Functionalisation of bolaamphiphiles with mononuclear bis(2,2′-bipyridyl)ruthenium(II) complexes for application in self assembled monolayers

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Received (in London, UK) 3rd March 2003, Accepted 14th May 2003
First published as an Advance Article on the web 9th June 2003

A novel ruthenium(II) polypyridyl complex connected covalently to a bolaamphiphile, containing amide linkages to provide rigidity *via* hydrogen bonding in the monolayer, has been prepared. The ruthenium(II) complexes of this ligand and of the intermediates in the synthesis were prepared by modification of the coordinated ligands, demonstrating the synthetic versatility and robustness of this family of complexes. All ruthenium complexes were characterised by electrochemical and spectroscopic techniques and were found to have similar properties to the parent complex $[Ru(bipy)_3]^{2+}$, and remain versatile photosensitisers, with well-defined properties, despite extensive substitution of the bipy ligand.

Introduction

Amphiphiles have been of interest in recent years due to their capacity to form a wide range of ordered assemblies in aqueous media, including layers, stacks and vesicles.[1–4] The exact nature of the assembly formed is dependent not only on the lipid but also on the conditions employed. Controlling the length of the chain, the nature of the head groups and the environment in which they are to be studied, allows for the formation of highly organised assemblies.[5–11]

It has been reported recently that, on gold surfaces, robust membranes of well-defined thickness can be formed *via* the self-assembly of bolaamphiphiles containing secondary amide groups.[12] Adsorption of bolas onto surfaces, which were previously rendered inhomogenous due to the presence of suitable steroids or porphyrins, allows for the formation of rigid membranes containing pores of uniform size (1–3 nm).[13] As the thickness of the membrane is well-defined by the amphiphiles, the surface may accurately be described as having a membrane coating with pores of a specific depth. The use of fluorescent porphyrins to create these membrane pores allows for the monitoring, by fluorescence detection, of diffusion of substrates (*e.g.* quenchers) into the pore.[14] Alternatively substrate diffusion into these membrane pores may be monitored by the use of redox active molecules.[15]

The modification of the membrane pores *in situ* may be achieved by utilising lipids containing functional groups other than those required for self-assembly. By judicious choice of functional group and conditions only the molecules which form the "picket fence"[16] around the porphyrin or steroid pore will be available to react, thus allowing modification of the pores without disturbance of the bulk structure of the membrane.[17]

In an effort to expand on the possible approaches to the closure of these membrane pores, the synthesis of a novel lipid, which should be capable of capping a pore *via* complexation with a suitable metal ion is reported (Fig. 1). 2,2′-Bipyridine (bipy) is the ligand of choice as it forms stable complexes with a wide range of metals and is relatively easily functionalised. In this contribution, the synthesis of a novel amphiphile containing amide linkages and a terminal 5-substituted bipy group are reported. The synthesis of a series of ruthenium complexes based on this ligand and some of its precursors is reported together with their electrochemical and spectroscopic properties. The surface chemistry of the system shall be reported in a future publication.

Results and discussion

Synthetic procedures

To date, a large number of bipy derivatives and their $[Ru(bipy)_2]$-complexes have been reported.[18,19] Most of these derivatives are substituted in the 4-position and are frequently 4,4′-disubstituted. 5-substituted 2,2′-bipyridyl compounds have attracted less attention than their 4- and 4,4′- substituted analogues. For the most part this lack of interest is due to the relative ease of the synthesis of 4,4′ derivatives in comparison with 5- and 5,5′- derivatives. While it may be possible to introduce substituents into the 4-position of a bipy *via* the N-oxide,[20] bipy's substituted in the highly deactivated 5-position are generally prepared either *via* aryl coupling reactions[21] or direct synthesis of substituted pyridines.[22] In the present study, substitution of bipy in the 5-position is preferred in order to facilitate correct positioning for the efficient closure of the membrane pore by *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ (see Fig. 1). The method chosen to prepare 5-methyl-2,2′-bipyridyl is the widely used route to a large range of pyridine derivatives devised by Kröhnke and coworkers.[23–25] Oxidation of the terminal methyl group to the acid (**i**) was accomplished with potassium permanganate in aqueous solution. This straightforward procedure has been shown previously as a general procedure for the oxidation of methylpyridines.[26]

 DOI: 10.1039/b302405a

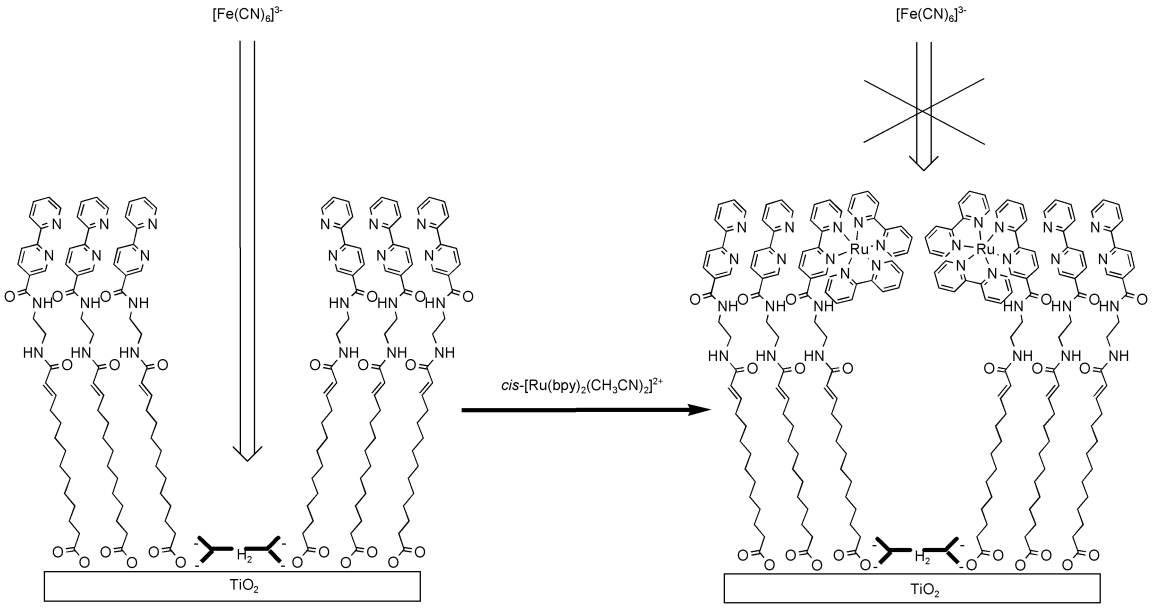
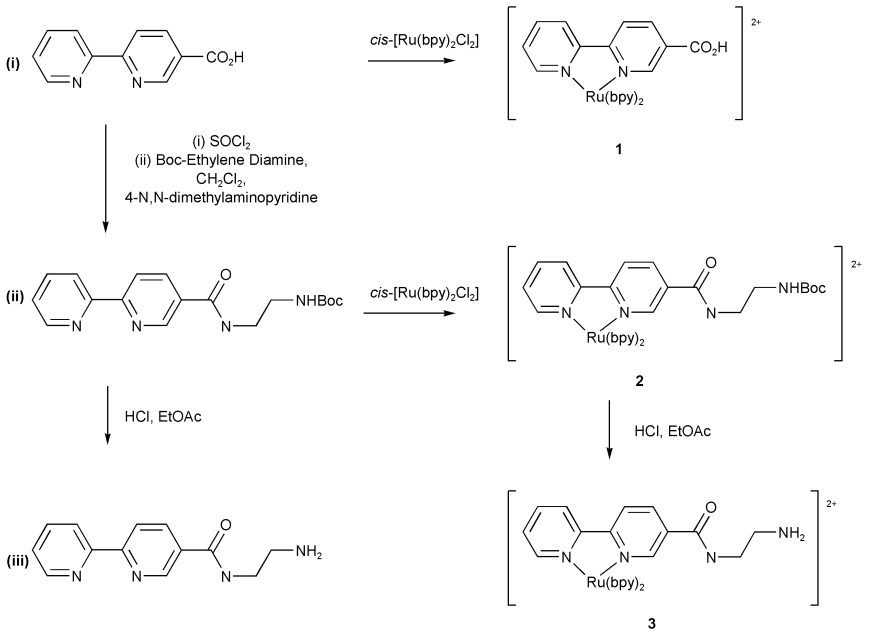


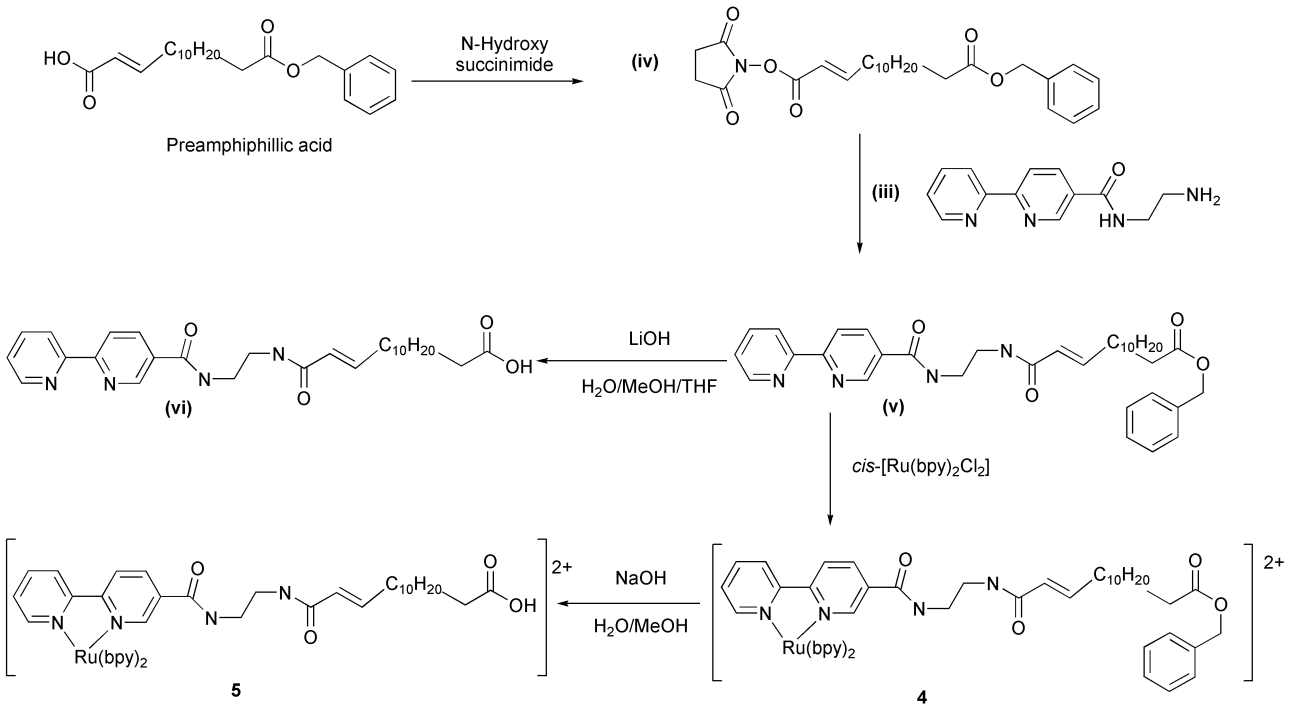
Fig. 1 Capping of pore by complexation.

Efforts to couple the acid (**i**) with the Boc-protected diamino ethane using DCC, BBC[27] and ethyl chloroformate were all found to be ineffective and more severe coupling conditions were required with the acid chloride procedure being adopted (Scheme 1).[28–30] Conversion to the acid chloride under reflux in thionyl chloride followed by treatment with Boc-protected ethylene diamine in dry dichloromethane, in the presence of 4-N,N-dimethylaminopyridine,[31] produced the amide (**ii**). The Boc protecting group was subsequently removed from (**ii**) at room temperature with hydrochloric acid in ethyl acetate to give the HCl salt of the free amine (**iii**). Although, this method of Boc cleavage has been shown to be effective in both methanol and dioxane, reaction in ethyl acetate gives improved yields for this system.[32]

Subsequent coupling of this new amine (**iii**) with the monobenzyl protected lipid (Scheme 2) was found to be problematic. The standard and generally successful method for the introduction of a new head group onto the amphiphile is *via* the mixed anhydride using ethyl chloroformate.[33] Although a highly versatile method, it proved unsuitable in the preparation of bipy-lipid compound resulting in only a very low yield ($< 5\%$). Direct reaction of (**iii**) with the protected preamphiphilic acid in the presence of DCC was also unsuccessful. In order to overcome this problem the preamphiphilic acid is activated by conversion to the N-hydroxy succinimide ester (Scheme 2). These esters are extremely useful as they can be made from the acid in very high yield, and are robust, being air-, moisture- and light-stable at room temperature.[34,35] The active ester (**iv**) reacted readily with the amine (**iii**) to give the amide (**v**) in a good yield. Purification of the amide is facilitated by the solubility of the by-product in water. Cleavage of the benzyl ester with lithium hydroxide was carried out without rupture of the peptide bonds in a heterogeneous reaction,[36] to yield the acid (**vi**).

The method normally used for the synthesis of complexes of the type $[Ru(bipy)_2(LL')]^{2+}$ is the reaction of *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ with the ligand. The target complex can indeed be prepared in this manner. However in this contribution we





Scheme 2

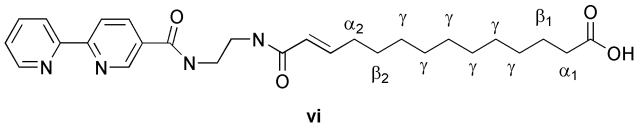
wish to illustrate the synthetic flexibility in ruthenium polypyridyl complexes.

The approach used takes advantage of the known chemical robustness of Ru(II) polpyridyl complexes.[37,38] By treating the complexes as organic molecules, it was possible to carry out standard reactions, in this case deprotection reactions, directly on the complexes (Scheme 1 and 2). The amine complex **3** ([Ru(bipy)$_2$(**iii**)]$^{2+}$) and the acid complex **5** ([Ru(bipy)$_2$(**vi**)]$^{2+}$) were prepared from **2** ([Ru(bipy)$_2$(**ii**)]$^{2+}$) and **4** ([Ru(bipy)$_2$(**v**)]$^{2+}$) respectively (Scheme 1 and 2). **3** was prepared by deprotection of **2** using the same method as used for the free ligand (**ii**), however, a longer reaction time was required. In the case of **5**, a slightly harsher method than that used for the ligand was necessary to deprotect the complex. Complete hydrolysis of the benzyl ester, without disturbance of the peptide bonds, was achieved by heating **4** at reflux in an alkaline mixture of H_2O–MeOH. Little purification of the subsequent complexes was required and high yields for the reactions were obtained, thus illustrating the usefulness of this approach in the preparation of metal complexes.

^{1}H NMR spectroscopy

The amphiphilic protons of **vi**, α- to the terminal functionalities are clearly visible at 2.19 and 2.28 ppm and show coupling with the adjacent protons (Fig. 2). The protons β- to the terminal functionalities were less well defined, being positioned close, at 1.41 and 1.60 ppm, to the signal due to the remaining 12 protons of the hydrocarbon chain at 1.27 ppm. The signals at 5.94 and 6.81 ppm are typical for vinylic protons.

For the functionalised bipyridine ligands, the inherent asymmetry arising from the introduction of a substituent onto one pyridyl ring removes the equivalency of the two rings. The chemical shifts of the 3 protons on the 5-substituted ring were found to change with the nature of the substituent. This change is clearest in the position of the signal from the H6 proton. Therefore, the H6 signal is useful in characterisation of the reaction products since it is a singlet and is separated from the remaining proton signals. For example, for methyl bipy it appears at 8.59 ppm, while the H6 signal in the corresponding amide compound (**iii**) is shifted downfield to 9.11 ppm. Full ^{1}H NMR spectral data are presented in the experimental section.



vi

Fig. 2 Structure of (**vi**).

Electrochemical properties

All complexes show a single reversible metal oxidation wave at potentials similar to that of the model complex [Ru(bipy)$_3$]$^{2+}$. In agreement with their luminescence properties (*vide infra*), the electron withdrawing nature of the carbonyl groups in the 5′ position results in an increase in the oxidation potential of the metal centres by as much as 80 mV. All ligand reductions, except the third reduction of **1** ($\Delta E_{p\frac{1}{2}}$ 150 mV), were found to be fully reversible. In contrast to complexes **1**, **3** and **4**, the first reduction of **2** and **5** are 200 mV lower than that of [Ru(bipy)$_3$]$^{2+}$. For **2**, in the presence of oxygen, the reduction peak at −1.16 V decays, forming a new redox wave at −1.36 V. This suggests that the first reduction may be of a functional group rather than of a bipyridyl group and may be related to electrochemical deprotection, with the formation of a new redox wave at a potential similar to that of **3**.

Electronic properties

The electronic spectra of complexes **1** to **5** show the expected strong ligand-based π–π* absorption bands at ~280 nm and overlapping d–π* MLCT bands at ~450 nm in agreement that reported for the unsubstituted [Ru(bipy)$_3$]$^{2+}$ (Table 1). The λ_{max} for each of the compounds varies only slightly from that of the parent complex [Ru(bipy)$_3$]$^{2+}$ in agreement with data obtained for complexes containing similar substituted 2,2′-bipyridines.[20]

The emission spectra are typical of charge transfer emitters, and are similar in shape both at 298 and 77 K to that of [Ru(bipy)$_3$]$^{2+}$, however the emission energies are red-shifted by between 40 and 60 nm, and show a marked decrease in emission lifetime.[39,40] This behaviour is in agreement with

Table 1 Electronic and redox properties of **1** to **5** and $[Ru(bipy)_3]^{2+}$

Compound	Abs. λ_{max}/nm (log ε)	[a] Em. λ_{max}/nm (τ/ns, 298 K)	[b] Ru_{II}/Ru^{III}Oxid./V	Ligand Red./V
1 $[Ru(bipy)_2$**(i)**$](PF_6)_2$	445 (0.88)	673 (170)	1.33	−1.40, −1.59, −1.85 (irr.)
2 $[Ru(bipy)_2$**(ii)**$](PF_6)_2$	452 (1.37)	652 (460)	1.30	−1.16, −1.51, −1.74
3 $[Ru(bipy)_2$**(iii)**$](PF_6)_2$	450 (0.82)	662 (490)	1.28	−1.38, −1.53, −1.73
4 $[Ru(bipy)_2$**(v)**$](PF_6)_2$	452 (1.15)	651 (480)	1.34	−1.29, −1.44, −1.73
5 $[Ru(bipy)_2$**(vi)**$](PF_6)_2$	450 (1.12)	655 (480)	1.33	−1.18, −1.50, −1.73
[c] $[Ru(bipy)_3](PF_6)_2$	452 (1.29)	612 (1000)	1.26	−1.35, −1.55, −1.80

All measurements in acetonitrile.[a] Samples in deaerated CH_3CN. [b] *vs.* SCE, measured in 0.1 M TEAP–CH_3CN. [c] From ref. 18

related substituted complexes[20] and is due to the introduction of electron withdrawing groups which reduce the σ-donor strength of the bipy ligand, destabilising the metal based dπ-orbitals and hence the energy gap between the emitting ^{3}MLCT state and the ground state is reduced.[41] In addition, the energy of the ^{3}MC state is reduced, and non-radiative deactivation *via* this state is increased.

In aerated acetonitrile, the emission lifetime of all complexes (except **1**) is approximately 170 ns with a marked increase in emission lifetime with deaeration as expected. For **1**, however, a pH dependence is observed with the deaerated lifetime of the protonated complex (170 ns) much shorter than for the deprotonated complex (840 ns). This is not unexpected given that the λ_{max} of the emission of the deprotonated complex (620 nm) is blue-shifted by 50 nm with respect to the protonated complex and hence the increase in lifetime may be attributed to the energy gap law.[39] For **2**–**5** the lifetimes measured are in range of 400 to 500 ns, which is comparable with $[Ru(bipy)_3]^{2+}$ (1 μs) and suggests that these derivatised complexes are well suited as photosensitisers. Substitution of bipy in $[Ru(bipy)_3]^{2+}$ for ligands which are stronger π-acceptors results in a higher metal oxidation potential. In addition, the first reduction potential is less negative in almost every case. Given the correlation between redox properties and electronic structure, observed for derivatised $[Ru(bipy)_3]^{2+}$ complexes and the lowering of emission energy in every case then it is likely that the lowest excited state (LUMO) is located upon the derivatised bipy ligand.

Conclusion

The synthesis of a novel lipid (**vi**) capable of immobilisation on a surface (such as TiO_2) with a terminal bipy group has been achieved. In every case recovered yields are satisfactory and purification is quite straightforward. The synthesis of the target ruthenium complex **5** can be achieved *via* modification of precursor complexes. Characterisation of these complexes by spectroscopic and electrochemical methods has shown the minimal differences which the introduction of these substituents produce in the properties compared with $[Ru(bipy)_3]^{2+}$.

The effect of immobilisation on the spectroscopic and electrochemical properties of the lipid derivatised Ru(II) polypyridyl complex (**5**) shall be presented in a later publication. Assemblies with metals other than Ru(II) will also be investigated.

Experimental

Materials

All solvents employed were of HPLC grade and used as received unless otherwise stated. All reagents employed in synthetic procedures were of reagent grade or better. *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$,[41] tetraethylammonium perchlorate (TEAP),[42] tetradec-2-enedioic acid 14-benzyl ester,[8] 5-methyl-2,2′-bipyridine[23–25] and (2-amino-ethyl)-carbamic acid tert-butyl ester[17] were prepared by literature methods.

Synthesis of ligands

2,2′-bipyridyl-5-carboxylic acid[26](i). 21.8 g (128 mmol) of 5-methyl-2,2′-bipyridine was suspended in 200 cm^3 of water at 70 °C. To this was added 41 g (250 mmol) of solid $KMnO_4$ over 3 h. A second portion of 41 g (total 500 mmol) was added over a further 3 h at 90 °C. After all of the $KMnO_4$ had been consumed, the dark brown mixture was filtered while hot and the precipitate washed with two 50 cm^3 portions of hot water. The combined filtrate and washings were concentrated *in vacuo* to approximately 40 cm^3. Slow addition, with external cooling, of 25% aq. HCl brought about the precipitation of the acid in a yield of 76%. mp 195 °C Lit 196–198 °C (decomp.)[43] ^{1}H NMR (250 MHz, $(CD_3)_2SO_2$) δ in ppm 7.82 (m, 1H, pyH5′), 8.37 (m, 3H, pyH4′, pyH3, pyH4), 8.55 (d, 2H, pyH3), 8.76 (d, 1H, pyH6′), 9.12 (s, 1H, pyH6). ^{13}C NMR (63 MHz, $(CD_3)_2SO_2$) δ in ppm 122.12, 123.81, 139.61, 143.30, 146.10, 149.93, 150.29, 153.46, 166.15.

2,2′-bipyridyl-5-carboxylic acid (2-amino-ethyl)-carbamic acid tert-butyl ester (ii). 5 g (25 mmol) of the bipyridine acid (**i**) were heated at reflux in 100 cm^3 of freshly distilled thionyl chloride for 3 h. This was then evaporated to complete dryness *in vacuo*. The formation of the acid chloride was assumed to be complete and was used immediately. 4 g (25 mmol) of mono Boc-protected ethylene diamine and a catalytic amount of 4-(N,N-dimethylamino)pyridine were dissolved in 50 cm^3 of dry dichloromethane and this solution added slowly to a stirred suspension of the acid chloride in 250 cm^3 of dry dichloromethane. This was then left to stir at room temperature overnight. The now dark solution was washed with aq. NaOH and then with water, before being dried to an orange oil *in vacuo*. Trituration of the oil with diethyl ether brought about the precipitation of a white solid which was filtered off and dried *in vacuo* to afford 4.3 g (50%) of (**ii**). mp 187–189 °C ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.41 (s, 9H, $(CH_3)_3$), 3.46 (m, 2H, CH_2NHBoc), 3.57 (m, 2H, CH_2), 5.09 (t, 1H, NHBoc), 7.42 (t, 1H, pyH5′), 7.65 (br, 1H, NH), 7.83 (t, 1H, pyH4′), 8.25 (d, 1H, pyH3′), 8.48 (m, 2H, pyH4, pyH6′), 8.69 (d, 1H, pyH3), 9.11 (s, 1H, pyH6) ^{13}C NMR (63 MHz, $CDCl_3$) δ 28.32, 39.94, 42.31, 80.10, 120.51, 121.68, 124.20, 129.36, 135.64, 136.98, 148.15, 149.22, 155.20, 157.76, 158.24, 165.89 MS EI (80 eV) m/z 342 $(M)^{\bullet+}$

2,2′-bipyridyl-5-carboxylic acid (2-amino-ethyl)-amide (iii). 3.3 g of the protected bipyridyl amine (**ii**) were dissolved in 18 cm^3 of 3 M HCl–ethyl acetate solution and stirred at room temperature for 1 h. After evaporating the mixture to dryness on the rotary evaporator and washing with diethyl ether, the resulting solid was redissolved in aqueous sodium hydroxide and extracted three times with chloroform. The chloroform fractions were combined, dried over magnesium sulfate and evaporated *in vacuo* to give 2.2 g (86%) of (**iii**) as a yellow waxy solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.87 (t, 2H, CH_2NH_2), 3.48 (m, 2H, CH_2NH), 7.32 (t, 1H, pyH5′), 7.76 (t, 1H, pyH4′), 8.28 (m, 3H, pyH4, pyH3′, pyH6′), 8.60 (d, 1H, pyH3), 9.05 (s, 1H, pyH6) ^{13}C NMR (63 MHz, $CDCl_3$) δ 40.91, 42.17, 120.28,

121.39, 124.02, 129.45, 135.64, 136.77, 147.87, 148.97, 154.75, 157.81, 165.93 MS (FAB, pos., Xe) m/z 243 $(M+H)^+$, 226 $(M-NH_2)^+$, 183 $(M–NHC_2H_4NH_2)^+$

Tetradec-13-en-dioic acid 1-benzyl ester 14-(2, 5-dioxo-pyrrolidin-1-yl) ester (iv). 1 g (2.9 mmol) of tetradec-2-enedioic acid 14-benzyl ester, 0.58 g (1 equiv.) of DCC and 0.33 g (1 equiv.) of N-hydroxy succinimide were dissolved in 10 cm^3 of dioxane and left to stand at 4 °C overnight. After filtration of the insoluble by-products and removal of the solvent *in vacuo*, a pale oil was obtained. This was recrystallised from chloroform–hexane (1 : 1 v/v) to give (**iv**) in a yield of 0.94 g (73%) as a white powder. mp 83–85 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.27 (s, 12H, $6\times CH_2$), 1.41 (m, 2H, CH_2), 1.55 (m, 2H CH_2), 3.37 (m, 4H, $2\times CH_2$), 2.84 (s, 4H, $OC(CH_2)_2CO$), 5.11 (s, 2H, CH_2Ph), 5.91 (d, 1H, vinyl α-H), 7.29 (m, 1H, vinyl β-H), 7.43 (s, 5H, Ph) ^{13}C NMR (63 MHz, $CDCl_3$) δ 24.92, 25.60, 27.55, 29.08, 29.16, 29.25, 39.33, 32.83, 34.30, 66.01, 103.86, 115.31, 126.29, 128.12, 128.51, 156.17, 169.26 MS EI (80 eV) m/z 443 $(M)^{\bullet+}$, 336 $(M–OCH_2Ph)^+$

13-{2-[([2,2′] bipyridinyl-5-carbonyl)-amino]-ethylcarbamoyl}-tridec-12-enoic acid benzyl ester (v). 0.9 g (2 mmol) of the lipid ester (**iv**) and 0.49 g (1 equiv.) of the bipyridyl amine (**iii**) were dissolved in 20 cm^3 of choroform–methanol (1 : 1) and stirred at room temperature overnight. After removal of the solvent under reduced pressure, the remainder was partitioned between aqueous HCl and chloroform. After 3 extractions, the combined organic phases were dried with magnesium sulfate and subsequently *in vacuo*. 1 g (86%) of (**v**) was obtained as a white powder. mp 147–150 °C. ^{1}H NMR (250 MHz, $CDCl_3$–CD_3OD 3 : 1) 1.09 (s, 12H, $6\times CH_2$), 1.25 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 2.10 (m, 2H, CH_2-vinyl), 2.33 (t, 2H, CH_2COO), 3.31 (m, 2H, CH_2NHCO-vinyl), 3.48 (m, 2H, CH_2NHCOBipy), 5.02 (s, 2H, CH_2Ph), 5.77 (d, 1H, vinyl α-H), 6.82 (m, 1H, vinyl β-H), 7.32 (s, 5H, Ph), 7.45 (m, 1H, pyH5′), 7.89 (t, 1H, pyH4′), 8.38 (m, 3H, pyH4, pyH3′, pyH6′), 8.69 (d, 1H, pyH3), 9.04 (s, 1H, pyH6). ^{13}C NMR (63 MHz, $CDCl_3$–CD_3OD 3 : 1) 24.61, 27.93, 28.73, 28.85, 29.04, 31.76, 34.02, 38.79, 40.11, 65.88, 120.74, 121.93, 122.84, 124.49, 127.78, 127.87, 128.21, 129.54, 136.16, 137.85, 145.21, 147.96, 148.50, 154.10, 154.39, 156.99, 166.24, 167.90. MS (EI, 80 eV) m/z 570 $(M)^{\bullet+}$, 479 $(M–C_7H_7)^+$

13-{2-[([2,2′]bipyridinyl-5-carbonyl)-amino]-ethylcarbamoyl}-tridec-12-enoic acid (vi). 0.09 g (2.2 mmol) of lithium hydroxide monohydrate was suspended in 25 cm^3 of water–methanol–THF (1 : 1 : 3) and added to a solution of 0.6 g (1.1 mmol) of the benzyl ester (**v**) in 25 cm^3 of the same solvent system. The resulting mixture was then stirred overnight at room temperature. After removal of the solvent under reduced pressure, the residue was taken up in acidic water and extracted three times with chloroform. The organic phases were dried and evaporated to give (**vi**) in a yield of 0.4 g (79%). mp 149–151 °C. ^{1}H NMR (400 MHz, CD_3OD–$CDCl_3$ 4 : 1) δ 1.27 (s, 12H, $6\times CH_2$), 1.41 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 2.19 (m, 2H, CH_2), 2.28 (t, 2H, CH_2), 3.54 (m, 2H, CH_2NHCO-vinyl), 3.60 (m, 2H, CH_2NHCOBipy), 5.94 (d, 1H, vinyl α-H), 6.81 (m, 1H, vinyl β-H), 8.05 (t, 1H, pyH5′), 8.53 (m, 2H, pyH4, pyH3′), 8.63 (t, 1H, pyH4′), 8.76 (d, 1H, pyH6′), 8.89 (d, 1H, pyH3), 9.28 (s, 1H, pyH6). ^{13}C NMR (100 MHz, CD_3OD–$CDCl_3$ 4 : 1) δ 26.56, 29.92, 30.72, 30.88, 31.02, 31.07, 33.67, 35.53, 35.64, 40.37, 118.54, 123.99, 124.91, 125.86, 129.01, 134.29, 139.74, 146.94, 150.34, 170.05, 178.43, 212.07. MS (EI, 80 eV) m/z 480 $(M^{+\bullet})$

Synthesis of complexes

$[Ru(bipy)_2(i)](PF_6)_2$ 1. 90 mg (0.35 mmol) of 2,2′-bipyridine-5-carboxylic acid (**i**) and 125 mg (0.24 mmol) of *cis*-$[Ru(bipy)_2Cl_2].2H_2O$ were heated at reflux for 4 h in 10 cm^3 of a 1 : 1 (v/v) mixture of ethanol and water. The reaction mixture was concentrated to approximately 5 cm^3 under reduced pressure. The PF_6^- salt of the complex was precipitated by adding a few drops of a saturated ammonium hexafluorophosphate solution, filtered and washed well with diethyl ether before drying *in vacuo*. The complex was purified by column chromatography on silica, with MeCN–H_2O–sat. aq. KNO_3 (80 : 20 : 1) as the eluent, to yield 125 mg (54%) of 1. ^{1}H NMR (400 MHz, CD_3CN) δ 7.45 (m, 5H, $5\times$H5), 7.83 (m, 5H, $5\times$H6), 8.12 (m, 6H, $6\times$H4), 8.56 (m, 7H, $6\times$H3, H6 (**i**)). Elemental Analysis Found: C 41.53, H 2.89, N 9.50; $C_{31}H_{24}N_6F_{12}O_2P_2Ru$ requires: C 41.23, H 2.68, N 9.31%

$[Ru(bipy)_2(ii)](PF_6)_2\cdot 2H_2O$ 2. 50 mg (0.14 mmol) of 2,2′-bipyridyl-5-carboxylic acid (2-amino-ethyl)-carbamic acid *tert*-butyl ester (**ii**) and 70 mg (0.13 mmol) of *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ were heated at reflux for 4 h in 10 cm^3 of a 1 : 1 (v : v) mixture of ethanol and water. After removal of most of the solvent, a few drops of a saturated ammonium hexafluorophosphate solution were added to crash out the complex as the PF_6^- salt. This was filtered, washed well with diethyl ether and dried *in vacuo*. 115 mg (84%) of the complex were obtained. The product obtained was pure by ^{1}H NMR spectroscopy and no further purification was necessary. ^{1}H NMR (400 MHz, CD_3CN) δ 1.35 (s, 9H, $3\times CH_3$), 3.17 (m, 2H, CH_2NHBoc), 3.33 (m, 2H, CH_2), 5.44 (m, 1H, NHBoc), 7.42 (m, 6H, $5\times$H5, NH), 7.76 (m, 5H, $5\times$H6), 8.08 (m, 6H, $5\times$H4, H6 (**ii**)), 8.28 (m, 1H, H4 (**ii**)), 8.55 (m, 6H, $6\times$H3). Elemental Analysis Found: C 42.51, H 3.55, N 10.17; $C_{38}H_{41}N_8F_{12}O_5P_2Ru$ requires: C 42.19, H 3.91, N 10.35%

$[Ru(bipy)_2(iii)](PF_6)_2\cdot 2NaCl\cdot 2H_2O$ 3. 50 mg (0.048 mmol) of **2** were dissolved in 5 cm^3 of a 3 M solution of HCl in ethyl acetate. After stirring overnight at room temperature, the solvent was removed *in vacuo*. The residue was taken up in dil. aq. NaOH and extracted three times with dichloromethane, which was dried with magnesium sulfate and evaporated to dryness to yield 35 mg (75%) of **3** as a red solid, which was recrystallised from acetone–water (2 : 1). ^{1}H NMR (400 MHz, CD_3CN) δ 2.52 (m, 2H, NH_2), 3.75 (m, 2H, J = 5 Hz, CH_2NHCO), 3.98 (t, 2H, J = 5 Hz, CH_2NH_2), 7.60 (m, 5H, $5\times$H5), 8.09 (m, 5H, $5\times$H6), 8.23 (m, 5H, $5\times$H4), 8.34 (s, 1H, H6 (**iii**)), 8.51 (d, 1H, H4(**iii**)), 8.85 (m, 6H, $6\times$H3). Elemental Analysis Found: C 36.65, H 2.83, N 9.83; $C_{33}H_{30}N_8F_{12}OP_2Ru\cdot 2NaCl\cdot 2H_2O$ requires: C 36.07, H 2.91, N 10.20%

$[Ru(bipy)_2(v)](PF_6)_2\cdot (CH_3)_2CO\cdot H_2O$ 4. 19 mg (0.033 mmol) of (**v**) and 15 mg (0.028 mmol) of *cis*-$[Ru(bipy)_2Cl_2]\cdot 2H_2O$ were refluxed for 4 h in 5 cm^3 of a 1 : 1 mixture of ethanol and water. After removal of most of the solvent, a few drops of a saturated ammonium hexafluorophosphate solution were added to precipitate the complex. This was filtered, washed well with diethyl ether and dried *in vacuo*. Subsequently, the complex was dissolved in acetonitrile and centrifuged to remove unreacted ligand, prior to recrystallisation from acetone–water (2 : 1). 29 mg (82%) of **4** was obtained. No further purification was necessary. ^{1}H NMR (400 MHz, CD_3CN) δ 2.52 (m, 2H, NH_2), 3.75 (m, 2H, J = 5 Hz, CH_2NHCO), 3.98 (t, 2H, J = 5 Hz, CH_2NH_2), 7.60 (m, 5H, $5\times$H5), 8.09 (m, 5H, $5\times$H6), 8.23 (m, 5H, $5\times$H4), 8.34 (s, 1H, H6 (**vi**)), 8.51 (d, 1H, H4 (**vi**)), 8.85 (m, 6H, $6\times$H3). Elemental Analysis Found: C 50.91, H 4.78, N 8.79; $C_{54}H_{57}N_8F_{12}O_4P_2Ru\cdot(CH_3)_2CO.H_2O$ requires: C 50.74, H 4.75, N 8.31%

$[Ru(bipy)_2(vi)](PF_6)_2\cdot (CH_3)_2O\cdot 4H_2O$ 5. 15 mg (0.012 mmol) of **4** were dissolved in 6 cm^3 of water–methanol (2 : 1) containing ~0.06 mmol NaOH. The solution was heated

at reflux for 1 h and cooled to room temperature. After removal of the volatile solvent under reduced pressure, a few drops of conc. $NH_4PF_{6(aq)}$ were added. The precipitate was filtered and washed well with water and diethyl ether, before being recrystallised from acetone–water at pH 4 (2 : 1) to yield 12 mg (86%) of **5** as a red solid. ^{1}H NMR (400 MHz, CD_3CN) δ 2.52 (m, 2H, NH_2), 3.75 (m, 2H, $J = 5$ Hz, CH_2NHCO), 3.98 (t, 2H, $J = 5$ Hz, CH_2NH_2), 7.60 (m, 5H, $5 \times$ H5), 8.09 (m, 5H, $5 \times$ H6), 8.23 (m, 5H, $5 \times$ H4), 8.34 (s, 1H, H6 (**vi**)), 8.51 (d, 1H, H4 (**vi**)), 8.85 (m, 6H, $6 \times$ H3). Elemental Analysis Found: C 45.13, H 4.54, N 8.49; $C_{47}H_{52}N_8F_{12}O_4P_2Ru.(CH_3)_2CO{\cdot}4H_2O$ requires: C 45.70, H 4.72, N 8.53%

Instrumentation

^{1}H NMR spectra were recorded on a Perkin Elmer AC250 (250 MHz) or a Bruker AC400 (400 MHz) NMR Spectrometer. All measurements were carried out in $(CD_3)_2SO$ for ligands and CD_3CN or $(CD_3)_2CO$ for complexes. Peak positions are relative to solvent peaks. Mass spectrometry was carried out on Varian-Mat CF 5 DF and MAT 711 spectrometers. UV-Vis absorption spectra were recorded on a Shimadzu UV-Vis-NIR 3100 spectrophotometer interfaced with an Elonex-466 PC using UV-Vis data manager software. Emission spectra were recorded using a LS50-B Luminescence spectrophotometer, equipped with a red sensitive Hamamatsu R928 PMT detector, interfaced with an Elonex-466 PC using Windows based fluorescence data manager software. Emission and excitation slit widths were 5 nm. Emission spectra are uncorrected for photomultiplier response. 1 cm path length quartz cells were used for recording spectra. Luminescence lifetime measurements were obtained using an Edinburgh Analytical Instruments (EAI) Time Correlated Single Photon Counting apparatus (TCSPC) described previously[44] Electrochemical measurements were made on a Model 660 Electrochemical Workstation (CH Instruments). Typical complex concentrations were 0.5 to 1 mM in anhydrous acetonitrile (Aldrich 99.8%), containing 0.1 M TEAP as the supporting electrolyte. A 5 mm diameter Teflon shrouded glassy carbon working electrode, a Pt wire auxiliary electrode and SCE reference electrode were employed in all measurements. Solutions for reduction measurements were deoxygenated by purging with N_2 or Ar gas for 15 min prior to the measurement. Measurements were taken in the range of -2.0 to $+2.0$ V (*vs.* SCE). The scan rate used was 100 mV s^{-1}. Elemental analysis was carried out at the Microanalytical Laboratory at University College Dublin.

Acknowledgements

The authors thanks Enterprise Ireland and EU TMR Network "Ru–Mn Artificial Photosynthesis" (CT 96-0031) for financial assistance.

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