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The Synthesis and Mesomorphism of Some Fluorinated 2,2′-Bipyridines and their Complexes with Rhenium(I)

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Tetrafluoro derivatives of four- and six-ring bipyridines were synthesised, along with their corresponding complexes of Re(I). The mesomorphism of the fluorinated and non-fluorinated materials was compared.

Keywords: Metallomesogens; bipyridines; rhenium; fluorination

INTRODUCTION

The effect of lateral substituents on thermotropic liquid crystals in terms of both mesophase stability, and physical properties, has been the subject of a number of investigations [1, 2]. Generally, however, the effect of a lateral substituent is to broaden a molecule, thereby reducing lateral interactions, which in turn suppresses the thermal stabilities of the mesophases, in particular smectic phases. However, if the substituent is dipolar in nature then more subtle effects on the mesomorphism may be observed. For example, dipole moments may act along the molecular long axis, enhancing the lateral interactions that stabilise smectic phases, or they may just as readily work against these lateral interactions, thereby destabilising the mesophase and promoting a nematic phase.

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Of all the lateral substituents studied, it is fluorine that has received the most attention. The advantage of using fluorine over other substituents is its small size and high electronegativity [3]. Fluorine is the smallest possible lateral substituent that can be incorporated into the molecular structure, with a van der Waals radius of 1.47 Å, comparable to the van der Waals radius of hydrogen which is 1.2 Å. Despite being only marginally larger than hydrogen, this substituent can influence mesomorphism, but as it does not reduce the structural anisotropy to the same extent as other substituents, the risk of total suppression of mesophase is reduced. The effect that fluorine substitution may have on a series of related mesogens is beautifully illustrated by the work of the Hull group with various terphenyls (Fig. 1) [4].

The incorporation of this small but highly polar group in a number of systems has been shown to alter molecular associations, which in turn effects the observed mesomorphism and the physical properties. Thus, understanding of its effects could lead to the generation of molecules with the desired properties for a particular application.

Fluorination has also been studied in relation to various metallomesogenic systems, and these are briefly discussed here. Courtieu [5] looked at the effect that a lateral halogen (either Cl or Br) would have on a series of salicylaldimine copper(II) complexes (Fig. 2), which were found to exhibit nematic phases.

The halogen was placed in either the 3- or the 5-position relative to the ring position bearing the imino carbon. It was found that the effect of

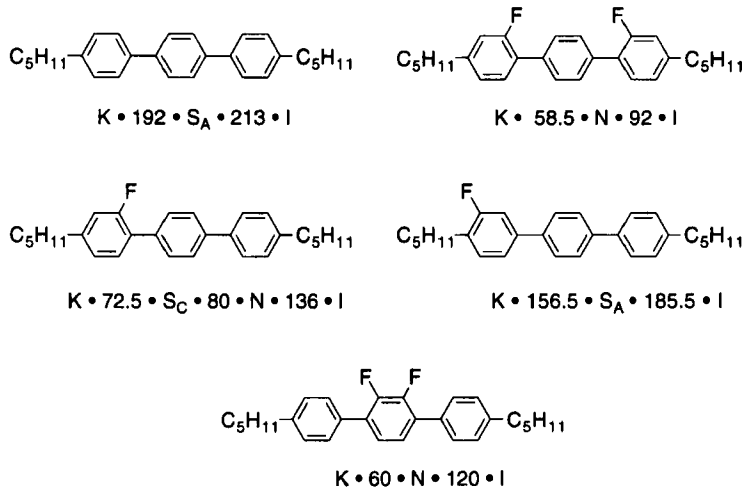

FIGURE 1 The effects of fluorination on the terphenyl systems.

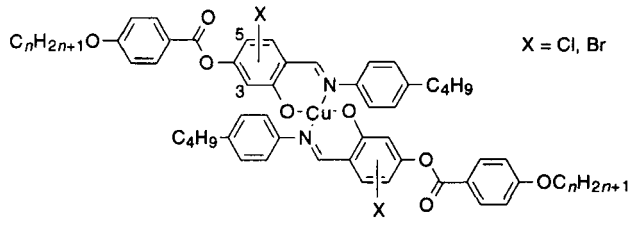

FIGURE 2 The halogenated copper(II) salicylaldimine complexes.

halogenation was to lower the clearing temperatures and to reduce the nematic phase range, without exception. The reduction in the clearing temperature was found to be greatest when X = Br. However, the effect on the clearing temperature due to the position of the halogen was somewhat curious. It was expected that the reduction in clearing temperature would be greatest for the 5-substitution, as the broadening effect of a halogen in the 3-position was expected to be negligible due to steric shielding by the rest of the molecule. Indeed, this was found to hold true when X = Cl with the reduction in clearing temperature being greatest for the 5-substitution. Curiously, however, when X = Br then no simple correlation was found between T_{NI} and the position of the substituent.

The fluorinated monosubstituted ferrocene derivative, shown in Figure 3 was been described by Imrie *et al.* [6], and was found to exhibit a nematic phase at a much lower temperature than its non-fluorinated analogue.

We carried out a rather systematic investigation of Ag(I) complexes of 2- or 3-fluorinated-4-alkoxystilbazoles (Fig. 4) [7].

The non-fluorinated silver complex with X = OTf (trifluoromethanesulphonate) was found to show crystal G, S_C, S_A and N mesophases [8], while when X = DOS (dodecyloxysulphate) then the mesomorphism observed was S_C, S_A, N and cubic [9].

The overriding effect of incorporating a fluorine in the 3-position (*ortho* to the alkoxy chain), was to promote S_A phase behaviour at the expense of the

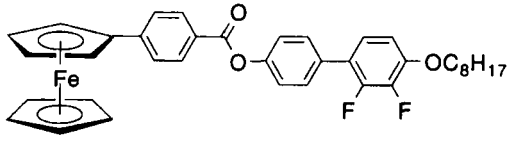

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FIGURE 3 A difluorinated ferrocene derivative.

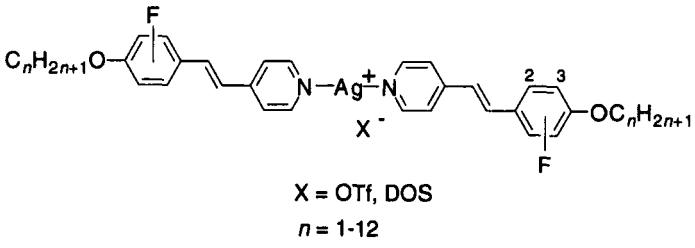


FIGURE 4 The silver complexes of the 2- and 3-fluorinated stilbazoles.

other mesophases seen in the unfluorinated derivatives. Thus, the N phase range was reduced, the crystal G phases and the cubic phases were no longer seen, and the thermal stability of the S_C phase was reduced.

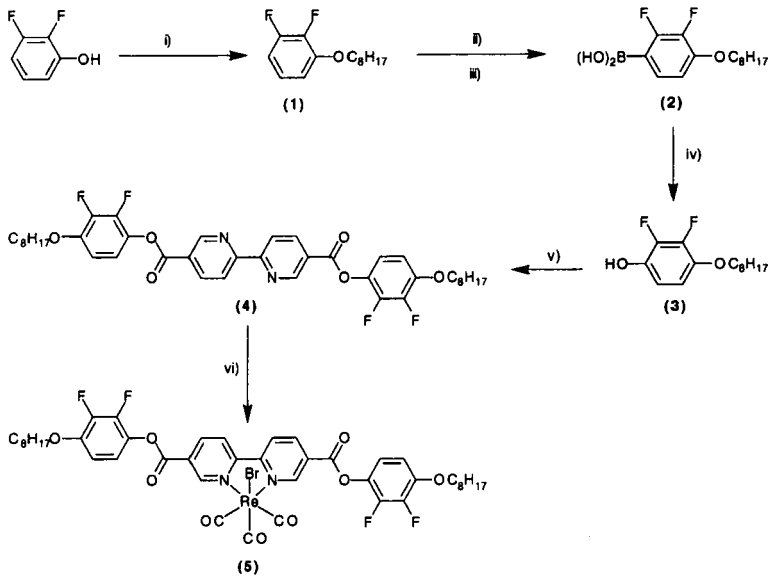
When a fluorine was incorporated into the 2-position, then both the melting and clearing temperatures were found to be lower than in the non-fluorinated analogues. The clearing point was lowered quite dramatically, with a decrease of ca 40–50°C for X = OTf, and a decrease of ca 60°C for X = DOS. The effect of fluorination in the 2-position was also found to lower the thermal stabilities of both the S_A and S_C phases (in fact totally destabilising the S_A phase for X = DOS), but to promote N phase formation, while retaining the cubic phases.

Other studies have been carried out on fluorinated salens [10], dithiobenzoates [11] stilbazole complexes of Ir(I) [12], β-diketonate complexes [13] and Re complexes of fluorinated imines [14].

Previously, we have reported on the mesomorphism of some 5,5′-disubstituted bipyridines [15] and their metal complexes [16], some of which have been found to be mesomorphic [17]. In the main, these have been rather high-melting systems both as free ligands and as complexes with Re(I) and we were therefore curious to see whether transition temperatures could be usefully reduced by using fluorinated ligands. Therefore, three ligand types were identified for synthesis of which complexes were obtained for two. The synthesis and mesomorphism of these ligands and complexes are now described.

SYNTHESIS

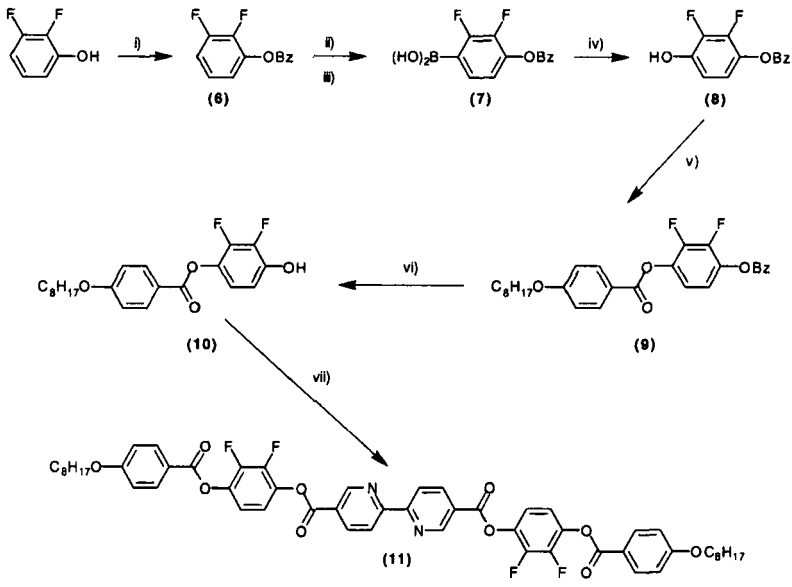
One four-ring and two six-ring ligands were identified, and their synthesis (and that of the related Re(I) complex) are shown in Schemes 1–3.



SCHEME 1 The synthesis of a fluorinated Re(I) complex. Reagents and conditions: i) C_8H_{17}/K_2CO_3/Acetone; ii) ^{n}BuLi; iii) Triisopropylborate/HCl; iv) H_2O_2/HCl; v) 2,2′-Bipyridine-5,5′-diacid dichloride/toluene/Et_3N; vi) [$ReBr(CO)_5$]/toluene/heptane.

Alkylation of 2,3-difluorophenol with 1-bromooctane gave 2,3-difluorooctyloxybenzene (**1**) in essentially quantitative yield (Scheme 1). It was then reacted with butyllithium in THF at −78°C to give 2,3-difluoro-4-lithiooctyloxybenzene, which was further reacted with triisopropylborate *in situ*, followed by 10% hydrochloric acid to give the related boronic acid (**2**). Conversion to the phenol (**3**) was achieved in a yield of 95% after treatment with hydrogen peroxide at reflux in THF [18]. The phenol so obtained, was subsequently reacted with the 2,2′-bipyridine-5,5′-diacid chloride in toluene at reflux, to give the ligand (**4**) in a yield of 36%. Reaction of the ligand with bromopentacarbonylrhenium(I) gave (**5**) as a bright red solid in quantitative yield.

Compound (**6**) (Scheme 2) was synthesised by heating 3,4-difluorophenol at reflux with benzyl bromide, and potassium carbonate in acetone. Conversion to the phenol (**8**) *via* the boronic acid was by an identical method to that described for (**2**), except that the yield of the boronic acid was found to be lower than expected (33%), probably due to competitive deprotonation from the CH_2 moiety in the benzyl group. Reaction of (**8**) with 4-octyloxybenzoic acid was *via* a standard DCC/DMAP esterification in dichloromethane at room temperature. Removal of the benzyl protecting



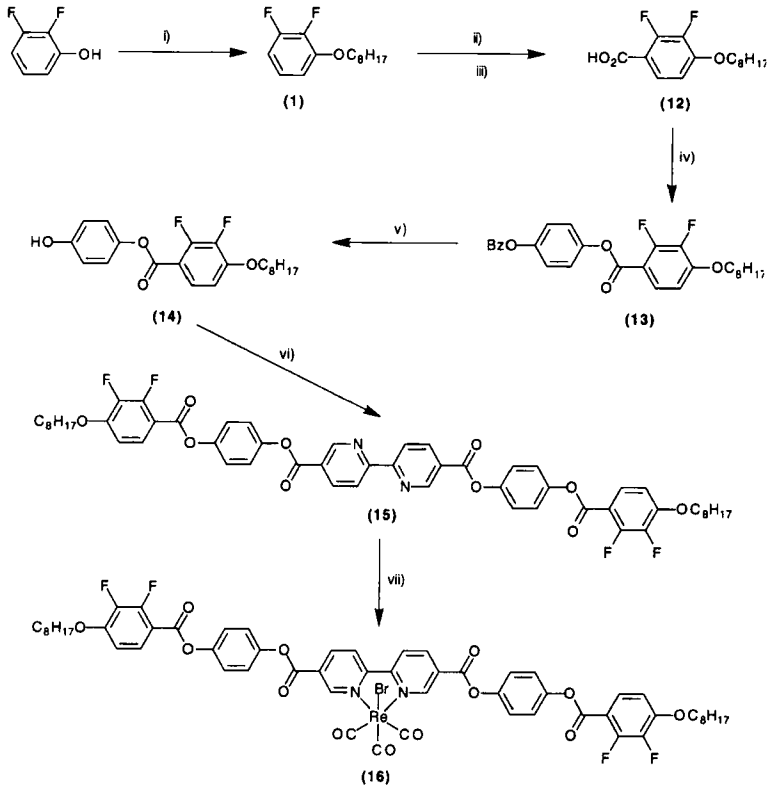
SCHEME 2 Synthesis of the six-ring ligand (**11**) with the inner ring fluorinated. Reagents and conditions: i) Benzyl bromide/K_2CO_3/acetone; ii) ^{n}BuLi; iii) Triisopropylborate/HCl; iv) H_2O_2/HCl; v) Octyloxybenzoic acid/DCC/DMAP; vi) H_2/Pd/C; vii) 2,2′-bipyridine-5,5′-diacid dichloride/toluene/Et_3N.

group by hydrogenolysis using palladium on charcoal gave quantitative yields of the phenol (**10**). Reaction of (**10**) with 2,2-bipyridine-5,5′-diacid-dichloride gave the target ligand (**11**) and subsequent reaction to give the Re(I) complex was as described above.

2,3-Difluorooctyloxybenzene (**1**) was lithiated and then converted *in situ* to the carboxylic acid (**12**) by the subsequent addition of solid CO_2, followed by an acidic work up (Scheme 3). Esterification with 4-benzyloxyphenol *via* a standard DCC/DMAP reaction gave (**13**) in ca 80% yield. The benzyl group was removed in quantitative yield by hydrogenolysis, and the resulting phenol (**14**) was esterified with 2,2-bipyridine-5,5′-diacid dichloride to give the target ligand (**15**). The Re(I) complex (**16**) was obtained as described above.

All of the compounds were characterised by ^{1}H, ^{13}C and ^{19}F spectroscopy, but in order to assign the ^{19}F spectra, it was necessary to obtain ^{19}F{^{1}H} spectra which was done using **12**.

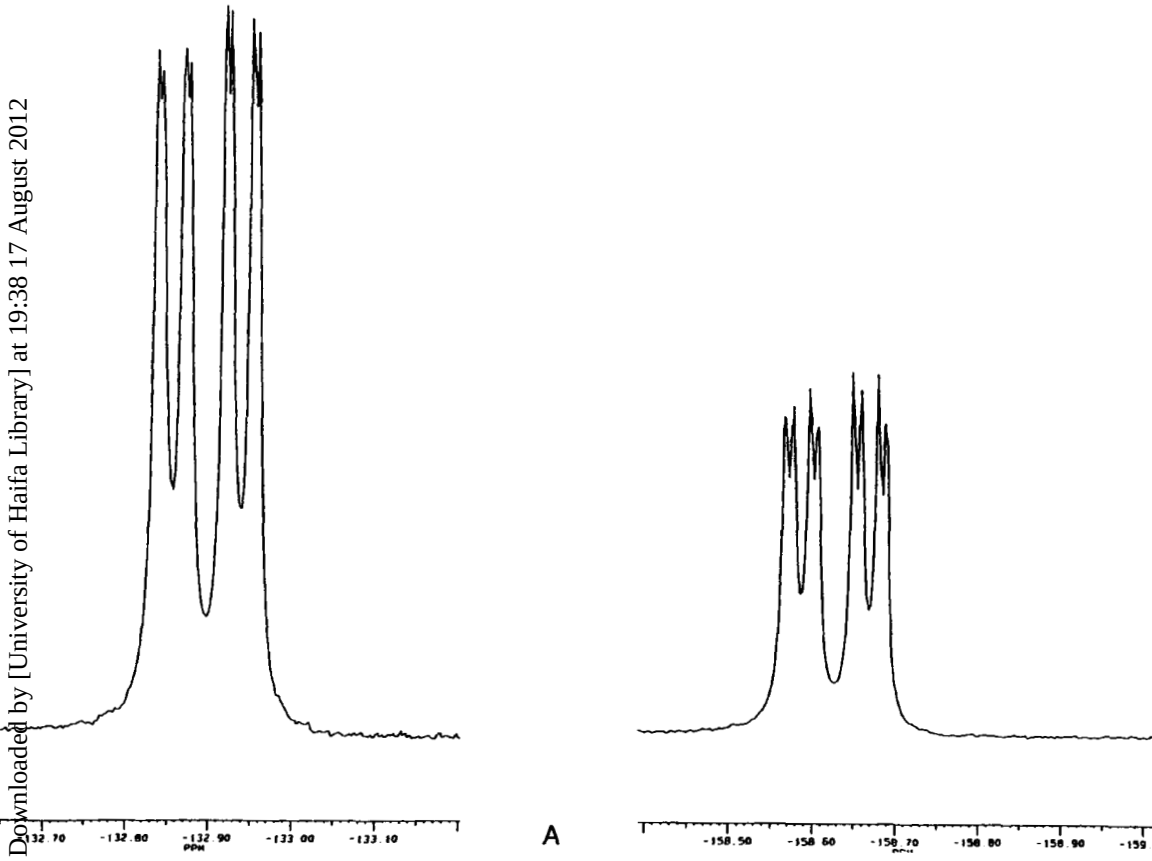
The ^{1}H spectrum showed two distinct signals in the aromatic region at 7.8 and 6.8 ppm, corresponding to the aromatic protons H6 and H5 (see figure in experimental), *ortho* and *meta* to the carboxylic acid group, respectively.



SCHEME 3 Synthesis of the six-ring Re(I) complex with the outer ring fluorinated. Reagents and conditions: i) $C_8H_{17}Br/K_2CO_3$/acetone; ii) $^nBuLi/CO_2$(s)/HCl; iii) 4-Benzyloxyphenol/DCC/DMAP; iv) H_2/Pd/C; v) 2,2′-bipyridine-5,5′-diacid dichloride/toluene/Et_3N; vi) $[ReBr(CO)_5]$/toluene/heptane.

These signals were assigned unambiguously from the formula $\delta_H = 7.27\Sigma + Z_i$ [19]. The protons are coupled to each other and also to both of the fluorine atoms giving rise to the splitting pattern observed, namely a doublets of doublets. The largest coupling constant arises from the *ortho* coupling between the two protons ($^3J_{HH} = 9.5$ Hz), the next largest coupling constant is attributed to the *meta* coupling between the protons and fluorines ($^4J_{HF}$ = ca 7 Hz), and the smallest coupling constant ($^5J_{HF}$ = ca 2 Hz), is attributed to the *para* coupling between the protons and fluorines.

The ^{19}F spectrum (Fig. 5A) of (**12**) shows two very clear signals, one for each of the fluorine atoms, which are approximately 25 ppm apart. Each signal shows a distinct doublet of doublets splitting pattern, due to coupling between the fluorine atoms and also to both of the protons. The largest



) ^{19}F NMR spectrum of (**12**); B) ^{19}F-{partial-^{1}H} NMR spectrum of (**12**) with decoupling of H6; C) ^{19}F-{partial-^{1}H} NMR spec
H5.

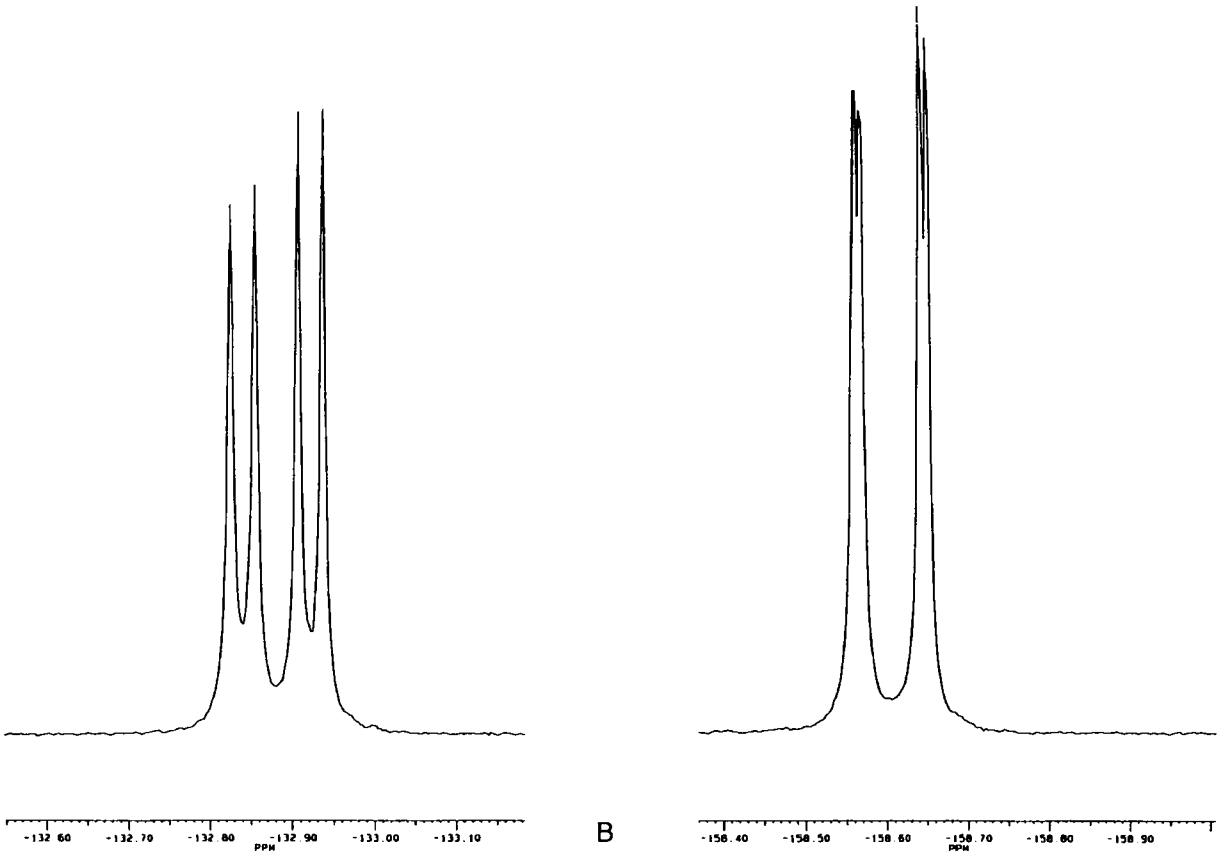


FIGURE 5 (Continued).

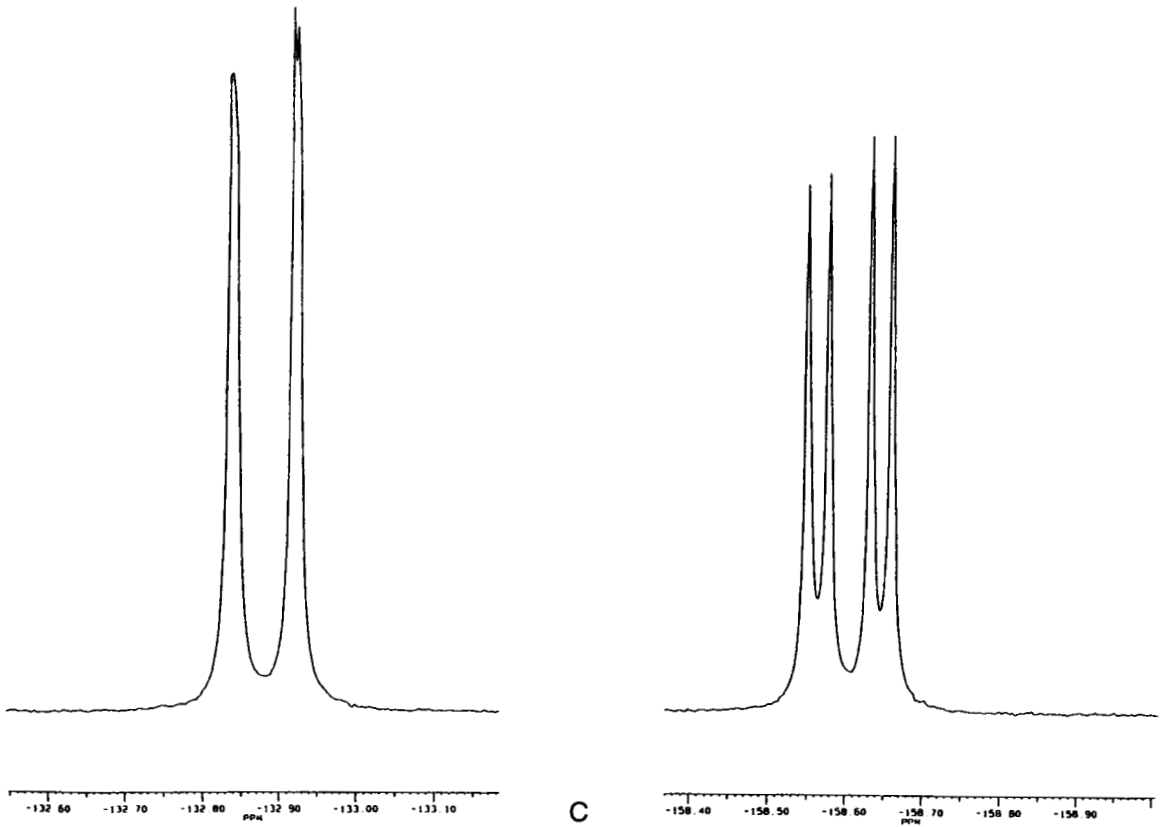


FIGURE 5 (Continued).

coupling constant arises from the *ortho* coupling between the two fluorines ($^3J_{FF}$ = ca 19 Hz), the next largest coupling constant is attributed to the *meta* coupling between the protons and fluorines ($^4J_{HF}$ = ca 7 Hz), and the smallest coupling constant ($^5J_{HF}$ = ca 2 Hz), is attributed to the *para* coupling between the protons and fluorines.

Despite the clarity of the spectra, it was not possible to ascertain which signal belonged to which fluorine, and so ^{19}F-{^1H} spectra were obtained with selective ^1H decoupling. Irradiation at 7.8 ppm (Fig. 5B) removed any coupling associated with H6 from the ^{19}F spectra, and resulted in the $^4J_{HF}$ coupling disappearing from the lower field signal and the fine coupling associated with $^5J_{HF}$ disappearing from the higher field signal. Hence, H6 must be *meta* to the lower field fluorine and *para* to the upper field fluorine, again leading to the assignments of F2 for the lower field signal, and F3 for the higher field signal.

These assignments can also be confirmed by irradiation at 6.8 ppm (Fig. 5C) which removed any coupling associated with the H5 from the ^{19}F spectra and led to the fine coupling ($^5J_{HF}$) in the lower field signal disappearing, with the $^4J_{HF}$ coupling disappearing from the higher field signal. Hence, H5 must be *para* to the lower field fluorine and *meta* to the upper field fluorine, leading to the assignments of F2 for the lower field signal, and F3 for the higher field signal.

MESOMORPHISM

Four-ring System: The thermal behaviour of the ligands is first compared with their non-fluorinated analogues. The non-fluorinated analogue of (**4**) is designated (**17**); similarly, (**18**) is the non-fluorinated analogue of complex (**5**). The thermal data for (**4**), (**17**), (**5**) and (**18**) are collected in Table I. For the ligands, the clearing point of **4** is destabilised by about 30°C relative to (**17**), the S_A phase of (**17**) has gone, as has the crystal smectic J phase, although interestingly, the crystal phase is stabilised in the fluorinated material. The S_C and N phase of (**4**) were identified by their characteristic textures, the former giving both schlieren and broken fan textures, while the latter gave a classic schlieren texture with both two- and four-brush disclinations. Transition bars were seen at the S_C–N transition. It would, therefore, appear that there has been a broadening effect on fluorination which has led to a reduction in clearing point. However, the ability of the 2,2′-bipyridine group to promote the S_C phase [15] has been suppressed on fluorination, presumably due to the presence of enhanced lateral dipoles

TABLE I Thermal data for the fluorinated and non-fluorinated ligands and their rhenium(I) complexes

Compound	*Transition*	*T/°C*	*ΔH/kJ mol⁻¹*	*ΔS/J K⁻¹ mol⁻¹*
Four-ring systems				
17	Crys → J	135	18.9	46
(Non-fluorinated)	J → S_C	155	30.5	71
	S_C → S_A	275	–†	–†
	S_A → N	280	–†	–†
	N → I	290	1.2	2
4	Crys → S_C	206	69.7	146
	S_C → N	232	1.8	4
	N → I	259	0.9	2
18	Crys → I	253	–	–
(Non-fluorinated)				
5	Crys → I	245	–	–
Six-ring systems				
19	Crys → S_C	231	52.3	104
(Non-fluorinated)	S_C → N‡	328	–	–
11	Crys → S_C	219	63.3	129
	S_C → N‡	256	1.1	2
15	Crys → Crys′	174	1.9	4
	Crys′ → S_C	239	53.1	105
	S_C → N‡	360	–	–
20	Crys → N	224	17.7	36
(Non-fluorinated)	N → I	315	0.9	2
16	Crys → S_C	224	18.5	37
	S_C → N‡	259	–†	–†
	N → I‡	304	–†	–†

† Not seen by DSC.
‡ With decomposition.

which would tend to destabilise the formation of lamellar phases (the S_A phase is also suppressed). Fluorination has little effect on the complex with both (**5**) and (**18**) melting at rather similar temperatures without showing a mesophase. Given that (**18**) is not mesomorphic, this is perhaps not such a surprising result.

Six-ring Systems (Tab. I): The mesomorphism of the ligands with fluorines on the inner ring (**11**) and on the outer ring (**15**) are compared with the non-fluorinated parent ligand (**17**) [16]. In each case, the mesophases observed were unaffected by the fluorine substitution, and both smectic C and nematic phases were seen in all three ligands. However, the extent to which the various phases were stabilised or not was different according to the pattern of fluorine substitution. Fluorine substitution at the inner rings (**11**) led to a small destabilisation of the crystal phase and a very strong destabilisation of the smectic C phase by some 70 K. Unfortunately, in none of these ligands was it possible to evaluate the effect on the nematic

phase as decomposition began in the nematic phase and so no clearing points could be measured. However, in the ligand with fluorine substitution at the outer rings (**15**), an additional crystal phase was added, the crystal phase was slightly stabilised and the smectic C phase was stabilised by some 30 K. Thus, it would appear that substitution close to the core of the molecule acted to give an enhanced lateral dipole which acted against the attractive lateral interactions stabilising the smectic C phase, while fluorine substitution closer to the end of the molecule acted a little more like an outboard dipole, reinforcing the forces acting to stabilise the smectic C phase. These differences are exemplified by the fact the smectic C phase range could be controlled from 37 – 121 K depending on the position of fluorine substitution.

The effect on the mesomorphism of the ligands on complexation was potentially more interesting, but a complete comparison was precluded by the very small amount of (**11**) obtained which did not allow the synthesis of the related Re complex. Time in the project mitigated against a resynthesis. However, comparison can be made between the mesomorphism of the non-fluorinated ligand (**19**), its complexes with Re(I) (**20**), and the mesomorphism of ligand (**15**) and *its* complex with Re(I) (**16**). Complexation of (**19**) to give (**20**) resulted [16] in the S_C phase of the ligand being lost with only a nematic phase being seen. The nematic phase was clearly destabilised on complexation as a clearing point of 315°C found for (**20**), while (**19**) decomposed in the nematic phase (without clearing) at 328°C. Interestingly, complexation led to a thermal stabilisation of the complex in that the isotropic phase of (**20**) was reached without decomposition. Complexation of (**15**) to give (**16**) however, did not lead to the S_C phase of the ligand being lost, although the S_C range was greatly reduced, mainly due to a destabilisation of the phase by 100 K. The nematic phase was also strongly destabilised in that clearing with decomposition was observed at 304°C for (**16**), while in (**15**) the nematic phase was seen to persist to 360°C.

It is interesting that the nematic phase of (**15**) was not totally destabilised on complexation. In our *ortho*-metallated imine complexes on Mn and Re, the smectic phases of the ligands are always suppressed on complexation, while in our Re complexes of diazabutadienes, the smectic phases of the ligands were only retained in the longest-chain homologues. Thus, we suspect that the general phase destabilisation reflects the perturbation to the anisotropy which the $[ReBr(CO)_3]$ represents, but the retention of the S_C phase in (**16**) is due to the dipolar effects of the fluorine substitution in the outer rings as discussed for the pure ligands. Thus, we would predict that the Re complex of (**11**) would have no S_C phase and only a nematic.

CONCLUSION

We have shown that by choice of the position of tetrafluorination in these large bipyridine mesogens, it is possible exert control over the stability of both the smectic C and nematic phases, both in the free ligands and in related complexes of Re(I).

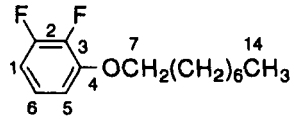
EXPERIMENTAL

The $^{19}F\{^1H\}$ spectra were obtained at Sheffield University on a Brüker AC250 spectrometer, while all other spectra were recorded in Exeter on a Brüker AMX400 machine. The ^{19}F chemical shifts are quoted relative to C_6F_6.

Synthesis of the Four-ring Fluorinated Ligand (4) and its Bromorhenium(I) Complex (5)

2,3-Difluorooctyloxybenzene (1)

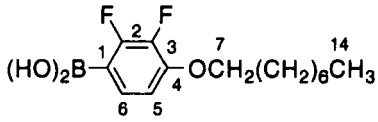
2,3-Difluorophenol (1 g, 7.69 mmol), potassium carbonate (2.45 g, 23.07 mmol), and 1-bromooctane (1.78 g, 9.2 mmol) were placed in acetone (50 cm^3) and heated at reflux for 48 hours. Distilled water (50 cm^3) was added and the aqueous layer extracted against diethyl ether (3 × 50 cm^3). The ethereal layers were combined and extracted against distilled water (2 × 50 cm^3), 5% sodium hydroxide solution (1 × 50 cm^3), and finally distilled water (3 × 50 cm^3), before being dried over $MgSO_4$, filtered and evaporated. Flash chromatography on silica gel using diethyl ether : hexane 1:1 as the eluent, gave the pure product as a yellow oil. Yield: 1.86 g, 99%.



^1H NMR δ ($CDCl_3$): 6.95 (1H, m, H6), 6.73 (2H, m, H1 and 5), 4.05 (2H, t, H7, $^3J_{HH}$ = 6.5 Hz), 1.83 (2H, quint, H8), 1.45 (2H, m, H9), 1.30 (8H, m, H10–13), 0.90 (3H, t, H14); ^{13}C NMR δ ($CDCl_3$): 151.5 (^2C, dd, $^1J_{CF}$ = 247 Hz, $^2J_{CF}$ = 10.5 Hz), 148.8 (^4C, dd, $^2J_{CF}$ = 7.5 Hz, $3J_{CF}$ = 3 Hz), 141.5 (^3C, dd, $^1J_{CF}$ = 247 Hz, $^2J_{CF}$ = 14.3 Hz), 123.0 (^6C, dd, $^4J_{HF}$ = 85 Hz, $^5J_{HF}$ = 5.2 Hz), 109.9 (^5C, d, $^4J_{HF}$ = 2.9 Hz), 108.8 (^1C, d, $^3J_{HF}$ = 175 Hz).

2,3-Difluoro-4-octyloxyphenylboronic acid (2)

^{n}Butyllithium (1.6 M in hexane, 6.8 cm^3, 10.9 mmol), was added dropwise to a stirred solution of 2,3-difluorooctyloxybenzene (2.64 g, 10.9 mmol) in freshly distilled and degassed THF (20 cm^3), under nitrogen at −78°C. Once the addition was complete the reaction was stirred for a further 2.5 hours under these conditions. A solution of triisopropylborate (4.23 g, 22 mmol), in THF (15 cm^3), at −78°C was added dropwise over 30 minutes, and the reaction was allowed to warm to room temperature overnight. Hydrochloric acid (10%, 10 cm^3) was added dropwise whilst cooling the reaction in an ethanol/ice bath, and the reaction stirred at room temperature for 1.5 hours. The reaction mixture was extracted with ether (3 × 50 cm^3), the ethereal layers combined, washed with water (100 cm^3), dried over $MgSO_4$, filtered and evaporated. The crude product was placed in petroleum ether (40 : 60) heated to reflux, allowed to cool to room temperature and collected to give the pure product as a white solid. Yield: 2.2 g, 71%.

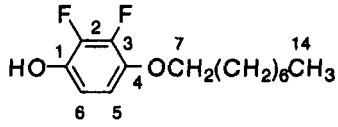


^{1}H NMR δ ($CDCl_3$): 7.50 (1H, ddd, H6, $^3J_{HH}$ = 8.5 Hz, $^4J_{HF}$ = 7.0 Hz, $^5J_{HF}$ = 2.5 Hz), 6.77 (1H, ddd, H5, $^3J_{HH}$ = 8.5 Hz, $^4J_{HF}$ = 6.5 Hz, $^5J_{HF}$ = 2.0 Hz). 4.98 and 4.95 (2H, s, OH), 4.06 (2H, t, H7, $^3J_{HH}$ = 6.5 Hz), 1.85 (2H, quint, H8), 1.48 (2H, m, H9), 1.30 (8H, m, H10–13), 0.90 (3H, t, H14); ^{13}C NMR δ ($CDCl_3$ and DMSO): 155.7 (^{2}C, dd, $^1J_{CF}$ = 242.5 Hz, $^2J_{CF}$ = 9.8 Hz), 150.7 (^{4}C, dd, $^3J_{CF}$ = 8.9 Hz, $^4J_{CF}$ = 4.8 Hz), 140.6 (^{3}C, dd, $^1J_{CF}$ = 248 Hz, $^2J_{CF}$ = 17.3 Hz), 130.2 (^{6}C, dd, $^3J_{CF}$ = 9.2 Hz, $^4J_{CF}$ = 5.0 Hz), 109.4 (^{5}C, d, $^3J_{CF}$ = 2.1 Hz), 69.6 (^{7}C), 31.7, 29.2, 29.1, 29.0, 25.8, 22.5 ($^{8-13}$C), 14.0 (^{14}C). No ^{1}C signal was observed, due to broadening caused by boron; ^{19}F NMR δ ($CDCl_3$): 28.88 (1F, d, F2, no coupling constants due to broadening of the signals caused by ^{11}B), 2.82 (1F, ddd, F3, $^3J_{FF}$ = 20.5 Hz, $^4J_{FH}$ = 6.7 Hz, $^5J_{FH}$ = 2.3 Hz).

2,3-Difluoro-4-octyloxyphenol (3)

Hydrogen peroxide (10%, 7.9 cm^3, 23 mmol) was added dropwise to a solution of compound (**2**) (2.1 g, 7.34 mmol) in THF (20 cm^3) heated at reflux. The reaction was heated at reflux for a further 2.5 hours, by which time TLC analysis indicated that the reaction had gone to completion. The

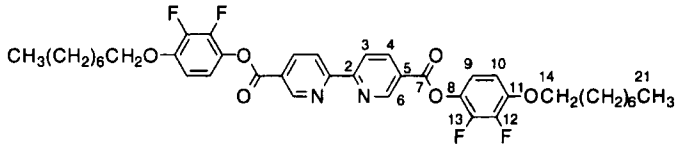
reaction mixture was cooled to room temperature, and the organic layer removed. The aqueous layer was washed with diethyl ether ($2 \times 50\,cm^3$), the ethereal layers combined and washed with sodium hydroxide solution (10%, $1 \times 50\,cm^3$). The separated aqueous layer was acidified with concentrated HCl and washed with diethyl ether ($2 \times 50\,cm^3$). The ethereal layers were combined, dried over $MgSO_4$, filtered and evaporated, to give the crude product. Chromatography on silica gel using hexane: diethyl ether 7:3 as the eluent, gave the pure product as a white solid. Yield: 1.79 g, 95%.



^{1}H NMR δ ($CDCl_3$): 6.65 (2H, m, H5 and 6), 4.96 (1H, s, OH), 3.97 (2H, t, H7, $^3J_{HH}$ = 6.5 Hz), 1.78 (2H, quint, H8), 1.50 (2H, m, H9), 1.30 (8H, m, H10–13), 0.90 (3H, t, H14); ^{13}C NMR δ ($CDCl_3$): 142.3 (^{2}C, dd, $^1J_{CF}$ = 243 Hz, $^2J_{CF}$ = 11.8 Hz), 141.9 (^{4}C, dd, $^2J_{CF}$ = 9.1 Hz, $^3J_{CF}$ = 1.2 Hz), 141.0 (^{3}C, dd, $^1J_{CF}$ = 240 Hz, $^2J_{CF}$ = 12.8 Hz), 138.6 (^{1}C, d, $^2J_{CF}$ = 11.8 Hz), 110.4 (^{6}C, dd, $^3J_{CF}$ = 3.4 Hz, $^4J_{CF}$ = 1.6 Hz), 110.3 (^{5}C, dd, $^3J_{CF}$ = 3.8 Hz, $^4J_{CF}$ = 1.6 Hz), 70.9 (^{7}C), 31.8, 29.3, 29.2, 25.8, 22.6 ($^{8-13}$C), 14.0 (^{14}C); ^{19}F NMR δ ($CDCl_3$): 7.54 (1F, m, F2), 2.96 (1F, m, F3).

Bis(2",3"-difluoro-4"-octyloxyphenyl)-2,2'-bipyridine-5,5'-dicarboxylate (4)

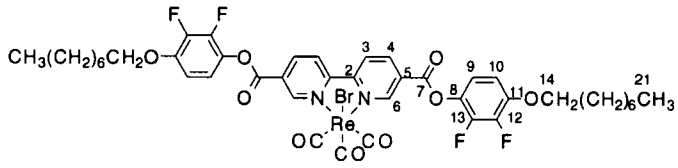
The apparatus was flame dried prior to use. 2,2'-Bipyridine-5,5'-diacid dichloride (0.5 g, 1.8 mmol), and 2,3-difluoro-4-octyloxyphenol (0.92 g, 3.6 mmol) were placed in freshly distilled toluene ($50\,cm^3$). Triethylamine ($1\,cm^3$) was added and the reaction heated at reflux, under nitrogen over night. The solvent was evaporated and dichloromethane added. This solution was extracted against 10% ammonia solution. The aqueous phase was then extracted with dichloromethane ($2 \times 100\,cm^3$), the organic extracts combined and the solvent evaporated to give a crude dark brown solid. The solid was twice placed in ethyl acetate, heated to reflux, allowed to cool to room temperature and the solid collected by centrifugation, before being crystallised from 1,4-dioxane. The crude product was placed in chloroform, heated to reflux and filtered hot through celite. The colourless solution was evaporated and the solid re-crystallised twice from 1,4-dioxane, giving the product as a cream solid. Yield: 0.47 g, 36%.



^{1}H NMR δ ($CDCl_3$): 9.46 (2H, dd, H6, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz), 8.72 (2H, dd, H3, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1 Hz), 8.62 (2H, dd, H4, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2 Hz), 7.00 (2H, ddd, H9, $^3J_{HH}$ = 9.5 Hz, $^4J_{HF}$ = 7.5 Hz, $^5J_{HF}$ = 2.5 Hz), 6.78 (2H, ddd, H10, $^3J_{HH}$ = 9.5 Hz, $^4J_{HF}$ = 7.5 Hz, $^5J_{HF}$ = 2.0 Hz), 4.07 (4H, t, H14, $^3J_{HH}$ = 6.5 Hz), 1.86 (4H, quint, H15), 1.50 (4H, m, H16), 1.30 (16H, m, H17–20), 0.90 (6H, t, H21); ^{19}F NMR δ ($CDCl_3$): 14.8 (1F, ddd, F13, $^3J_{FF}$ = 19.5 Hz, $^4J_{FH}$ = 7.7 Hz, $^5J_{FH}$ = 2.3 Hz), 8.54 (1F, ddd, F12, $^1J_{FF}$ = 19.5 Hz, $^4J_{FH}$ = 8.0 Hz, $^5J_{FH}$ = 2.5 Hz); Microanalysis % Expected (Found) C 66.3 (66.3) H 6.1 (6.2) N 3.9 (3.8).

Bis(2",3"-difluoro-4"-octyloxyphenyl)-2,2'-bipyridine-5,5'-dicarboxylate)-bromopentacarbonylrhenium(I) (5)

Compound (**4**) (0.05 g, 6.9×10^{-5} mol), and bromopentacarbonylrhenium(I) (0.028 g, 6.9×10^{-5} mol) were placed in freshly distilled toluene (50 cm^3) under N_2 and the reaction was heated at reflux. After 3.5 hours the reaction was cooled to room temperature filtered and the solvent evaporated to give a red solid as the product. Yield: 0.07 g, 95%.



^{1}H NMR δ ($CDCl_3$): 9.78 (2H, dd, H6, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz), 8.83 (2H, dd, H4, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2 Hz), 8.48 (2H, d, H3, $^3J_{HH}$ = 8.5 Hz), 7.00 (2H, ddd, H9, $^3J_{HH}$ = 9.5 Hz, $^4J_{HF}$ = 7.5 Hz, $^5J_{HF}$ = 2.5 Hz), 6.78 (2H, ddd, H10, $^3J_{HH}$ = 9.5 Hz, $^4J_{HF}$ = 7.5 Hz, $^5J_{HF}$ = 2.5 Hz), 4.07 (4H, t, H14, $^3J_{HH}$ = 6.5 Hz), 1.86 (4H, quint, H15), 1.50 (4H, m, H16), 1.30 (16H, m, H17–20), 0.90 (6H, t, H21); ^{13}C NMR δ ($CDCl_3$): 195.6 (CO), 187.6 (CO), 160.1 (^{7}C), 158.1 (^{4}C), 155.0 (^{2}C), 147.6 (^{11}C, dd, $^2J_{CF}$ = 8 Hz, $^3J_{CF}$ = 2.2 Hz), 143.9 (^{13}C, dd, $^1J_{CF}$ = 251.5 Hz, $^2J_{CF}$ = 12.6 Hz), 142.1 (^{12}C, dd, $^1J_{CF}$ = 251 Hz, $^2J_{CF}$ = 12 Hz), 140.5 (^{6}C), 131.6 (^{8}C, d, $^2J_{CF}$ = 11 Hz), 128.6 (^{5}C),

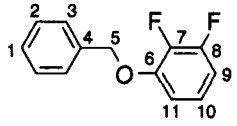
124.1 (^{3}C), 116.6 (^{9}C, d, $^{3}J_{CF}$ = 4 Hz), 108.6 (^{10}C, d, $^{3}J_{CF}$ = 3 Hz), 70.2 (^{14}C), 31.8, 29.7, 29.3, 29.2, 25.9, 22.6 ($^{15-20}$C), 14.1 (^{21}C). ^{19}F NMR δ ($CDCl_3$): 15.27 (1F, ddd, F13, $^{1}J_{FF}$ = 19.5 Hz, $^{4}J_{FH}$ = 7.7 Hz, $^{5}J_{FH}$ = 2.3 Hz), 9.02 (1F, ddd, F12, $^{3}J_{FF}$ = 19.5 Hz, $^{4}J_{FH}$ = 8.0 Hz, $^{5}J_{FH}$ = 2.5 Hz); IR (DCM): $\nu_{C\equiv O}$ 2029, 1933, 1909, $\nu_{C=O}$ 1761 (m); Microanalysis % Expected (Found) C 48.0 (48.3) H4.1 (4.3) N 2.6 (2.5) Br 7.4 (7.8).

Synthesis of the Six-ring Fluorinated Ligands (11 and 15) and the Bromorhenium(I) Complex (16)

Synthesis of (11)

Benzyloxy-2,3-difluorobenzene (6)

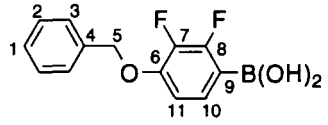
2,3-Difluorophenol (1.5 mg, 11.5 mmol), potassium carbonate (3.66 g, 26.5 mmol), and benzylbromide (2.17 g, 12.7 mmol) were placed in acetone (50 cm^3) and heated at reflux for 48 hours, under nitrogen. Distilled water (50 cm^3) was added and the aqueous layer extracted against diethyl ether (3 × 50 cm^3). The ethereal layers were combined and extracted against distilled water (2 × 50 cm^3), 5% sodium hydroxide solution (1 × 50 cm^3), and finally distilled water (3 × 50 cm^3), before being dried over $MgSO_4$, filtered and evaporated, to give the crude product as a waxy solid. Yield: 2.4 g, 95%.



^{1}H NMR δ ($CDCl_3$): 7.40 (5H, m, H1 – 3), 6.95 (1H, m, H10), 6.80 (2H, m, H9 and 11), 5.16 (2H, s, H5); ^{13}C NMR δ ($CDCl_3$): 151.5 (^{8}C, dd, $^{1}J_{CF}$ = 246.5 Hz, $^{2}J_{CF}$ = 10.5 Hz), 148.4 (^{6}C, dd, $^{2}J_{CF}$ = 7.5 Hz, $^{3}J_{CF}$ = 3.0 Hz), 141.8 (^{7}C, dd, $^{1}J_{CF}$ = 248 Hz, $^{2}J_{CF}$ = 14.5 Hz), 136.2 (^{4}C), 128.7, 128.3, 127.4 ($^{1-3}$C), 123.1 (^{10}C, dd, $^{3}J_{CF}$ = 9.0 Hz, $^{4}J_{CF}$ = 5.3 Hz), 110.7 (^{11}C, d, $^{3}J_{CF}$ = 3 Hz), 109.6 (^{9}C, d, $^{2}J_{CF}$ = 17.5 Hz), 71.7 (^{5}C); ^{19}F NMR δ ($CDCl_3$): 26.62 (1F, dddd, F8, $^{2}J_{FF}$ = 19.8 Hz, $^{3}J_{HF}$ = 9.8 Hz, $^{4}J_{HF}$ = 6 Hz, $^{5}J_{HF}$ = 2.0 Hz), 5.14 (1F, dddd, F7, $^{2}J_{FF}$ = 19.8 Hz, $^{3}J_{HF}$ = 9.2 Hz, $^{4}J_{HF}$ = 6.9 Hz, $^{5}J_{HF}$ = 2.0 Hz).

4-Benzyloxy-2,3-difluorophenylboronic acid (7)

^{n}Butyllithium (1.6 M in hexane, 6.8 cm^3, 10.9 mmol), was added dropwise to a stirred solution of benzyloxy-2,3-difluorobenzene (2.4 g, 10.9 mmol) in freshly distilled and degassed THF (20 cm^3), under nitrogen at −78°C. Once the addition was complete the reaction was stirred for a further 2.5 hours under these conditions. A solution of triisopropylborate (4.23 g, 22 mmol), in THF (15 cm^3), at −78°C was added dropwise over 30 minutes, and the reaction was allowed to warm to room temperature overnight. Hydrochloric acid (10%, 10 cm^3) was added dropwise whilst cooling the reaction in an ethanol/ice bath, and the reaction stirred at room temperature for 1.5 hours. The reaction mixture was extracted with ether (3 × 50 cm^3), the ethereal layers combined, washed with water (1 × 100 cm^3), dried over $MgSO_4$, filtered and evaporated. The crude product was placed in petroleum ether (40 : 60) heated to reflux, allowed to cool to room temperature and collected to give the pure product as a white solid. Yield: 1.0 g, 33%.

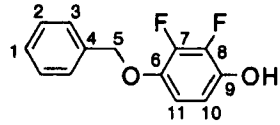


^{1}H NMR δ ($CDCl_3$): 7.43 (6H, m, H1 – 3 and H10), 6.85 (1 H, ddd, H11, $^3J_{HH}$ = 8.5 Hz, $^4J_{HF}$ = 6.5 Hz, $^5J_{HF}$ = 2 Hz), 5.20 (2H, s, H5), 4.80 and 4.83 (2H, 2s, OH); ^{13}C NMR δ ($CDCl_3$): 153.0 (^{8}C, dd, $^1J_{CF}$ = 246 Hz, $^2J_{CF}$ = 9.0 Hz), 149.4 (^{6}C, dd, $^2J_{CF}$ = 8.3 Hz, $^3J_{CF}$ = 3.8 Hz), 141.8 (^{7}C, dd, $^1J_{CF}$ = 245.5 Hz, $^2J_{CF}$ = 17.3 Hz), 136.7 (^{4}C), 130.0 (^{10}C, dd, $^3J_{CF}$ = 10.1 Hz, $^4J_{CF}$ = 5.2 Hz), 128.9, 128.6, 128.3 ($^{1-3}$C), 110.7 (^{11}C, $^3J_{CF}$ = 2.8 Hz), 71.03 (^{5}C); ^{19}F NMR δ ($CDCl_3$): 33.79 (1F, ddd, F8, $^3J_{FF}$ = 22.0 Hz, $^4J_{FH}$ = 6.5 Hz, $^5J_{FH}$ = 1.3 Hz), 2.07 (1F, ddd, F7, $^3J_{FF}$ = 21.9 Hz, $^4J_{FH}$ = 7.1 Hz, $^5J_{FH}$ = 2.2 Hz).

4-Benzyloxy-2,3-difluorophenol (8)

Hydrogen peroxide (10%, 3.85 cm^3, 11.3 mmol) was added dropwise to a solution of (7) (0.95 g, 3.59 mmol), in THF (20 cm^3) heated at reflux. The reaction was heated at reflux for a further 3.5 hours, by which time TLC analysis indicated that the reaction had gone to completion. The reaction was cooled to room temperature, and the organic layer removed. The aqueous layer was washed with diethyl ether (2 × 50 cm^3), the ethereal layers

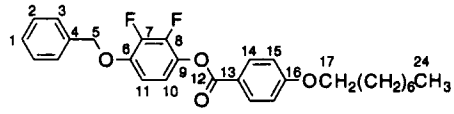
combined and washed with 10% sodium hydroxide solution ($1 \times 50\,cm^3$). The aqueous layer was then acidified with concentrated hydrochloric acid and washed with diethyl ether ($2 \times 50\,cm^3$). The ethereal layers were combined, dried over $MgSO_4$, filtered and evaporated, to give the crude product. Purification was achieved by chromatography on silica gel using hexane : diethyl ether 7 : 3 as the eluent, to give the pure product as a white solid. Yield: 0.78 g, 92%.



^{1}H NMR δ ($CDCl_3$); 7.37 (5H, m, H1 – 3), 6.67 (2H, m, H10 and 11), 5.09 (2H, s, H5), 5.05 (1H, s, OH); ^{13}C NMR δ ($CDCl_3$): 142.6 (^{8}C, dd, $^1J_{CF}$ = 249 Hz, $^2J_{CF}$ = 12.0 Hz), 141.4 (^{6}C, m), 141.0 (^{7}C, dd, $^1J_{CF}$ = 240 Hz, $^2J_{CF}$ = 12.8 Hz), 139.2 (^{9}C, $^2J_{CF}$ = 11.8 Hz), 136.4 (^{4}C), 128.6, 128.2, 127.6 ($^{1-3}$C), 111.4 (^{10}C, dd, $^3J_{CF}$ = 3.6 Hz, $^4J_{CF}$ = 1.5 Hz), 110.4 (^{11}C, $^3J_{CF}$ = 3.7 Hz, $^4J_{CF}$ = 1.5 Hz), 71.03 (^{5}C); ^{19}F NMR δ ($CDCl_3$): 8.58 (1F, m, F8), 3.27 (1F, m, F7).

4-Benzyloxy-2,3-difluorophenyl-4'-octyloxybenzoate (9)

4-Octyloxybenzoic acid (0.83 g, 3.3 mmol), 4-benzyloxy-2,3-difluorophenol (0.78 g, 3.3 mmol), and DCC (0.68 g, 3.3 mmol), were dissolved in dichloromethane. To this 4-(*N*,*N*-Dimethylamino)pyridine (0.04 g 0.03 mmol) was added and the reaction was stirred at room temperature for 24 hours. The white precipitate was removed by filtration and the solvent was evaporated. Crystallisation from ethanol ($75\,cm^3$) gave the product as a white solid. Yield: 1.3 g, 86%.

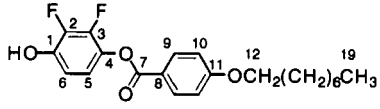


^{1}H NMR δ ($CDCl_3$): 8.13 (2H, AA'XX', H14, $J_{AA'XX'}$ = 9 Hz), 7.40 (5H, m, H1 – 3), 6.97 (2H, AA'XX', H15, $J_{AA'XX'}$ = 9 Hz), 6.93 (1H, ddd, H10, $^3J_{HH}$ = 9.5 Hz, $^4J_{HF}$ = 7.5 Hz, $^5J_{HF}$ = 2.2 Hz), 6.78 (1H, ddd, H11 $^3J_{HH}$ = 9.5 Hz, $^4J_{HF}$ = 7.5 Hz, $^5J_{HF}$ = 2.2 Hz), 5.16 (2H, s, H5), 4.05 (2H, t, H17, $^3J_{HH}$ = 6.5 Hz), 1.84 (2H, quint, H18), 1.50 (2H, m, H19), 1.35 (8H,

m, H20–23), 0.90 (3H, t, H24); ^{13}C NMR δ ($CDCl_3$): 163.9 ($^{12}CO_2$), 145.9 (^{6}C, dd, $^{2}J_{CF}$ = 8.3 Hz, $^{3}J_{CF}$ = 2.5 Hz), 144.3 (^{8}C, dd, $^{1}J_{CF}$ = 251.5 Hz, $^{2}J_{CF}$ = 13 Hz), 142.5 (^{7}C, dd, $^{1}J_{CF}$ = 250 Hz, $^{2}J_{CF}$ = 13 Hz), 136.0 (^{16}C), 133.4 (^{9}C, d, $^{2}J_{CF}$ = 10.5 Hz), 132.5 (^{14}C), 128.7, 128.3, 127.5 ($^{1-3}$C), 120.4 (^{13}C), 117.2 (^{10}C, d, J_{CF} = 4.5 Hz), 114.4 (^{15}C), 109.5 (^{11}C, d, $^{3}J_{CF}$ = 3 Hz), 72.1 (^{5}C), 68.4 (^{17}C), 31.8, 29.3, 29.2, 29.1, 26.0, 22.6 ($^{18-23}$C), 14.1 (^{24}C); ^{19}F NMR δ ($CDCl_3$): 14.96 (1F, ddd, F8, $^{1}J_{FF}$ = 19.7 Hz, $^{4}J_{FH}$ = 7.7 Hz, $^{5}J_{FH}$ = 2.3 Hz), 8.99 (1F, ddd, F7, $^{3}J_{FF}$ = 19.7 Hz, $^{4}J_{FH}$ = 8 Hz, $5J_{FH}$ = 2.4 Hz).

4-Hydroxy-2,3-difluorophenyl-4′-octyloxybenzoate (10)

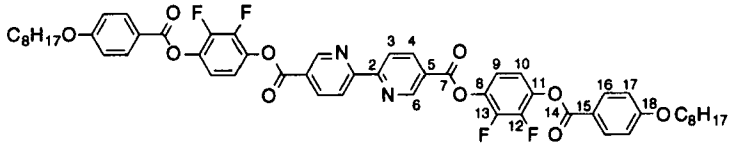
Compound (**9**) (1.1 g, 2.35 mmol) was dissolved in freshly distilled THF (100 cm^3), triethylamine (1 cm^3), and 10% wet degassu Pd/C catalyst (0.05 g), was added. The reaction flask was evacuated and placed under hydrogen three times, before being stirred at room temperature under an atmosphere of hydrogen. After the calculated amount of hydrogen had been taken up the catalyst was removed by filtration through celite and the solvent was evaporated. Flash chromatography on silica gel, using diethyl ether as the eluent, gave the product as a white solid. Yield: 1.03 g, 98%.



^{1}H NMR δ ($CDCl_3$): 8.14 (2H, AA′XX′, H9, $J_{AA'XX'}$ = 9 Hz), 6.98 (2H, AA′XX′, H10, $J_{AA'XX'}$ = 9 Hz), 6.87 (1H, ddd, H5, $^{3}J_{HH}$ = 9.5 Hz, $^{4}J_{HF}$ = 7.5 Hz, $^{5}J_{HF}$ = 2.2 Hz), 6.78 (1H, ddd, H6, $^{3}J_{HH}$ = 9.5 Hz, $^{4}J_{HF}$ = 7.5 Hz, $^{5}J_{HF}$ = 2.2 Hz), 5.90 (1H, s, OH), 4.05 (2H, t, H12, $^{3}J_{HH}$ = 6.5 Hz), 1.84 (2H, quint, H13), 1.48 (2H, m, H14), 1.30 (8H, m, H15–18), 0.90 (3H, t, H19); ^{13}C NMR δ ($CDCl_3$): 164.4 (^{11}C), 164.0 ($^{7}CO_2$), 143.8 (^{2}C, dd, $^{1}J_{CF}$ = 251.5 Hz, $^{2}J_{CF}$ = 12 Hz), 143.0 (^{4}C, d, $^{2}J_{CF}$ = 10.5 Hz), 140.8 (^{3}C, dd, $^{1}J_{CF}$ = 242 Hz, $^{2}J_{CF}$ = 12.8 Hz), 132.6 (^{9}C), 132.3 (^{1}C, d, $^{2}J_{CF}$ = 10.5 Hz), 120.3 (^{8}C), 117.9 (^{5}C, d, $^{3}J_{CF}$ = 3.8 Hz), 114.5 (^{10}C), 11.2 (^{6}C, dd, $^{3}J_{CF}$ = 3.8 Hz, $^{4}J_{CF}$ = 1.5 Hz), 68.4 (^{12}C), 31.8, 29.3, 29.2, 29.1, 26.0, 22.6, 21.2 ($^{13-18}$C), 14.1 (^{19}C); ^{19}F NMR δ ($CDCl_3$): 14.55 (1F, ddd, F3, $^{3}J_{FF}$ = 20.3 Hz, $^{4}J_{FH}$ = 7.6 Hz, $^{5}J_{FH}$ = 2.3 Hz), 3.99 (1F, ddd, F2, $^{1}J_{FF}$ = 20.3 Hz, $^{4}J_{FH}$ = 8 Hz, $^{5}J_{FH}$ = 2.3 Hz).

Bis(4"-(4"'-octyloxybenzoyloxy)-2",3"-difluorophenyl)-2,2'-bipyridine-5,5'-dicarboxylate (11)

The apparatus was flame dried prior to use. 2,2'-Bipyridine-5,5'-diacid dichloride (0.37 g, 1.3 mmol), and compound (**10**) (1 g, 2.6 mmol) were placed in freshly distilled toluene (50 cm^3). Triethylamine (1 cm^3) was added and the reaction mixture heated at reflux, under nitrogen over night. The solvent was evaporated and dichloromethane added. This was extracted against 10% ammonia solution. The aqueous phase was then extracted with dichloromethane (2 × 100 cm^3), the organic extracts combined and the solvent evaporated to give a crude dark brown solid. The solid was twice placed in ethyl acetate, heated to reflux, allowed to cool to room temperature and the solid collected by centrifugation. The crude product was placed in chloroform, heated to reflux and filtered hot through celite. The colourless solution was evaporated and the solid re-crystallised twice from 1,4-dioxane, giving the product as a white solid. Yield: 0.07 g, 6%.



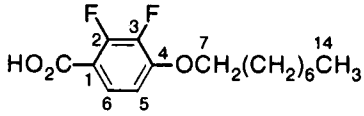
^{1}H NMR δ ($CDCl_3$): 9.50 (2H, dd, H6, $^4J_{HH}$ = 2 Hz, $^5J_{HH}$ = 1 Hz), 8.75 (2H, dd, H3, $^3J_{HH}$ = 8.5 Hz, $^5J_{HH}$ = 1 Hz), 8.65 (2H, dd, H4, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2 Hz), 8.16 (2H, AA'XX', H16, $J_{AA'XX'}$ = 9 Hz), 7.16 (4H, m, H9 and 10), 7.00 (2H, AA'XX', H17, $J_{AA'XX'}$ = 9 Hz), 4.07 (4H, t, H19, $^3J_{HH}$ = 6.5 Hz), 1.85 (4H, quint, H20), 1.50 (2H, m, H21), 1.35 (16 H, m, H22–25), 0.90 (6H, t, H26); ^{19}F NMR δ ($CDCl_3$): 16.91 (1F, m), 16.4 (1F, m); Microanalysis % Expected (Found): C 67.2 (66.8) H 5.4 (5.3) N 2.9 (2.8).

Synthesis of (15) and (16)

2,3-Difluoro-4-octyloxybenzoic acid (12)

"Butyllithium (1.6 M in hexane, 4.8 cm^3, 7.68 mmol), was added dropwise to a stirred solution of octyloxy-2,3-difluorobenzene in THF (20 cm^3), under nitrogen at −78°C. Once the addition was complete the reaction was stirred for a further 2.5 hours in these conditions. Excess solid CO_2 was added and the reaction stirred for a further hour at −78°C, before being allowed to warm to room temperature. The reaction was poured onto distilled water

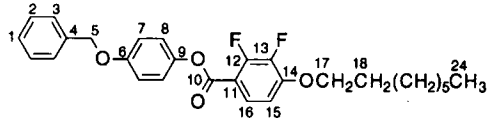
and acidified with hydrochloric acid (concentrated, 5 cm^3). The aqueous layer was extracted against diethyl ether (2 × 50 cm^3), the ethereal layers combined dried over $MgSO_4$, filtered and evaporated. Crystallisation from ethanol : water 5 : 1 gave the product as a cream solid. Yield: 1.05 g, 47%.



^{1}H NMR δ ($CDCl_3$): 7.76 (1H, ddd, H6, $^3J_{HH}$ = 9.5 Hz, $^4J_{HF}$ = 7.5 Hz, $^5J_{HF}$ = 2.5 Hz), 6.79 (2H, ddd, H5, $^3J_{HH}$ = 9.5 Hz, $^4J_{HF}$ = 7.0 Hz, $^5J_{HF}$ = 2.0 Hz), 4.12 (2H, t, H7, $^3J_{HH}$ = 6.5 Hz), 1.85 (2H, quint, H8), 1.48 (2H, m, H9), 1.30 (8H, m, H10–13), 0.90 (3H, t, H14); ^{13}C NMR δ ($CDCl_3$): 165.7 (CO_2H), 152.2 (^{4}C, dd, $^2J_{CF}$ = 8.3 Hz, $^3J_{CF}$ = 3.8 Hz), 151.6 (^{2}C, dd, $^1J_{CF}$ = 261 Hz, $^2J_{CF}$ = 11.3 Hz), 141.3 (^{3}C, dd, $^1J_{CF}$ = 247 Hz, $^2J_{CF}$ = 14.3 Hz), 126.7 (^{6}C, dd, $^3J_{CF}$ = 4.5 Hz, $^4J_{CF}$ = 1 Hz), 112.3 (^{1}C, d, $^2J_{CF}$ = 6.8 Hz), 108.1 (^{5}C, d, $^3J_{CF}$ = 3.5 Hz); ^{19}F NMR δ ($CDCl_3$): 31.45 (1F, ddd, F2, $^3J_{FF}$ = 19.2 Hz, $^4J_{FH}$ = 7.6 Hz, $^5J_{FH}$ = 1.6 Hz), 5.74 (1F, ddd, F3, $^3J_{FF}$ = 19.3 Hz, $^4J_{FH}$ = 7 Hz, $^5J_{FH}$ = 2.3 Hz).

4-Benzyloxyphenyl-2',3'-difluoro-4'-octyloxybenzoate (13)

2,3-Difluoro-4-octyloxybenzoic acid (1.05 g, 3.67 mmol), 4-benzyloxyphenol (0.74 g, 3.67 mmol), and dicyclohexylcarbodiimide (0.76 g, 3.67 mmol), were dissolved in dichloromethane (80 cm^3). 4-(*N*,*N*-Dimethylamino)pyridine (0.045 g, 0.367 mmol) was then added and the reaction stirred at room temperature overnight. The white precipitate was removed by filtration and the solvent evaporated. Crystallisation from ethanol gave the product as a white solid. Yield: 1.3 g, 81%.

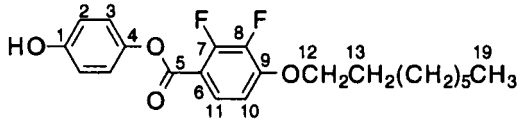


^{1}H NMR δ ($CDCl_3$): 7.76 (1H, ddd, H16, $^3J_{HH}$ = 9.5 Hz, $^4J_{HF}$ = 7.5 Hz, $^5J_{HF}$ = 2.5 Hz), 7.40 (5H, m, H1–3), 7.14 (2H, AA'XX', H8 $J_{AA'XX'}$ = 9 Hz), 7.00 (2H, AA'XX', H7, $J_{AA'XX'}$ = 9 Hz), 6.81 (1H, ddd, H15, $^3J_{HH}$ = 9.5 Hz,

$^4J_{HF}$ = 7.0 Hz, $^5J_{HF}$ = 2.0 Hz), 5.07 (2H, s, H5), 4.12 (2H, t, H17, $^3J_{HH}$ = 6.5 Hz), 1.86 (2H, quint, H18), 1.50 (2H, m, H19), 1.35 (8H, m, H20–23), 0.90 (3H, t, H24); ^{13}C NMR δ ($CDCl_3$): 162.4 (^{10}C, dd, $^3J_{CF}$ = 4.5 Hz, $4J_{CF}$ = 3.8 Hz), 156.6 (^{6}C), 153.05 (^{14}C, dd, coupling constants uncertain due to overlap of signals with ^{12}C), 151.8 (^{12}C, dd, $^2J_{CF}$ = 12 Hz, J_{CF} coupling constant uncertain due to overlap of signals with ^{14}C), 144.3 (^{9}C), 141.6 (^{13}C, dd, $^1J_{CF}$ = 249 Hz, $^2J_{CF}$ = 14.5 Hz), 136.9 (^{4}C), 128.6, 128.0 and 127.5 ($^{1-3}$C), 126.9 (^{16}C, d, $^3J_{CF}$ = 4.0 Hz), 122.4 (^{8}C), 115.5 (^{7}C), 111.5(^{11}C, d, $^2J_{CF}$ = 7.5 Hz), 108.5 (^{15}C, d, $^3J_{CF}$ = 3.0 Hz); ^{19}F NMR δ ($CDCl_3$): 31.60 (1F, ddd, F12, $^1J_{FF}$ = – 19.3 Hz, $^4J_{FH}$, = 7.5 Hz, $^5J_{FH}$ = 1.8 Hz), 5.85 (1F, ddd, F13, $^1J_{FF}$ = 19.4 Hz, $^4J_{FH}$ = 7 Hz, $^5J_{FH}$ = 2.3 Hz).

4-Hydroxyphenyl-4'-octyloxy-2',3'-difluorobenzoate (14)

To a solution of compound (**13**) (1.3 g, 2.7 mmol) in freshly distilled THF (50 cm^3), a 10% wet degassu Pd/C catalyst was added (50 mg). The reaction was three times placed under vacuum and hydrogen before being left to stir under an atmosphere of hydrogen at room temperature. After hydrogen (70 cm^3) had been used the reaction was filtered through celite and the solvent evaporated. Flash chromatography on silica using diethyl ether as the eluent gave the product as a white solid. Yield: 1.03 g, 98%.



^{1}H NMR δ ($CDCl_3$): 7.82 (1H, ddd, H11, $^3J_{HH}$ = 9.0 Hz, $^4J_{HF}$ = 7.5 Hz, $^5J_{HF}$ = 2.0 Hz), 7.05 (2H, AA'XX', H3, $J_{AA'XX'}$ = 9 Hz), 6.81 (3H, m, H2 and 10), 5.32 (1H, s, OH), 4.13 (2H, t, H12, $^3J_{HH}$ = 6.5 Hz), 1.86 (2H, quint, H13), 1.46 (2H, m, H14), 1.34 (8H, m, H15–18), 0.90 (3H, t, H19); ^{13}C NMR δ ($CDCl_3$): 162.8 (^{5}C), 153.6 (^{1}C), 153.2 (^{9}C, coupling constants uncertain due to overlap of signals with ^{7}C), 151.8 (^{7}C, dd, 263 > $^1J_{CF}$ > 259 Hz, J_{CF} coupling constant uncertain due to overlap of signals with ^{9}C, $^2J_{CF}$ = 11.3 Hz), 144.0 (^{4}C), 141.5 (^{8}C, dd, $^1J_{CF}$ = 249 Hz, $^2J_{CF}$ = 15.1 Hz), 127.0 (^{11}C, d, $^3J_{CF}$ = 4.5 Hz), 122.5 (^{3}C), 116.1 (^{2}C), 111.3 (^{6}C, d, $^2J_{CF}$ = 7.5 Hz), 108.5 (^{10}C, d, $^3J_{CF}$ = 3.0 Hz); ^{19}F NMR δ ($CDCl_3$): 31.64 (1F, ddd, F7, $^3J_{FF}$ = 19.4 Hz, $^4J_{FH}$ = 7.5 Hz, $^5J_{FH}$ = 1.7 Hz), 5.9 (1F, ddd, F8, $^3J_{FF}$ = 19.3 Hz, $^4J_{FH}$ = 7 Hz, ^{5}FH = 2.3 Hz).

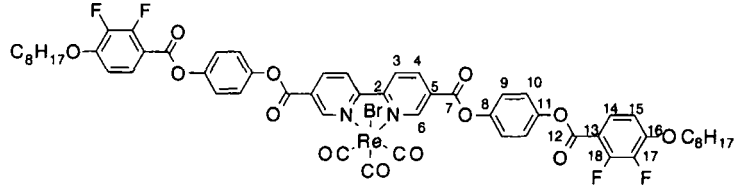
Bis(4"-(2"',3"'-difluoro-4"'-octyloxybenzoyloxy)phenyl)-2,2'-bipyridine-5,5'-dicarboxylate (15)

The apparatus was flame dried prior to use. 2,2'-Bipyridine-5,5'-diacid dichloride (0.37 g, 1.3 mmol), and compound (**14**) (1 g, 2.6 mmol) were placed in freshly distilled toluene (50 cm^3). Triethylamine (1 cm^3) was added and the reaction heated at reflux, under nitrogen over night. The solvent was evaporated and dichloromethane added. This was extracted against 10% ammonia solution. The aqueous phase was then extracted with dichloromethane ($2 \times 100\,cm^3$), the organic extracts combined and the solvent evaporated to give a crude dark brown solid. The solid was twice placed in ethyl acetate, heated to reflux, allowed to cool to room temperature and the solid collected by centrifugation. The crude product was crystallised twice from 1,4-dioxane, giving the product as a cream solid. Yield: 0.31 g, 25%.

MS *m/z*: [M +] 964.01; No NMR data could be obtained due to the products insolubility. Microanalysis % Expected (Found): C 67.2 (66.3) H 5.4 (5.2) N 2.9 (3.0).

Bis(4"-(2"',3"'-difluoro-4"'-octyloxybenzoyloxy)phenyl)-2,2'-bipyridine-5,5'-dicarboxylatebromotricarbonylrhenium(I) (16)

Compound (**15**) (0.05 g, 6.9×10^{-5} mol), and bromopentacarbonylrhenium(I) (0.028 g, 6.9×10^{-5} mol) were placed in freshly distilled toluene (50 cm^3) under N_2 and the reaction was heated at reflux. After 3.5 hours the reaction was cooled to room temperature filtered and the solvent evaporated to give a red solid as the product. Yield: 0.065 g, 95%.



^{1}H NMR δ ($CDCl_3$): 9.80 (2H, d, H6, $^4J_{HH}$ = 2 Hz), 8.78 (2H, dd, H4, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2 Hz), 8.49 (2H, d, H3, $^3J_{HH}$ = 8.5 Hz), 7.85 (2H, ddd, H14, $^3J_{HH}$ = 9.0 Hz, $^4J_{HF}$ = 7.5 Hz, $^5J_{HF}$ = 2.0 Hz), 7.37 (8H, s, H9 and 10), 6.84 (2H, ddd, H15, $^3J_{HH}$ = 9.0 Hz, $^4J_{HF}$ = 7.0 Hz, $^5J_{HF}$ = 2.0 Hz), 4.15 (4H, t, H19, $^3J_{HH}$ = 6.5 Hz), 1.86 (2H, quint, H20), 1.50 (4H, m, H21), 1.30 (16H, m, 22 - 25), 0.90 (6H, t, H26); ^{13}C NMR δ ($CDCl_3$): 195.7 and 187.8 (CO), 161.8 (^{12}C, m), 160.9 (^{7}C), 158.0 (^{2}C), 154.8 (^{6}C), 153.3(^{16}C, m due to

overlap of signals with ^{18}C), 152.0 (^{18}C, dd, $^{1}J_{CF}$ = ca 250 Hz this value is approximate due to overlap of signals with ^{16}C, $^{2}J_{CF}$ = 12 Hz), 148.8 and 147.5 ($^{8\text{ and }11}C$), 141.5 (^{17}C, dd, $^{1}J_{CF}$ = 235 Hz, $^{2}J_{CF}$ = 14 Hz), 140.3 (^{4}C), 129.3 (^{5}C), 127.1 (^{14}C, d, $^{3}J_{CF}$ = 4 Hz), 124.2 (^{3}C), 123.1 and 122.3 ($^{9\text{ and }10}C$), 110.8 (^{13}C, d, $^{2}J_{CF}$ = 7 Hz), 108.5 (^{15}C, $^{3}J_{CF}$ = 3 Hz), 70.0 (^{19}C), 31.8, 29.7, 29.2, 28.9, 25.8, 22.6 ($^{20-25}C$), 14.1 (^{26}C); ^{19}F NMR δ ($CDCl_3$): 31.77 (1F, dd, F18, $^{3}J_{FF}$ = 19.6 Hz, $^{4}J_{HF}$ = 7.5 Hz, $^{3}J_{HF}$ = 1.3 Hz), 6.08 (1F, dd, F17, $^{3}J_{FF}$ = 19.6 Hz, $^{4}J_{HF}$ = 7 Hz, $^{3}J_{HF}$ = 2.2 Hz) IR (DCM): $\upsilon_{C\equiv O}$ 2028, 1932, 1907, $\upsilon_{C=O}$ 1751 (m), 1735 (m); Microanalysis % Expected (Found): C 52.1 (51.7) H 4.00 (3.8) N 2.1 (2.1) Br 6.1(6.4).

Acknowledgements

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