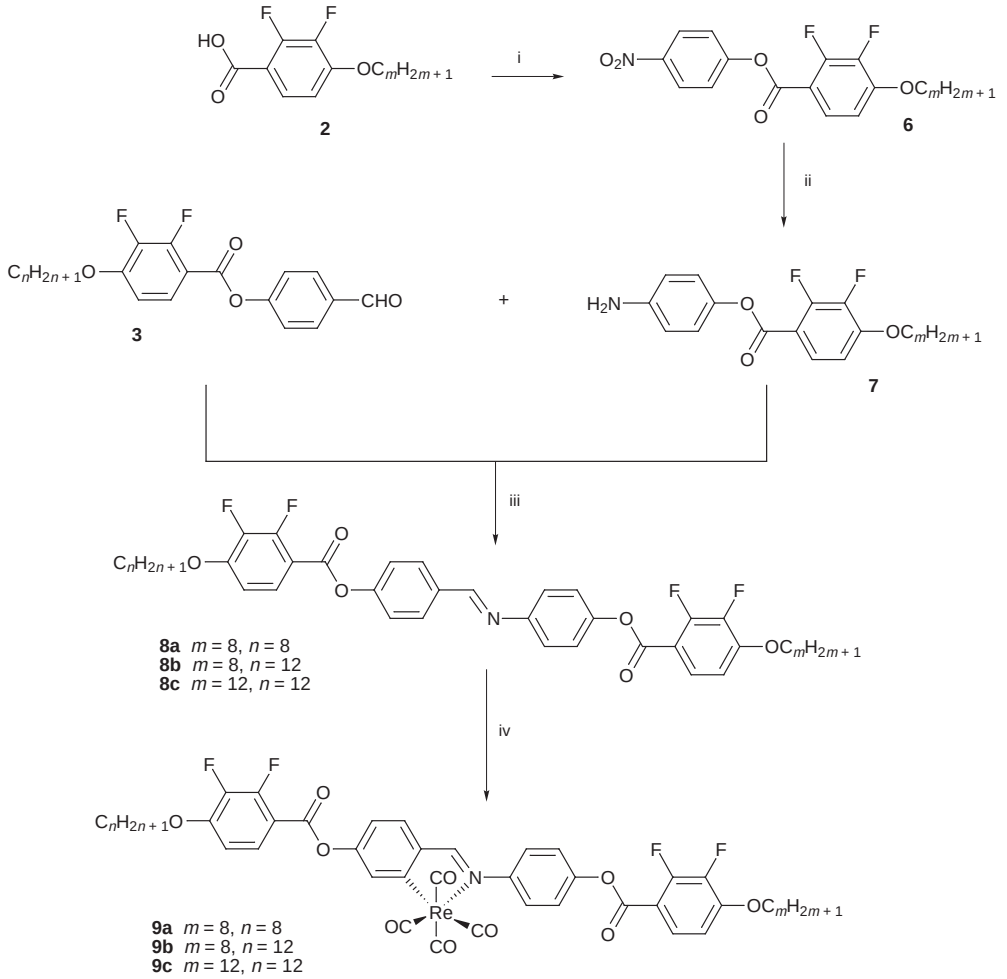
Synthesis

Difluoroimines were synthesized in a four-step reaction (Scheme 1). The unsymmetrical ether **1** was first obtained in a Williamson ether synthesis using 2,3-difluorophenol and the related 1-bromoalkane in dimethylformamide. Lithiation was then effected with an equimolar amount of butyllithium at −78 °C, followed by quenching with solid carbon dioxide to give a single product as detected by chromatographic (TLC) analysis of the crude product mixture. The crude product was isolated by adding aqueous sodium hydrogen carbonate, acidifying with cold, concentrated hydrochloric acid, and then extracting with chloroform. After crystallisation from chloroform, compound **2** (4-alkoxy-2,3-difluorobenzoic acid) was obtained as colourless crystals in *ca.* 85% yield. Compound **2** was then esterified with 4-hydroxybenzaldehyde using DCC–DMAP to give the aldehyde, **3**, which was then condensed with various anilines. Crystallisation of the resulting imines from dichloromethane–methanol, and then from toluene, gave the pure difluorinated imines, **4**, which were reacted with $[ReMe(CO)_5]$ in toluene at reflux. The resulting rhenium(I) complexes (**5**) were purified by flash column chromatography (neutral alumina), eluting with 20% hexanes–CH_2Cl_2 (v/v) to obtain the desired product in *ca.* 80% yield after crystallisation from dichloromethane and hexanes.

The synthesis of the tetrafluoro-substituted rhenium complexes, **9**, (Scheme 2) required 4′-(4-alkoxy-2,3-difluorobenzoyloxy)aniline derivatives in addition to the difluorobenzaldehydes **3**. Thus, 4-alkoxy-2,3-difluorobenzoic acid was esterified with 4-hydroxynitrobenzene using DCC–DMAP to give the 4-alkoxy-2,3-difluorobenzoyloxy-4′-nitrobenzene **6** which was then reduced to 4-alkoxy-2,3-difluorobenzoyloxy-4′-aniline derivatives using tin(II) chloride. The 4-alkoxy-2,3-difluorobenzoyloxyaniline derivatives **7** were purified by flash chromatography (silica gel), eluting with a solution of 1% triethylamine in 10% MeOH–CH_2Cl_2 (v:v:v). A brownish product, **7**, was obtained in *ca.* 70% yield, which was then condensed with the difluorinated aldehyde derivatives **3** and



Scheme 1 Synthetic route to difluoro-substituted rhenium complexes **5**. *Reagents and conditions*: i, $C_nH_{2n+1}Br$, K_2CO_3, DMF; ii, BuLi, $CO_{2(s)}$, THF; iii, DCC, DMAP, DCM; iv, toluene–acetic acid; v, $[ReMe(CO)_5]$–toluene.



Scheme 2 Synthetic route to tetrafluoro-substituted rhenium complexes **9**. *Reagents and conditions*: i, DCC, DMAP, DCM, 4-nitrophenol; ii, $SnCl_2{\cdot}2H_2O$, ethanol; iii, toluene–acetic acid; iv, $[ReMe(CO)_5]$–toluene.

crystallised from CH_2Cl_2–hexanes and then toluene to give compound **8** as colourless crystals. The tetrafluorinated imines **8** were reacted with $[ReMe(CO)_5]$ in toluene and the product purified by flash column chromatography (neutral alumina), eluting with 10% hexane–CH_2Cl_2 (v/v) to give the desired complexes **9** as yellow crystals in *ca.* 80% yield following crystallisation from CH_2Cl_2–hexane.

Ligand mesomorphism

Table 1 shows the transition temperatures for the parent, unsubstituted imine ligands **10**, **11** and **12**,[14] and those of their di- and tetra-fluorinated analogues, **4** and **8**. Thus, **11** and **12** exhibit crystal J, smectic I, C and nematic phases, while **10** exhibits crystal G, smectic C and nematic phases. The mesomorphism of these parent ligands and their fluorinated analogues is collected in Fig. 4.

The mesomorphism of the di- and tetra-fluorinated derivatives was rather similar in that all showed both a smectic C and a nematic phase, with none of the more ordered smectic phases being observed. The smectic C phase was characterised by its *schlieren* texture and the observation of transition bars on its transition to the nematic phase. The largest smectic C ranges were consistently observed for the difluoro imines, reaching nearly 150 °C in **4c**, but this range was obtained by a destabilisation of the crystal phase. The highest thermal stability for the S_C phase is with the tetrafluoro derivatives, while the highest nematic phase stability was found in the unsubstituted imines; the reduction in nematic range on increased fluoro substitution is nicely illustrated in Fig. 5.

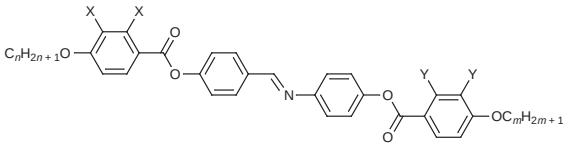
Clearly then, because of the position of the fluoro groups towards the end of the molecules, smectic phases are being stabilised in the shorter chain compound, while nematic phases are destabilised in the longer chain compounds. It is also of interest that all of the more highly ordered smectic phases have been suppressed. Further, if melting is taken to be the formation of a fluid smectic phase, then melting points are systematically lowered in the difluoro compounds and raised in the tetrafluoro compounds. The former may be explained by the unsymmetric nature of the imine, while the latter reflects increased (and symmetric) intermolecular dipolar associations.

Mesomorphism of the complexes

The mesomorphism behaviour of the complexes is collected in Table 2 along with the mesomorphism of the parent unfluorinated complexes; the behaviour is also illustrated graphically in Fig. 6.

Reaction of the parent imines with $[ReMe(CO)_5]$ led to complexes whose melting points (taken as the transition into a fluid phase) increased by 20–30 °C and whose nematic phase stability decreased by about 120 °C; all other phases were suppressed. In the case of the fluorinated ligands, complexation again led to the suppression of the S_C phase and the destabilisation of the nematic phase. This destabilisation was quite constant in the case of the tetrafluoro systems at 127 ± 1 °C, while it varied much more for the difluoro systems. In fact, the drop in T_{NI} on going from **4c** to **5c** is undetermined (except that it is at least 118 °C) as the complex simply melted at 141 °C with no sign of a monotropic phase before crystallisation on cooling. Another interesting point is that the stabilisation of the crystal phase on complexation shows a strong depen-

Table 1 Thermal behaviour for the fluoro-substituted imines and their parent compounds



Compound	X	Y	*n*	*m*	transition	*T*/°C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
10	H	H	8	8	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
4a	F	H	8	8	Crys–S_C	97	27.5	74
					S_C–N	213	2.6	5
					N–I	299	1.9	3
8a	F	F	8	8	Crys–S_C	127	33.2	83
					S_C–N	222	4.0	8
					N–I	288	1.1	2
11	H	H	12	8	Crys–J	91	13.5	38
					J–S_I	110	0.4	1
					S_I–S_C	118	0.8	2
					S_C–N	224	1.4	3
					N–I	284	1.0	1
4b	F	H	12	8	Crys–S_C	96	32.4	88
					S_C–N	216	2.1	4
					N–I	270	1.7	3
8b	F	F	12		Crys–S_C	120	32.2	82
					S_C–N	226	4.5	9
					N–I	264	1.4	3
12	H	H	12	12	Crys–J	99	32.6	88
					J–S_I	105	0.1	>1
					S_I–S_C	113	1.0	3
					S_C–N	234	3.3	7
					N–I	269	1.8	3
4c	F	H	12	12	Crys–S_C	86	31.0	86
					S_C–N	234	6.2	12
					N–I	259	2.4	5
8c	F	F	12	12	Crys–S_C	120	32.6	83
					S_C–N	231	5.2	10
					N–I	252	1.2	2

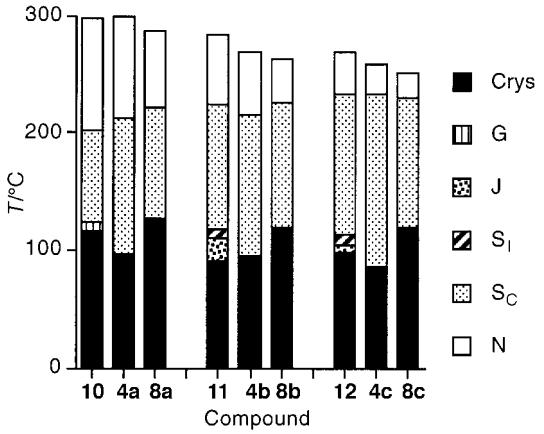


Fig. 4 Schematic representation of the mesomorphism of the non-fluorinated, di- and tetra-fluorinated imines

dence on the degree of fluorination, with difluorinated systems being stabilised by between 47 and 55 °C, while tetrafluorinated systems are stabilised by only 5–11 °C. We have no simple explanation for this phenomenon. However, the net effect is to produce complexes with shorter mesomorphic ranges due to destabilisation of the mesophase and stabilisation of the crystal phase. This behaviour is true for all of the systems examined and indeed, it would appear that the chain length has a larger influence.

These results are perhaps surprising given the more beneficial

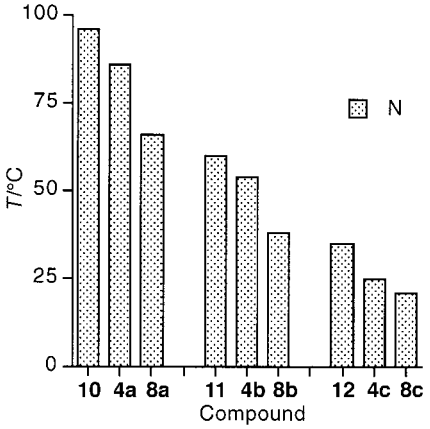
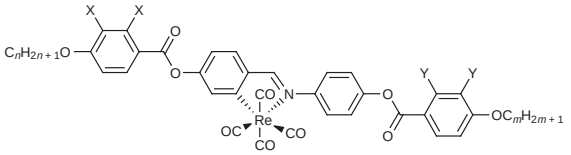


Fig. 5 Plot to show the decrease in the nematic range with increasing fluorine substitution

Table 2 Thermal behaviour for the rhenium complexes of the fluoro-substituted imines and their parent complexes



Compound	X	Y	*n*	*m*	transition	*T*/°C	ΔH/ kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
13	H	H	8	8	Crys–Crys'	135	6.8	17
					Crys'–N	154	32.2	75
					N–I	176	1.2	3
5a	F	H	8	8	Crys–Crys'	48	17.1	53
					Crys'–N	153	51.1	120
					N–I	164	2.6	6
9a	F	F	8	8	Crys–N	137	52.1	127
					N–I	160	1.6	4
14	H	H	12	8	Crys–N	130	48.0	118
					N–I	164	0.9	2
5b	F	H	12	8	Crys–Crys'	123	18.5	47
					Crys'–N	143	47.0	113
					N–I	149	1	2
9b	F	F	12	8	Crys–N	125	47.6	120
					N–I	138	0.7	2
15	H	H	12	12	Crys–Crys'	96	22.8	62
					Crys'–N	131	53.4	132
					N–I	145	0.9	2
5c	F	H	12	12	Crys–Crys'	95	33.2	90
					Crys'–I	141	30.6	74
9c	F	F	12	12	Crys–Crys'	61	19.1	57
					Crys'–I	131	43.2	107
					(N–I)	(125)	0.5	1

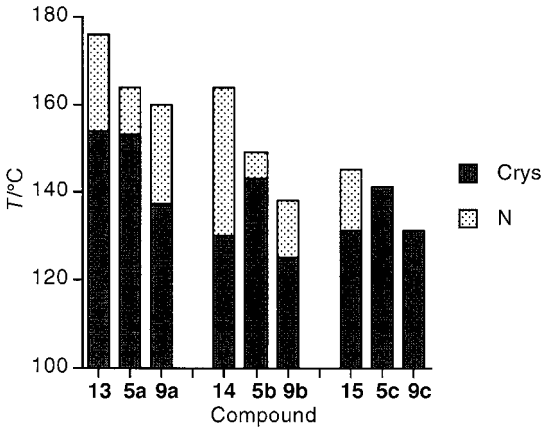


Fig. 6 Schematic representation of the mesomorphism in rhenium(I) complexes of non-fluorinated, di- and tetra-fluorinated imines

effects observed by Imrie and coworkers[7] with fluorinated ferrocenes, although it may just be that there is a more advantageous fluorine substitution pattern in these imines which will offer the chance of wider ranges and at lower temperatures. This awaits further study.

Experimental

Characterisation

Microanalyses were performed at Department of Chemistry, University of Exeter and Quantitative Technologies Inc., Whitehouse, NJ, Micro-analytical Service. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in electron impact (EI) mode. All chemicals were used as received unless otherwise specified. IR spectra were recorded on a Nicolet Magna 550 IR spectrometer at University of Toronto. Spectra were recorded as Nujol mulls between polythene plates, or as CH_2Cl_2 solutions, or KBr disks. ^{1}H NMR spectra were recored on a Varian Gemini 200 spectrometer; chemical shifts are quoted relative to an internal duterium lock. ^{19}F NMR spectra were recorded on a Varian Gemini 300 spectrometer and $CFCl_3$ was used as reference. The melting points and phase transitions of liquid crystal materials were observed by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC7 system with a Perkin-Elmer 7000 data station using TAS 7 software. Visual characterisation of the liquid-crystalline properties of the bulk materials was performed using a polarising optical microscope equipped with a Mettler FP82 hot stage and FP80 central processor at University of Toronto.

Toluene and tetrahydrofuran were distilled over sodium/benzophenone under nitrogen immediately before use. Dichloromethane was dried over molecular sieves (4A) for at least 24 h before use. All other solvents were used as received without further purification.

Synthesis

In all cases, the synthesis for one example is given along with the relevant spectroscopic data. All other homologues were the same with analogous spectra. Analytical data and yields are collected in Table 3.

2,3-Difluoro-4-octyloxybenzene 1. A mixture of 4-hydroxy-2,3-difluorobenzene (5.0 g, 38.4 mmol), 1-bromooctane (8.9 g, 46.1 mmol) and potassium carbonate (14.0 g, 96 mmol) in DMF (130 cm^3) was refluxed for 6 h. After cooling to room temperature, water (100 cm^3) was added in the flask to dissolve salt and then the product was extracted with diethyl ether three times. The extracts were washed with water and then dried over $CaCl_2$ overnight. After filtration, ether was evaporated under vacuum to give a yellow oil. Distillation under vacuum at 69 °C (5×10^{-3} mm Hg) afforded a colourless oil.

Yield 92%, ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.90 (t, 3H, CH_3), 1.31–1.55 (m, 10H, $5CH_2$), 1.80 (m, 2H, OCH_2CH_2), 4.03 (t, 2H, $J=6.6$ Hz, OCH_2), 6.75 (m, 2H, aromatic) and 6.97 (m, 1H, aromatic). MS: m/z 242 (M^+).

Table 3 Analytical data for the ligands and complexes

		calc. (found)		
compound	yield (%)	C	H	N
ligands				
4a	83	72.0 (72.4)	6.9 (6.9)	1.9 (2.0)
4b	75	73.3 (73.2)	7.5 (7.3)	1.8 (1.8)
4c	78	74.1 (73.8)	7.9 (7.8)	1.7 (1.7)
8a	83	68.9 (68.7)	6.3 (6.2)	1.9 (1.8)
8b	81	70.0 (70.1)	7.0 (7.3)	1.9 (1.8)
8c	76	71.1 (70.9)	7.4 (7.2)	1.6 (1.6)
complexes				
5a	77	55.8 (55.6)	4.8 (4.9)	1.4 (1.4)
5b	82	57.4 (57.1)	5.3 (5.1)	1.3 (1.3)
5c	78	58.8 (58.5)	5.7 (5.6)	1.3 (1.2)
9a	83	53.9 (53.6)	4.4 (4.3)	1.3 (1.3)
9b	72	55.5 (55.2)	4.9 (5.1)	1.3 (1.3)
9c	75	57.0 (56.6)	5.4 (5.3)	1.2 (1.2)

2,3-Difluoro-4-octyloxybenzoic acid 2. A solution of the 2,3-difluoro-4-octyloxybenzene **1** (3.0 g, 12.4 mmol) in dry THF (100 cm^3) was blanketed with nitrogen and then treated dropwise at −78 °C with butyllithium in hexane (7.75 cm^3 in 1.6 M hexanes). When the addition was complete, the mixture was stirred for *ca.* 5 h at the same temperature and then poured into *ca.* 100 g of crushed, solid carbon dioxide. After 15 h the residue was treated with 10% aqueous sodium bicarbonate and then with diethyl ether. The aqueous layer was separated, washed with diethyl ether, acidified with cold concentrated hydrochloric acid, and extracted with chloroform. The combined chloroform extracts were dried over anhydrous Na_2SO_4, and TLC analysis of the extract showed the presence of one significant product. The solvent was removed *in vacuo* to give a white residue, which was purified by crystallisation from chloroform.

Yield, 2.99 g (84.6%), ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.90 (t, 3H, CH_3), 1.25–1.65 (m, 10H, $5CH_2$), 1.86 (m, 2H, OCH_2CH_2), 4.09 (t, 2H, OCH_2), 6.8 (m, 1H, aromatic) and 7.8 (m, 1H, aromatic), 9.0 (br s, CO_2H). ^{19}F NMR (300 MHz, CD_2Cl_2), δ −132.93 (dd), −158.65 (dd). MS: m/z 286 (M^+) (HRMS: found: M^+, 286.1381. $C_{15}H_{20}F_2O_3$ requires 286.1368).

4′-(4-Alkoxy-2,3-difluorobenzoyloxy)benzaldehyde 3. All esters were obtained using this general procedure.

Dicyclohexyl carbodiimide (5.94 g, 28.8 mmol) and 4-(*N,N*-dimethylamino)pyridine (0.15 g) were added to a stirred solution of the relevant acid (24 mmol) and hydroxybenzaldehyde (3.0 g, 24.0 mmol) in dry dichloromethane (100 cm^3). The reaction mixture was stirred at room temperature for 6 h. The precipitated dicyclohexyl urea was removed by filtration and the residue was reduced to dryness on a rotary evaporator. The crude product was purified by column chromatography (silica gel, CH_2Cl_2) to give the product as a colourless solid.

$n=8$; yield: 67.3%, ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.90 (t, 3H, CH_3), 1.25–1.65 (m, 10H, $5CH_2$), 1.86 (m, 2H, OCH_2CH_2), 4.09 (t, 2H, OCH_2), 6.8 (m, 1H, aromatic), 7.45 (d, 2H, AA′XX′), 7.87 (dd, 1H, aromatic), 8.0 (dd, 2H, AA′XX′), 10.0 (s, 1H, CHO). ^{19}F NMR (300 MHz, CD_2Cl_2), δ −132.14 (dd), −157,64 (dd). MS: m/z 391 (MH^+), 269, 157(100%) (HRMS: found: MH^+, 391.1721. $C_{22}H_{24}F_2O_4$ requires M, 391.1711).

4′-(4-Alkyloxy-2,3-difluorobenzoyloxy)nitrobenzene 6. For the compounds **6**, the synthesis was performed in an analogous manner as **3** above.

$m=8$; yield: 74.2%, ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.90 (t, 3H, CH_3), 1.25–1.65 (m, 10H, $5CH_2$), 1.86 (m, 2H, OCH_2CH_2), 4.15 (t, 2H, OCH_2), 6.86 (dd, 1H, aromatic), 7.43 (d, 2H, AA′XX′), 7.87 (dd, 1H, aromatic), 8.34 (dd, 2H, AA′XX′).

4′-(4-Alkyloxy-2,3-difluorobenzoyloxy)aniline 7. All anilines were obtained from the parent nitro compound according to the following general method.

A mixture of the nitrobenzene (13 mmol) and $SnCl_2{\cdot}2H_2O$ (15.2 g, 65 mmol) was heated at reflux in ethanol (100 cm^3) for 6 h. After cooling, the mixture was poured into ice and the pH was adjusted to *ca.* 7–8 using sodium hydroxide. The mixture was then extracted with ethyl acetate. The ethyl acetate solution was washed three times with brine and was then dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure. The brownish solid was purified by column chromatography (silica gel: 1% Net_3–CH_2Cl_2, v/v) and then crystallised from ethanol to give an off-white solid.

$n=8$; yield: 71%, ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.90 (t, 3H, CH_3), 1.25–1.65 (m, 10H, $5CH_2$), 1.86 (m, 2H, OCH_2CH_2), 3.35 (br s, 2H, NH_2), 4.1 (t, 2H, OCH_2), 6.7 (dd, 2H, AA'XX'), 6.8 (dd, 1H, aromatic), 7.0 (dd, 2H, AA'XX'), 7.82 (dd, 1H, aromatic). ^{19}F NMR (300 MHz, CD_2Cl_2), δ −132.77 (dd), −158.03 (dd). MS: m/z 377 (M^+), 269, 157 (100%), 108, 57 (HRMS: found: M^+, 377.1803. $C_{21}H_{25}F_2O_3$ requires M, 377.1809).

Difluoro-substituted imines 4. All imines were obtained using the following general procedure.

The relevant aniline (19.2 mmol) was dissolved in toluene (25 cm^3) and then acetic acid (2 drops) was added to the solution. The relevant aldehyde (19.2 mmol) was added to the solution which was stirred for a few minutes then left unstirred overnight. The crude product was filtered and crystallised from CH_2Cl_2–MeOH and then from toluene, to give a colourless, crystalline product.

4a: ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.88 (t, 6H, $2CH_3$), 1.25–1.65 (m, 20H, $10CH_2$), 1.86 (m, 4H, $2OCH_2CH_2$), 4.05 (t, 2H, $J=6.6$ Hz, OCH_2), 4.14 (t, 2H, $J=6.5$ Hz, OCH_2), 6.81 (ddd, 1H, aromatic), 7.0 (dd, 2H, AA'XX'), 7.2–7.4 (m, 6H, AA'XX'), 7.82 (ddd, 1H, aromatic), 8.0 (d, 2H, AA'XX'), 8.17 (d, 2H, AA'XX'), 8.5 (s, 1H, CH=N). ^{19}F NMR (300 MHz, CD_2Cl_2), δ −132.30 (dd, 1F, $J=19.7$, 8.2 Hz), −157.74 (dd, 1F, $J=18.7$, 8.1 Hz).

Difluoro-substituted rhenium(I) complexes 5. All difluoro-substituted rhenium(I) complexes **5** were synthesised in an analogous manner using the following method.

Ligand **4a** (0.15 g, 0.21 mmol) and (pentacarbonylmethyl)-rhenium (0.07 g, 0.21 mmol) were dissolved in dry toluene and heated at reflux for 12–16 h under nitrogen. Solvent was then removed *in vacuo* and passed through a column of neutral alumina eluting with hexanes–CH_2Cl_2 (1:4, v/v) to obtain the desired rhenium(I) complex fraction. Following crystallisation from CH_2Cl_2–MeOH, a yellow crystalline product was obtained.

5a; yield 76.7%, IR (CH_2Cl_2 solution) ν/cm^{-1}: 2093w (CO), 1992vs (CO), 1987s (CO), 1934m (CO) and 1731(C=O), 1606 (C=N). ^{1}H NMR (200 MHz, CD_2Cl_2), δ 0.88 (t, 6H, $2CH_3$), 1.25–1.65 (m, 20H, $10CH_2$), 1.86 (m, 4H, $2OCH_2CH_2$), 4.05 (t, 2H, $J=6.6$ Hz, OCH_2), 4.14 (t, 2H, $J=6.5$ Hz, OCH_2), 6.9 (ddd, 1H, aromatic), 7.05 (m, 3H), 7.4 (m, 4H, AA'XX'), 7.82 (dd, 2H), 7.9 (d, 1H, aromatic), 8.15 (d, 2H, AA'XX'), 8.67 (s, 1H, CH=N). ^{19}F NMR (300 MHz, CD_2Cl_2), δ −132.43 (dd, 1F, $J=19.3$, 7.8 Hz), −157.82 (dd, 1F, $J=19.2$, 6.6 Hz).

Tetrafluoro substituted imine ligands 8. The imine ligands **8** were obtained in an analogous manner as those of ligands **4.**

8a: ^{1}H NMR (200 MHz, $CDCl_3$), δ 0.88 (t, 6H, $2CH_3$), 1.25–1.65 (m, 20H, $10CH_2$), 1.86 (m, 4H, $2OCH_2CH_2$), 4.15 (t, 4H, $J=6.5$ Hz, $2OCH_2$), 6.81 (ddd, 2H, aromatic), 7.2–7.4 (m, 6H, AA'XX'), 7.87 (ddd, 2H, aromatic), 8.0 (d, 2H, AA'XX'), 8.5 (s, 1H, CH=N). ^{19}F NMR (300 MHz, CD_2Cl_2), δ −132.30 (dd, 1F, $J=19.6$, 7.9 Hz), −132.47 (dd, 1F, $J=19.7$, 7.1 Hz), −157.73 (dd, 1F, $J=18.7$, 8.1 Hz), −157.85 (dd, 1F, $J=19.3$, 8.5 Hz).

Tetrafluoro-substituted rhenium(I) complexes 9. Tetrafluoro-substituted rhenium(I) complexes **9** were obtained in a manner analogous to that used in complexes **5**.

9a: IR (CH_2Cl_2 solution) ν_{max}/cm^{-1}: 2093w (CO), 1992vs (CO), 1934m (CO) and 1735m (C=O), 1623w (C=N). ^{1}H NMR (200 MHz, CD_2Cl_2), δ 0.9 (t, 6H, $2CH_3$, overlapped), 1.25–1.65 (m, 20H, $10CH_2$), 1.86 (m, 4H, $2OCH_2CH_2$), 4.15 (t, 4H, $J=6.6$ Hz, OCH_2), 6.9 (ddd, 2H, aromatic, overlapped), 7.08 (dd, 1H, $J=8.2$ Hz, 2.4), 7.36 (m, 4H, AA'XX'), 7.8–7.93 (m, 4H, 2AMX + 2aromatic), 8.65 (s, 1H, CH=N). ^{19}F NMR (300 MHz, CD_2Cl_2), δ −132.26 (dd, 1F, $J=19.3$, 8.1 Hz), −132.44 (dd, 1F, $J=19.3$, 8.1 Hz), −157.72 (dd, 1F, $J=19.2$, 6.6 Hz), −157.83 (dd, 1F, $J=19.3$, 7.1 Hz).

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