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A Modular Approach to Luminescent Dinuclear Ruthenium(II) and Rhenium(I) Complexes

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A series of dinuclear (bipyridine)tricarbonylrhenium(I) and tris(bipyridine)ruthenium(II) complexes have been isolated and characterised, bridged by a flexible diamido ethylene glycol chain. A new stepwise synthetic pathway has been investigated to heterometallic complexes, with the rhenium(I) complexes exhibiting an unusual configuration and inequivalence of the metal centres potentially arising from a surprising hydrogen-bonding interaction between an Re–CO group and an amide proton in low-polarity solvents. This interaction appears to be broken by competing hydrogen-bonding species such as dihydrogen phosphate. This effect was not observed in the corresponding ruthenium(II) complexes, which showed very little interaction with anions. The photophysical characterisation shows that the inclusion of two ester/amide groups to the rhenium centre effectively quenches the fluorescence at room temperature. The ruthenium(II) complexes have considerably stronger fluorescence than the rhenium species, and are less affected by the inclusion of ester and amide groups to the 2,2′-bipyridine chelating group.

Introduction

The investigation of the photophysical properties of a large number of polypyridine transition metal complexes has attracted considerable attention,[1] with potential application in molecular sensing[2] and light-emitting diodes.[3] Initially concentrated on the ubiquitous $[Ru(bpy)_3]^{2+}$ motif,[4,5] the family of photoactive transition metals has extended to include the analogous osmium complexes,[6–9] the acetylene complexes of platinum[10] and the cyclometallated benzopyridine complexes of iridium(III).[11] Interest in (bipyridyl)tricarbonylrhenium(I) complexes has given rise to a wealth of new luminescent materials[12] with potential application in metal-mediated photo-induced reduction of carbon dioxide[13–15] and sensing devices.[16–20] Materials prepared to recognise a number of anions have been reported in recent years, demonstrating the synthetic versatility of this fluorescent motif. Examples include a rotaxane-based structure reported by Curiel et al. with a selectivity for hydrogen sulfate,[21] the cationic squares of Sloan[22] and Tzeng[23] and a dimetallic diamide complex reported by the group of Lees.[24] The pioneering work of Beer illustrated that a simple dinuclear neutral Re^{I} complex can have selectivity for dihydrogen phosphate.[25]

The idea of preparing fluorescent polynuclear transition-metal complexes has been a growing area of chemistry,[26] with particular interest in the area of electron- and energy-transfer processes.[27] Key to this has been the development of bridged 2,2′-bipyridine species leading to a diverse and exciting array of ligand systems.[28] The preparation of polymetallic rhenium(I) complexes, such as the tetrametallic rectangles of Benkstien et al.[29] have led to some interesting new materials, but the isolation of heterometallic complexes with rhenium(I) has not been widely investigated. Reports are limited to platinum/rhenium systems,[30,31] a (porphyrin)zinc/ruthenium/carbonylrhenium triad[32] and a ruthenium/tris(tricarbonylrhenium) tetranuclear complex with photocatalytic activity in the reduction of carbon dioxide.[33] In a recent paper, the group of Ward demonstrated the isolation of a tris(bipyridine)ruthenium complex with a macrocyclic spacer as bridge to a tricarbonylrhenium complex; the effect of binding barium cations to the photo-induced energy transfer between the metal centres was investigated.[34] Heterometallic complexes are frequently isolated by low yielding, and synthetically challenging routes. One option is to use a stepwise "metal-as-ligand" strategy as employed in the preparation of metallic dendrimers,[35] where successive layers can be introduced by using suitable protecting groups to control the structure.[36,37]

Recently we reported a neutral dinuclear (bipyridine)-tricarbonylrhenium(I) bromide complex (Figure 1), with the two metal centres bridged by a very flexible 2,2′-(ethylenedioxy)bis(ethylamine) chain.[38] The complex exhibited an unusual conformation in non-polar solution, with evidence leading to the conclusion that there is a hydrogen bond between the amide and possibly one of the carbonyl groups on the rhenium centre. This results in an observed inequivalence of the two chelating groups. On the addition of dihy-

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drogen phosphate, the anion competes for the opportunity to hydrogen-bond to the system, breaking the observed restricted conformation. The results were confirmed by solution electrochemical and IR studies. In this study we illustrate a synthetic strategy whereby a modular approach can be adopted leading to the isolation of linear chains of fluorophores in an attempt to improve the synthetic methodology in the isolation of heterometallic complexes. By using this strategy, it is possible to include additional functional groups that allow for the incorporation of new components, or even be used to attach these materials to solid supports. Care has been taken to investigate whether the restricted conformation can be observed in related molecular systems.

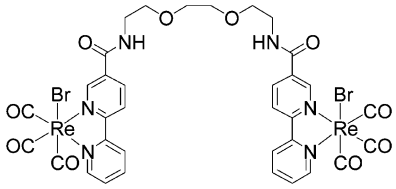
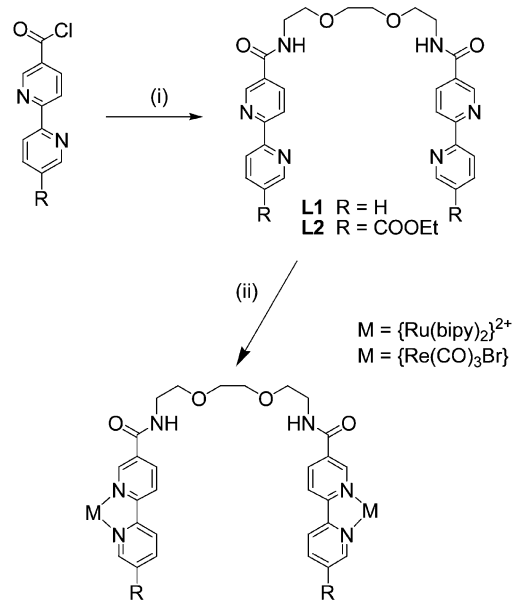


Figure 1. Previously reported dinuclear rhenium(I) complex.[38]



Scheme 1. Isolation of dinuclear metal complexes: (i) 2,2′-(ethylenedioxy)bis(ethylamine), NEt_3, dry THF; (iia) $[Re(CO)_5Br]$, dry toluene; (iib) $[Ru(bpy)_2Cl_2]$, aqueous ethanol.

Results and Discussion

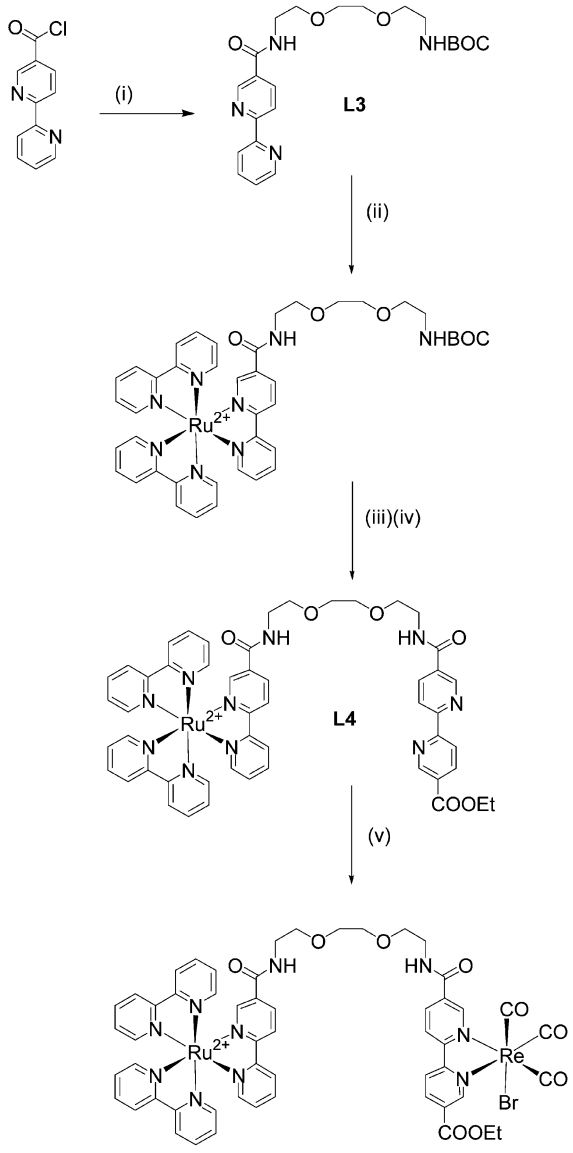
Synthesis

The ligand **L2** was prepared in an analogous fashion to the previously reported ligand **L1**[38] by the condensation of an excess of 5′-ethoxycarbonyl-2,2′-bipyridine-5-carboxylic acid[39,40] with 2,2′-(ethylenedioxy)bis(ethylamine) in a reasonable 60% yield following chromatography (Scheme 1). Refluxing of the ligand with a slight excess of $Re(CO)_5Br$ in dry toluene gave the respective dinuclear tricarbonylrhenium(I) bromide complex and $[\{Re(CO)_3Br\}_2(\mu\text{-}\mathbf{L2})]$ as an orange solid in 36% yield. This does not compare favourably with the preparation of $[\{Re(CO)_3Br\}_2(\mu\text{-}\mathbf{L1})]$, where a yield of 80% was found. Both ligands **L1** and **L2** were treated with *cis*-$[Ru(bpy)_2Cl_2]$ to give the complexes $[\{Ru(bpy)_2\}_2(\mu\text{-}\mathbf{L1})](PF_6)_4$ and $[\{Ru(bpy)_2\}_2(\mu\text{-}\mathbf{L2})](PF_6)_4$ as red solids in 68% and 36% yield, respectively, following purification by preparative silica-plate chromatography. The disappointing yields seen with the complexation of **L2** are partially explained by de-esterification of the ligand during the reaction to give the resulting carboxylic acid, which appears in both cases to have good water solubility. In addition, a quantity of the mononuclear complex, $[Ru(bpy)_2(\mathbf{L2})](PF_6)_2$, was also isolated.

Routes to mixed-metal complexes are more problematic. Given the low yields for the dinuclear complexes, isolation and separation of the mononuclear complexes from the dinuclear species and starting materials proved challenging and did not readily lend themselves to a reasonable synthetic procedure. In order to overcome these difficulties, a "metal-as-ligand" synthetic strategy was adopted, whereby the chelating groups are added sequentially. The condensation of 5-(chlorocarbonyl)-2,2′-bipyridine with 1 equiv. of BOC-protected 1,8-diamino-3,6-dioxaoctane in the presence of an excess of triethylamine afforded ligand **L3** in a typical yield of 80–90%, following purification by silica gel chromatography. The deprotection of this intermediate could then be achieved in up to 80% yield.

The introduction of a bis(bipyridine)ruthenium(II) core to this then proved very disappointing, with a 21% yield of the red compound, following purification by preparative plate chromatography, and the free amine showing signs of decomposition upon standing in air. The subsequent attempts at the addition of a second chelating site also proved disappointing, with the amide synthesis to $[Ru(bpy)_2(\mathbf{L4})](PF_6)_2$ being achieved in only 38%, presumably due to the de-esterification of the 5′-ester function.

To obtain this complex in a more satisfactory yield, metal complexation was attempted before deprotection (Scheme 2). The complex $[Ru(bpy)_2(\mathbf{L3})](PF_6)_2$ was obtained in 70% yield after purification by cation-exchange chromatography and characterised by ^1H NMR spectroscopy. The subsequent deprotection step again yielded a product that decomposed rapidly, and while identified by ^1H NMR spectroscopy, it was used immediately in the subsequent condensation with 5-(chlorocarbonyl)-5′-(ethoxycarbonyl)-2,2′-bipyridine. The resulting complex bears a free ethyl ester group, which can be readily deprotected in basic solution to allow the addition of further chelating sites in future studies. To demonstrate the isolation of heterometallic complexes, the final coordination site was treated with pentacarbonylrhenium bromide to give the mixed-metal complex $[\{Re(CO)_3Br\}\{Ru(bpy)_2\}(\mu\text{-L4})](PF_6)_2$.



Scheme 2. Synthetic pathway for a heterodimetallic complex: (i) *tert*-butyl {2-[2-(2-aminoethoxy)ethoxy]ethyl}carbamate,[41] NEt_3, dry THF; (ii) $[Ru(bpy)_2Cl_2]$, aqueous ethanol, KPF_6; (iii) 3 M HCl, MeOH; (iv) 5-(chlorocarbonyl)-5′-(ethoxycarbonyl)-2,2′-bipyridine, dry CH_3CN, KPF_6: (v) $[Re(CO)_5Br]$, dry toluene.

^{1}H NMR Characterisation

All of the complexes where characterised by ^{1}H NMR spectroscopy. In our preceding study we noted that the ^{1}H NMR spectrum of $[\{Re(CO)_3Br\}_2(\mu\text{-}\mathbf{L1})]$ presented an unusual splitting of the aromatic bipyridine proton signals, attributed to a conformational arrangement of the molecule in low-polarity solvents potentially arising from hydrogen-bonding interactions.[38] Compound $[\{Re(CO)_3Br\}_2(\mu\text{-}\mathbf{L2})]$ behaved similarly confirming our previously reported studies, whereas $[\{Ru(bpy)_2\}_2(\mu\text{-}\mathbf{L1})](PF_6)_4$ and $[\{Ru(bpy)_2\}_2(\mu\text{-}\mathbf{L2})](PF_6)_4$ indicated that both ends of the ligand have equivalent chemical shifts. Significantly though, complex $[\{Re(CO)_3Br\}\{Ru(bpy)_2\}(\mu\text{-}\mathbf{L4})](PF_6)_2$ demonstrated a splitting of the bipyridine peaks coordinated to just the rhenium centre, shown in Figure 2. As expected, the chemical shift of the ^{1}H NMR signals of the ruthenium-containing half of the complex are not affected by the coordination of tricarbonylrhenium, although the peaks were observed to broaden significantly (Figure 2). Upon the addition of the rhenium(I) fragment, the signals of the bipyridine protons H^{3}*, H^{4}* and H^{6}* are all shifted downfield by 0.3–0.4 ppm. Interestingly, the signal of one of the NH protons is shifted downfield by 0.8 ppm as well, which would suggest that the electronic environment of one of the amide groups is modified upon the rhenium coordination consistent with the formation of a hydrogen bond. The compound isolated appears to be a mixture of isomers. Indeed, the signals for the protons H6*, H6*′, H4* and H6 appear as distinct sets of signals. Because there is only one rhenium centre in this complex, this can only be explained by considering the diastereoisomerism of the metal centres. The ruthenium centre can be Δ or Λ, while the rhenium centre can have an *R* or *S* configuration (Figure 3). The centres are, however, far too remote from each other to permit an observed diastereomeric discrimination (Δ*R*/Λ*S* and Δ*S*/Λ*R*) unless they are brought sufficiently close together with an interaction akin to that previously proposed for $[\{Re(CO)_3Br\}_2(\mu\text{-}\mathbf{L1})]$, with the amidic proton forming a hydrogen bond with a

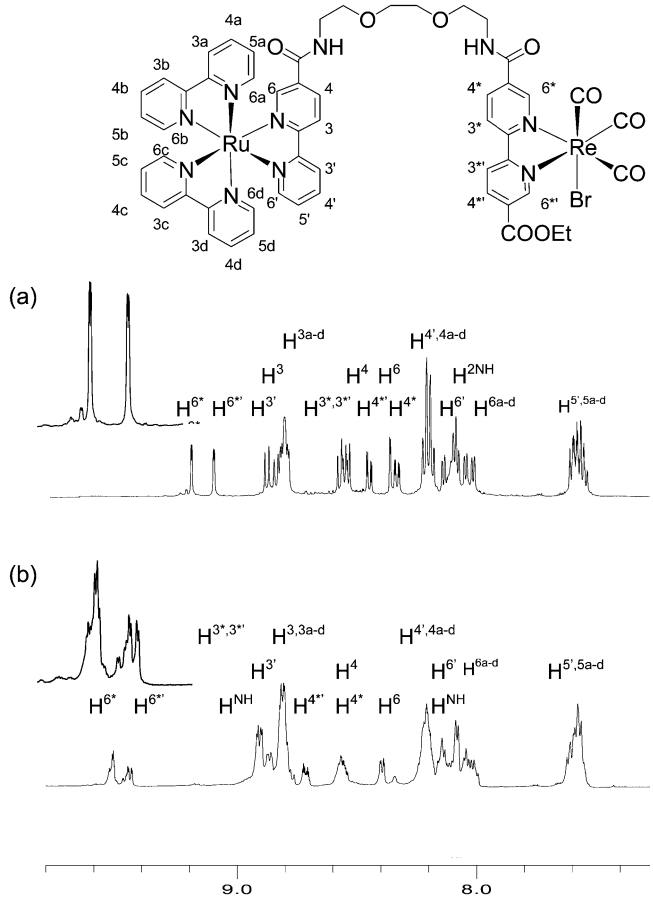


Figure 2. ^{1}H NMR spectra (500 MHz, $[D_6]$acetone, 25 °C) of (a) $[Ru(bpy)_2(\mathbf{L4})](PF_6)_2$ and (b) $[\{Re(CO)_3Br\}\{Ru(bpy)_2\}(\mu\text{-}\mathbf{L4})](PF_6)_2$.

rhenium–carbonyl or –bromide group. Reger et al. have observed close C–H···Br–Re contacts in the solid state with several bis(pyrazolyl)methane complexes.[42,43] However, a DFT calculation using the SIESTA code,[44] indicated that the formation of a hydrogen bond to the oxygen atom of one of the three carbonyl groups is lower in energy by 0.06 eV than to the bromide ion, suggesting that this is the probable site for coordination in this case.

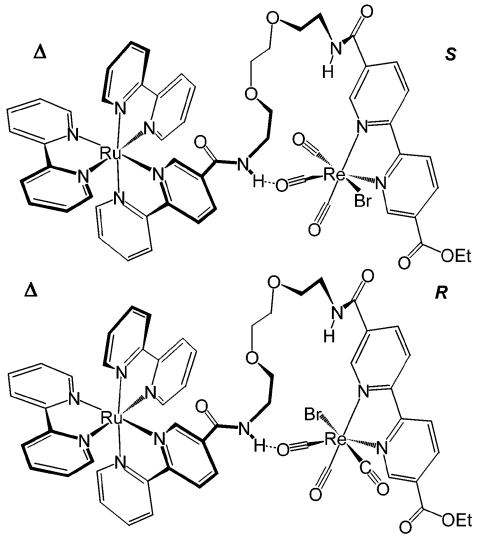


Figure 3. The proposed folded diastereoisomers of [{Re(CO)$_3$Br}{Ru(bpy)$_2$}(μ-**L4**)](PF$_6$)$_2$.

Photophysical Characterisation

The electronic UV/Vis absorption spectra of [{Re(CO)$_3$Br}$_2$(μ-**L**)], [{Ru(bpy)$_2$}$_2$(μ-**L**)](PF$_6$)$_4$ (**L** = **L1** and **L2**) and [{Re(CO)$_3$Br}{Ru(bpy)$_2$}(μ-**L4**)](PF$_6$)$_2$ are shown in Figure 4, and significant absorption bands are given in Table 1. The absorptions of [{Re(CO)$_3$Br}$_2$(μ-**L1**)] and [{Re(CO)$_3$Br}$_2$(μ-**L2**)] are in keeping with the parent complex [Re(CO)$_3$(bpy)Br][45] (λ_{max} = 288 and 372 nm), although significantly redshifted as a result of the electron-withdrawing nature of the amide/ester groups. It is also observed that the additional ester groups in ligands **L2** significantly enhanced the extinction coefficient of the π–π* ligand-centred transitions. Similarly, the complexes [{Ru(bpy)$_2$}$_2$(μ-**L1**)](PF$_6$)$_4$ and [{Ru(bpy)$_2$}$_2$(μ-**L2**)](PF$_6$)$_4$ are lower in energy when compared to [Ru(bpy)$_3$](PF$_6$)$_2$.[4,46] Further, the complex [{Ru(bpy)$_2$}$_2$(μ-**L2**)](PF$_6$)$_4$ presented a significant shoulder at 500 nm tentatively assigned as an MLCT transition to the amide/ester-functionalised bipyridine group. For the heterodimetallic complex [{Re(CO)$_3$Br}{Ru(bpy)$_2$}(μ-**L4**)](PF$_6$)$_2$, the spectral characteristics are dominated by the ruthenium moiety due to its large extinction coefficient, but is effectively the average of [{Re(CO)$_3$Br}$_2$(μ-**L2**)] and [{Ru(bpy)$_2$}$_2$(μ-**L1**)](PF$_6$)$_4$. Luminescence measurements were attempted in acetonitrile at room temperature as depicted in Figure 5 and tabulated in Table 1. [{Re(CO)$_3$Br}$_2$(μ-**L1**)] gave a weak emission with a very low quantum yield (calculated by comparison to the parent complex [Re(CO)$_3$(bpy)Br]).[47] With the addition of two ester functions, the detected emission from [{Re(CO)$_3$Br}$_2$(μ-**L2**)] was negligible. Similarly, [{Ru(bpy)$_2$}$_2$(μ-**L1**)](PF$_6$)$_4$ gave a weaker luminescence in comparison to [Ru(bpy)$_3$](PF$_6$)$_2$, whereas the fluorescence observed for [{Ru(bpy)$_2$}$_2$(μ-**L2**)](PF$_6$)$_4$ was significantly quenched and redshifted by over 50 nm due to the ester groups. The heterometallic complex [{Re(CO)$_3$Br}{Ru(bpy)$_2$}(μ-**L4**)](PF$_6$)$_2$ gave a reasonable emission, character-

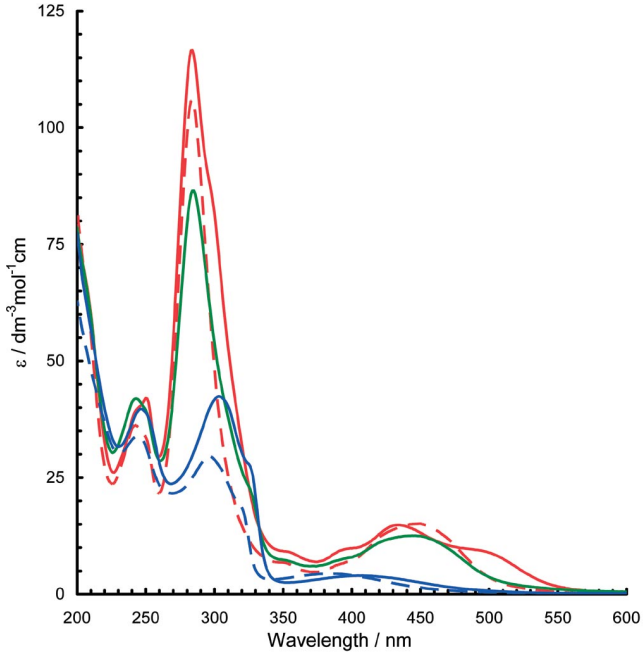


Figure 4. UV/Vis spectra of [{Ru(bpy)$_2$}$_2$(μ-**L1**)](PF$_6$)$_4$ (red, dashed), [{Re(CO)$_3$Br}$_2$(μ-**L1**)] (blue, dashed), [{Re(CO)$_3$Br}$_2$(μ-**L2**)] (blue, solid), [{Ru(bpy)$_2$}$_2$(μ-**L2**)](PF$_6$)$_4$ (red, solid) and [{Re(CO)$_3$Br}{Ru(bpy)$_2$}(μ-**L4**)] (green, solid) in MeCN at 25 °C.

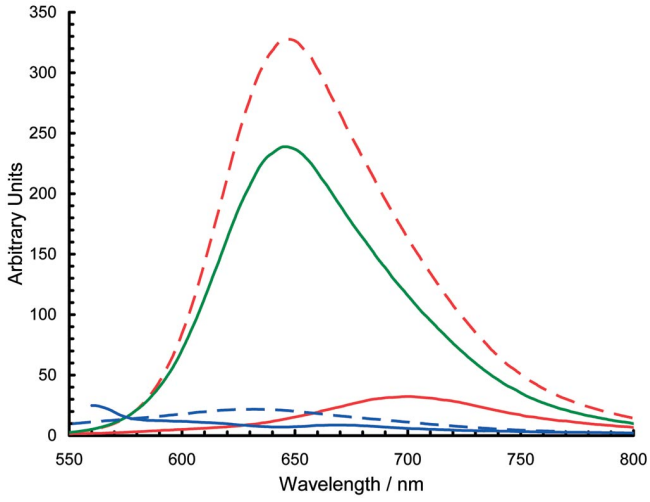


Figure 5. Fluorescence spectra of [{Ru(bpy)$_2$}$_2$(μ-**L1**)](PF$_6$)$_4$ (red, dashed), [{Re(CO)$_3$Br}$_2$(μ-**L1**)] (blue, dashed), [{Re(CO)$_3$Br}$_2$(μ-**L2**)] (blue, solid), [{Ru(bpy)$_2$}$_2$(μ-**L2**)](PF$_6$)$_4$ (red, solid) and [{Re(CO)$_3$Br}{Ru(bpy)$_2$}(μ-**L4**)] (green, solid) in MeCN at 25 °C.

Table 1. Photophysical properties of the isolated rhenium(I) and ruthenium(II) complexes.

Complex	Absorption[b]				Emission[b]	
	λ_{max} ±1 nm	$\varepsilon \times 10^3$ $dm^{-3}\,mol^{-1}\,cm$	λ_{max} ±1 nm	$\varepsilon \times 10^3$ $dm^{-3}\,mol^{-1}\,cm$	λ_{max} ±1 nm	Φ_{em}[c] ± 10%
[{Re(CO)$_3$Br}$_2$(L1)]	296	29.6	383	4.44	632	0.5×10^{-3}[c]
	320	(sh)				
[{Re(CO)$_3$Br}$_2$(L2)]	303	42.2	402	3.97	–	–
	325	(sh)				
[{Ru(bpy)$_2$}$_2$(L1)]$^{4+}$[a]	284	105.9	449	15.1	647	0.039[d]
[{Ru(bpy)$_2$}$_2$(L2)]$^{4+}$[a]	284	116.6	434	14.8	700	4.3×10^{-3}[d]
	293	(sh)				
[{Re(CO)$_3$Br}	285	86.5	446	12.6	642	0.025[d]
{Ru(bpy)$_2$}(L4)]$^{2+}$[a]	325	(sh)				

[a] Recorded as the hexafluorophosphate salts. [b] Recorded in aerated CH_3CN at 298 K. [c] Excited at 400 nm, emission quantum yields (Φ_{em}) were calculated relative to [Re(CO)$_3$Br(bpy)] (7.8×10^{-3})[47] in acetonitrile. [d] Excited at 450 nm, emission quantum yields (Φ_{em}) were calculated relative to [Ru(bpy)$_3$](PF$_6$)$_2$ as a standard in acetonitrile (0.062).[48,49]

istic of the ruthenium(II) moiety, although with a reduced quantum yield when compared to [{Ru(bpy)$_2$}$_2$(μ-**L1**)](PF$_6$)$_4$. Given the redshift observed in going from the ligand **L1** to **L2**, it would be expected that the lowest energy emissive state should be from the rhenium fragment. However, given the poor luminescence of [{Re(CO)$_3$Br}$_2$(μ-**L2**)], energy transfer between the two metal atoms does not appear to be observed at room temperature, but could account for the small reduction in quantum yield, in keeping with the findings of the Ward group.[34,50]

Table 2. Electrochemical data.

Complex	$E_{1/2}$ [V][b] Oxidation		$E_{1/2}$ [V][b] Reduction			
[Re(CO)$_3$Br(bpy)]	1.46		–1.39	–1.70		
[{Re(CO)$_3$Br}$_2$(**L1**)]	1.41	1.49	–1.09	–1.65	–1.90	
[{Re(CO)$_3$Br}$_2$(**L2**)]	1.45	1.55	–0.80	–1.13	–1.26	
[Ru(bpy)$_3$]$^{2+}$	1.39		–1.32	–1.59	–1.93	
[{Ru(bpy)$_2$}$_2$(**L1**)]$^{4+}$[a]	1.42		–1.09	–1.54	–1.85	
[{Ru(bpy)$_2$}$_2$(**L2**)]$^{4+}$[a]	1.44		–0.84	–1.26	–1.62	–1.85
[{Re(CO)$_3$Br}	1.43	1.51	–0.80	–1.11	–1.47	–1.53 (sh)
{Ru(bpy)$_2$}(**L4**)]$^{2+}$[a]						

[a] Recorded in a 25% mixture of methanol and acetonitrile. [b] Values quoted relative to an Ag/AgCl reference electrode.

Electrochemical Characterisation

The relevant electrochemical data was collected by a combination of cyclic and square-wave voltammetry in acetonitrile (Table 2). The rhenium complex [{Re(CO)$_3$Br}$_2$(μ-**L2**)] displays two resolved partially reversible oxidation waves as previously reported for [{Re(CO)$_3$Br}$_2$(μ-**L1**)] (Figure 6).[38] These are assigned as Re$^{I/II}$ couples in keeping with the parent complex [Re(bpy)(CO)$_3$Br] (1.46 V). This observed splitting is unlikely to arise from the formation of a mixed-valence complex, due to the length and flexibility of the bridging group. Consequently, the two metal centres must be in two different environments; either due to the stereochemistry (the *rac SS*/*RR* and *meso SR* forms), or more likely due to intramolecular hydrogen-bonding interactions bringing one amidic proton and a carbonyl group on one of the rhenium centres giving the dissimilarity of the two metal environments as highlighted by the previously reported ^{1}H NMR spectroscopic studies.[38] In contrast, [{Ru(bpy)$_2$}$_2$(μ-**L1**)](PF$_6$)$_4$ and [{Ru(bpy)$_2$}$_2$(μ-**L2**)](PF$_6$)$_4$ gave a single reversible Ru$^{II/III}$ oxidation couple indicating that under the experimental conditions, the two metal centres are equivalent. The heterometallic complex [{Re(CO)$_3$Br}{Ru(bpy)$_2$}(μ-**L4**)](PF$_6$)$_2$, presented two poorly resolved waves corresponding to the Ru$^{II/III}$ couple followed by the irreversible Re$^{I/II}$ oxidation (Figure 6).

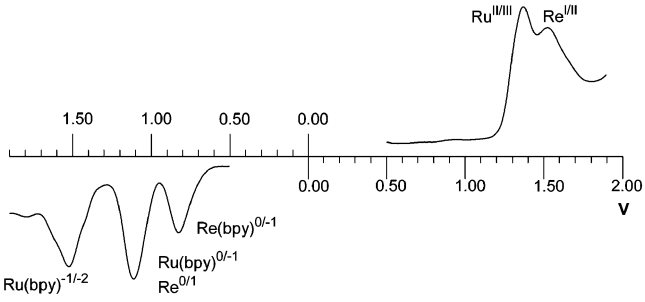


Figure 6. Square-wave voltammogram of [{Re(CO)$_3$Br}{Ru(bpy)$_2$}(**L4**)](PF$_6$)$_2$ in MeCN at 25 °C against an Ag/Ag$^+$ reference electrode.

The complex [{Re(CO)$_3$Br}$_2$(μ-**L1**)] gave a pseudo-reversible ligand-based bpy$^{0/-1}$ reduction (–1.09 V), which is significantly cathodically shifted when compared to [Re(CO)$_3$Br(bpy)] (–1.39 V) due to the electron-withdrawing nature of **L1**. This effect is further enhanced with [{Re(CO)$_3$Br}$_2$(μ-**L2**)] (–0.80 V). For both these complexes, a second irreversible reduction is assigned as an Re$^{I/0}$ reduction in keeping with literature data.[33,47,51–53] Both complexes also demonstrated a further reduction tentatively assigned as a second ligand-based reduction, although for the complex [{Re(CO)$_3$Br}$_2$(μ-**L2**)] a rather complex manifold of reduction waves were present. The analogous ruthenium

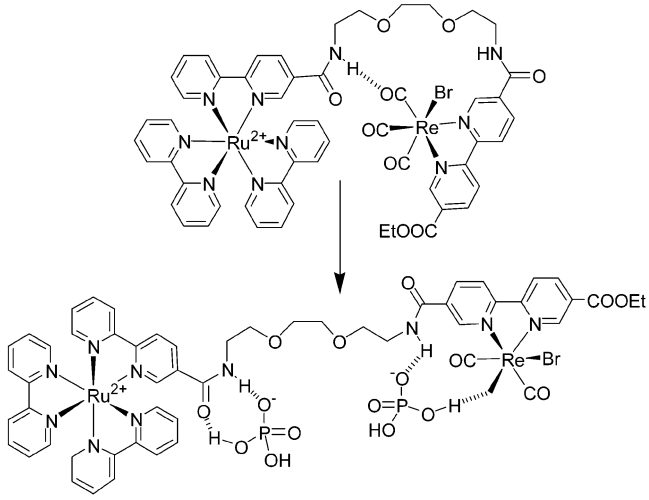
complexes demonstrated the sequential reduction of the ligands, the first two being reversible. As for the rhenium complexes, these reductions are cathodically shifted with respect to the control $[Ru(bpy)_3]^{2+}$ as a result of the electron-withdrawing nature of the ligands.[4] The heterometallic complex $[\{Re(CO)_3Br\}\{Ru(bpy)_2\}(\mu\text{-}\mathbf{L4})](PF_6)_2$ gave what is in effect a supposition of the reductions for $[\{Re(CO)_3Br\}_2(\mu\text{-}\mathbf{L2})]$ and $[\{Ru(bpy)_2\}_2(\mu\text{-}\mathbf{L1})](PF_6)_4$ indicating that the two metal centres do not influence each other significantly (Figure 6).

Interactions with Anions

In our earlier publication we reported that the complex $[\{Re(CO)_3Br\}_2(\mathbf{L1})]$ demonstrates a selective fluorescent enhancement on the addition of dihydrogen phosphate in an aprotic solvent.[38] ^1H NMR studies indicated that this uncharged rhenium complex gives surprisingly high stability constants with both dihydrogen phosphate ($\beta_2 = 3.5\times10^5$ M^{-1}) and chloride ($\beta_2 = 1.5\times10^4$ M^{-1}) for an uncharged rhenium complex. Preliminary ^1H NMR titrations with $[\{Re(CO)_3Br\}_2(\mathbf{L2})]$ indicate that this complex behaves similarly, although the absence of luminescence in solution hinders further and detailed analysis of the material and consideration as a potential sensor. However, this interaction is expressed by a large electrochemical cathodic shift in the electrochemistry of the two rhenium centres, indicating that the metal atoms themselves and not the bipyridine moieties are involved in the anion interactions and could possibly be caused by the displacement of the bromide ion.

In contrast, the two ruthenium(II) complexes $[\{Ru(bpy)_2\}_2(\mathbf{L1})](PF_6)_2$ and $[\{Ru(bpy)_2\}_2(\mathbf{L2})](PF_6)_2$ give an immediate precipitate on the addition of both chloride and dihydrogen phosphate in both acetonitrile and DMSO solution preventing detailed analysis and the calculation of stability constants by ^1H NMR spectroscopy. At much lower concentrations (approx. 10^{-5} M) no significant change in the UV/Vis absorption and emission spectra was observed on the introduction of a range of anions. Similarly, no significant changes in any of the redox waves were observed (performed in 25% methanol acetonitrile solution to prevent precipitation). Given the similarity of the complexes to those reported by Beer et al.,[25] it would be reasonable to assume that the ruthenium complexes can associate with the anions; however, this appears to be dominated by ion pairing and weak interactions with the amide group and do not give a visible change in the spectroscopic properties.

Given the significant difference in anion-binding behaviour between the ruthenium and rhenium complexes, the properties observed for $[\{Re(CO)_3Br\}\{Ru(bpy)_2\}(\mathbf{L4})](PF_6)_2$ should be a combination of the two families of complexes. Unfortunately, attempted titrations with a range of anions, followed by ^1H NMR spectroscopy proved very difficult due to the complexity of the aromatic region, preventing determination of the signal position of the amide proton. In addition, precipitation at higher anion concentrations caused problems. The UV/Vis absorption and emission spectroscopy, being dominated by the tris(chelate)-ruthenium(II) complex did not show a significant interaction with either dihydrogen phosphate or chloride, replicating the results observed for $[\{Ru(bpy)_2\}_2(\mathbf{L1})](PF_6)_2$. The introduction of anions to the heterometallic complex did, however, give a notable change in the electrochemistry; it is observed that the addition of dihydrogen phosphate modifies the oxidation with the processes becoming irreversible and slightly shifted, surprisingly in opposite directions. The oxidation of the ruthenium centre becomes easier (–60 mV), whereas the oxidation of the rhenium centre becomes harder (+30 mV), on the addition of 10 equiv. of the anion. In the reduction waves, a shift of the first peak attributed to the reduction of the rhenium-coordinated bipyridine (–40 mV) is observed. It is conceivable that the dihydrogen phosphate displaces the coordinated bromide, giving rise to these observations, but the observed changes are only small and a formal ligand exchange would have been apparent in the UV/Vis spectroscopic study. They can, however, be explained by the structural changes occurring upon binding of a dihydrogen phosphate anion, replicating the behaviour observed for the rhenium complex $[\{Re(CO)_3Br\}_2(\mu\text{-}\mathbf{L1})]$. By assuming that initially the complex $[\{Re(CO)_3Br\}\{Ru(bpy)_2\}(\mu\text{-}\mathbf{L4})](PF_6)_2$ adopts a folded conformation due to the existence of a hydrogen bond between the amide proton close to the ruthenium centre and one of the equatorial carbonyl groups coordinated to the rhenium centre as highlighted above. The presence of $H_2PO_4^-$ competes for the positions to form hydrogen bonds, thereby releasing the folded conformation; the amide proton previously engaged in the hydrogen bond holding the folded conformation now binds the anion, while the carbonyl groups hydrogen-bond to the phosphate hydroxy groups to give rise to the observed changes on the rhenium-centred processes (Scheme 3).



Scheme 3.Proposed mechanism for conformational change on the introduction of $[(n\text{-}C_4H_9)_4]H_2PO_4$ to $[\{Re(CO)_3Br\}\{Ru(bpy)_2\}(\mathbf{L4})](PF_6)_2$.

Conclusions

In the course of our studies, we have demonstrated that a modular approach can be used to introduce two chromophores to a nanometer-dimensioned complex. There is strong evidence suggesting that the neutral complex [{Re(CO)$_3$Br}$_2$(μ-**L2**)] and the heterometallic complex [{Re(CO)$_3$Br}{Ru(bpy)$_2$}(μ-**L4**)](PF$_6$)$_2$ appear to adopt an unusual folded conformation in organic solvents arising from the interaction of an amidic proton and the carbonyl group on the rhenium(I) centre in keeping with the complex [{Re(CO)$_3$Br}$_2$(μ-**L1**)]. This remarkable interaction can be opened by competing interactions with oxo anions. In comparison, the analogous positively charged fluorescent ruthenium(II) complexes, while potentially having a greater ion-pairing interaction with the anions, do not show the same degree of selectivity for protic anions, the associations being more reliant on simple electrostatic interactions. However, the application of rhenium(I) as a suitable fluorophore in future devices is very limited. In comparison to the ruthenium(II) complexes, the quantum yield appears to be dramatically affected by the substitution pattern of the appended 2,2′-bipyridine. The addition of one electron-withdrawing carbonyl group to the bipyridine chromophore effectively forces the quantum yield to drop by over 50%, while the introduction of two groups kills all emissive behaviour limiting the inclusion of this functionality in future studies.

Experimental Section

Instrumentation: ^{1}H and ^{13}C NMR spectra were recorded with a Bruker DPX 300 and DRX 500 using the solvent as an internal reference; electronic spectra were recorded with a Perkin–Elmer Lambda 800 spectrophotometer. Emission spectra were recorded with a Perkin–Elmer LS 55 spectrofluorimeter having adjusted the sample concentration to give a UV/Vis absorption of 0.1 at the excitation wavelength. Emission quantum yields (Φ_{em}) were calculated by using [Re(CO)$_3$Br(bpy)] (7.8×10^{-3}) for the rhenium complexes[47] and [Ru(bpy)$_3$](PF$_6$)$_2$ (0.062) for the ruthenium complexes[48,49] as standards in acetonitrile. Electrochemical measurements were carried out by using square-wave voltammetry in nitrogen-purged acetonitrile or a 25% mixture of methanol and acetonitrile by using a BAS CV-50W voltammetric analyzer and Voltalab PG 301 dynamic-EIS voltameter in a three-electrode cell with a glassy carbon working, Ag/AgCl reference, and platinum wire counter electrode and 0.01 M tetrabutylammonium hexafluorophosphate as electrolyte. Microanalyses and EI mass spectrometry were performed by The School of Chemistry, Queen's University Belfast.

Materials: All starting materials were used as received from the supplier. Laboratory-grade solvents were used unless otherwise specified. Dichloromethane (DCM), tetrahydrofuran (THF) and toluene were distilled under N$_2$ from calcium hydride, potassium, and sodium, respectively. SP Sephadex C25 and Sephadex LH20 were used for chromatographic purification of the metal complexes. Re(CO)$_5$Br was purchased from Strem, [Ru(bpy)$_2$Cl$_2$],[54] 2,2′-bipyridine-5-carboxylic acid,[55] 2,2′-bipyridine-5,5′-dicarboxylic acid,[40,56] 5′-(ethoxycarbonyl)-2,2′-bipyridine-5-carboxylic acid,[39,40] *tert*-butyl {2-[2-(2-aminoethoxy)ethoxy]ethyl}-carbamate,[41] *N*,*N*′-bis(2,2′-bipyridin-5-ylcarbonyl)-2-[2-(2-aminoethoxy)ethoxy]ethylamine (**L1**)[38] [Ru(bpy)$_3$](PF$_6$)$_2$,[4] and [Re(bpy)(CO)$_3$Br][39] were prepared according to literature procedures.

Synthesis

***N*,*N*′-Bis[5′-(ethoxycarbonyl)-2,2′-bipyridin-5′-ylcarbonyl]-2-[2-(2-aminoethoxy)ethoxy]ethylamine (L2):** 5-(Ethoxycarbonyl)-2,2′-bipyridine-5-carboxylic acid (0.40 g, 1.47 mmol) was refluxed in thionyl chloride (50 mL) for 1 h. The thionyl chloride was removed under reduced pressure, and the pale yellow solid was dried in vacuo for 2.5 h. The resulting solid was dissolved in dry THF (50 mL) to which was added dropwise a solution of 2,2′-(ethylenedioxy)bis(ethylamine) (0.110 g, 0.74 mmol) and Et$_3$N (5 mL) in dry THF (40 mL). The reaction mixture was stirred under nitrogen for 16 h, during which the product precipitated. The solvent was removed and distilled water (50 mL) added. The ligand was isolated by filtration and rinsed with copious amounts of water, acetone and diethyl ether. The off-white compound was dried in vacuo for 3 h and subsequently at 50 °C for 16 h (yield 310 mg, 63%). ^{1}H NMR (500 MHz, CDCl$_3$/TFA): δ = 9.40 (s, 2 H, H$^{6/6'}$), 8.91 (d, J = 8.3 Hz, 1 H, H$^{4/4'}$), 8.88 (d, J = 8.3 Hz, 1 H, H$^{4/4'}$), 8.52 (d, J = 8.3 Hz, 1 H, H$^{3/3'}$), 8.46 (d, J = 8.3 Hz, 2 H, H$^{3/3'}$, NH), 4.53 (q, J = 7.2 Hz, 2 H, COOEt), 3.73 (m, 6 H, CH$_2$), 1.47 (t, J = 7.2 Hz, 3 H, COOEt) ppm. ^{13}C NMR (125.8 MHz, CDCl$_3$/TFA): δ = 164.5, 162.7, 160.4, 160.0, 148.3, 148.0, 147.7, 145.3, 143.5, 143.2, 133.2, 130.2, 123.7, 123.2, 117.9, 115.6, 113.4, 111.1, 69.9, 68.9, 63.5, 40.5, 13.9 ppm. EI-MS: m/z (%) = 255 (100) [M – 2 COOEt]$^{2+}$. C$_{34}$H$_{36}$N$_6$O$_8$·0.5H$_2$O (665.71): calcd. C 60.51, H 5.53, N 12.59; found C 60.51, H 5.68, N 12.46.

[{Re(CO)$_3$Br}$_2$(μ-L1)]: This compound was prepared according to a previously published procedure.[38]

[{Re(CO)$_3$Br}$_2$(μ-L2): Ligand **L2** (35 mg, 0.05 mmol) was dissolved under nitrogen in hot toluene (30 mL), then [Re(CO)$_5$Br] (45 mg, 0.11 mmol) in dry toluene (20 mL) was added slowly. The reaction mixture was heated at 60–80 °C for 16 h, during which a yellow-orange precipitate formed which was isolated by filtration, rinsed with diethyl ether (50 mL) and dried in vacuo (yield 28 mg, 39%). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 9.53 (s, 1 H, H$^{6/6'}$), 9.51 (s, 1 H, H$^{6/6'}$), 9.04–8.53 (m, 5 H, H$^{3,3',4,4'}$, NH), 4.50 (q, J = 7.2 Hz, 2 H, COOEt), 3.65 (m, 6 H, CH$_2$), 1.44 (t, J = 7.2 Hz, 3 H, COOEt) ppm. LSIMS-NOB: m/z = 1277 (100) [M – Br]$^+$. C$_{40}$H$_{36}$Br$_2$N$_6$O$_{14}$Re$_2$·1.5H$_2$O (1384.00): calcd. C 34.73, H 2.85, N 6.08; found C 34.54, H 2.41, N 5.90.

[{Ru(bpy)$_2$}$_2$(μ-L1)](PF$_6$)$_4$: A mixture of ligand **L1** (35 mg, 0.07 mmol) and *cis*-Ru(bpy)$_2$Cl$_2$ (73 mg, 0.14 mmol) was refluxed in 50% aqueous ethanol (40 mL) for 16 h. The reaction mixture was filtered through Celite® and purified by preparative silica-plate chromatography eluting with DMF/ethanol (4:1), saturated with ammonium chloride. The lower red band was collected; the product was removed from the silica by using a saturated KPF$_6$ solution in acetone. The solvent was removed, the residue dissolved in water (25 mL), and the ruthenium complex was extracted with DCM (3 × 15 mL) (yield 49 mg, 38%). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 8.88 (d, J = 8.5 Hz, 1 H, H^3), 8.85 (d, J = 8.5 Hz, 1 H, H$^{3'}$), 8.83–8.77 (m, 4 H, H$^{3a–d}$), 8.48 (dd, J = 8.2, 7.8 Hz, 1 H, H$^{4'}$), 8.33 (s, 1 H, H^6), 8.25–8.17 (m, 5 H, H^4, H$^{4a–d}$), 8.13–8.00 (m, 6 H, H$^{6'}$, H$^{6a–d}$, NH), 7.64–7.51 (m, 5 H, H$^{5'}$, H$^{a–d}$), 3.52–3.20 (m, 6 H) ppm. MALDI-MS: m/z (%) = 1775 (100) [M – PF$_6$]$^+$. C$_{68}$H$_{60}$F$_{24}$N$_{14}$O$_4$P$_4$Ru$_2$·3KPF$_6$ (2471.50): calcd. C 33.01, H 2.45, N 7.93; found C 33.47, H 2.71, N 8.27.

[{Ru(bpy)$_2$}$_2$(μ-L2)](PF$_6$)$_4$: Complex [{Ru(bpy)$_2$}$_2$(μ-**L2**)](PF$_6$)$_4$ was obtained by using a similar procedure as the one described for

[{Ru(bpy)$_2$}$_2$(μ-**L1**)](PF$_6$)$_4$ using **L2** (40 mg, 0.06 mmol). The two red bands were extracted from the preparative plate to afford both the product and [Ru(bpy)$_2$(μ-**L2**)](PF$_6$)$_4$ in 5% yield (yield 14 mg, 11%). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 8.99 (d, J = 8.1 Hz, 1 H, H$^{3'}$), 8.97 (d, J = 8.1 Hz, 1 H, H^3), 8.89 (d, J = 7.5 Hz, 1 H, H^{3b}), 8.82 (m, 3 H, H^{3a,c,d}), 8.61 (d, J = 8.1 Hz, 1 H, H^4), 8.53 (m, 1 H, H$^{4'}$), 8.39 (br. s, 1 H, H^6), 8.31 (m, 2 H, H$^{6',4b}$), 8.27–8.19 (m, 3 H, H^{4a,c,d}), 8.08–7.98 (m, 4 H, H$^{6a–d}$), 8.02 (m, 1 H, NH), 7.68 (dd, J = 7.5, 5.2, Hz, 1 H, H^{5b}), 7.63 (dd, J = 7.5, 5.2, Hz, 1 H, H^{5d}), 7.58–7.52 (m, 2 H, H^{5a,c}), 4.16 (q, J = 7.0 Hz, COOEt), 3.42–3.24 (m, 6 H), 1.14 (t, J = 7.0 Hz, COOEt) ppm. MALDI-MS: m/z (%) = 1919 (100) [M – PF$_6$]$^+$. C$_{74}$H$_{68}$F$_{24}$N$_{14}$O$_8$P$_4$Ru$_2$·2.5KPF$_6$·2H$_2$O (2559.63): calcd. C 33.05, H 3.07, N 7.29; found C 33.30, H 3.53, N 6.82.

***tert*-Butyl [2-(2-{2-[(2,2′-Bipyridin-5-ylcarbonyl)amino]ethoxy}ethoxy)ethyl]carbamate (L3):** 2,2′-Bipyridine-5-carboxylic acid (1.00 g, 5.00 mmol) was refluxed in thionyl chloride (100 mL) for 1 h. The thionyl chloride was removed under reduced pressure, and the pale yellow solid was dried in vacuo for 2.5 h. The resulting solid was dissolved in dry THF (80 mL) to which was added dropwise a solution of *tert*-butyl {2-[2-(2-aminoethoxy)ethoxy]ethyl}carbamate[41] (1.20 g, 5.00 mmol) and Et$_3$N (10 mL) in dry THF (40 mL). The reaction mixture was stirred under nitrogen for 16 h, filtered through Celite®, and the Celite® rinsed with THF (100 mL). The filtrate was concentrated to a dark oily residue which was purified by silica column chromatography eluting with up to 3% MeOH in DCM collecting the first yellow band (R_f = 0.40; DCM/5% MeOH). The product was dried with MgSO$_4$, filtered, and the solvent removed to leave a brown oil (yield: 1.90 g, 90%). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 9.05 (s, 1 H, H^6), 8.57 (d, J = 5.2 Hz, 1 H, H$^{6'}$), 8.32 (d, J = 8.1 Hz, 1 H, H$^{3'}$),8.30 (d, J = 8.2 Hz, 1 H, H^3), 8.17 (d, J = 8.2 Hz, 1 H, H^4), 7.71 (dd, J = 7.8, 8.1 Hz, 1 H, H$^{4'}$), 7.44 (s, 1 H, NH^{bpy}), 7.22 (d, J = 5.2, 7.8 Hz, 1 H, H$^{5'}$), 5.30 (s, 1 H, NH^{BOC}), 3.59 (br., 4 H), 3.53 (br., 4 H), 3.44 (t, J = 5.3 Hz, 2 H, CONHCH_2), 3.20 (br., 2 H, CH_2NHBOC), 1.33 (s, 9 H, H^{BOC}) ppm. ^{13}C NMR (125.8 MHz, CDCl$_3$): δ = 166.1, 158.5, 156.5, 155.5, 149.6, 148.4, 137.4, 136.3, 130.1, 124.6, 122.0, 120.9, 79.6, 70.9, 70.6, 70.5, 70.0, 40.7, 40.2, 28.8 ppm. ES-MS: m/z (%) = 431 [M + 1]$^+$, 453 [M + Na]$^+$. C$_{22}$H$_{30}$N$_4$O$_5$·0.25CH$_2$Cl$_2$ (451.74): calcd. C 59.16, H 6.80, Cl 3.92, N 12.40; found C 59.39, H 6.66, Cl 3.51, N 11.99.

[Ru(bpy)$_2$(L3)](PF$_6$)$_2$: A mixture of ligand **L3** (236 mg, 0.55 mmol) and *cis*-[Ru(bpy)$_2$Cl$_2$] (290 mg, 0.56 mmol) was refluxed in 50% aqueous ethanol (40 mL) for 16 h. The reaction mixture was filtered through Celite® and purified by cation-exchange Sephadex C-25 chromatography eluting with aqueous 0.3 M NaCl. The first red band was collected and the product extracted as the hexafluorophosphate salt by extraction with DCM. The solvent was removed to give the product as red solid (yield 460 mg, 74%). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 8.92–8.76 (m, 6 H, H$^{3,3',3a–d}$), 8.53 (d, J = 8.1 Hz, 1 H, H^4), 8.33 (s, 1 H, H^6), 8.28–8.16 (m, 5 H, 4, H$^{4',4a–d}$), 8.13–8.00 (m, 5 H, H$^{6',6a–d}$), 7.97 (br. s, NH), 7.64–7.51 (m, 5 H, H$^{5',5a–d}$), 5.88 (br. s, 1 H, NH^{BOC}), 3.54 (br., 6 H), 3.46 (m, 4 H), 3.17 (m, 2 H, CH_2NHBOC), 1.37 (s, 9 H, H^{BOC}) ppm. ES-MS: m/z (%) = 989 [M – PF$_6$]$^+$.

[Ru(bpy)$_2$(L4)](PF$_6$)$_2$: A mixture of complex [Ru(bpy)$_2$(**L3**)](PF$_6$)$_2$ (235 mg, 0.20 mmol) and 3 M HCl in MeOH was stirred for 16 h. The solvent was removed and the residue dissolved in water. After addition of a few drops of a saturated aqueous KPF$_6$ solution, the product was extracted with DCM. The solvent was removed to give the intermediate product as red solid (yield 128 mg, 60%). 5′-(Ethoxycarbonyl)-2,2′-bipyridine-5-carboxylic acid (30 mg, 0.11 mmol) was refluxed with thionyl chloride (10 mL) for 3 h. The thionyl chloride was removed by distillation and the product dried in vacuo for 1 h. The resulting 5-(chlorocarbonyl)-5′-(ethoxycarbonyl)-2,2′-bipyridine was dissolved in dry DCM (30 mL) and added to a solution of the preceding red ruthenium(II) complex and triethylamine (1 mL) in dry acetonitrile (10 mL). The reaction mixture was refluxed for 16 h, and the solvent was removed. The residue was dissolved in water and the product precipitated by the addition of several drops of a saturated aqueous solution of KPF$_6$ and isolated by filtration (yield 32 mg, 38%). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 9.20 (s, 1 H, H^{6*}), 9.11 (s, 1 H, H$^{6*'}$), 8.89 (d, J = 8.1 Hz, 1 H, H$^{3'}$), 8.85 (d, J = 8.1 Hz, 1 H, H^3), 8.84–8.79 (m, 4 H, H$^{3a–d}$), 8.60–8.53 (m, 3 H, H$^{4,3*,3*'}$), 8.46 (d, J = 8.1 Hz, 1 H, H$^{4*'}$), 8.37 (s, 1 H, H^6), 8.34 (d, J = 8.1 Hz, 1 H, H^{4*}), 8.25–8.18 (m, 5 H, H$^{4',4a–d}$), 8.15 (m, 1 H, H$^{6'}$), 8.13–8.01 (m, 6 H, H$^{6a–d}$, NH, NH), 7.63–7.53 (m, 5 H, H$^{5',5a–d}$), 4.43 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 3.65–3.36 (m, 12 H), 1.41 (t, J = 7.2 Hz, 3 H, CH$_3$) ppm. ES-MS: m/z (%) = 1143 (100) [M – PF$_6$]$^+$.

[{Re(CO)$_3$Br}{Ru(bpy)$_2$}(μ-L4)](PF$_6$)$_2$: A mixture of complex [Ru(bpy)$_2$(**L4**)](PF$_6$)$_2$ (50 mg, 0.04 mmol) and Re(CO)$_5$Br (17 mg, 0.04 mmol) was refluxed in a 50% mixture of DCM/THF (50 mL) for 16 h. The solvent was removed, water was added, and the insoluble product was isolated by filtration. Purification was achieved by silica plate chromatography eluting with butanol/acetonitrile/NaNO$_3$-saturated water (1:1:1). The red band was collected to afford a red/orange crystalline solid (yield 10 mg, 16%). ^{1}H NMR (500 MHz, [D$_6$]acetone): δ = 9.50 (br., 1 H, H^{6*}), 9.45 (2 s, 1 H, H$^{6*'}$), 8.98–8.75 (m, 9 H, H$^{3,3',3*,3*',3a–d}$, NH), 8.72 (d, J = 8.1 Hz, 1 H, H$^{4*'}$), 8.61–8.51 (m, 2 H, H$^{4',4*}$), 8.42 (2 s, 1 H, H^6), 8.27–7.98 (m, 11 H, H$^{4a–d,4,6',6a–d}$, NH), 7.66–7.50 (m, 5 H, H$^{5',5a–d}$), 4.51 (2 q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 3.69–3.34 (m, 12 H), 1.44 (2 t, J = 7.2 Hz, 3 H, OCH_2CH$_3$) ppm. MALDI and ES-MS: m/z (%) = 1492 [M – PF$_6$]$^+$, 1448 [M – PF$_6$ – OEt]$^+$. C$_{54}$H$_{48}$F$_{12}$N$_{10}$O$_9$P$_2$ReRu·3(CH$_3$)$_2$CO (1559): calcd. C 41.72, H 3.49, N 7.73; found C 41.95, H 3.49, N 7.56.

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