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Mesomorphic 2,2′-bipyridine diesters and their related metal complexes

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Esterification of 2,2′-bipyridine-5,5′- and 4,4′-dicarboxylic acids with 4-alkoxyphenols leads to new mesomorphic bipyridine esters which are subsequently complexed with various metals. The synthesis and properties of these compounds are discussed.

1. Introduction

Metallomesogens have the potential to yield novel and useful materials in terms of, for example, colour, magnetism, and electrical properties. Indeed a number of suitable ligands have been utilized in the formation of metallomesogens, but as the vast majority of calamitic, metal-containing liquid crystals possess either a linear or square planar geometry, the choice of metals has been largely restricted to groups 9–11 of the periodic table [1]. As a result, recent attempts have been directed towards the formation of mesomorphic transition metal complexes with high coordination number metal centres. Until recently these have been limited to square pyramidal complexes of V(IV), or Fe(III), or to ferrocene derivatives [2, 3], but in the last year, reports have appeared of mesomorphic complexes of Schiff's bases bound to octahedral Mn(I) and Re(I) [4] and of diazabutadienes bound to octahedral Re(I) [5] (see figure 1). The structures of these complexes indicate that when mesomorphic ligands of sufficiently high structural anisotropy are used (i.e. at least four rings in the backbone of the ligand), the introduction of relatively bulky metal fragments can be tolerated without destroying the mesomorphism [6].

As 2,2′-bipyridine enjoys an extensive coordination chemistry [7] and is readily modified, we therefore sought suitably functionalized 2,2′-bipyridines which might also lead to a range of mesomorphic metal complexes. Indeed, 2,2′-bipyridines have recently been utilized in the formation of liquid crystals (figure 2). Hanabusa described derivatives of 2,2′-bipyridine polymerized through the 5- and 5′-positions, whose mesomorphism was lost when significant quantities of six-coordinate cations were introduced [8]. Reports have also appeared of metal complexes of alkanoyl derivatives of 6,6′-diamino-2,2′-bipyridine [9], and of lyotropic systems based on 4-alkylated-2,2′-bipyridine complexes of Ru(II) [10]. Of particular note in the context of the present work are the alkoxyphenylvinylbipyridines described by Ziessel *et al.* (**3d** in figure 2), which bear some conceptual similarity to the systems now described. Preliminary reports of both their work [11] and our own [12] appeared together in this journal.

2. Results and discussion

2.1. *Ligand synthesis*

The coupling of either 3- or 4-picoline over Raney nickel led to the appropriate 5,5′- or 4,4-dimethyl-2,2′-bipyridine precursors, respectively, in high yield [13]. These were subsequently oxidized using aqueous permanganate to give the corresponding (and very insoluble) diacids [14]. The 5,5′-dicarboxylic acids were first esterified with aliphatic alcohols under acid-catalysed conditions. Unfortunately none of the alkyl esters (**4a–d**) was mesomorphic, simply clearing to isotropic liquids; for example, clearing points for $n=8$ and 12 were 117 and 120°C, respectively.

The diacids were then converted into the acid chlorides using thionyl chloride, before being esterified with 4-alkoxyphenols in pyridine at room temperature (5,5′-diesters) or toluene under reflux (4,4′-diesters). The 4-alkoxyphenols were obtained in moderate yields (50–60 per cent) by alkylating hydroquinone using an alkyl bromide and base in 1,4-dioxane/water for $R < C_{10}H_{21}$ and poly(etheneglycol)/1,4-dioxane for $R > C_{10}H_{21}$ [15]. Unfortunately, yields for the final esterification step were disappointingly low. Esterification with 4-alkoxyphenols and the bipyridine

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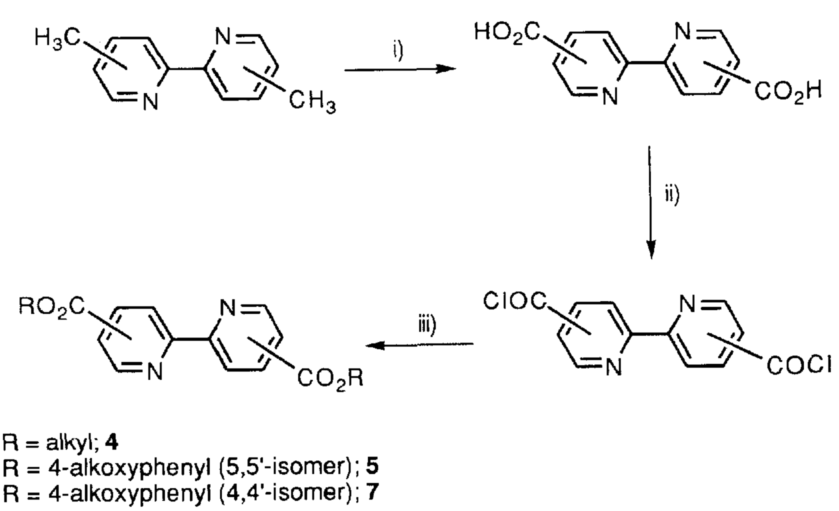
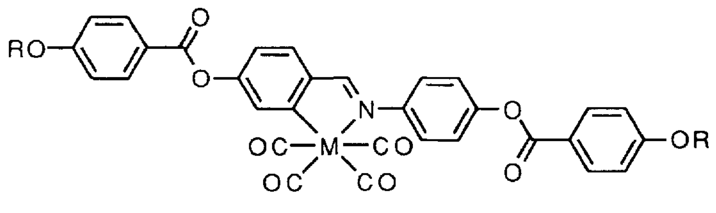
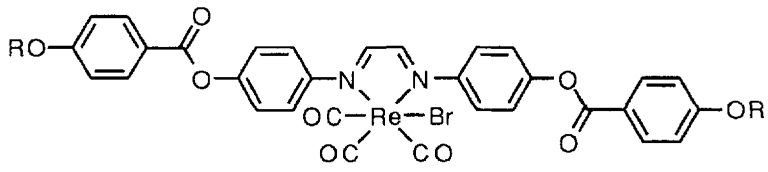


Scheme Synthesis of the bipyridine esters. (i) $KMnO_4$; (ii) $SOCl_2$; (iii) *R*OH/py (for 5,5′-isomer); toluene/*R*OH (for 4,4′-isomer)



(1)



(2)

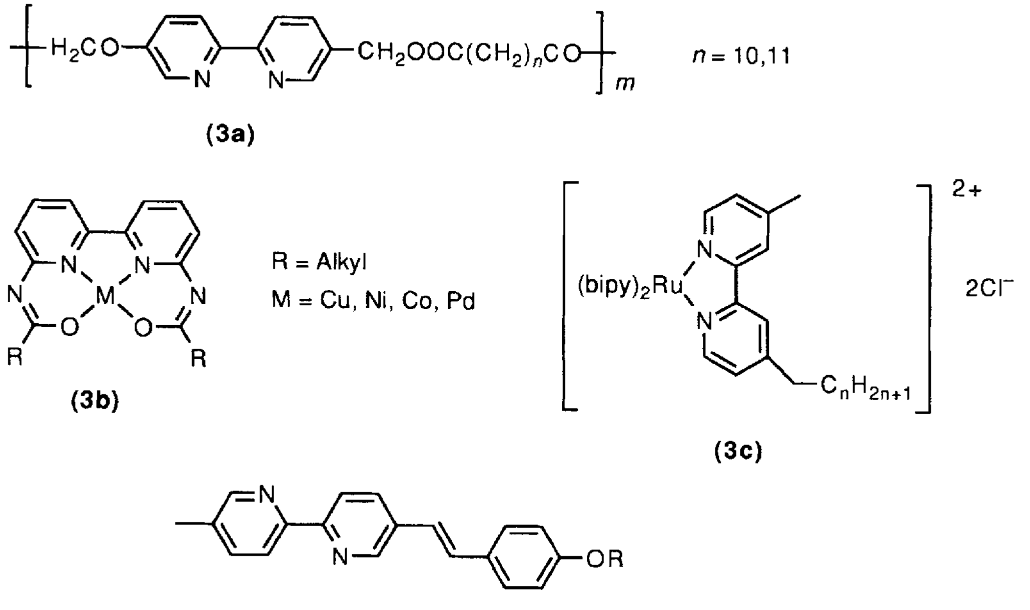
Figure 1. Mesomorphic Schiff's base (**1**) and diazabutadiene (**2**) complexes.

diacid chloride to form the diesters gave only 18–25 per cent yields for the 5,5′-isomer, whilst formation of the corresponding 4,4′-diesters resulted in even lower yields of between 8–12 per cent. Attempts to improve these yields by other methods failed completely on account of the almost total insolubility of the diacids, and the acid chloride route was found to be the only one that gave the desired product.

2.2. *5,5′-Diesters*

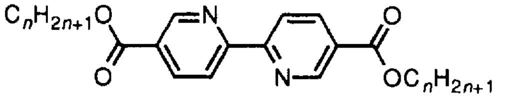
Four 2,2′-bipyridine-5,5′-diester derivatives (**5a–d**) were synthesized with $n = 1$, 4, 8 and 12.

The mesomorphism was dominated by long range nematic phases for the shorter chain lengths and wide range S_C phases for the longer chain lengths, with shorter range S_A phases appearing in the first 3 derivatives. In two derivatives, a crystal smectic phase was found below the S_C phase and on the basis of optical microscopy alone, a preliminary assignment as a J phase has been made. As the alkoxy chain length was increased two trends were observed. Firstly, the smectic phases were stabilized above that of the nematic phase. For example the methoxyphenyl diester (**5a**) exhibited a nematic range over 190°, compared to a 5° range for the dodecyloxy derivative (**5d**). Secondly, the S_C phase was stabilized above and at the expense of the S_A phase. For example, the methoxyphenyl diester exhibited a S_A range over 20°, but did not show a S_C phase (the S_C phase first appeared at the butoxy derivative). By comparison, the dodecyloxyphenyl ester exhibited a S_C phase over a



(3d)

Figure 2. Examples of mesomorphic 2,2-bipyridines. **3a**, 2,2′-Bipyridine metal containing polymers; **3b**, Metal complexes of alkanoyl derivatives of 6,6′-diamino-2,2′-bipyridine; **3c**, Lyotropic Ru(II) tris-2,2′-bipyridine complexes; **3d** The alkoxyphenylvinyl-2,2′-bipyridines.



(4)

n = 1 **(4a)**
4 **(4b)**
8 **(4c)**
12 **(4d)**

Figure 3. Dialkyl 2,2′-bipyridine-5,5′-dicarboxylates.

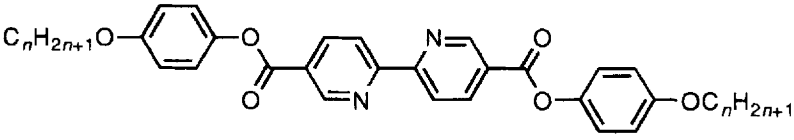
120° range, and by this time the S_A phase was no longer stabilized.

It was then of interest to compare these new compounds with their biphenyl analogues (see figure 6) synthesized by Samulski *et al.* [16].

Only the methyl and butyl derivatives may be compared directly as follows:

(Methoxy ester-bipyridine)
$Cr \cdot 220 \cdot S_A \cdot 241 \cdot N \cdot {>}428 \cdot I$
(Methoxy ester-biphenyl)
$Cr \cdot 193 \cdot S_A \cdot 231 \cdot N \cdot {>}400 \cdot I$
(Butoxy ester-bipyridine)
$Cr \cdot 194 \cdot S_C \cdot 256 \cdot S_A \cdot 299 \cdot N \cdot 370 \cdot I$
(Butoxy ester-biphenyl)
$Cr \cdot 171 \cdot S_A \cdot 339 \cdot N \cdot 367 \cdot I$

The mesomorphism of the two methoxyphenyl diesters is rather similar, but comparison of the data for the two butoxyphenyl diesters shows for the bipyridyl derivative a destabilization of the smectic A phase in favour of a



(5)

n = 1 **(5a)**
4 **(5b)**
8 **(5c)**
12 **(5d)**

Figure 4. Bis(alkoxyphenyl) 2,2′-bipyridine-5,5′-dicarboxylates.

Table 1. Thermal data for bis(alkoxyphenyl) 2,2′-bipyridine-5,5′-dicarboxylates.

R	Transition[a]	T/°C	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
CH_3	$Cr \rightarrow S_A$	220	40·4	81·9
	$S_A \rightarrow N$	241	—[c]	
	$N \rightarrow I$	428[b]	—	
C_4H_9	$Cr \rightarrow S_C$	194	31·5	67·5
	$S_C \rightarrow S_A$	256	—[c]	
	$S_A \rightarrow N$	299		
	$N \rightarrow I$	370[b]		
C_8H_{17}	$Cr \rightarrow J$	135	18·9[d]	46·3
	$J \rightarrow S_C$	155	30·5	71·3
	$S_C \rightarrow S_A$	275	—[c]	
	$S_A \rightarrow N$	280	—[c]	
	$N \rightarrow I$	290	1·23	2·2
$C_{12}H_{25}$	$Cr \rightarrow S_C$	140	33·5	81·1
	$(S_C \rightarrow J)$	(138)		
	$S_C \rightarrow N$	260	1·67	3·1
	$N \rightarrow I$	265	2·03	3·8

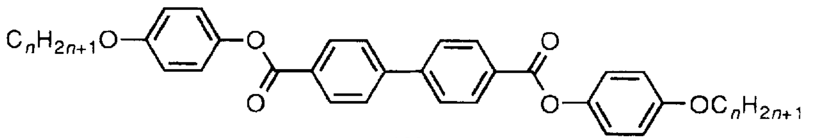
[a] Assignment as a J phase is preliminary.

[b] These temperatures are influenced by decomposition of the materials (see text).

[c] Not seen by DSC.

[d] Enthalpy is that of Cr–Cr–J which is identified by DSC but not readily seen by microscopy.

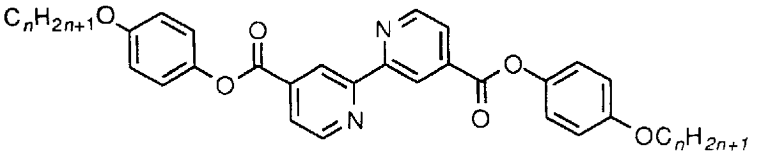
Parentheses denote a monotropic transition.



(6)

n = 1 **(6a)**
4 **(6b)**
7 **(6c)**

Figure 5. Bis(alkoxyphenyl) 1,1′-biphenyl-4,4′-dicarboxylates.



(7)

n = 1 **(7a)**
4 **(7b)**
8 **(7c)**

Figure 6. Bis(alkoxyphenyl) 2,2′-bipyridine-4,4′-dicarboxylates.

nematic phase and the preferential introduction of a smectic C phase. Although not directly comparable, it is interesting that in the heptoxyphenyl diester with a biphenyl core, the smectic C range is 72° with a 107° range for the smectic A phase and a 2° nematic range. This compares with the octyloxyphenyl diester with the bipyridine core which has a 120° smectic C range, a 5° smectic A range and a 10° nematic range.

(octyloxy ester-bipyridine)
$Cr \cdot 135 \cdot J \cdot 155 \cdot S_C \cdot 175 \cdot S_A \cdot 280 \cdot N \cdot 290 \cdot I$
(heptyloxy ester-biphenyl)
$Cr \cdot 116 \cdot Cr_2 \cdot 139 \cdot S_C \cdot 211 \cdot S_A \cdot 318 \cdot N \cdot 320 \cdot I$

Thus, it would appear that the 2,2′-bipyridine core is able strongly to promote the smectic C phase and to some extent the nematic phase compared to the 1,1′-biphenyl analogue.

2.3. *4,4′-Diesters*

In order to examine the relationship between structure and mesomorphism in these systems, we also undertook the synthesis of the related diesters of the 4,4′-dicarboxylic acid.

Here, only three derivatives were synthesized and the thermal data are collected in table 2. As can be seen readily from figure 5, the 4,4′-diesters were much less anisometric than the 5,5′-diesters and this was reflected in the much lower clearing point for the nematic phase of the methoxy- and butoxy-phenyl diesters. However, melting points were little affected by the change in substitution and the nematic phases now appear just enantiotropically for the methoxyphenyl diester and monotropically for the butoxyphenyl diester. Thus, the chains have a greater destabilizing effect on the nematic phase as opposed to the crystal phase. While the molecular shape of the 4,4′-diesters is (obviously) able to support nematic phase formation, it is clear from the thermal behaviour of the octyloxyphenyl diester that smectic phases are not similarly supported and mesomorphism is lost at these chain lengths.

Table 2. Thermal data for bis(alkoxyphenyl) 2,2′-bipyridine-4,4′-dicarboxylates.

R	Transition	*T*/°C
CH_3	$Cr \rightarrow N$	208
	$N \rightarrow I$	210
C_4H_9	$Cr \rightarrow I$	199
	$(I \rightarrow N)$	(195)
C_8H_{17}	$Cr \rightarrow I$	169

Parentheses denote a monotropic transition.

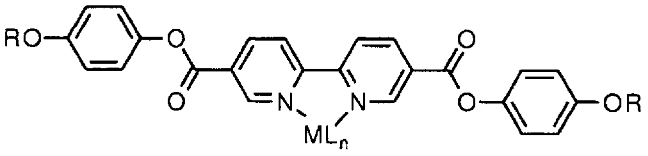
2.4. *Metal complexes*

Having now in our hands a series of ligands with excellent complexing ability, we wished to see how useful they were in the promotion of mesomorphism when complexed to various metal fragments, in particular those with high coordination numbers.

Heating a 2,2′-bipyridine-5,5′-diester ligand with either $[Mo(CO)_6]$, $Cu(NO_3) \cdot 6H_2O$, or $CoCl_2$ at reflux in THF afforded the corresponding complexes (**8**), (**13**), and (**12**). Complexation with $[W(CO)_6]$, $[ReBr(CO)_5]$, or $NiCl_2$ was also achieved thermally to give the resulting complexes, (**9**), (**14**), (**11**). However, in these cases the solvent systems used were toluene, toluene : heptane 3 : 2, and THF : ethanol 3 : 2, respectively. No heating was required when reacting $[PdCl_2(PhCN)_2]$ with a 2,2′-bipyridine-5,5′-diester ligand in CH_2Cl_2, as addition of the metal fragment to a solution of the ligand instantly yielded a yellow precipitate which analysed for the desired complex (**10**).

Thus, several metal fragments of differing geometry were coordinated to the 5,5′-diester-2,2′-bipyridine ligands. Unfortunately none of these complexes exhibited mesomorphism, all of them decomposing before reaching the isotropic liquid except for that with the $ReBr(CO)_3$ fragment which melted at 253°C.

This lack of success was highly unexpected, especially in view of the knowledge that a series of structurally similar Schiff's base and diazabutadiene ligands have



ML_n =	$Mo(CO)_4$	(**8**)	Decomposed on heating
	$W(CO)_4$	(**9**)	
	$PdCl_2$	(**10**)	
	$NiCl_2$	(**11**)	
	$CoCl_2$	(**12**)	
	$Cu(NO_3)_2$	(**13**)	
	$Re(CO)_3Br$	(**14**)	Mpt = 253 °C

Figure 7. Metal complexes of 2,2′-bipyridine-5,5′-diesters.

been successfully coordinated to rhenium(I) and manganese(I) to yield octahedral metal-containing liquid crystals [4, 5].

It has also been observed, firstly with Deshenaux's ferrocene derivatives [3], and then with the Schiff's base and diazabutadiene systems that at least 4 rings are normally required in the ligand backbone in order to gain sufficient anisotropy to compensate for the disruption caused by the addition of a bulky side group and thus to stabilize mesophases in the resulting complexes. Hence it was anticipated that complexation of the 2,2′-bipyridine-5,5′-diesters would yield mesomorphic complexes.

However there is one difference between these complexes and the 2,2′-bipyridine-5,5′-diester complexes, namely that they all contain 4 rings *in addition* to the core (although this is not *so* clear-cut for the Schiff's base complexes (**1**)), whereas the 2,2′-bipyridine complexes all contain 4 rings *including* the core. Thus, by comparison, the 2,2′-bipyridine ligands may not be sufficiently anisometric in this context. Studies are underway to synthesize more extended bipyridines to test this hypothesis.

Another factor which may be of significance is the dipolar nature of the 2,2′-bipyridine unit itself [17]. X-ray studies have shown that in the solid state 2,2′-bipyridine adopts a planar *trans*-conformation, but in solution intramolecular forces are insufficient to maintain this rigid conformation and rotation around an appreciable angle of approximately 20° readily occurs. This gives rise to a measured dipole moment, of between 0·6–0·91 D, which is still negligible when compared with the (calculated) dipole moment associated with the *cisoid* conformation of 2,2′-bipyridine (as found in metal complexes) which is 3·8 D [17].

It is reasonable therefore to assume that the ligand will adopt a *transoid* conformation, and hence will have a negligible dipole moment associated with its coordinating centre. However the complexed ligand will adopt a *cisoid* conformation. Consequently a large dipole moment will be present, which may be instrumental in stabilizing crystal phases above that of the mesophases.

At present, it is not possible to delineate the relative contributions of these two factors and thus, further experiments are planned to see whether such delineation is possible.

3. Experimental

Toluene and THF were distilled over sodium and benzophenone prior to use, and dichloromethane was stored over calcium chloride, followed by anhydrous magnesium sulphate, followed by basic alumina, all for at least 24 h prior to use. Elemental analyses were determined by the University of Sheffield Microanalysis Service. Mass spectra were recorded using the Fast Atom Bombardment technique (FAB), by the University of Sheffield Mass Spectrometry Service. Infrared spectra were measured using a Perkin–Elmer 1600 FT infrared spectrometrometer. NMR spectra were recorded on either a Brucker AM250 or a Brucker AMX 400 spectrometer, where the chemical shifts are reported relative to the internal standard of the deuteriated solvent used. Analysis by DSC was carried out on a Perkin–Elmer DSC7 instrument using heating and cooling rates of either 5 or 10 K min^{-1}. Analysis by hot stage microscopy was carried out using a Zeiss Labpol microscope equipped with a Linkam TH600 hot stage and PR600 controller. Silica gel particle size was 40–63 μm.

3.1. *5,5′-Dimethyl-2,2′-bipyridine*

Nickel aluminium alloy (125 g) was added slowly over a period of 2 h to a stirred solution of sodium hydroxide (160 g) in water (600 cm^3), in an ice bath, under reduced pressure. The temperature rose rapidly during the addition of the alloy. When the temperature had stabilized, the vacuum was removed and the mixture heated at reflux for 30–45 min. The solution was allowed to cool to room temperature and the supernatant liquid decanted. The residue was washed with water (20 × 500 cm^3), until the excess of sodium hydroxide had been removed. The wet catalyst was placed in a 500 cm^3 3-necked flask equipped with a condenser, dropping funnel and water pump. The flask was heated under reduced pressure for *c*. 3 h to remove any residual water and then 3-methylpyridine (150 cm^3, 1·71 mol) was added dropwise to the reaction vessel under reduced pressure, with cooling in an ice bath. Once the catalyst was thoroughly wetted, the pressure was adjusted to atmospheric and the mixture heated at reflux for 40–48 h under N_2. The catalyst was then filtered off and washed with hot chloroform (2 × 150 cm^3). On reducing the volume of solvent, a brown solid precipitated. This was collected, crystallized from ethanol, and washed with water, to yield colourless needles of 5,5′-dimethyl-2,2′-bipyridine. Yield 48·65 g (32 per cent); M.p. 117°C; ^{1}H NMR ($CDCl_3$) 8·48 (2 H, d, H6), 8·24 (2 H, d, H3), 7·60 (2 H, dd, H4), 2·38 (6 H, s, CH_3); ^{13}C NMR ($CDCl_3$) 153·8 (^{2}C), 149·5 (^{6}C), 137·4 (^{4}C), 133·0 (^{5}C), 120·3 (^{3}C), 18·3 (^{7}C); Microanalysis: Calculated (Found) C 78·2 (78·1); H 6·6 (6·6); N 15·2 (15·1) per cent.

3.2. *2,2′-Bipyridine-5,5′-dicarboxylic acid*

5,5′-Dimethyl-2,2′-bipyridine (4 g, 0·02 mol) was added to a solution of potassium permanganate (22 g, 0·14 mol) in water (380 cm^3). The mixture was heated at reflux until the solution became colourless (*c*. 6 h). The precipitated manganese oxide was filtered off, and the colourless aqueous layer washed with diethyl ether (3 × 150 cm^3).

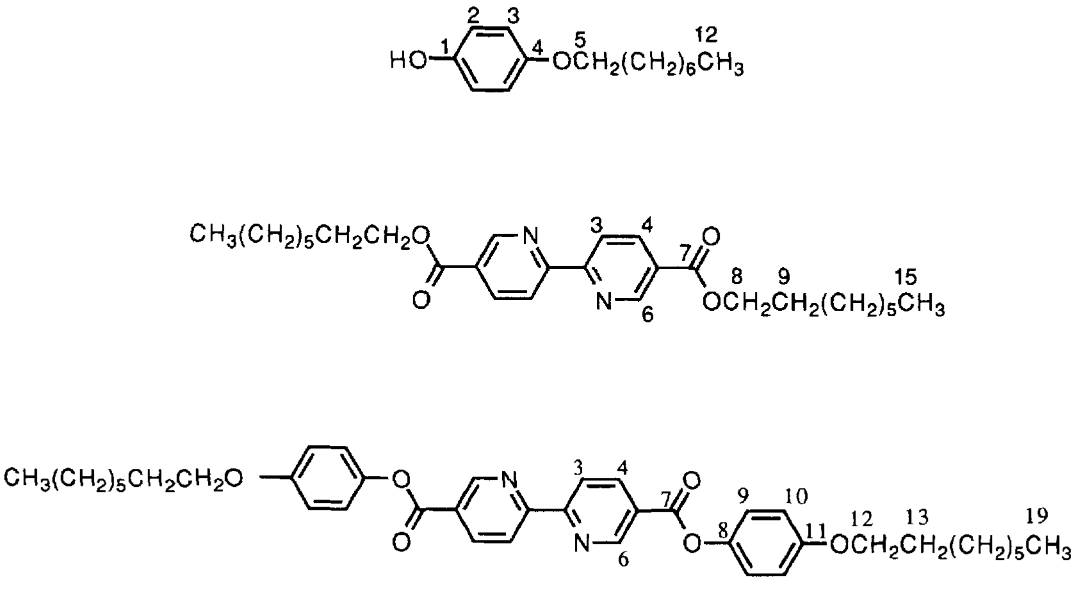


Figure 8. The labelling schemes for NMR data.

The now yellow aqueous layer was acidified with concentrated hydrochloric acid ($50\,cm^3$). The resulting fine white precipitate was collected, washed with a water/methanol mixture and dried to yield 2,2′-bipyridine-5,5′-dicarboxylic acid. Yield 4·68 g (92 per cent); No characterization was achieved due to the product's insolubility.

3.3. *Dimethyl 2,2′-bipyridyl-5,5′-dicarboxylate (4a)*

2,2′-Bipyridine-5,5′-dicarboxylic acid (0·5 g, 2 mmol), methanol ($20\,cm^3$) and a catalytic amount of concentrated sulphuric acid (*c.* 5 drops) were heated under refluxed for 72 h. The resulting white precipitate was filtered off, and washed with a water/methanol mixture. The crude product was crystallized from 1,4-dioxane, and dried, giving the product as a colourless crystalline solid. Yield 0·13 g (24 per cent); M.p. 261·5°C; Microanalysis: Calculated (Found) C 61·7 (61·5); H 4·4 (4·5); N 10·3 (10·3) per cent.

3.5. *Diethyl 2,2′-bipyridyl-5,5′-dicarboxylate (4b)*

All apparatus was pre-dried for 24 h in the oven. Oxalyl chloride ($0·22\,cm^3$, 0·5 mmol) and a drop of DMF were added to a suspension of 2,2′-bipyridine-5,5′-dicarboxylic acid (0·25 g, 1 mmol) in dry dichloromethane ($4\,cm^3$) under nitrogen. The mixture was stirred at room temperature for 3 h before the solvent was evaporated. To the dry acid chloride, a mixture of absolute ethanol ($4\,cm^3$) and pyridine ($0·166\,cm^3$, 2·5 mmol) was added, and the mixture stirred at room temperature overnight. The solvent was evaporated, dichloromethane added and the solution filtered. This was washed with water ($3 \times 50\,cm^3$), dried over magnesium sulphate, filtered and evaporated. The crude product was purified by flash chromatography on silica (hexane:ethyl acetate 7:3), giving the product as a cream solid. Yield 0·058 g (19 per cent); M.p. 150°C; ^{1}H NMR ($CDCl_3$) 9·24 (2 H, d, H6), 8·52 (2 H, d, H3), 8·37 (2 H, dd, H4), 4·39 (4 H, q, OCH_2), 1·38 (6 H, t, CH_3).

3.6. *Dioctyl 2,2′-bipyridyl-5,5′-dicarboxylate (4c)*

2,2′-Bipyridine-5,5′-dicarboxylic acid, (1 g, 4 mmol), toluene ($20\,cm^3$), octanol ($6·35\,cm^3$, 40 mmol), and a catalytic amount of concentrated sulphuric acid (10 drops) were heated at reflux for 72 h. The reaction was cooled to room temperature and the solvent removed under vacuum (*c.* 2 h). The resulting white solid was taken up in dichloromethane and washed with saturated sodium hydrogen carbonate solution ($1 \times 100\,cm^3$). The aqueous layer was then shaken with dichloromethane ($1 \times 150\,cm^3$). The organic extract was washed with water ($4 \times 100\,cm^3$), dried over magnesium sulphate, filtered and evaporated. The crude product was purified by flash chromatography (2 ×) on neutral alumina, using dichloromethane:hexane 3:7 followed by dichloromethane:hexane 1:1, to give the product as a colourless solid. Yield 1 g (52 per cent); M.p. 117°C; ^{1}H NMR ($CDCl_3$) 9·20 (2 H, d, H6), 8·52 (2 H, d, H3), 8·34 (2 H, dd, H4), 4·28 (4 H, t, OCH_2), 1·73 (4 H, m, H9), 1·25 (20 H, m, CH_2), 0·84 (6 H, t, CH_3); ^{13}C NMR (CD_2Cl_2) 165·5 (^{7}C), 158·7 (^{2}C), 150·9 (^{6}C), 138·4 (^{4}C), 127·2 (^{5}C), 121·5 (^{3}C), 66·1 (^{8}C), 32·3, 29·7, 29·1, 26·5, 23·1 ($^{9-14}$C), 14·3 (^{15}C); Microanalysis: Calculated (Found) C 71·8 (71·5); H 8·60 (8·7); N 6·0 (5·7) per cent.

3.7. *Didodecyl 2,2′-bipyridyl-5,5′-dicarboxylate (**4d**)*

This was prepared using the procedure described for dioctyl 2,2′-bipyridyl-5,5′-dicarboxylate, to give the product as a cream solid. Yield 0·08 g (34 per cent); M.p. 118°C; ^{1}H NMR ($CDCl_3$) 9·26 (2 H, dd, H6), 8·58 (2 H, dd, H3), 8·40 (2 H, dd, H4), 4·35 (2 H, t, OCH_2), 1·78 (4 H, m, H9), 1·25 (36 H, m, CH_2), 0·86 (3 H, t, CH_3); Microanalysis: Calculated (Found) C 74·4 (74·5); H 9·7 (10·0); N 4·8 (4·8) per cent.

3.8. *4-Butoxyphenol*

Hydroquinone (5·5 g, 0·05 mol), potassium hydrogen carbonate (5 g, 0·05 mol) and 1-bromobutane (7·45 g, 0·05 mol) were dissolved under nitrogen in 1,4-dioxane/water (1/1, 200 cm^{3}), and heated at reflux for 12 h. The 1,4-dioxane was removed and 6 M hydrochloric acid added dropwise until pH 6 was reached. The aqueous phase was shaken with diethyl ether (3 × 100 cm^{3}); the organic extracts were combined and their volume reduced before washing with water (3 × 100 cm^{3}), drying over magnesium sulphate, filtration and evaporation. The crude brown solid was purified by chromatography on silica (2 ×) using diethyl ether : hexane 1 : 3 followed by diethyl ether : hexane 1 : 1, to give 4-butoxyphenol as a colourless solid. Yield 2·82 g (34 per cent); ^{1}H NMR ($CDCl_3$) 6·75 (4 H, Ar–H), 4·60 (1 H, s, OH), 3·90 (2 H, t, OCH_2), 1·72 (2 H, m, H6), 1·47 (2 H, q, H7), 0·95 (3 H, t, CH_3); ^{13}C NMR ($CDCl_3$) 153·2 (^{4}C), 149·4 (^{1}C), 116·1 (^{2}C), 115·8 (^{3}C), 68·6 (^{5}C), 31·4 (^{6}C), 19·2 (^{7}C), 13·7 (^{8}C).

3.9. *4-Octyloxyphenol*

This was prepared using the procedure described for 4-butoxyphenol. The crude brown solid was purified by chromatography on silica (2 ×) using diethyl ether : hexane 1 : 4, to give 4-octyloxyphenol as a colourless solid. Yield 4·85 g (44 per cent); ^{1}H NMR ($CDCl_3$) 6·76 (4 H, Ar–H), 4·60 (1 H, s, OH), 3·88 (2 H, t, OCH_2), 1·75 (2 H, qt, H6), 1·35 (10 H, m, CH_2), 0·85 (3 H, t, CH_3).

3.10. *4-Dodecyloxyphenol*

This was prepared using the procedure described for 4-butoxyphenol. The crude brown solid was purified by chromatography on silica (2 ×), using diethyl ether : hexane 3 : 7, to give the colourless solid, 4-dodecyloxyphenol. Yield 4·6 g (34 per cent); ^{1}H NMR ($CDCl_3$) 6·76 (4 H, Ar–H), 4·60 (1 H, s, OH), 3·89 (2 H, t, OCH_2), 1·75 (2 H, m, H6), 1·35 (18 H, m, CH_2), 0·88 (3 H, t, CH_3); ^{13}C NMR ($CDCl_3$) 153·3 (^{4}C), 149·4 (^{1}C), 116·1 (^{2}C), 115·7 (^{3}C), 68·8 (^{5}C), 31·9, 29·7, 29·6, 29·4, 26·1, 22·7 ($^{6-15}$C), 14·1 (^{16}C); Microanalysis: Calculated (Found) C 77·7 (77·8); H 10·9 (11·0) per cent.

3.11. *Bis(4-methoxyphenyl) 2,2′-bipyridine-5,5′-dicarboxylate (**5a**)*

All apparatus was pre-dried for 24 h in the oven. 2,2′-Bipyridine-5,5′-dicarboxylic acid (1 g, 4 mmol), thionyl chloride (30 cm^{3}), and dimethyl formide (5 drops) were stirred for 48 h at room temperature. The excess of thionyl chloride was removed under vacuum with mild heat (*c.* 40°C). The resulting dry red solid was cooled in an ethanol/ice bath and a solution of 4-methoxyphenol (0·99 g 8 mmol) in pyridine (15 cm^{3}) was added. The reaction was stirred at room temperature for 4 h, and the pyridine evaporated. The resulting dark brown solid was taken up in aqueous ammonia solution and dichloromethane. The aqueous phase was extracted with dichloromethane (3 × 100 cm^{3}), the organic extracts were combined and the solvent was evaporated. Ethyl acetate was added and the solid collected. The solid was placed in dichloromethane, heated to reflux, allowed to cool to room temperature and the solid collected 2 × . The solid was then heated to reflux in 1,4-dioxane; after hot filtration the product crystallized from the mother liquor. The product was finally recrystallized from 1,4-dioxane, to yield yellow platelets. Yield 0·36 g (20 per cent); ^{1}H NMR ($CDCl_3$) 9·40 (2 H, dd, H6), 8·63 (2 H, dd, H3), 8·53 (2 H, dd, H4), 7·12 (4 H, AA′XX′, H9), 6·90 (4 H, AA′XX′, H10), 3·78 (6 H, s, OCH_3); ^{13}C NMR ($CDCl_3$) 164·1 (^{7}C), 158·6 (^{11}C), 157·6 (^{2}C), 151·1 (^{6}C), 143·9 (^{8}C), 138·7 (^{4}C), 126·0 (^{5}C), 122·3 (^{9}C), 121·5 (^{3}C), 114·6 (^{10}C), 55·6 (^{12}C); Microanalysis: Calculated (Found) C 68·1 (68·4); H 4·2 (4·3); N 5·9 (6·1) per cent.

3.12. *Bis(4-butoxyphenyl) 2,2′-bipyridine-5,5′-dicarboxylate (**5b**)*

This was prepared using the procedure described for bis(4-methoxyphenyl) 2,2′-bipyridine-5,5′-dicarboxylate, to yield the product as colourless platelets. Yield 0·55 g (25 per cent); ^{1}H NMR ($CDCl_3$) 9·46 (2 H, dd, H6), 8·68 (2 H, dd, H3), 8·60 (2 H, dd, H4), 7·15 (4 H, AA′XX′, H9), 6·95 (4 H, AA′XX′, H10), 3·98 (4 H, t, OCH_2) 1·78 (4 H, m, H13), 1·50 (4 H, m, H14), 0·99 (6 H, t, CH_3); ^{13}C NMR ($CDCl_3$) 164·1 (^{7}C), 158·6 (^{11}C), 157·2 (^{2}C), 151·1 (^{6}C), 143·8 (^{8}C), 138·7 (^{4}C), 126·1 (^{5}C), 122·2 (^{9}C), 121·5 (^{3}C), 115·2 (^{10}C), 68·1 (^{12}C), 31·3 (^{13}C), 19·3 (^{14}C), 13·8 (^{15}C); Microanalysis: Calculated (Found) C 71·1 (70·9); H 6·0 (5·9); N 5·2 (5·0) per cent.

3.13. *Bis(4-octyloxyphenyl) 2,2′-bipyridine-5,5′-dicarboxylate (**5c**)*

5c was obtained similarly to **5a** as a light yellow solid. Yield 0·47 g (18 per cent); ^{1}H NMR ($CDCl_3$) 9·40 (2 H, dd, H6), 8·82 (2 H, dd, H3), 8·53 (2 H, dd, H4), 7·10 (4 H, AA′XX′, H9), 6·89 (4 H, AA′XX′, H10), 3·90 (4 H, t, OCH_2), 1·74 (4 H, m, H13), 1·35 (20 H, m, CH_2), 0·82 (6 H, t, CH_3); ^{13}C NMR ($CDCl_3$) 164·1 (^7C), 158·6 (^{11}C), 157·2 (^2C), 151·1 (^6C), 143·8 (^8C), 138·7 (^4C), 126·0 (^5C), 122·2 (^9C), 121·5 (^3C), 115·2 (^{10}C), 68·4 (^{12}C), 31·8, 29·3, 29·2, 26·0, 22·7 ($^{13-19}C$), 14·1 (^{20}C); Microanalysis: Calculated (Found) C 73·6 (73·0); H 7·4 (7·4); N 4·3 (4·3) per cent.

3.14. *Bis(4-dodecyloxyphenyl) 2,2′-bipyridine-5,5′-dicarboxylate (**5 d**)*

5 d was obtained similarly to **5 a** as a colourless solid. Yield 0·583 g (19 per cent); ^1H NMR ($CDCl_3$) 9·46 (2 H, dd, H6), 8·70 (2 H, dd, H3), 8·60 (2 H, dd, H4), 7·16 (4 H, AA′XX′, H9), 6·94 (4 H, AA′XX′, H10), 3·97 (4 H, t, OCH_2), 1·78 (4 H, m, H13), 1·35 (36 H, m, CH_2), 0·88 (6 H, t, CH_3); ^{13}C NMR ($CDCl_3$) 164·1 (^7C), 158·6 (^{11}C), 157·2 (^2C), 151·1 (^6C), 143·8 (^8C), 138·7 (^4C), 126·0 (^5C), 122·2 (^9C), 121·5 (^3C), 115·2 (^{10}C), 68·4 (^{12}C), 31·9, 29·6, 29·4, 29·2, 26·0, 22·7 ($^{13-23}C$), 14·1 (^{24}C); Microanalysis: Calculated (Found) C 75·4 (75·1); H 8·4 (8·2); N 3·7 (3·6) per cent.

3.15. *4,4′-Dimethyl-2,2′-bipyridine*

This was prepared using the procedure described for 5,5′-dimethyl-2,2′-bipyridine, yielding the product as colourless crystals. Yield 55 g (35 per cent); Sublimes >170°C; ^1H NMR ($CDCl_3$) 2·35 (6 H, s, CH_3), 7·06 (2 H, dd, H5), 8·15 (2 H, d, H3), 8·47 (2 H, dd, H6); ^{13}C NMR ($CDCl_3$) 156·0 (^2C), 148·9 (^6C), 148·1 (^4C), 124·6 (^5C), 122·0 (^3C), 21·1 (^7C); Microanalysis: Calculated (Found) C 78·2 (78·1); H 6·6 (6·6); N 15·2 (15·2) per cent.

3.16. *2,2′-Bipyridine-4,4′-dicarboxylate*

This was prepared using the procedure described for 2,2′-bipyridine-5,5′-dicarboxylate, yielding the product as a colourless powder. Yield 2·39 g (45 per cent); No characterization was achieved due to the product's insolubility.

3.17. *Bis(4-methoxyphenyl) 2,2′-bipyridine-4,4′-dicarboxylate (**7 a**)*

All apparatus was pre-dried for 24 hours in the oven.

2,2′-Bipyridine-4,4′-dicarboxylate (1 g, 4 mmol), thionyl chloride (30 cm^3), and dimethyl formide (5 drops), were placed in a 2-necked flask equipped with a calcium chloride guard tube. A clear orange solution was obtained by stirring for 90 min at room temperature. The excess thionyl chloride was removed under vacuum with a mild heat (*c.* 40°C). A solution of methoxy phenol (0·99 g, 8 mmol), in toluene was added to the dry acid chloride under nitrogen. The reaction was heated at reflux for 2 h and the excess solvent was removed. The resulting dark brown solid was taken up in aqueous ammonia solution and dichloromethane. The aqueous phase was extracted with dichloromethane (3 × 100 cm^3), the organic extracts combined and the solvent evaporated. Ethyl acetate was added and the solid collected. The solid was placed in dichloromethane, heated to reflux, allowed to cool to room temperature and the solid collected. The solid was then heated to reflux in 1,4-dioxane, filtered hot and the product crystallized from the mother liquor. The product was finally recrystallized from 1,4-dioxane, to yield the product as a colourless solid. Satisfactory elemental analyses were never obtained for this compound, although analysis by hplc gave a purity of 98·6 per cent and it was found to melt quite cleanly. Yield 0·15 g (8 per cent); ^1H NMR ($CDCl_3$) 9·10 (2 H, dd, H3), 8·88 (2 H, dd, H6), 8·00 (2 H, dd, H5), 7·12 (4 H, AA′XX′, H9), 6·90 (4 H, AA′XX′, H10), 3·77 (6 H, s, OCH_3); Microanalysis: Calculated (Found) C 68·4 (66·3); H 4·4 (4·5); N 6·1 (5·8) per cent; MS *m/z* 458 $[M]^+$, 457 $[M\text{-}H]^+$.

3.18. *Bis(4-butoxyphenyl) and bis(4-octyloxyphenyl) 2,2′-bipyridine-4,4′-dicarboxylate (**7 b**) and (**7 c**)*

Two further esters were prepared similarly and obtained as colourless solids: **7 b**: Yield 0·24 g (11 per cent); ^1H NMR ($CDCl_3$) 9·15 (2 H, dd, H3), 8·92 (2 H, dd, H6), 8·05 (2 H, dd, H5), 7·16 (4 H, AA′XX′, H9), 6·90 (4 H, AA′XX′, H10), 3·97 (4 H, t, OCH_2) 1·77 (4 H, m, H13), 1·55 (4 H, m, H14), 0·98 (6 H, t, CH_3), ^{13}C NMR ($CDCl_3$) 164·2 (^7C), 157·2 (^{11}C), 156·6 (^2C), 150·3 (^6C), 143·8 (^8C), 138·3 (^4C), 123·7 (^5C), 122·2 (^9C), 120·9 (^3C), 115·2 (^{10}C), 68·1 (^{12}C), 31·3 (^{13}C), 19·2 (^{14}C), 13·9 (^{15}C); Microanalysis: Calculated (Found) C 71·1 (70·4); H 6·0 (6·0); N 5·2 (5·1) per cent.

7 c: Yield 0·3 g (12 per cent); ^1H NMR ($CDCl_3$) 9·15 (2 H, dd, H3), 8·95 (2 H, dd, H6), 8·05 (2 H, dd, H5), 7·18 (4 H, AA′XX′, H9), 6·96 (4 H, AA′XX′, H10), 4·00 (4 H, t, OCH_2) 1·81 (4 H, m, H13), 1·35 (20 H, m, CH_2) 0·90 (6 H, t, CH_3); ^{13}C NMR ($CDCl_3$) 164·1 (^7C), 157·2 (^{11}C), 156·6 (^2C), 150·3 (^6C), 143·8 (^8C), 138·3 (^4C), 123·7 (^5C), 122·1 (^9C), 120·9 (^3C), 115·2 (^{10}C), 68·4 (^{12}C), 31·8, 29·3, 29·2, 26·0, 22·6 ($^{13-18}C$), 14·1 (^{19}C); Microanalysis: Calculated (Found) C 73·6 (73·3); H 7·4 (7·5); N 4·3 (4·2) per cent.

3.19. *(2,2′-Bipyridyl-5,5′-bis(dodecyloxybenzoato)) tetracarbonylmolybdenum(0) (**8**)*

Molybdenum hexacarbonyl (0·0172 g, 0·0065 mmol) and THF (60 cm^3) were placed in a flask equipped with a Soxhlet apparatus containing bis(4-dodecyloxyphenyl) 2,2′-bipyridine-5,5′-dicarboxylate (0·05 g, 0·0065 mmol) in the thimble and heated at reflux in a nitrogen atmosphere for 4 h, giving a dark purple solution. The solvent was removed and the crude solid was crystallized from THF and hexane, to yield the product as a dark purple solid. Decomposes >160°C; ^1H NMR ($CDCl_3$) 9·84

(2 H, dd, H6), 8·59 (2 H, dd, H4) 8·05 (2 H, dd, H3), 7·12 (4 H, AA'XX', H9), 6·90 (4 H, AA'XX', H10), 3·90 (4 H, t, OCH_2) 1·75 (4 H, m, H13), 1·20 (36 H, m, CH_2) 0·80 (6 H, t, CH_3); ^{13}C NMR ($CDCl_3$) 222·2 (CO), 203·8 (CO), 162·3 (^7C), 157·4 (^{11}C), 156·7 (^2C), 154·4 (^6C), 143·4 (^8C), 138·4 (^4C), 127·8 (^5C), 122·8 (^3C), 122·1 (^9C) 115·2 (^{10}C), 68·5 (^{12}C), 31·9, 29·7, 29·6, 29·4, 29·3, 29·2, 26·0, 22·7 ($^{13-21}C$), 14·1 (^{22}C); IR (DCM) $\nu_{C=O}$ 2017 (m), 1911 (s), 1885 (sh), 1838 (m), $\nu_{C=O}$ 1743 (m); MS *m/z* 974 $[M]^+$, 949 $[M\text{-}CO]^+$, 919 $[M\text{-}2CO]^+$, 890 $[M\text{-}3CO]^+$, 828 $[M\text{-}(CO)_4CH_2CH_3]^+$, 765 $[M\text{-}Mo(CO)_4]^+$, 737 $[M\text{-}Mo(CO)_4CH_2CH_3]^+$, 709 $[M\text{-}Mo(CO)_4\ (CH_2CH_3)_2]^+$, 487 $[M]^{2+}$, 459 $[M\text{-}2CO]^+$, Microanalysis: Calculated (Found) C 64·2 (64·3); H 6·6 (6·8); N 2·9 (3·1) per cent.

3.20. *(2,2'-Bipyridyl-5,5'-bis(octyloxybenzoato))tetracarbonyltungsten(0) (9)*

Bis(4-octyloxyphenyl) 2,2'-bipyridine-5,5'-dicarboxylate (0·05 g, 7·67 × 10^{-5} mol), and tungsten hexacarbonyl (0·069 g, 1·96 × 10^{-4} mol) were placed in toluene (30 cm^3) under nitrogen and heated at reflux for 26 h, followed by stirring at room temperature for 60 h. The toluene was then evaporated and the excess of tungsten hexacarbonyl removed by sublimation onto a cold finger (56°C, 0·25 mmHg). Dichloromethane (7 cm^3) was added, and the solid precipitated by the addition of an excess of hexane was collected by centrifugion, washed with hexane and dried, to give the product as a black solid. Yield 0·055 g (79 per cent); Decomposes >200°C; ^1H NMR ($CDCl_3$) 10·00 (2 H, d, H6), 8·68 (2 H, dd, H4), 8·41 (2 H, dd, H3), 7·20 (4 H, AA'XX', H9), 6·96 (4 H, AA'XX', H10), 3·98 (4 H, t, OCH_2), 1·80 (4 H, qt, H13), 1·4 (20 H, m, CH_2), 0·90 (6 H, t, CH_3); ^{13}C NMR ($CDCl_3$) 214·8 (CO), 199·9 (CO), 162·0 (^7C), 157·8, 157·5 (^2C, ^{11}C), 154·7 (^6C), 143·5 (^8C), 138·1 (^4C), 128·6 (^5C), 123·5 (^3C), 122·1 (^9C) 115·3 (^{10}C), 68·1 (^{12}C), 31·3, 29·6, 29·4, 26·0, 22·7 ($^{13-18}C$), 14·1 (^{19}C); IR (DCM) $\nu_{C=O}$ 2009 (m), 1900 (vs), 1883 (sh), 1837 (m), $\nu_{C=O}$ 1742 (m); Microanalysis: Calculated (Found) C 55·7 (55·3); H 5·1 (5·6); N 3·0 (2·8) per cent.

3.21. *(2,2'-Bipyridyl-5,5'-bis-octyloxybenzoato)palladium(II)chloride (10)*

A solution of palladiumdichloride-bis-benzonitrile (0·00294 g, 7·67 × 10^{-5} mol) was added to a solution of bis(4-octyloxyphenyl) 2,2'-bipyridine-5,5'-dicarboxylate (0·05 g, 7·67 × 10^{-5} mol) at room temperature under nitrogen. A yellow precipitate immediately formed. The suspension was stirred at room temperature for 1 h before the solvent was evaporated and the yellow solid dried. Yield 0·06 g (94 per cent); M.p. unchanged >350°C; Microanalysis: Calculated (Found) C 57·9 (57·5); H 5·8 (5·9); N 3·4 (3·1); Cl 8·5 (8·7) per cent. No NMR data could be obtained due to the product's insolubility.

3.22. *(2,2'-Bipyridyl-5,5'-bis-octyloxybenzoato)nickel(II)chloride (11)*

Bis(4-octyloxyphenyl) 2,2'-bipyridine-5,5'-dicarboxylate (0·05 g, 7·67 × 10^{-5} mol) and nickel(II) chloride (0·0182 g, 7·67 × 10^{-5} mol) were placed in THF : ethanol (3 : 2, 30 cm^3), under nitrogen. The mixture was heated at reflux for 4·5 h and then stirred at room temperature for 60 h. The resulting yellow precipitate was collected by centrifugion, washed with hexane and dried to give the product as a bright yellow solid. Yield 0·058 g (97 per cent); Decomposes >300°C; Microanalysis: Calculated (Found) C 61·4 (61·0); H 6·2 (6·4); N 3·6 (3·6); C 19·1 (9·3) per cent; MS *m/z*, 745 $[M\text{-}Cl]^+$, 710 $[M\text{-}2Cl]^+$, 653 $[M\text{-}NiCl_2]^+$.

3.23. *(2,2'-Bipyridyl-5,5'-bis-octyloxybenzoato)cobalt(II)chloride (12)*

Bis(4-octyloxyphenyl) 2,2'-bipyridine-5,5'-dicarboxylate (0·05 g, 7·67 × 10^{-5} mol) and cobalt(II)chloride (0·01 g, 7·67 × 10^{-5} mol) were placed in THF under nitrogen. The mixture was heated at reflux for 2 h and then stirred at room temperature for 24 h. The precipitate was collected by centrifugion and washed with hexane 2 ×, to give the product as a dark green solid. Yield 0·051 g (85 per cent); Decomposes >160°C; MS *m/z* 746 $[M\text{-}Cl]^+$; Microanalysis: Calculated (Found) C 61·4 (60·8); H 6·2 (6·3); N 3·6 (3·5); Cl 9·1 (9·3) per cent.

3.24. *(2,2'-Bipyridyl-5,5'-bis-octyloxybenzoato)copper(II)nitrate (13)*

Copper(II)nitrate hexahydrate (0·0371 g, 0·15 mmol) was placed in THF, under nitrogen, in a flask to which a Soxhlet apparatus containing bis(4-octyloxyphenyl) 2,2'-bipyridine-5,5'-dicarboxylate (0·1 g, 0·15 mmol) in the thimble was attached. After heating at reflux for 5 h, the solution was cooled to room temperature and the solvent evaporated. The minimum amount of THF required to form a solution was added, followed by an excess of hexane. The resulting precipitate was collected by centrifugion, and washed with hexane. The product crystallized from THF and hexane as a green solid. Yield 0·088 g (76 per cent); Microanalysis: Calculated (Found) C 57·2 (56·6); H 5·8 (5·6); N 6·7 (6·3) per cent.

3.25. *(2,2'-Bipyridyl-5,5'-bis-octyloxybenzoato)pentacarbonylrheniumbromide (14)*

Bis(4-octyloxyphenyl) 2,2'-bipyridine-5,5'-dicarboxylate (0·05 g, 7·67 × 10^{-5} mol) and rhenium pentacarbonylbromide (0·031 g, 7·67 × 10^{-5} mol) were placed in toluene : heptane (3 : 2, 30 cm^3) under nitrogen, and heated at reflux and the reaction course followed by FTIR.

After 3·5 h the solution was cooled to room temperature, and the resulting orange precipitate collected by centrifugion and washed with heptane. It was then redissolved in dichloromethane, reprecipitated by the addition of hexane, collected by centrifugion, washed with hexane and dried to yield the product. Yield 0·055 g (72 per cent); M.p. 253°C; ^{1}H NMR ($CDCl_3$) 9·80 (2 H, d, H6), 8·80 (2 H, dd, H4), 8·45 (2 H, dd, H3), 7·20 (4 H, AA′XX′, H9), 6·97 (4 H, AA′XX′, 10), 3·98 (4 H, t, OCH_2), 1·80 (4 H, qt, H13), 1·35 (20 H, m, CH_2), 0·90 (6 H, t, CH_3); ^{13}C NMR ($CDCl_3$) 161·4 (^{7}C), 157·8, 157·6 (^{2}C, ^{11}C), 154·8 (^{6}C), 143·3 (^{8}C), 140·3 (^{4}C), 129·6 (^{5}C), 124·1 (^{3}C), 122·0 (^{9}C), 115·3 (^{10}C), 68·5 (^{12}C), 31·8, 29·4, 29·3, 26·1, 22·7 ($^{13-18}$C), 14·1 (^{19}C); IR (KBr) $\nu_{C\equiv O}$ 2023 (s), 1930 (s), 1908 (s), $\nu_{C=O}$ 1740 (m); MS *m*/*z* 1002 $[M]^+$, 974 $[M\text{-}CO]^+$, 923 $[M\text{-}Br]^+$; Microanalysis: Calculated (Found) C 51·5 (51·1); H 4·8 (4·5); N 2·8 (2·7); Br 8·0 (8·1) per cent.

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