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Spectral and electrochemical recognition of halide anions by acyclic mononuclear ruthenium(II) bipyridyl receptor molecules

Paul D. Beer,*[a] Simon W. Dent[a] and Trevor J. Wear[b]

[a] *Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK*
[b] *Kodak Ltd., Headstone Drive, Harrow, Middlesex HA1 4TY, UK*

New acyclic mononuclear ruthenium(II) bipyridyl amide receptors containing phenolic and sterically bulky *tert*-butyl pendant arms have been prepared and characterised. Spectroscopic and electrochemical anion-co-ordination studies have shown these receptors to bind chloride, bromide and iodide anions *via* a combination of electrostatic attraction and favourable amide CONH and phenolic ROH hydrogen-bonding interactions. Stability constant determinations from NMR titration data and electrochemical observations indicate that the presence of additional phenolic hydrogen-bonding units significantly enhances the strength of anion complexation. In addition, incorporation of sterically bulky *tert*-butyl groups to the amide units confers improved selectivity for chloride over iodide anions. Fluorescence-emission spectroscopic studies show that the relative emission intensities of the metal-to-ligand charge-transfer emission bands of the receptors is enhanced in the presence of chloride and bromide but diminished by iodide anions.

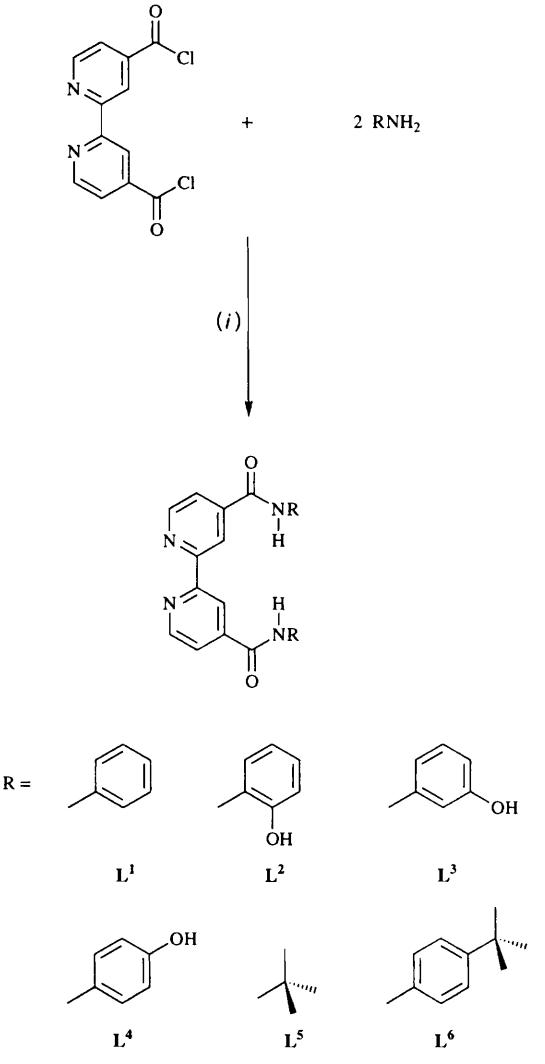
The molecular recognition of anionic guest species of biochemical, medical and environmental importance continues to be an area of intense interest.[1] Examples of anion receptors reported to date include electron-deficient tin-,[2] mercury-,[3] silicon-[4] and uranyl-containing[5] ligands, protonated polyammonium[6] and expanded porphyrin macrocycles[7] and guanidinium derivatives.[8] Surprisingly, however, reports of the design and syntheses of ligands capable of optically or electrochemically detecting anions in aqueous or non-aqueous media are very scarce. The ability of the positively charged $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) species to act as an optical *and* electrochemical sensing unit is very well documented and understood.[9-11] For example, the detection of oxygen,[12] alkali-metal cations,[13] NADH (reduced nicotinamide adenine dinucleotide)[14] and glucose[15] are known. To date, however, comparatively little work has been conducted on the $[Ru(bipy)_3]^{2+}$ fragment in relation to anion recognition.

As part of a research programme dedicated to designing new spectro- and electro-chemical sensory devices for anion recognition, we have recently reported anion recognition by ruthenium(II) 4,4′- and 5,5′-bis(amide-substituted) bipyridyl derivatives which have the ability to selectively discriminate between dihydrogen phosphate and chloride anions.[16-19] In an effort to enhance the strength of anion complexation by these types of system we decided to incorporate additional hydrogen-bonding units into the ruthenium(II) bipyridyl amide framework. Also attempts were made to alter the lipophilicity and steric bulk of the attached amide functional groups such as to afford binding selectivity between halide anions. To this end this paper details the synthesis, halide-anion co-ordination studies, electrochemical and photochemical studies of a series of new ruthenium(II) bipyridyl amide receptor molecules containing such functional groups.

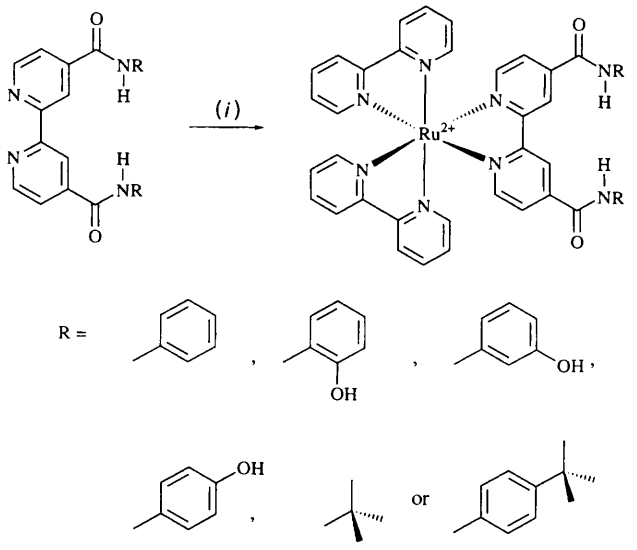
Results and Discussion

Ligand syntheses

The condensation of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine[20] with an excess of the appropriate amine in the presence of triethylamine in anhydrous dichloromethane or tetrahydrofuran (thf) solvent gave the respective acyclic 4,4′-amide disubstituted bipyridine ligands in good yields as extremely insoluble powders (Scheme 1). These new ligands were characterised using ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis (see Experimental section).



Scheme 1 (*i*) 2 NEt_3, CH_2Cl_2 or thf



Scheme 2 (*i*) $[RuCl_2(bipy_2]\cdot 2H_2O$; NH_4PF_6

Co-ordination studies

The monoruthenium(II) receptors, $[RuL(bipy)_2][PF_6]_2$ (L = L^1–L^6), were prepared by refluxing the appropriate ligand with 1 equivalent of $[RuCl_2(bipy)_2]\cdot 2H_2O$[21] in an ethanol–water–acetic acid mixture for 24–48 h (Scheme 2). After removing the volatiles *in vacuo*, the products were obtained by metathesis from aqueous solution with an excess of ammonium hexafluorophosphate. Pure samples were obtained after size-exclusion column chromatography on Sephadex LH-20-100 eluting with an acetonitrile–methanol gradient. Satisfactory analytical data was obtained for all these new heteroleptic ruthenium(II) anion receptors (see Experimental section).

Anion-complexation studies

Proton NMR titrations. Proton-NMR titration experiments were conducted in $(CD_3)_2SO$ solutions due to problems with receptor-anion complex solubility. The receptor $[RuL^5(bipy)_2][PF_6]_2$, which contained an aliphatic *tert*-butyl group, exhibited better solubility than the other receptors and thus NMR titration experiments were performed in CD_3CN solution as well as in $(CD_3)_2SO$.

The addition of tetrabutylammonium chloride, bromide and iodide to the ruthenium(II) bipyridyl receptors resulted in significant downfield shifts of the amide CONH and substituted 3,3′-bipy proton resonance signals. For example, the addition of 1 equivalent of tetrabutylammonium chloride to $[RuL^6(bipy)_2][PF_6]_2$ in $(CD_3)_2SO$ caused the amide resonance to shift by 0.55 ppm and the substituted 3,3′-bipy protons to shift by 0.22 ppm. The downfield shifts observed in acetonitrile solution were even greater, in keeping with the lower polarity of this solvent, which disrupts the amide-anion hydrogen-bonding interactions to a lesser extent. Addition of 1 equivalent of chloride to $[RuL^5(bipy)_2][PF_6]_2$ resulted in the amide and 3,3′-bipy protons being perturbed by 1.62 and 1.58 ppm respectively. As noted previously[19] these results suggest that favourable CONH-anion hydrogen-bonding interactions play a key role in the overall anion complexation process. This is further supported by the phenol functionalised receptors, $[RuL^{2\text{–}4}(bipy)_2][PF_6]_2$, which show downfield shifts in their respective phenol, OH protons of up to 0.3 ppm upon the addition of an excess of chloride anions. The resulting titration curves, (for example Fig. 1) imply all the receptors form receptor:halide anion complexes with a 1:1 stoichiometry. Analysis of the titration curves using the computer program EQNMR[22] allows stability constants to be elucidated and these are presented in Table 1.

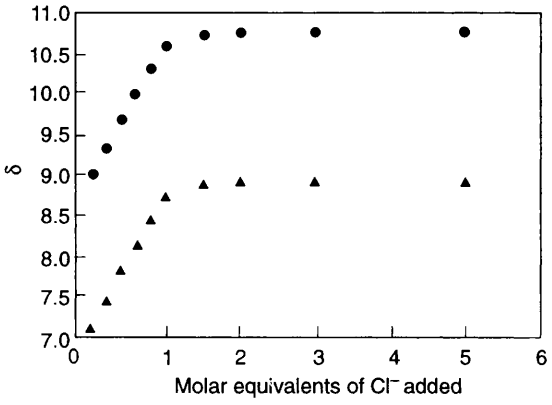


Fig. 1 Proton NMR titration curves of $[RuL^5(bipy)_2][PF_6]_2$ with Cl^- in CD_3CN; ●, 3,3′-bipy and ▲, amide proton

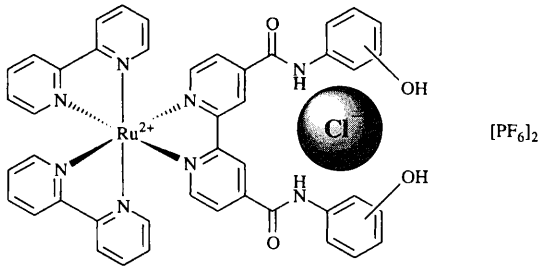


Fig. 2 Proposed structure in solution of anion complexes of ruthenium(II) bipyridyl receptors

Table 1 Halide-anion stability constant data in $(CD_3)SO$[a]

Receptor	$K(Cl^-)$/dm^3 mol^{-1}	$K(Br^-)$/dm^3 mol^{-1}	$K(I^-)$/dm^3 mol^{-1}
$[RuL^1(bipy)_2][PF_6]_2$	40	20	10
$[RuL^2(bipy)_2][PF_6]_2$	20	—	< 5
$[RuL^3(bipy)_2][PF_6]_2$	140	30	15
$[RuL^4(bipy)_2][PF_6]_2$	150	35	20
$[RuL^5(bipy)_2][PF_6]_2$	80	20	< 5
	6700[b]	—	120[b]
$[RuL^6(bipy)_2][PF_6]_2$	205	95	25

[a] Errors estimated to be ≤5%. [b] In CD_3CN.

It is noteworthy that all the receptors show a selectivity preference $Cl^- > Br^- > I^-$. The presence of additional *meta*- and *para*-substituted phenol groups significantly enhances the strength of chloride-anion complexation *via* additional hydrogen-bonding interactions when compared to the unsubstituted aniline analogue (Fig. 2). Interestingly the binding enhancement is most noticeable for chloride anions (over a three-fold increase in the stability constant) but is less prominent for bromide and iodide anions. The *ortho*-substituted phenol however exhibited weaker anion binding possibly due to steric crowding of the amide binding site and/or intramolecular hydrogen bonding between the amide and phenol groups.

The selectivity trend $Cl^- > I^-$ is greatest for the *tert*-butyl aliphatic receptor $[RuL^5(bipy)_2][PF_6]_2$ in dimethyl sulfoxide and acetonitrile solution. This may be explained in terms of the steric bulk of the *tert*-butyl group in close proximity to the amide CONH group which inhibits complexation of the larger iodide anion to a greater extent. This argument is supported by the observation that the shift for the 3,3′-bipy and amide protons are virtually the same during the chloride titration, which may be indicative of a very tight binding fit. However in the case of iodide the shift of the amide proton (0.63 ppm with an excess of iodide in CD_3CN) is much greater than that of the 3,3′-bipy proton (0.12 ppm). The selectivity trend is not as

marked for the aromatic-linked *tert*-butyl receptor $[RuL^6(bipy)_2][PF_6]_2$ which possesses a larger pseudo-macrocyclic cavity. However in this instance the binding strength for both chloride and iodide is increased and the increase is more marked for iodide than chloride. This observation may be attributed to the lower charge density on the iodide anion which renders it more tolerant of the lipophilic environment which the *tert*-butyl group creates.

Electrochemical anion-recognition studies

Cyclic voltammetry was used to investigate the electrochemical anion recognition properties of the new ruthenium(II) bipyridyl receptors in acetonitrile solution. The results are summarised in Table 2. Comparison with the prototype $[Ru(bipy)_3][PF_6]_2$ revealed that each compound exhibited typical redox behaviour for ruthenium(II) tris(bipyridyl)-based systems, namely a metal-centred oxidation (1.1 to 1.0 V) and three bipyridyl ligand centred reductions (−1.4 to −2.1 V). Due to the presence of electron-withdrawing carbonyl amide moieties, the least cathodic bipyridyl ligand centred reduction wave can be assigned to the amide-substituted bipyridyl groups within each receptor. This is supported by the observation that this is the redox couple which exclusively underwent cathodic perturbations upon the addition of anions. The magnitudes of the cathodic shifts of the first bipy reduction waves were consistent with the findings of the ^1H NMR titration experiments and are presented in Table 3. Addition of excess amounts of chloride anions in acetonitrile solution resulted in cathodic shifts of up to 50 mV {for $[RuL^5(bipy)_2][PF_6]_2$}, but smaller shifts (5–20 mV) with bromide and iodide. Interestingly, the addition of an excess of iodide anions to electrochemical solutions of $[RuL^5(bipy)_2][PF_6]_2$ had no effect on the amide-substituted bipy redox wave at all. This corroborates the finding from the ^1H NMR titrations that this receptor binds iodide very weakly in acetonitrile solution.

Electronic-absorption and fluorescence-emission spectra anion-recognition studies

Ruthenium(II) bipyridyl complexes exhibit intraligand, metal-centred and low-energy metal-to-ligand charge-transfer (m.l.c.t.) absorption bands. Electronic absorption λ_{max} and ε data for all the ruthenium(II) receptors in acetonitrile solution are summarised and contrasted with the prototype $[Ru(bipy)_3][PF_6]_2$ in Table 4. The electron-withdrawing nature of the amide groups confers hypsochromic (blue) shifts of up to 25 nm of the lowest energy m.l.c.t. bands when compared to the prototype. Interestingly, the addition of chloride and iodide anions has no effect on the absolute position of any of the λ_{max} absorption bands, but does result in significant changes in ε of both the m.l.c.t. and intraligand-centred absorption bands (an example is shown in Fig. 3). Notably, the addition of anions generally resulted in a decrease in ε for the intraligand-centred bands but an increase in the m.l.c.t. bands. No effect on the metal-centred absorption bands was observed.

Fluorescence-emission data is also summarised in Table 4. All the receptors exhibit m.l.c.t. emission maxima in the range 630–650 nm at lower energy than the prototype $[Ru(bipy)_3][PF_6]_2$. Addition of chloride and bromide anions resulted in marked emission intensity increases. For example, a 42% increase in the m.l.c.t. emission maxima with a concomitant hypsochromic shift of 8 nm was observed with an excess of chloride (see Fig. 4). This intensity enhancement may be attributed to the complexation process imparting a degree of rigidity to the receptor, thus disfavouring receptor-mobility non-radiative decay processes in solution. Interestingly iodide anions caused an intensity decrease with no shift in the position of the maxima. This emission quenching may be a manifestation of the so-called 'heavy atom effect'.[23]

Table 2 Electrochemical data ($E_{\frac{1}{2}}$/V)*

Receptor	Metal-based Ru^{II}–Ru^{III}	bipy-based +2/+1	+1/0	0/−1
$[Ru(bipy)_3][PF_6]_2$	1.025	−1.610	−1.820	−2.115
$[RuL^1(bipy)_2][PF_6]_2$	1.090	−1.500	−1.690	−2.120
$[RuL^2(bipy)_2][PF_6]_2$	1.100	−1.465	−1.680	−2.115
$[RuL^3(bipy)_2][PF_6]_2$	1.100	−1.470	−1.550	−2.130
$[RuL^4(bipy)_2][PF_6]_2$	1.095	−1.460	−1.605	−2.125
$[RuL^5(bipy)_2][PF_6]_2$	1.070	−1.515	−1.860	−2.080
$[RuL^6(bipy)_2][PF_6]_2$	1.100	−1.465	−1.850	−2.070

* Obtained in acetonitrile solution containing 0.1 mol dm^{-3} $NBu^n_4PF_6$ as supporting electrolyte. Solutions were 5 × 10^{-4} mol dm^{-3} in receptor and potentials were determined with reference to a Ag–Ag^+ electrode (330 ± 5 mV *vs.* SCE) at 21 ± 1 °C and 100 mV s^{-1} scan rate.

Table 3 Cathodic shifts induced upon first (substituted) bipyridyl redox wave on addition of an excess of halide anions

Receptor	$\Delta E_{\frac{1}{2}}$/mV Cl^-	Br^-	I^-
$[Ru(bipy)_3][PF_6]_2$	0	0	0
$[RuL^1(bipy)_2][PF_6]_2$	15	5	< 5
$[RuL^2(bipy)_2][PF_6]_2$	10	5	< 5
$[RuL^3(bipy)_2][PF_6]_2$	30	10	5
$[RuL^4(bipy)_2][PF_6]_2$	35	15	5
$[RuL^5(bipy)_2][PF_6]_2$	50	20	0
$[RuL^6(bipy)_2][PF_6]_2$	45	—	15

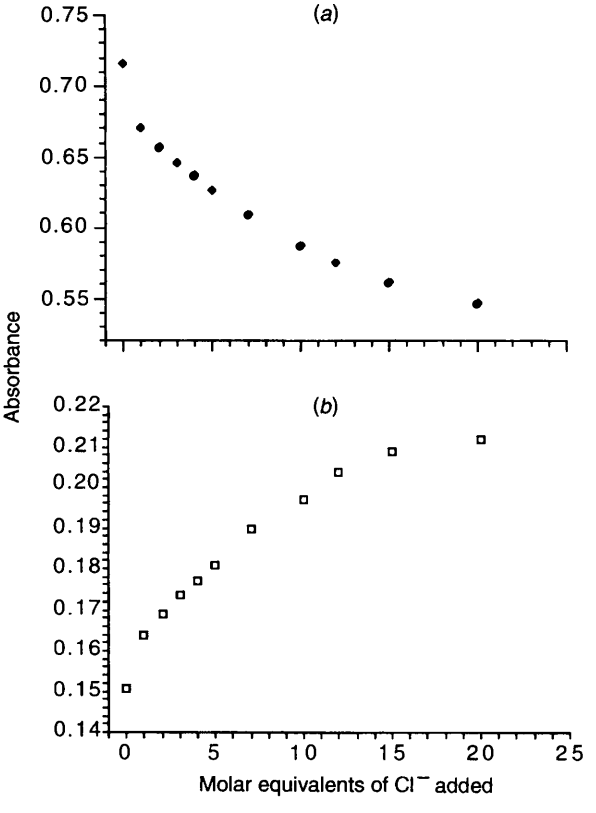


Fig. 3 Effect of addition of equivalents of Cl^- on the intraligand-centred (*a*) and m.l.c.t. (*b*) absorption intensity of $[RuL^5(bipy)_2][PF_6]_2$ in MeCN

Conclusion

New acyclic mononuclear ruthenium(II) bipyridyl amide containing receptors have been prepared and demonstrated to co-ordinate chloride, bromide and iodide anions. Spectroscopic

Table 4 Electronic-absorption and fluorescence-emission data[a]

Receptor	m.l.c.t. λ/nm	m.l.c.t. ε/dm³ mol⁻¹ cm⁻¹	Intraligand-centred λ/nm	Intraligand-centred ε/dm³ mol⁻¹ cm⁻¹	m.l.c.t. λ/nm	m.l.c.t. ε/dm³ mol⁻¹ cm⁻¹	λ_{max}[b]/nm
$[Ru(bipy)_3][PF_6]_2$	244	27 200	287	79 800	452	14 300	609
$[RuL^1(bipy)_2][PF_6]_2$	244	31 500	288	67 000	459	15 700	640
$[RuL^2(bipy)_2][PF_6]_2$	245	32 400	288	71 900	470	16 700	650
$[RuL^3(bipy)_2][PF_6]_2$	244	31 900	287	71 000	473	16 200	643
$[RuL^4(bipy)_2][PF_6]_2$	245	33 000	286	72 800	468	17 100	646
$[RuL^5(bipy)_2][PF_6]_2$	246	31 800	287	71 600	458	15 100	633
$[RuL^6(bipy)_2][PF_6]_2$	247	32 700	287	72 300	472	17 500	639

[a] Recorded in acetronitrile at 20 °C. Solutions were 2.0×10^{-5} mol dm^{-3} in receptor. Errors estimated to be ≤10%. [b] m.l.c.t. fluorescence-emission maximum.

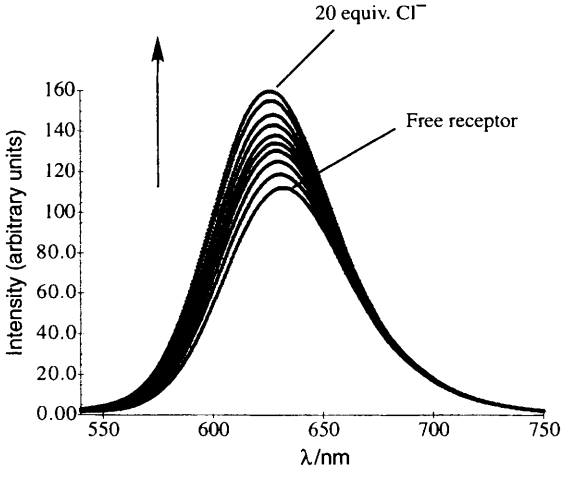


Fig. 4 Effect of addition of equivalents of Cl^- on the m.l.c.t. emission intensity of $[RuL^5(bipy)_2][PF_6]_2$ in MeCN

and electrochemical investigations reveal that these receptors sense halide anions through mutual electrostatic attraction and favourable amide CONH hydrogen-bonding interactions. Stability constant determinations from NMR titration data in corroboration with electrochemical observations demonstrate that the presence of additional phenolic hydrogen-bonding functionalities cooperatively enhance the strength of anion complexation. Further studies also indicate that the presence of a sterically hindered *tert*-butyl group attached directly to the amide functionality confers significant selectivity for chloride anions over larger iodide anions in acetonitrile solution. In addition, fluorescence-emission spectroscopic studies show that the relative emission intensities of the m.l.c.t. emission bands of the receptors is enhanced in the presence of chloride and bromide but diminished by iodide anions.

Experimental

Instrumentation

Nuclear magnetic resonance spectra were recorded on either a Bruker AM300 instrument (300 MHz) using solvent deuterium signal as an internal reference or on a Varian-Unity 500 instrument (500 MHz for ^{1}H, 125.7 MHz for ^{13}C NMR spectra). The NMR assignments for the ruthenium(II) receptors were made with the aid of ^{1}H–^{1}H correlation techniques. Mass spectrometry (electron impact and fast-atom bombardment) was performed by the analytical services at Kodak Ltd., Harrow and elemental analyses were performed at the Inorganic Chemistry Laboratory, Oxford. Electrochemical measurements were conducted using an EG and G Princeton Applied Research 362 scanning potentiostat. A three-electrode system was employed with platinum-wire working electrodes and a platinum-mesh counter electrode. Electrode potentials were measured and are quoted with respect to a $Ag–Ag^+$ reference electrode [+0.330 V *vs.* saturated calomel electrode (SCE)] at 22 (±2) °C. Both counter and reference electrodes were separated from the working-electrode compartment of the electrochemical cell by glass frits. No IR compensation was used. Measurements were carried out in deoxygenated acetonitrile solutions containing 0.1 mol dm^{-3} support electrolyte ($NBu^n_4BF_4$). Electronic absorption spectra were recorded on a Philips UV-PU 8745 spectrophotometer. A Perkin-Elmer luminescence LS 50 spectrometer was used for recording the fluorescence-emission spectra. Measurements were conducted at 25 °C using a 1 × 1 cm rectangular quartz cuvette and deoxygenated solutions.

Materials

Where necessary, solvents were purified prior to use and stored under dinitrogen. Tetrahydrofuran and toluene were distilled from sodium using benzophenone as indicator, triethylamine, dichloromethane and acetonitrile from calcium hydride. All other solvents employed were of commercial grade and used as received. 4,4′-Bis(chlorocarbonyl)-2,2′-bipyridine[20] and *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$[21] were prepared as described elsewhere. All tetrabutylammonium salts were recrystallised from anhydrous toluene and dried rigorously *in vacuo* prior to use.

Ligand syntheses

4,4′-Bis[(phenyl)aminocarbonyl]-2,2′-bipyridine, L^1. A solution of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (0.52 g, 1.85 mmol) in anhydrous thf (100 cm^3) was added dropwise to a vigorously stirred solution of aniline (0.60 g, 6.5 mmol, 3.5 equiv.) and triethylamine (0.75 g, 7.4 mmol) in thf (150 cm^3) over 30 min. The reaction was stirred for 18 h under nitrogen at room temperature and the precipitate removed by filtration and washed with thf (3 × 50 cm^3), aqueous ammonia solution (1 mol dm^{-3}, 100 cm^3) and water (100 cm^3). Following drying in an oven (70 °C) a white powder was obtained (0.34 g, 60.6%) (Found: C, 72.8; H, 5.1; N, 13.9. $C_{24}H_{18}N_4O_2$ requires C, 73.1; H, 4.6; N, 14.2%). NMR [$(CD_3)_2SO$]: ^{1}H (300 MHz), δ 7.22 (t, 4 H, J = 8.1, aryl $H^{3,3'}$ and $H^{5,5'}$), 7.37 (d, 2 H, J = 8.0, aryl $H^{4,4'}$), 7.82 (d, 4 H, J = 8.0, aryl $H^{2,2'}$ and $H^{6,6'}$), 8.07 (d, 2 H, J = 5.5, bipy $H^{6,6'}$), 8.95 (d, 2 H, J = 5.2 Hz, bipy $H^{5,5'}$), 9.00 (s, 2 H, bipy $H^{3,3'}$) and 10.69 (br s, 2 H, CONH); ^{13}C (125.7 MHz), δ 115.32, 119.74, 121.39, 122.42, 127.11, 139.00, 141.22, 149.52, 155.81 and 167.47 (C=O). Mass spectrum (EI): m/z 396 $(M\mathrm{H})^+$.

4,4′-Bis[(2-hydroxyphenyl)aminocarbonyl]-2,2′-bipyridine, L^2. A solution of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (0.67 g, 2.38 mmol) in anhydrous thf (100 cm^3) was added dropwise to a vigorously stirred solution of 2-aminophenol (0.91 g, 8.31 mmol, 3.5 equiv.) and triethylamine (0.95 g, 9.5 mmol) in thf

($150\ cm^3$) over 20 min. The reaction was stirred for 16 h under nitrogen at room temperature and the precipitate removed by filtration and washed with thf ($3 \times 50\ cm^3$), aqueous ammonia solution ($1\ mol\ dm^{-3}$, $100\ cm^3$) and water ($100\ cm^3$). Following drying in an oven (70 °C) a pale yellow powder was obtained (0.78 g, 76.7%) (Found: C, 68.0; H, 4.3; N, 12.8. $C_{24}H_{18}N_4O_4$ requires C, 67.6; H, 4.2; N, 13.1%). NMR [$(CD_3)_2SO$]: ^1H (300 MHz), δ 6.65 (t, 2 H, J = 7.4, aryl $H^{5,5'}$), 6.94 (d, 2 H, J = 7.2, aryl $H^{6,6'}$), 7.09 (t, 2 H, J = 6.7, aryl $H^{4,4'}$), 7.62 (d, 2 H, J = 7.1, aryl $H^{3,3'}$) 7.99 (d, 2 H, J = 4.9, bipy $H^{6,6'}$), 8.91 (d, 2 H, J = 3.7 Hz, bipy $H^{5,5'}$), 8.94 (s, 2 H, bipy $H^{3,3'}$), 9.74 (br s, 2 H, CONH) and 10.01 (s, 2 H, aryl OH); ^{13}C (125.7 MHz), δ 105.75, 114.55, 117.23, 119.17, 121.32, 130.21, 139.12, 142.88, 150.69, 158.50, 159.02 and 168.41 (C=O). Mass spectrum (EI): m/z 427 $(M\mathrm{H})^+$.

4,4′-Bis[(3-hydroxyphenyl)aminocarbonyl]-2,2′-bipyridine, L³. A solution of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (0.47 g, 1.67 mmol) in anhydrous thf ($100\ cm^3$) was added dropwise to a vigorously stirred solution of 3-aminophenol (0.64 g, 5.85 mmol, 3.5 equiv.) and triethylamine (1.01 g, 10 mmol) in thf ($150\ cm^3$) over 20 min. The reaction was stirred for 14 h under nitrogen at room temperature and the precipitate removed by filtration and washed with thf ($3 \times 50\ cm^3$), aqueous ammonia solution ($1\ mol\ dm^{-3}$, $100\ cm^3$) and water ($100\ cm^3$). Following drying in an oven (70 °C) a pale grey powder was obtained (0.52 g, 72.9%) (Found: C, 67.1; H, 4.4; N, 13.5. $C_{24}H_{18}N_4O_4$ requires C, 67.6; H, 4.2; N, 13.1%). NMR [$(CD_3)_2SO$]: ^1H (300 MHz), δ 6.56 (d, 2 H, J = 7.7, aryl $H^{6,6'}$), 7.15 (t, 2 H, J = 7.9, aryl $H^{5,5'}$), 7.22 (d, 2 H, J = 8.1, aryl $H^{4,4'}$), 7.38 (s, 2 H, aryl $H^{2,2'}$), 8.02 (d, 2 H, J = 5.0, bipy $H^{6,6'}$), 8.94 (d, 2 H, J = 4.6 Hz, bipy $H^{5,5'}$), 8.97 (s, 2 H, bipy $H^{3,3'}$), 9.92 (br s, 2 H, CONH) and 10.65 (s, 2 H, aryl OH); ^{13}C (125.7 MHz), δ 107.69, 111.32, 111.43, 118.64, 122.40, 129.41, 139.67, 143.61, 150.18, 155.47, 157.61 and 163.93 (C=O). Mass spectrum (EI): m/z 427 $(M\mathrm{H})^+$.

4,4′-Bis[(4-hydroxyphenyl)aminocarbonyl]-2,2′-bipyridine, L⁴. A solution of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (0.50 g, 1.78 mmol) in anhydrous thf ($100\ cm^3$) was added dropwise to a vigorously stirred solution of 4-aminophenol (0.68 g, 6.22 mmol, 3.5 equiv.) and triethylamine (0.81 g, 8.0 mmol) in thf ($150\ cm^3$) over 30 min. The reaction was stirred for 18 h under nitrogen at room temperature and the precipitate removed by filtration and washed with thf ($3 \times 50\ cm^3$), aqueous ammonia solution ($1\ mol\ dm^{-3}$, $100\ cm^3$) and water ($100\ cm^3$). Following drying in an oven (70 °C) a pale yellow powder was obtained (0.49 g, 64.6%) (Found: C, 67.3; H, 3.9; N, 12.7. $C_{24}H_{18}N_4O_4$ requires C, 67.6; H, 4.2; N, 13.1%). NMR [$(CD_3)_2SO$]: ^1H (300 MHz), δ 6.52 (d, 4 H, J = 7.6, aryl $H^{3,3'}$ and $H^{5,5'}$), 7.09 (d, 4 H, J = 7.6, aryl $H^{2,2'}$ and $H^{6,6'}$), 7.90 (d, 2 H, J = 5.0, bipy $H^{6,6'}$), 8.83 (d, 2 H, J = 4.6 Hz, bipy $H^{5,5'}$), 8.87 (s, 2 H, bipy $H^{3,3'}$), 9.79 (br s, 2 H, CONH) and 10.21 (s, 2 H, aryl OH); ^{13}C (125.7 MHz), δ 110.56, 116.98, 120.34, 121.50, 129.11, 135.77, 138.43, 142.39, 150.90, 158.04, 160.62 and 169.89 (C=O). Mass spectrum (EI): m/z 427 $(M\mathrm{H})^+$.

4,4′-Bis[(*tert*-butyl)aminocarbonyl]-2,2′-bipyridine, L⁵. A solution of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (0.54 g, 1.92 mmol) in anhydrous CH_2Cl_2 ($100\ cm^3$) was added dropwise to a vigorously stirred solution of *tert*-butylamine (0.56 g, 7.68 mmol, 4.0 equiv.) and triethylamine (1.13 g, 11.2 mmol) in CH_2Cl_2 ($150\ cm^3$) over 45 min. The reaction was stirred for 18 h under nitrogen at room temperature and the precipitate removed by filtration and washed with CH_2Cl_2 ($3 \times 50\ cm^3$), aqueous ammonia solution ($1\ mol\ dm^{-3}$, $100\ cm^3$) and water ($100\ cm^3$). Following drying a white, hydrophobic powder was obtained (0.46 g, 67.4%) (Found: C, 67.5; H, 7.5; N, 16.2. $C_{20}H_{26}N_4O_2$ requires C, 67.8; H, 7.4; N, 15.8%). NMR [$(CD_3)_2SO$]: ^1H (300 MHz), δ 1.41 (s, 18 H, Bu^t), 7.78 (d, 2 H, J = 5.0, bipy $H^{6,6'}$), 8.29 (s, 2 H, CONH), 8.69 (s, 2 H, bipy $H^{3,3'}$) and 8.82 (d, 2 H, J = 4.9 Hz, bipy $H^{5,5'}$); ^{13}C (125.7 MHz), δ 28.42, 51.25, 118.47, 122.13, 144.36, 149.77, 155.32 and 164.94 (C=O). Mass spectrum (EI): m/z 355 $(M\mathrm{H})^+$ and 297 $(M - \mathrm{Bu}^t)^+$.

4,4′-Bis[(4-*tert*-butylphenyl)aminocarbonyl]-2,2′-bipyridine, L⁶. A solution of 4,4′-bis(chlorocarbonyl)-2,2′-bipyridine (0.39 g, 1.39 mmol) in anhydrous CH_2Cl_2 ($100\ cm^3$) was added dropwise to a vigorously stirred solution of 4-*tert*-butylaniline (0.83 g, 5.57 mmol, 4.0 equiv.) and triethylamine (0.68 g, 6.68 mmol) in CH_2Cl_2 ($150\ cm^3$) over 45 min. The reaction was stirred for 18 h under nitrogen at room temperature and the precipitate removed by filtration and washed with CH_2Cl_2 ($3 \times 50\ cm^3$), aqueous ammonia solution ($1\ mol\ dm^{-3}$, $100\ cm^3$) and water ($100\ cm^3$). Following drying a white, hydrophobic powder was obtained (0.51 g, 72.5%) (Found: C, 75.4; H, 6.5; N, 10.8. $C_{32}H_{34}N_4O_2$ requires C, 75.9; H, 6.8; N, 11.1%). NMR [$(CD_3)_2SO$]: ^1H (300 MHz), δ 1.29 (s, 18 H, Bu^t), 7.41 (d, 4 H, J = 8.7, aryl H), 7.72 (d, 4 H, J = 8.7, aryl H), 7.97 (d, 2 H, J = 5.1, bipy $H^{6,6'}$), 8.91 (s, 2 H, bipy $H^{3,3'}$), 8.95 (d, 2 H, J = 5.0 Hz, bipy $H^{5,5'}$) and 10.66 (s, 2 H, CONH); ^{13}C (125.7 MHz), δ 31.23, 34.17, 118.58, 120.43, 122.39, 125.39, 136.05, 143.51, 146.70, 150.21, 155.51 and 163.75 (C=O). Mass spectrum (EI): m/z 506 (M^+) 491 $(M - CH_3)^+$ and 449 $(M - \mathrm{Bu}^t)^+$.

General procedure for the preparation of the ruthenium(II) bipyridyl receptors

The appropriate 4,4′-amide disubstituted bipyridyl receptor ligand was suspended in a mixture of water ($20\ cm^3$), ethanol ($20\ cm^3$) and acetic acid ($10\ cm^3$) and heated to 50 °C. A slight excess (1.1 equivalents) of *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$ was added and the mixture refluxed under nitrogen for 24–48 h. After cooling and filtering, the solvents were removed from the filtrate and the red-black solid dried *in vacuo* for 4 h. The solid was redissolved in water ($10\ cm^3$) and treated with a saturated aqueous solution of NH_4PF_6 ($5\ cm^3$) which precipitated the desired product. Further purification by repeated size-exclusion column chromatography on Sephadex LH-20-100 using acetonitrile–methanol (1 : 1 v/v) as eluent yielded the receptors as red glassy solids.

$[RuL^1(bipy)_2][PF_6]_2$. Prepared from the amide L^1 (0.175 g, 0.44 mmol) and *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$ (0.254 g, 0.48 mmol). Yield 0.345 g, 70.9% (Found: C, 47.9; H, 3.2; N, 10.0. $C_{44}H_{34}F_{12}N_8O_2P_2Ru$ requires C, 48.1, H, 3.1; N, 10.2%). ^1H NMR (300 MHz, CD_3CN): δ 7.29 (t, 4 H, J = 8.1, aryl $H^{3,3'}$ and $H^{5,5'}$), 7.39 (d, 2 H, J = 8.0, aryl $H^{4,4'}$), 7.72 (m, 4 H, bipy $H^{4,4'}$), 7.86 (d, 4 H, J = 8.0, aryl $H^{2,2'}$ and $H^{6,6'}$), 7.95 (m, 8 H, bipy $H^{3,3'}$ and $H^{5,5'}$), 8.21 (d, 4 H, J = 8.2, bipy $H^{6,6'}$), 8.53 (d, 4 H, J = 8.3 Hz, L^1 bipy $H^{5,5'}$ and $H^{6,6'}$), 9.51 (s, 2 H, L^1 bipy $H^{3,3'}$) and 9.86 (br s, 2 H, CONH). Mass spectrum (FAB): m/z 953 $(M - PF_6)^+$ and 404 $(M - 2PF_6)^{2+}$.

$[RuL^2(bipy)_2][PF_6]_2$. Prepared from the amide L^2 (0.110 g, 0.26 mmol) and *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$ (0.149 g, 0.29 mmol). Yield 0.174 g, 59.2% (Found: C, 46.2; H, 3.5; N, 10.3. $C_{44}H_{34}F_{12}N_8O_4P_2Ru$ requires C, 46.7; H, 3.1; N, 9.9%). ^1H NMR (500 MHz, CD_3CN): δ 6.97 (t, 2 H, J = 7.5, aryl $H^{5,5'}$), 7.01 (d, 2 H, J = 8.2, aryl $H^{6,6'}$), 7.15 (t, 2 H, J = 7.4, aryl $H^{4,4'}$), 7.79 (m, 4 H, bipy $H^{4,4'}$), 7.88 (d, 2 H, J = 6.0, aryl $H^{3,3'}$), 7.96 (m, 8 H, bipy $H^{3,3'}$ and $H^{5,5'}$), 8.10 (dd, 4 H, J = 7.9 and 1.4, bipy $H^{6,6'}$), 8.27 (br s, 2 H, CONH), 8.53 (dd, 4 H, J = 8.2 Hz, L^2 bipy $H^{5,5'}$ and $H^{6,6'}$), 9.56 (s, 2 H, L^2 bipy $H^{3,3'}$) and 9.79 (s, 2 H, aryl OH). Mass spectrum (FAB): m/z 986 $(M - PF_6)^+$ and 420 $(M - 2PF_6)^{2+}$.

$[RuL^3(bipy)_2][PF_6]_2$. Prepared from the amide L^3 (0.152 g, 0.36 mmol) and *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$ (0.204 g, 0.39 mmol).

Yield 0.250 g, 62.1% (Found: C, 46.5; H, 3.2; N, 10.0. $C_{44}H_{34}F_{12}N_8O_4P_2Ru$ requires C, 46.7; H, 3.1; N, 9.9%). ^1H NMR (500 MHz, CD_3CN): δ 6.75 (d, 2 H, J = 8.2, aryl $H^{6,6'}$), 7.12 (t, 2 H, J = 7.5, aryl $H^{5,5'}$), 7.34 (d, 2 H, J = 7.4, aryl $H^{4,4'}$), 7.73 (m, 4 H, bipy $H^{4,4'}$), 7.93 (s, 2 H, aryl $H^{2,2'}$), 7.99 (m, 8 H, bipy $H^{3,3'}$ and $H^{5,5'}$), 8.21 (dd, 4 H, J = 7.9 and 1.4, bipy $H^{6,6'}$), 8.59 (dd, 4 H, J = 8.2 Hz, L^3 bipy $H^{5,5'}$ and $H^{6,6'}$), 9.17 (br s, 2 H, CONH), 9.72 (s, 2 H, L^3 bipy $H^{3,3'}$) and 10.08 (s, 2 H, aryl OH). Mass spectrum (FAB): m/z 986 $(M - PF_6)^+$ and 420 $(M - 2PF_6)^{2+}$.

$[RuL^4(bipy)_2][PF_6]_2$. Prepared from the amide L^4 (0.134 g, 0.31 mmol) and *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$ (0.180 g, 0.35 mmol). Yield 0.234 g, 65.8% (Found: C, 47.1; H, 3.1; N, 9.5. $C_{44}H_{34}F_{12}N_8O_4P_2Ru$ requires C, 46.7; H, 3.1; N, 9.9%). ^1H NMR (500 MHz, CD_3CN): δ 6.66 (d, 4 H, J = 8.0, aryl $H^{3,3'}$ and $H^{5,5'}$), 7.29 (d, 4 H, J = 7.5, aryl $H^{2,2'}$ and $H^{6,6'}$), 7.82 (m, 4 H, bipy $H^{4,4'}$), 8.10 (m, 8 H, bipy $H^{3,3'}$ and $H^{5,5'}$), 8.35 (d, 4 H, J = 7.5 and 2.5, bipy $H^{6,6'}$), 8.41 (d, 2 H, J = 8.5, L^4 bipy $H^{6,6'}$), 8.55 (d, 2 H, J = 8.0 Hz, L^4 bipy $H^{5,5'}$), 9.03 (s, 2 H, L^4 bipy $H^{3,3'}$), 9.93 (br s, 2 H, CONH) and 10.65 (s, 2 H, aryl OH). Mass spectrum (FAB): m/z 986 $(M - PF_6)^+$ and 420 $(M - 2PF_6)^{2+}$.

$[RuL^5(bipy)_2][PF_6]_2$. Prepared from the amide L^5 (0.200 g, 0.56 mmol) and *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$ (0.323 g, 0.62 mmol). Yield 0.475 g, 80.1% (Found: C, 45.1; H, 4.0; N, 11.0. $C_{40}H_{42}F_{12}N_8O_2P_2Ru$ requires C, 45.4; H, 4.0; N, 10.6%). ^1H NMR (500 MHz, CD_3CN): δ 1.45 (s, 18 H, Bu^t), 7.09 (br s, 2 H, CONH), 7.39 (m, 4 H, bipy $H^{5,5'}$), 7.67 (dd, 2 H, J = 5.5 and 1.5, L^5 bipy $H^{5,5'}$), 7.71 (dd, 4 H, J = 8.0, bipy $H^{3,3'}$), 7.83 (d, 2 H, J = 6.5, L^5 bipy $H^{6,6'}$), 8.06 (m, 4 H, bipy $H^{4,4'}$), 8.50 (dd, 4 H, J = 8.0 and 2.5 Hz, bipy $H^{6,6'}$) and 8.96 (s, 2 H, L^5 bipy $H^{3,3'}$). Mass spectrum (FAB): m/z 913 $(M - PF_6)^+$ and 384 $(M - 2PF_6)^{2+}$.

$[RuL^6(bipy)_2][PF_6]_2$. Prepared from the amide L^6 (0.254 g, 0.50 mmol) and *cis*-$[RuCl_2(bipy)_2]\cdot 2H_2O$ (0.287 g, 0.55 mmol). Yield 0.470 g, 77.5% (Found: C, 51.7; H, 4.2; N, 9.8. $C_{52}H_{50}F_{12}N_8O_2P_2Ru$ requires C, 51.6; H, 4.2; N, 9.3%). ^1H NMR (500 MHz, CD_3CN): δ 1.29 (s, 18 H, Bu^t), 7.42 (d, 4 H, J = 8.6, aryl $H^{3,3'}$ and $H^{5,5'}$), 7.58 (m, 4 H, bipy $H^{5,5'}$), 7.70 (d, 4 H, J = 8.0, aryl $H^{2,2'}$ and $H^{6,6'}$), 7.76 (d, 2 H, J = 5.2, L^6 bipy $H^{6,6'}$), 7.80 (d, 2 H, J = 5.2, L^6 bipy $H^{5,5'}$), 7.96 (d, 4 H, J = 8.0, bipy $H^{6,6'}$), 8.20 (m, 4 H, bipy $H^{4,4'}$), 8.87 (d, 4 H, J = 8.0 Hz, bipy $H^{3,3'}$), 9.46 (br s, 2 H, CONH) and 10.72 (s, 2 H, L^6 bipy $H^{3,3'}$). Mass spectrum: (FAB): m/z 1065 $(M - PF_6)^+$ and 460 $(M - 2PF_6)^{2+}$.

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