Amphiphilic Terpyridine Complexes of Ruthenium and Rhodium displaying Lyotropic Mesomorphism

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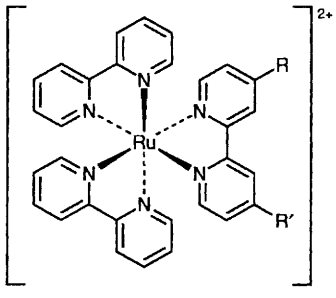
New 4'-alkyl-substituted 2,2':6',2"-terpyridine (4'R-terpy) compounds have been synthesised from 4'-methyl-2,2':6',2"-terpyridine and an appropriate 1-bromoalkane and complexed with ruthenium and rhodium to yield new bis(terpyridine) complexes $[Ru(terpy)(4'R\text{-}terpy)]^{2+}$ ($R = C_{19}H_{39}$ or $C_{31}H_{63}$) and $[Rh(terpy)(4'R\text{-}terpy)]^{3+}$ ($R = C_{19}H_{39}$) as chloride and hexafluorophosphate salts. These complexes are amphiphilic being structurally related to surfactant tris(bipyridine)ruthenium complexes. Both ruthenium and rhodium complexes with $R = C_{19}H_{39}$ and chloride counter ions show lyotropic mesomorphism in water, and the ruthenium complex with $R = C_{31}H_{63}$ shows mesophase formation in ethylene glycol.

For several years we have been looking at the synthesis and properties of metal-containing liquid crystals. These have primarily been thermotropic mesogens where liquid-crystalline behaviour is mediated by temperature. The incorporation of a metal complex[1] can be used to introduce novel physical modifications to the underlying properties of the mesophase (*i.e.* magnetism, colour, chirality, electronic properties). More recently we have started to look at metal-containing lyotropic liquid-crystal systems where mesomorphism is mediated by concentration in solution. The mesogenic units are molecular aggregates comprising either micelles or columns.

Metal-containing lyotropic liquid crystals have not been widely studied although interest in this area is growing. Notable contributions have been made by Usol'tseva *et al.*[2] with studies of anionic phthalocyanine derivatives in water and by Praefcke, Usol'tseva and co-workers[3] on tetrapalladium organyl complexes which have a disc-like structure and form lyotropic mesophases in oil-continuous solutions (*i.e.* tetradecane). In both examples, lyotropic mesophases are formed through aggregation of the disc-like molecules into short columns which become ordered. These materials can show nematic and hexagonal phases, analogous to the columnar discotic mesophases shown by some thermotropic materials. This phase behaviour is common for many dye molecules[4] but is not typical of the most common lyotropic materials, surfactants. Surfactants have an amphiphilic structure comprising a hydrophilic head and one or more hydrophobic (usually hydrocarbon) chains. They form micelles above the critical micelle concentration (c.m.c.) which interact at higher concentrations to form lyotropic liquid-crystal phases.

We have centred our effort on materials which have a structural motif similar to simple surfactants, having successfully prepared transition-metal complexes which show surfactant-type mesomorphism[5,6] in water (*i.e.* the mesomorphism is based on the formation and ordering of micelles). The lyotropic behaviour of amphiphilic tris(2,2'-bipyridine)-ruthenium surfactants (Fig. 1), synthesised using the method described by Seddon and Yousif,[7b] has been investigated.[8] These materials show remarkable stability compared with our earlier examples,[5,6] allowing complete mesophase characterisation by microscopy and small-angle X-ray scattering measurements.[9]



R = Me, alkyl
R' = alkyl

Fig. 1 Tris(2,2'-bipyridine)ruthenium surfactants

We have expanded the scope of these systems by the synthesis of related surfactant tris(2,2'-bipyridine)rhodium complexes, these being the first examples of cationic surfactants containing three positive charges. Even more remarkable, the charge is localised on a single head group. This is not possible in conventional surfactants and illustrates the flexibility of metal-containing surfactants. Lyotropic mesophases were observed for the rhodium complexes which are similar to those for the ruthenium complexes but which showed instability to photochemical decomposition when in solution and could not be fully characterised.

In order to address the aspects of stability of the complexes in solution and mesophases, and to extend the range of this work, we have looked at some related ligand systems. Here we report on the synthesis of two new 4'-substituted 2,2':6',2"-terpyridine derivatives (**I**, **II** in Scheme 1) and their complexes **1**–**3** with either ruthenium and rhodium. Transition-metal complexes of terpyridine (terpy) and its derivatives (*i.e.* 4'-phenyl-2,2':6',2"-terpyridine) have been widely investigated,[10] with the tridentate, conjugated aromatic nature of the ligand leading to interesting modifications of the electronic and photochemical properties[11] of the metal centre (*i.e.* redox potentials, absorption and emission spectra) and also showing increased stability when compared to 2,2'-bipyridine (bipy) complexes and the potential to stabilise more than one oxidation state. Platinum terpyridine complexes have been shown to intercalate with DNA and this behaviour has been extensively studied[12] with reference to potential anticancer activity. Bis-(terpyridine)metal complexes are also intrinsically achiral in

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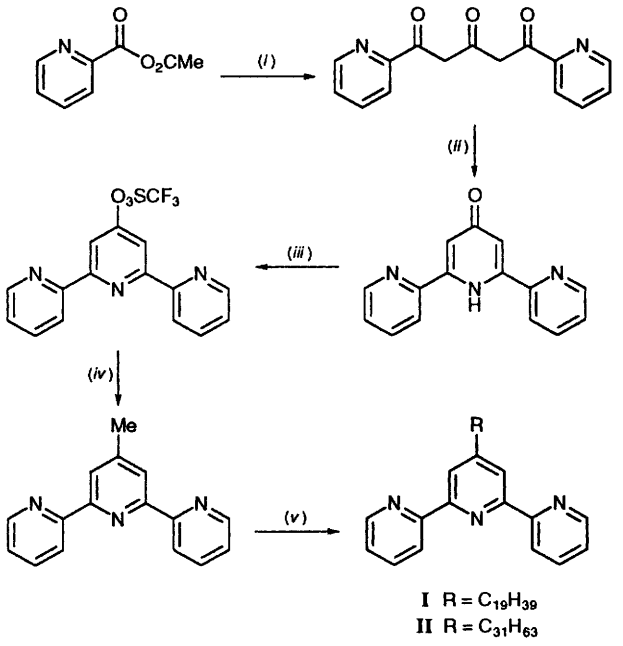
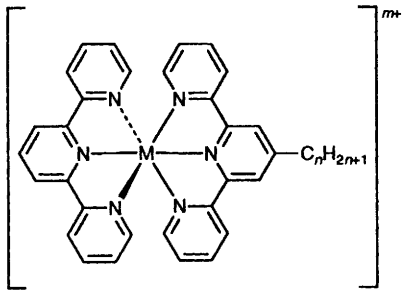


Scheme 1 Synthesis of 4′-alkyl-2,2′:2″,6″-terpyridines. (*i*) Me_2CO, NaH, tetrahydrofuran (thf); (*ii*) NH_4O_2CMe; (*iii*) $(CF_3SO_2)_2O$; (*iv*) $SnMe_4$, $[PdCl_2(PPh_3)_2]$; (*v*) (*a*) $LiNPr^i_2$, thf, < 0 °C, (*b*) $C_{18}H_{37}Br$ or $C_{30}H_{31}Br$



	M	*n*	*m*
1	Rh	19	3
2	Ru	19	2
3	Ru	31	2

contrast to tris(bipyridine)metal complexes which exhibit two isomers, the Δ and Λ forms.

The lyotropic mesophases formed for a surfactant depend on structural features of the individual molecules (*i.e.* ratio of head group cross-section to hydrophobic volume and length) and have been described by Mitchell and co-workers.[13] From models of the terpyridine and bipyridine complexes (Fig. 2) it is clear that both have very similar structures, the metal co-ordination sphere containing six pyridine rings. The size of the polar head group should not change for the terpyridine complexes compared to the bipyridine complexes, and we would anticipate that a similar mesomorphic behaviour would be observed (*i.e.* formation of an micellar I_1 cubic phase).

Synthesis

2,2′:6′,2″-Terpyridine compounds alkylated at the 4′ position were prepared from commercially available ethyl pyridine-2-carboxylate in good overall yield using a five-step synthesis (see Scheme 1). Using a combination of the methods of Potts[14] and Constable[15] and co-workers, ethylpyridine-2-carboxylate and acetone were combined in a Claisen condensation followed by Hantzsch cyclisation of the resulting 1,2,5-triketone to yield 2,6-di-2-pyridyl-4(1*H*)-pyridone. This was converted into 2,2′:6′,2″-terpyridine-4′-trifluoromethanesulfonate with trifluoromethanesulfonic anhydride and methylated using a palladium-catalysed coupling[16] with tetramethyltin, to yield 4′-methyl-2,2′:2″,6′-terpyridine. The long alkyl chains were then added by direct alkylation of the methyl group with lithium diisopropylamide and the corresponding 1-bromoalkane $Br(CH_2)_{n-1}CH_3$ under similar conditions to those used earlier for the alkylated bipyridines. The 4′-alkylated derivatives show reduced melting points compared to the parent 4′-methylterpyridines, in agreement with the melting points of other 4′-functionalised terpyridine derivatives.

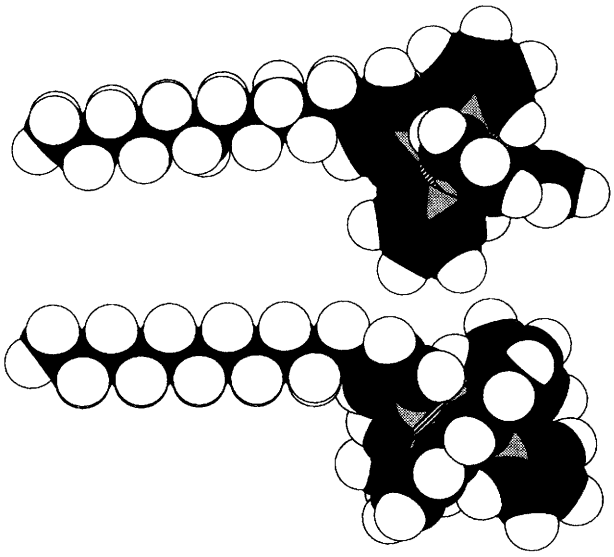


Fig. 2 Space-filling models of (4′-substituted terpyridine)(terpyridine)metal (above) and bis(bipyridine)(4′-substituted 4-methylbipyridine)metal complexes (below)

Rhodium and ruthenium complexes of the new 4′-alkylated terpyridine compounds with the general formula $[M(terpy)(4'R\text{-}terpy)]^{m+}\cdot mX^-$ [M = Ru (*m* = 2) or Rh (*m* = 3); R = $C_{19}H_{39}$ or $C_{31}H_{63}$; X = Cl or PF_6] were prepared from $[MCl_3(terpy)]$. A *trans*-dialkyl complex, $[Ru(4'R\text{-}terpy)_2]Cl_2$ **4** (R = $C_{19}H_{39}$) was synthesised from $RuCl_3$ and the 4′-alkylterpyridine.

Bis(terpyridine)ruthenium complexes were conveniently prepared by reaction of $[RuCl_3(terpy)]$ and a 4′-functionalised terpyridine in ethanol at reflux, to yield the desired product. However the reaction was considerably slower than the corresponding reaction between *cis*-$[RuCl_2(bipy)_2]$ and a bipyridine. In contrast, direct combination of $[RhCl_3(terpy)]$ with a second terpyridine failed to yield any reaction due the strength of the bonds between the Rh^{3+} centre and the three remaining chlorides. The inertness of $[RhCl_3(terpy)]$ to simple substitution of the chlorines by other ligands has been noted by Sauvage *et al.*[17] and the method described in their work has been used to prepare the bis(terpyridine)rhodium complexes. Thus, $[RhCl_3(terpy)]$ was first treated with a silver salt (either $AgNO_3$ or $AgBF_4$) in a weakly co-ordinating solvent (acetone is used for terpyridine complexes). The silver cation acts as both a Lewis acid and chloride-ion scavenger to remove the co-ordinated chloride ions from the metal centre. In the resulting intermediate, $[Rh(terpy)(solv)_3]^{3+}$, the weakly co-ordinating solvent (solv) molecules can easily be displaced by a second, functionalised terpyridine ligand.

Reaction of $[RhCl_3(terpy)]$ with the substituted 4′-alkylterpyridine and a silver salt yielded the nitrate or tetrafluoroborate salt (depending on the silver salt used) which was not isolated. The crude product was dissolved in water and precipitated as the hexafluorophosphate salt by addition of aqueous ammonium hexafluorophosphate. The hexafluorophosphate anions were readily exchanged for chloride by precipitation

from dry acetone solution using LiCl to yield the bis(terpyridine)rhodium complex, $[Rh(terpy)(4'R\text{-}terpy)]Cl_3$ **3** ($R = C_{19}H_{39}$), as a colourless powder which was extremely hygroscopic when isolated.

The complex $[RuCl_3(terpy)]$ was treated with a substituted terpyridine using a silver salt to promote the removal of chloride from the ruthenium complex, which allowed efficient formation of the $[Ru(terpy)(4'R\text{-}terpy)]^{2+}$ dication which was obtained as the hexafluorophosphate salt. However, anion exchange to the chloride salt could not be achieved. The addition of LiCl to solutions of the hexafluorophosphate or tetrafluoroborate salts (from the crude reaction mixture) in acetone precipitated the metal complex with mixed counter ions, $[Ru(terpy)(4'R\text{-}terpy)]Cl_mX_{2-m}$ ($X = PF_6$, BF_4 or NO_3 depending on the initial counter ion). The solubility of these complexes was intermediate between those of the hexafluorophosphate and chloride salts which allowed ready formation of the PF_6 salt, but precluded subsequent efficient conversion into the desired complex with chloride counter ions. Similarly, ion-exchange chromatography (Sephadex LH-20) yielded poor conversion into the chloride salt.

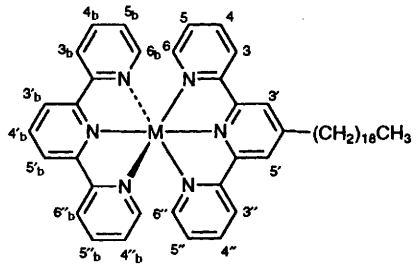
The ruthenium complexes were obtained as stable, red powders. The rhodium complex was obtained as a colourless, hygroscopic powder as the chloride salt and as a pale yellow to pale violet solid for the hexafluorophosphate salt, the colour depending on the purity and the residual solvent in the complex. Rhodium terpyridine complexes[18] have been reported to vary from colourless for chloride and perchlorate salts through yellow to red for iodide salts, as a function of anion polarisability. This is interpreted as a decrease in inner-sphere hydration through closer covalent approach of the ions lowering the energy gap for the charge-transfer process. We have found that a solution of the rhodium complexes in a highly co-ordinating solvent such as dimethyl sulfoxide changes from colourless to yellow as the complex dissolves.

Proton NMR assignments for the terpyridine complexes of ruthenium and rhodium are shown in Table 1. Spectra were obtained in $(CD_3)_2SO$ (all ruthenium complexes), $(CD_3)_2CO$ (rhodium hexafluorophosphate salts) and CD_3OD (rhodium chloride salts). The complexes contain two, orthogonal C_2 symmetry axes which simplify the NMR spectra and two sets of four signals are expected for each terpyridine ligand with a further signal for the 4″-proton of the unsubstituted terpyridine. In practice, signals from the two terpyridine ligands were indistinguishable to the limiting resolution of the NMR experiment and the observed spectra were simplified further to give a signal (each 4 H) for each of positions 3/3″, 4/4″, 5/5″ and 3′/5′ of terpyridine and a signal (1 H) for the unsubstituted terpyridine 4′ position. The 6/6″ signals showed a distinct upfield shift for the complexes compared to the free terpyridines. The shielding of the nuclei was indicative of their location over the central ring of the opposing terpyridine. In spectra of the rhodium complexes hyperfine J(Rh–H) coupling (< 0.25 Hz) was observed for the protons of the terpyridine rings, especially in the 3, 4, 5 positions.

Proton NMR spectra in $(CD_3)_2SO$ were obtained for complexes containing ruthenium with chloride and hexafluorophosphate anions. The chemical shift of the signals showed no anion dependency, which has also been reported[19] for surfactant tris(bipyridine)ruthenium complexes. Spectra taken in different solvents [$(CD_3)_2SO$, CD_3OD, $(CD_3)_2CO$, D_2O] did show a solvent dependence.

The chloride salts of the ruthenium complexes, in contrast to the very high water solubility of the analogous bipyridine complexes, were only slightly soluble in water. The chloride salt of the rhodium complex was very hygroscopic in air and, unlike the ruthenium complexes, was very soluble in water. Ruthenium and rhodium complexes as chloride salts were investigated for lyotropic mesomorphism in water and in ethylene glycol, an organic polar solvent.

Table 1 Proton NMR shift assignments (J/Hz) for $[M(terpy)(4'R\text{-}terpy)]^{n+}\cdot nX^-$ complexes ($R = C_{19}H_{39}$)



M	Rh^{III}	Rh^{III}	Ru^{II}
X, n	PF_6, 3	Cl, 3	Cl, 2
Solvent	$(CD_3)_2CO$	CD_3OD	$(CD_3)_2SO$
Terminal CH_3	0.88	0.9	0.83
	(3 H, t, J = 6.5)	(3 H, t, J = 6.5)	(3 H, t, J = 7)
Alkyl	1.29	1.30	1.05–1.65, (32 H, m)
	(32 H, m)	(34 H, m)	2.03 (2 H, m)
$C_\alpha H_2$	3.30	2.10	3.14
	(2 H, t, J = 7)	(2 H, t)	(2 H, t, J = 7.5)
5,5″/5$_b$,5″$_b$	7.62	7.78, 7.61	7.23, 7.27
	(4 H, 2 × dd)	(4 H, 2 × dd)	(4 H, 2 × d, J = 7)
6,6″/6$_b$,6″$_b$	8.11, 8.14	7.88, 7.92	7.37
	(4 H, 2 × d, J = 6.5)	4 H, 2 × d)	(4 H, m)
4,4″/4$_b$,4″$_b$	8.40, 8.44	8.34, 8.37	8.00
	(4 H, 2 × dd)	(4 H, 2 × dd)	(4 H, dd, J = 6.5)
3,3″/3$_b$,3′$_b$	8.97	8.93	8.88
	(4 H, d, J = 7)	(4 H, dd)	(4 H, d, J = 7)
4′$_b$	9.13	9.0	8.50
	(1 H, d, J = 7)	(1 H, d, J = 7)	(1 H, dd, J = 7)
3′,5′	9.18	9.07	9.09
	(2 H, s)	(2 H, s)	(2 H, s)
3′$_b$,5′$_b$	9.50	9.18	9.14
	(2 H, d, J = 7)	(2 H, d, J = 7)	(2 H, d, J = 7.5)

Lyotropic Mesomorphism

The mesomorphic behaviour of the complexes in water was investigated by optical microscopy using the Lawrence penetration experiment[20] where solvent is introduced onto a microscope slide containing surfactant. A concentration gradient is created at the interface between neat surfactant and the solvent and lyotropic mesophases are observed across the boundary and can be monitored with changing temperature.

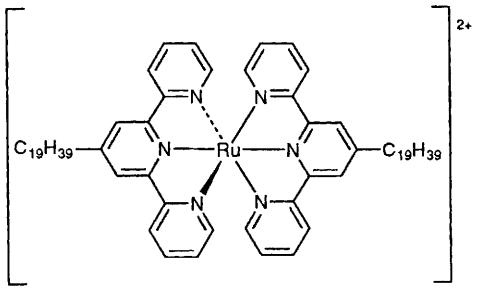
The ruthenium complex [Ru(terpy)(4′R-terpy)]Cl_2 (R = $C_{19}H_{39}$) showed mesomorphism broadly similar to that of the analogous tris(bipyridine)ruthenium complex, exhibiting a normal micellar cubic (I_1) mesophase between the solution and solid regions. However the specific behaviour varied because of the difference in solubility between the two ruthenium complexes. In the penetration experiment the complex showed only limited solubility in water and no mesophase formation at room temperature or on gentle warming. A distinct increase in solubility was observed when the temperature was raised to between 65 and 70 °C and a viscous, isotropic cubic phase then formed at the solid–solution interface from around 73 °C; the mesophase persisted to < 100 °C. In ethylene glycol the complex was soluble from room temperature, solubility increasing with increasing temperature up to 150 °C; however, no evidence of lyotropic mesophase formation was found.

The bis(terpyridine)ruthenium complex with the longer alkyl chain, [Ru(terpy)(4′R-terpy)]Cl_2(R = $C_{31}H_{63}$), failed to show any mesophase formation in the penetration experiment with water. This complex was insoluble in water until the temperature was raised to *ca.* 70 °C and showed only limited solubility between 70 and 100 °C. The reduced solubility of this complex compared to both the shorter-chain analogue and the corresponding bipyridine complex was responsible for the lack of mesophase formation in water. The penetration experiment in ethylene glycol did show a viscous, isotropic lyotropic mesophase (assigned as I_1 cubic) at high temperatures. The material was insoluble in ethylene glycol until 82 °C at which point it started to dissolve. The solubility increased with increasing temperature and a viscous, isotropic mesophase formed at the solution–solid interface from 96 °C. This phase grew into the solid on increasing temperature and was stable to > 150 °C. From 136 °C the mesophase began to clear to an isotropic solution from the solution–mesophase boundary.

The rhodium complex, [Rh(terpy)(4′R-terpy)]Cl_3 (R = $C_{19}H_{39}$), proved to be very hygroscopic, absorbing moisture from the air at room temperature to yield a viscous, optically isotropic material from room temperature. In the penetration experiment this material was heated to 110 °C to remove water, then cooled to room temperature; the crystalline solid so formed was contacted with water and observed to form a viscous, isotropic mesophase from room temperature which persisted on heating to 100 °C. Small air-bubbles trapped within this phase became very angular and formed perfect hexagonal shapes. These were reminiscent of the profile along the long diagonal axis of a cube. The shapes of the bubbles formed in cubic mesophases have been analysed[21] and used as a method of characterising the phase type.

Conclusion

Using terpyridine derivatives, we have prepared amphiphilic ruthenium and rhodium complexes that are comparable with existing surfactant tris(bipyridine) complexes. However, the solubility of the bis(terpyridine)ruthenium complexes with chloride counter ions is much lower than that of the related tris(bipyridine) complexes, so that in order to obtain a sufficiently high surfactant concentration in water for micelle formation the ruthenium complex **2** must be heated to above 70 °C. A cubic phase forms from 73 °C. The ruthenium complex **3**, which had proportionately a much higher hydrophobic content, showed comparably lower solubility and did not show any mesophase formation up to 100 °C, but did show a cubic phase in ethylene glycol. The much more soluble bis(terpyridine)rhodium complex **1** showed a cubic phase, assigned I_1, from room temperature.



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The reduced solubility limits the range of temperature over which lyotropic mesophase formation is observed, but these complexes do act as surfactant systems, forming the expected cubic mesophase. The reduced solubility helps in our qualitative understanding of the requirements for formation of transition metal-containing lyotropic liquid crystals. We have found that the Krafft point (minimum temperature at which micelles can form) is high (> 70 °C) for these terpyridine complexes whereas for the structurally very similar ruthenium tris(bipyridine) surfactants it is much lower being typically around ambient temperature.

We have also synthesised the related terpyridine complex with two *trans* alkyl chains, $[Ru(4'R\text{-terpy})_2]^{2+}$ **4** (R = $C_{19}H_{39}$), prepared from $RuCl_3$ and 2 equivalents of the alkyl-substituted terpy. This complex, as the chloride salt, failed to show any mesophase formation, being insoluble in water and was only sparingly soluble in glycol even at elevated temperatures. However it is interesting to speculate on the structure of a possible mesophase formed from an amphiphile with two tails and the head group placed symmetrically in the centre of the molecule.

Experimental

Microanalyses were performed at the University of Sheffield. All chemicals were used as received unless otherwise specified. Infrared spectra were recorded on a Perkin-Elmer 684 infrared spectrometer as KBr discs, ^1H NMR spectra on a Bruker WM250 spectrometer; proton chemical shifts are quoted relative to an internal deuterium lock. Mesomorphism was studied by heated-stage polarising microscopy using a Zeiss Labpol microscope equipped with a Linkam TH600 hot stage and PR600 temperature controller.

Synthesis of 4″-Alkyl-2,2′:6′,2″-terpyridines.—*1,5-Di-2-pyridylpentane-1,3,5-trione.* To NaH (2.25 g, 80% dispersion in oil, 75 mmol) in thf (50 cm^3) heated to reflux under N_2 was added a solution of ethylpyridine-2-carboxylate (10.1 cm^3, 75 mmol) and acetone (1.8 cm^3, 25 mmol) in dry thf (30 cm^3), dropwise over *ca.* 4 h, and the reaction mixture heated for 2 h giving an orange solution. The reaction mixture was then cooled, the solvent removed under reduced pressure and the residue dissolved in water (200 cm^3). After filtration through Celite, the solution was neutralised by the addition of acetic acid, precipitating a fine, intense yellow powder. This was filtered off and crystallised from diethyl ether (yield 4.5 g, 71%). M.p. 103 °C (lit.,[15] 103–105 °C).

2,6-Di-2-pyridyl-4(1H)-pyridone. Ammonium acetate (4.0 g) and 2,5-di-2-pyridylpentane-1,3,5-trione (2.0 g, 7.46 mmol) were dissolved in absolute EtOH (50 cm^3) and heated to reflux. After 6 h the resultant brown solution was concentrated to *ca.* 8 cm^3 and cooled to 0 °C, precipitating the product as colourless crystals which were crystallised from ethanol (1.76 g, 94%). M.p. 165–166 °C (lit., 165,[15] 166–168 °C[16]) IR (KBr): ν_{NH} 3300,

ν_{CO} 1630 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 9.9 (1 H, br, NH), 8.73 [2 H , d, $^3J(H^{6,5}H^{6'',5''})$ = 6, $H^{6,6''}$], 7.87 [2 H, d, $^3J(H^{3,4}H^{3'',4''}$ = 7.5, $H^{3,3''}$] 7.77 [2 H, dd, $^3J(H^{4,5}H^{4'',5''})$ = 6, $^3J(H^{3,4}H^{3'',4''})$ = 7.5, $H^{4,4''}$], 7.42 [2 H, dd, ^3J-$(H^{5,4}H^{5'',4''})$ = 6, $^3J(H^{5,6}H^{5'',6''})$ = 6Hz, $H^{5,5''}$] and 7.29 (2 H, s, $H^{3',5'}$).

4'-(Trifluoromethylsulfonyl)-2,2':6',2''-terpyridine. Trifluoromethanesulfonic anhydride (600 mg, 2 mmol) was added over 30 min to a stirred solution of 2,6-di-2-pyridyl-4(1*H*)-pyridone (500 mg, 2 mmol) in anhydrous pyridine (5 cm^3) cooled to 0 °C under N_2. The solution was allowed to warm to room temperature, stored for 48 h, then poured onto ice–water (50 cm^3) and stirred for 30 min. The pale brown precipitate was filtered off, washed with cold water (50 cm^3) and air dried. The solid was dissolved in hexane (10 cm^3) with warming, the insoluble portion was filtered off and the filtrate concentrated yielding colourless crystals on cooling (0.43 g, 57%). M.p. 108 °C (lit.,[15] 108 °C). ^1H NMR (250 MHz, $CDCl_3$): δ 8.75 [2 H, d, $^3J(H^{6,5}H^{6'',5''})$ = 4, $H^{6,6''}$], 8.60 [2 H, d, $^3J(H^{3,4}$-$H^{3'',4''})$ = 7, $H^{3,3''}$], 8.41 (2 H, s, $H^{3',5'}$), 7.87 [2 H, dd, $^3J(H^{4,5}H^{4'',5''})$ = 7, $^3J(H^{3,4}H^{3'',4''})$ = 7, $H^{4,4''}$] and 7.40 [2 H, dd, $^3J(H^{5,4}H^{5'',4''})$ = 7, $^3J(H^{5,6}H^{5'',6''})$ = 4 Hz, $H^{5,5''}$].

4'-Methyl-2,2':6',2''-terpyridine. Tetramethyltin (1 cm^3, 7 mmol), 4'-(trifluoromethylsulfonyl)-2,2':2'',6'-terpyridine (1.9 g, 5 mmol), $[PdCl_2(PPh_3)_2]$ (100 mg) and LiCl (1 g, excess) were dissolved in dimethylformamide (100 cm^3) and heated at reflux under N_2 for 4 h, forming a palladium mirror. The dark reaction mixture was concentrated *in vacuo* to a dark oil which was taken up in water (100 cm^3) and extracted into CH_2Cl_2 (3 × 100 cm^3). The organic extracts were combined and the solvent removed under reduced pressure to give a brown gum. Purification by column chromatography (neutral alumina, pentane–ethyl acetate 9:1) yielded a white crystalline solid (0.67 g). M.p. 101 °C (lit.,[22] 97–100 °C) (Found: C, 77.3; H, 5.45; N, 16.8. $C_{16}H_{13}N_3$ requires C, 77.7; H, 5.3; N, 17.0%). ^1H NMR (250 MHz, $CDCl_3$): δ 8.67 [2 H, d, $^3J(H^{6,5}H^{6'',5''})$ = 4, $H^{6,6''}$], 8.60 [2 H, d, $^3J(H^{3,4}H^{3'',4''})$ = 7.5, $H^{3,3''}$], 8.28 (2 H, s, $H^{3',5'}$), 7.84 [2 H, dd, $^3J(H^{4,5}H^{4'',5''})$ = 7, $^3J(H^{3,4}$-$H^{3'',4''})$ = 7.5, $H^{4,4''}$], 7.30 [2 H, dd, $^3J(H^{5,4}H^{5'',4''})$ = 7, $^3J(H^{5,6}H^{5'',6''})$ = 4 Hz, $H^{5,5''}$] and 2.55 (3 H, s, CH_3).

4'-Nonadecyl-2,2':6',2''-terpyridine, **I**. To a stirred solution of diisopropylamine (0.36 cm^3) in thf (2.5 cm^3) cooled to 0 °C under N_2 was added dropwise LiBu (1.56 cm^3, 1.6 mol dm^{-3} solution in hexane) and stirred for 1 h. A solution of 4'-methyl-2,2':2'',6'-terpyridine (0.6 g, 2.43 mmol) in thf (5 cm^3) was added and stirred for 1 h followed by addition of a solution of 1-bromooctadecane (0.81 g, 2.4 mmol) in thf (20 cm^3). The reaction mixture was stirred at 0 °C for 1 h, allowed to come to room temperature and stirred at room temperature for 12 h. Water (10 cm^3) was added and the thf removed under reduced pressure, water (30 cm^3) was added and the yellow precipitate filtered off, washing with water and Et_2O to give a white powder. Crystallisation from ethanol yielded colourless crystals (0.80 g, 66%). M.p. 78–79.5 °C (Found: C, 81.8; H, 10.1; N, 8.2. $C_{34}H_{49}N_3$ requires C, 81.7; H, 9.9; N, 8.4%). ^1H NMR (250 MHz, $CDCl_3$): δ 8.67 [2 H, d, $^3J(H^{6,5}H^{6'',5''})$ = 4, $H^{6,6''}$], 8.63 [2 H, d, $^3J(H^{3,4}H^{3'',4''})$ = 7.5, $H^{3,3''}$], 8.28 (2 H, s, $H^{3',5'}$), 7.85 [2 H, dd, $^3J(H^{4,5}H^{4'',5''})$ = 7, $^3J(H^{3,4}H^{3'',4''})$ = 7.5, $H^{4,4''}$], 7.32 [2 H, dd, $^3J(H^{5,4}H^{5'',4''})$ = 7, $^3J(H^{5,6}$-$H^{5'',6''})$ = 4, $H^{5,5''}$], 2.77 (2 H, t, ^3J = 7.5, $C_\alpha H_2$), 1.75 (2 H, m, $C_\beta H_2$), 1.27 (32 H, m, alkyl) and 0.86 (3 H, t, ^3J = 7 Hz, CH_3).

4'-Hentriacontyl-2,2':6',2''-terpyridine **II**. This compound was prepared from 4'-methyl-2,2':6',2''-terpyridine (0.60 g, 2.43 mmol) in an analogous manner to that of **I** and crystallised from ethanol as white microcrystals (1.53 g, 94%). M.p. 93.5–95.5 °C (Found: C, 82.7; H, 11.1; N, 5.9. $C_{46}H_{73}N_3$ requires C, 82.7; H, 11.0; N, 6.2%). ^1H NMR (250 MHz, $CDCl_3$): δ 8.67 [2 H, d, $^3J(H^{6,5}H^{6'',5''})$ = 4, $H^{6,6''}$], 8.63 [2 H, d, $^3J(H^{3,4}H^{3'',4''})$ = 7.5, $H^{3,3''}$], 8.28 (2 H, s, $H^{3',5'}$), 7.85 [2 H, dd, $^3J(H^{4,5}$-$H^{4'',5''})$ = 7, $^3J(H^{3,4}H^{3'',4''})$ = 7.5, $H^{4,4''}$], 7.32 [2 H, dd, $^3J(H^{5,4}H^{5'',4''})$ = 7, $^3J(H^{5,6}H^{5'',6''})$ = 4, $H^{5,5''}$], 2.77 (2 H, t, ^3J = 7.5, $C_\alpha H_2$), 1.75 (2 H, m, $C_\beta H_2$), 1.27 (58 H, m, alkyl) and 0.86 (3 H, t, ^3J = 7 Hz, CH_3).

Synthesis of Metal–Terpyridine Complexes.—The starting complexes $[RuCl_3(terpy)]$ and $[RhCl_3(terpy)]$ were prepared from $RuCl_3 \cdot xH_2O$ or $RhCl_3 \cdot xH_2O$ (Johnson Matthey) and 2,2':6',2''-terpyridine (Aldrich) by literature methods.[23]

$[Rh(terpy)(4'R\text{-}terpy)][PF_6]_3$ **1** (R = $C_{19}H_{39}$, X = PF_6). To $[RhCl_3(terpy)]$ (0.25 g, 0.5 mmol) dissolved in acetone–ethanol (250 cm^3, 6:1 ratio) was added $AgNO_3$ (0.22 g, 1.5 mmol, 3 equivalents) and the mixture heated to reflux under N_2. After 3 h the solvent was removed under reduced pressure and the residue dissolved in BuOH (200 cm^3), filtered through Celite and 4'-nonadecyl-2,2':6',2''-terpyridine (0.25 g, 0.5 mmol) was added. The mixture was heated at reflux under N_2 for 12 h, cooled and the solvent removed under reduced pressure. The residue was dissolved in water (*ca.* 200 cm^3), filtered and the hexafluorophosphate salt precipitated upon careful addition of aqueous NH_4PF_6 as a fine grey powder and recrystallised from dry acetone (Found: C, 42.1; H, 5.5; N, 6.4. $C_{44}H_{66}F_{18}N_6O_3$-P_3Rh requires C, 41.8; H, 5.3; N, 6.6%).

$[Rh(terpy)(4'R\text{-}terpy)]Cl_3$ **1** (R = $C_{19}H_{39}$, X = Cl). To a filtered solution of the hexafluorophosphate salt (0.617 g) in acetone (50 cm^3) was added dropwise a saturated solution of LiCl in acetone until precipitation ceased. The chloride salt was obtained as a hygroscopic white powder, filtered off, dried *in vacuo* (0.40 g, 81% yield) and stored over silica gel. It is light and moisture sensitive and was stored in the dark.

$[Ru(terpy)(4'R\text{-}terpy)]Cl_2$ **2** (R = $C_{19}H_{39}$, X = Cl). The complex $[RuCl_3(terpy)]$ (0.25 g, 0.57 mmol) and 4'-nonadecyl-2,2':6',2''-terpyridine (0.25 g, 0.50 mmol) in ethanol (100 cm^3) were heated at reflux under N_2 for 24 h during which time, the mixture changed to a dark red-brown. It was filtered and the filtrate evaporated to dryness under reduced pressure. Chromatography [Sephadex LH-20, ethanol–water (3:1) eluent] yielded the product as the major, deep red band which was dried *in vacuo* to give a red glass (0.35 g, 73%) (Found: C, 58.8; H, 7.0; Cl, 7.2; N, 8.05. Hexahydrate requires C, 58.1; H, 7.2; Cl, 7.0; N, 8.3. Pentahydrate requires C, 59.1; H, 7.1; Cl, 7.1; N, 8.45%). Samples gained weight on standing.

$[Ru(terpy)(4'R\text{-}terpy)][PF_6]_2$ **2** (R = $C_{19}H_{39}$, X = PF_6). The complex $[RuCl_3(terpy)]$ (0.25 g, 0.5 mmol) and $AgBF_4$ (0.32 g, 1.3 mmol) in acetone (100 cm^3) were heated at reflux in air for 2 h to yield a dark purple mixture. The solvent was removed under reduced pressure and the residue dissolved in BuOH (50 cm^3), filtered and 4'-nonadecyl-2,2':6',2''-terpyridine (0.25 g, 0.5 mmol) was added. The reaction mixture was heated at reflux for 3 h to give a deep red solution which was cooled, the solvent removed under reduced pressure and the residue redissolved in acetonitrile, filtered and concentrated to yield the orange-brown tetrafluoroborate salt. The trihydrate of the hexafluorophosphate salt was prepared as an orange-red power (0.47 g, 80%) from the crude tetrafluoroborate in ethanolic solution by precipitation with aqueous NH_4PF_6 (Found: C, 49.7; H, 5.3; N 7.0. Calc.: C, 50.0; H, 5.7; N, 7.1%).

$[Ru(terpy)(4'R\text{-}terpy)]Cl_2$ **3** (R = $C_{31}H_{63}$, X = Cl). The complex $[RuCl_3(terpy)]$ (0.187 g, 0.42 mmol) and 4'-hentriacontyl-2,2':6',2''-terpyridine (0.124 g, 0.19 mmol) in ethanol (95%, 70 cm^3) were heated at reflux under N_2 for 24 h to yield a dark, red-brown mixture This was filtered and the filtrate evaporated to dryness under reduced pressure. Chromatography [Sephadex LH-20, ethanol–water (3:1) eluent] yielded the product as the major, deep red band which was dried *in vacuo* to give a red glass (0.196 g, 87%) (Found: C, 61.4; H, 7.7; N, 6.6. (Hexahydrate requires C, 62.0; H, 8.2; N, 7.1%.)

$[Ru(4'R\text{-}terpy)_2]Cl[NO_3]$ **6** (R = $C_{19}H_{39}$). A mixture of $RuCl_3 \cdot 3H_2O$ (0.014 g, 5.35×10^{-5} mol) and 4'-nonadecyl-2,2':6',2''-terpyridine (0.054 g, 1.1×10^{-4} mol) in 95% ethanol (50 cm^3) was heated at reflux for 1 h, $AgNO_3$ (0.055 g, 6 equivalents) was added and the mixture heated for

12 h until it had changed to a dark red-brown. The mixture was cooled, filtered and the solvent removed under reduced pressure to give a dark gum which was purified by chromatography (Sephadex LH-20, absolute ethanol). The red band was collected, the solvent removed under reduced pressure and dried *in vacuo* to give a red glass (0.064 g, 93%). The product was insoluble in water and elemental analysis for chlorine indicated mixed chloride–nitrate counter ions (Found: Cl, 3.3. Calc.: 3.0%). ^{1}H NMR (250 MHz, $CDCl_3$); δ 0.82 (3 H, CH_3), 1.1–1.6 (alkyl), 1.95 (2 H, $C_\beta H_2$), 3.20 (2 H, $C_\alpha H_2$), 7.2 (4 H), 7.85 (2 H), 8.75 (2 H) and 8.85 (2 H).

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