New Alkynyl- and Vinyl-linked Benzo- and Aza-crown Ether-bipyridyl Ruthenium(II) Complexes which Spectrochemically recognize Group IA and IIA Metal Cations†

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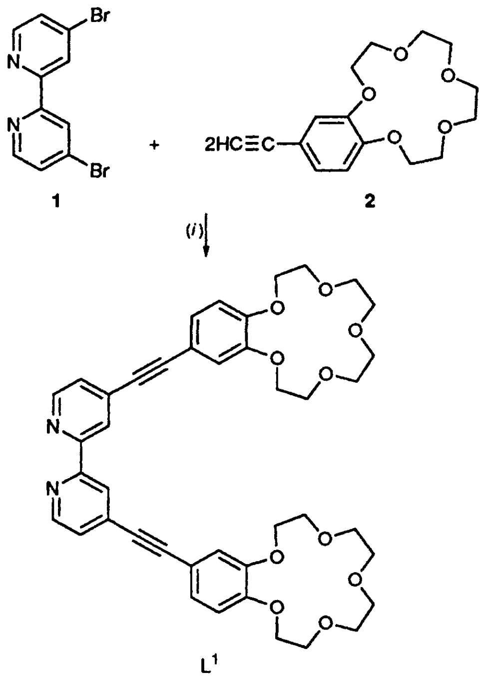
A new alkynyl-linked bis(benzo-15-crown-5) bipyridyl ligand and new mono- and bis-benzo-15-crown-5 and aza-15-crown-5 bipyridyl ligands containing *trans*-conjugated olefinic linkages between the crown ethers and the 4,4′-disubstituted 2,2′-bipyridine (bipy) moieties have been synthesised. The corresponding $[RuL(bipy)_2][PF_6]_2$ and $[RuL_3][PF_6]_2$ complexes have been prepared and the latter electropolymerized onto optically transparent conducting glass electrodes. Electronic absorption and fluorescence-emission spectroscopic measurements have demonstrated spectrochemical recognition of Group IA and IIA metal cations by the novel functionalized crown ethers both as solution complexes and as polymeric films. The λ_{max} and ε values for both the low-energy ligand-based π–π^* transition and the metal-to-ligand charge transfer band observed for the complexes are sensitive to the binding of sodium and magnesium cations. The spectral measurements further demonstrate the presence of residual unsaturated linkages in the electropolymerized films, providing a technique that could be applied to probe the mechanisms and efficiencies of such electropolymerizations.

The prospect of developing new materials of relevance to the emerging field of molecular electronics, modelling electron-transfer processes in biological systems and producing new electro- and photo-active catalysts has led in recent years to considerable interest in transition-metal polypyridyl complexes.[1–3] However, the application of these types of systems to chemical sensor technology has not been fully exploited. Rare examples include luminescent oxygen[4] and pH sensors,[5] the latter based on di(2,2′-bipyridyl)(5,5′-diaminomethyl-2,2′-bipyridyl)ruthenium(II) complexes, and the determination of copper using electrodes modified with appropriate ligands incorporated by ion exchange into electropolymerized thin films of $[Ru(mvbipy)_3]^{2+}$ (mvbipy = 4-methyl 4′-vinyl-2,2′-bipyridine).[6] This paper reports the syntheses, co-ordination and electronic absorption/fluorescence emission spectroscopy studies of new alkynyl- and vinyl-linked benzo- and aza-crown ether–bipyridyl ruthenium(II) complexes. The complexes are designed with conjugated linkages between the 2,2′-bipyridine (bipy) moiety and the macrocyclic binding sites in order to provide an efficient mechanism for recognition of Group IA and IIA metal cations by the $[Ru(bipy)_3]^{2+}$ reporter group. Furthermore, the presence of the alkynyl or vinyl linkages allows production of novel polymeric films[7] based on the general reductive electrochemical polymerization technique pioneered by Abruña *et al.*[8] A preliminary report of this work has recently appeared.[9]



Scheme 1 (*i*) $[Pd(PPh_3)_2Cl_2]$, CuI, NEt_3

Results and Discussion

Ligand Syntheses.—The reaction of 4,4′-dibromo-2,2′-bipyridine **1**[10] with 2 mol of 4-ethynylbenzo-15-crown-5 **2**[11] in the presence of $[Pd(PPh_3)_2Cl_2]$ and CuI gave L^1 in 85% yield, Scheme 1 (benzo-15-crown-5 = 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzapentaoxacyclopentadecine). Monolithiation of 4,4′-dimethyl-2,2′-bipyridine **3** using 1 equivalent of lithium diisopropylamide in tetrahydrofuran (thf) gave compound **4**[12] which on reaction with the appropriate aldehyde, 4-formylbenzo-15-crown-5, 4-formylphenylaza-15-crown-5 or 3,4-dimethoxybenzaldehyde produced the intermediate alcohol **5a**–**5c** in excellent yield. Dehydration of **5a**–**5c** using pyridinium toluene-*p*-sulfonate (ptps) in boiling toluene afforded the *trans*

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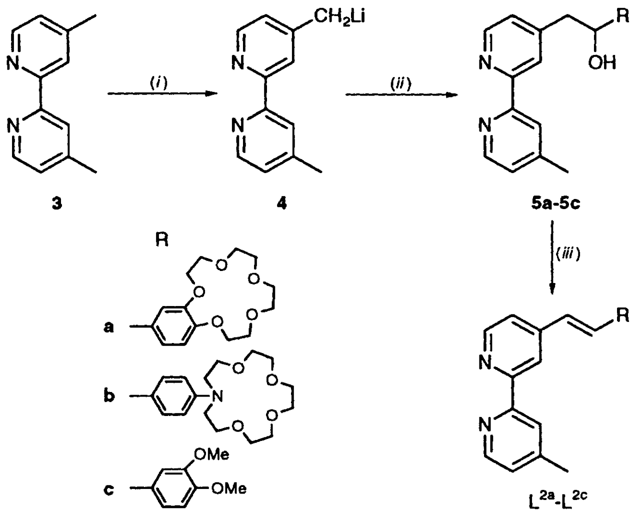
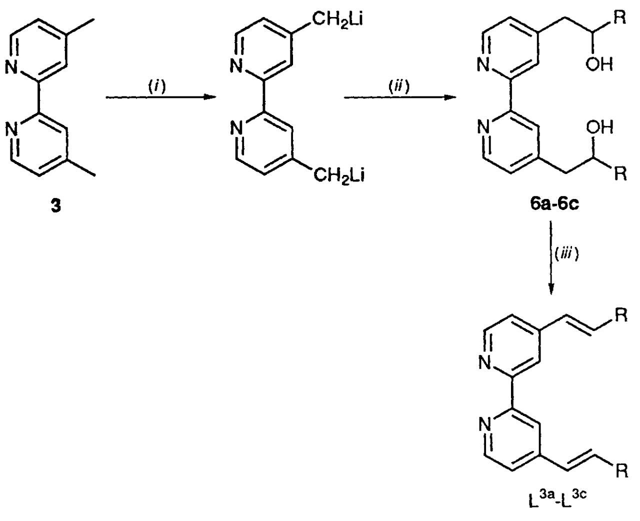
† *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.



Scheme 2 (*i*) $LiNPr^i_2$; (*ii*) RCHO; (*iii*) ptps

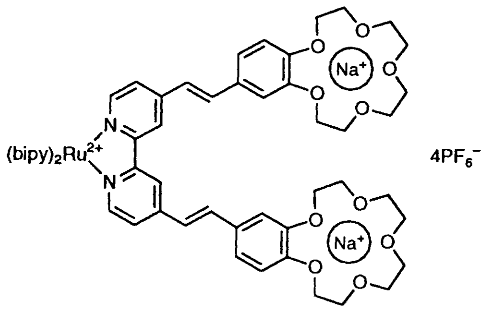


Scheme 3 R as in Scheme 2. (*i*) $2LiNPr^i_2$; (*ii*) 2RCHO; (*iii*) ptps

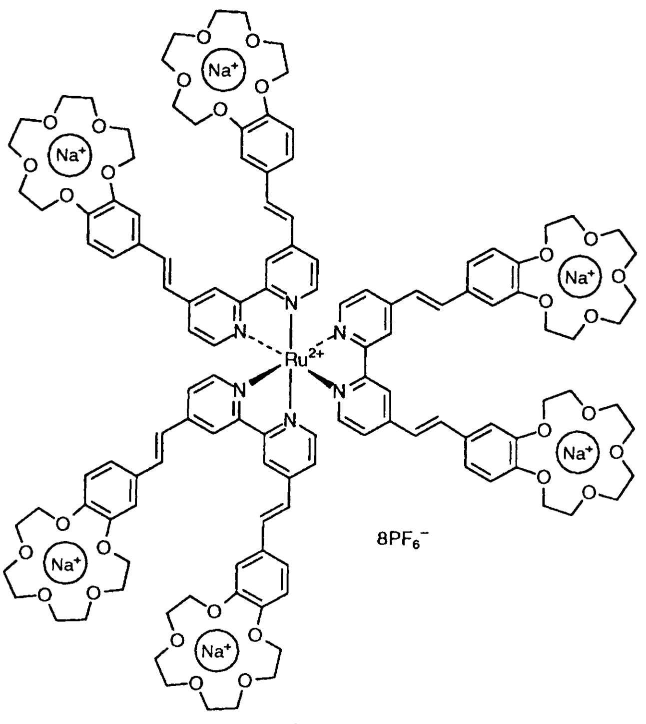
vinyl compounds L^{2a}–L^{2c} in quantitative yields, Scheme 2. Dilithiation of **3** followed by analogous synthetic procedures produced the corresponding bis *trans* vinylic ligands L^{3a}–L^{3c} in very good yields, Scheme 3. All of these new ligands were characterized using ^1H and ^{13}C NMR, mass spectrometry and elemental analysis (see Experimental section).

Co-ordination Studies.—The monoligand ruthenium(II) complexes $[RuL(bipy)_2][PF_6]_2$ and corresponding tris(ligand) ruthenium(II) complexes $[RuL_3][PF_6]_2$ ($L = L^1$–L^3) were obtained by refluxing the appropriate ligand with $[RuCl_2(bipy)_2]\cdot 2H_2O$[13] and $RuCl_3\cdot 3H_2O$, respectively in dimethylformamide (dmf), followed by purification on Sephadex LH-20 and precipitation of the complexes on addition of ammonium hexafluorophosphate. Heteropolymetallic ruthenium(II)–sodium complexes such as $[(bipy)_2RuL^{3a}Na_2][PF_6]_4$ and $[RuL^{3a}_3Na_6][PF_6]_8$ were isolated from complexation reactions of $[RuL^{3a}(bipy)_2][PF_6]_2$ and $[RuL^{3a}_3][PF_6]_2$ with excess amounts of sodium hexafluorophosphate. Subsequent solution ^{13}C NMR titration studies with these ruthenium(II) complexes and sodium perchlorate suggested the same sodium cation stoichiometries as those found in the isolated complexes in which each benzocrown ether moiety binds one sodium cation.

Electrochemical Polymerization Investigations.—We have recently shown that the $[RuL_3][PF_6]_2$ ($L = L^{2a}$–L^{2c}) complexes can be electropolymerized onto platinum to form smooth, adherent, electroactive orange films.[7,9] Fig. 1 illustrates the electropolymerization process onto optically transparent conducting glass, a substrate amenable to electronic absorption/emission spectral measurements of the polymer films. Complexes $[RuL_3][PF_6]_2$ ($L = L^{3a}$–L^{3c}) can also be electropolymerized although less efficiently (lower current increase on sequental scanning), due to steric crowding of the 4,4′ substituents, and complexes $[RuL(bipy)_2][PF_6]_2$ ($L = L^2$ or L^3) only exhibited solution redox processes analogous to the prototype $[Ru(bipy)_3][PF_6]_2$.[7,9] As for $[RuL(bipy)_2]^{2+}$ [L = 1,2-bis(4-pyridyl)acetylene],[14] the alkynyl-substituted complex $[RuL^1_3][PF_6]_2$ was successfully electropolymerized, with a higher efficiency than for the analogous vinyl-linked complex.[9] All poly-$[RuL_3]^{2+}$ ($L = L^1$–L^3) modified electrodes in complex-free supporting electrolyte revealed current for the Ru^{III}–Ru^{II} and ligand-centred redox processes.



$[(bipy)_2RuL^{3a}Na_2][PF_6]_4$



$[RuL^{3a}_3Na_6][PF_6]_8$

Electronic Absorption Spectra of the Ligands.—Electronic absorption λ_{max} and ε data for the vinyl-linked benzo- and aza-crown ether-bipyridyl ligands are contrasted with data for 4,4′-dimethyl-2,2′-bipyridine, benzo-15-crown-5, and *N*-phenyl-aza-15-crown-5 (*N*-phenyl-1,4,7,10-tetraoxa-13-azacyclopentadecane) in Table 1. The π–π*(1) and π–π*(2) transitions exhibited by L^{2a} and L^{2b} have λ_{max} values close to that of 4,4′-dimethyl-2,2′-bipyridine, with increased absorbances due to the

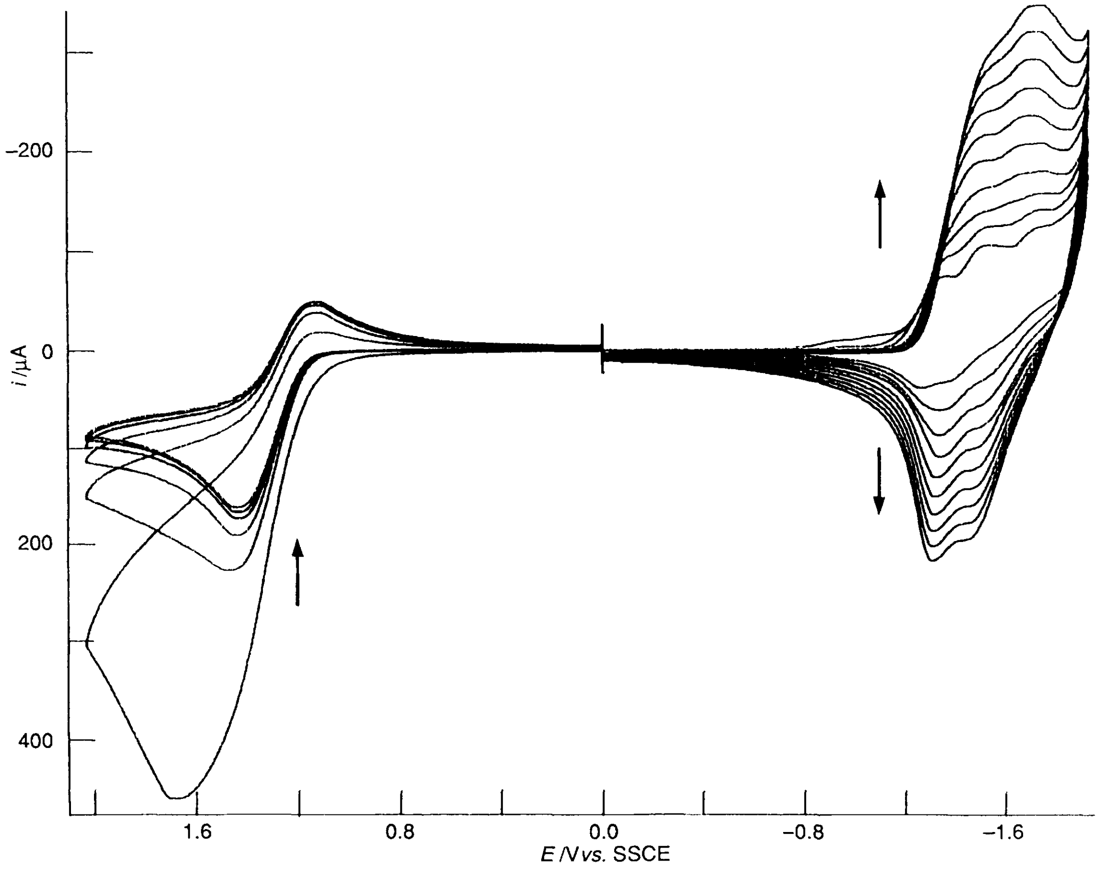


Fig. 1 Sequential cyclic voltammograms for an acetonitrile solution containing 1.33 mmol dm^{-3} [RuL$^{2a}_{3}$][PF$_6$]$_2$ in 0.1 mol dm^{-3} NBu$_4$BF$_4$ at 100 mV s^{-1} employing an optically transparent conducting glass electrode (surface area 0.3 cm^2) as working electrode. First ten cycles 0.00 ⟷ −1.90 V, with arrows indicating current increase; second six cycles 0.00 ⟷ +2.00 V, with arrows indicating current decrease. The ΔE_p values are higher than for platinum[7] due to the resistance of the conducting glass substrate. The benzo-15-crown-5 ether irreversible electrooxidation electrocatalysed by ruthenium(III) sites[7] dominates the first potential sweep from 0.00 to +2.00 V

Table 1 Electronic absorption data (298 K) in acetonitrile for the vinyl-linked benzo- and aza-crown ether-bipyridyl ligands[a] contrasted with data for related compounds

Ligand	λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})
L^{2a}	π–π*(2) 238 (2.33)
(pale yellow)	π–π*(1) 282 (2.41)
	π–π* 338 (2.96)
L^{2b}	π–π*(2) 246 (2.51)
(red)	π–π*(1) 282 (2.15)
	π–π* 380 (2.38)
L^{3a}	π–π*(2) 242 (4.23)
(pale yellow)	π–π*(1) 288 (4.08)
	π–π* 344 (6.67)
L^{3b}	π–π* 394 (4.30)
(orange)	
4,4′-Dimethyl-2,2′-bipyridine[b]	π–π*(2) 241 (0.93)
(white)	π–π*(1) 283 (1.32)
Benzo-15-crown-5	276 (0.23)
(white)	
N-Phenylaza-15-crown-5	257 (1.57)
(grey-light blue)	303 (0.24)

[a] Error in λ is ±2 nm; absorption bands below 220 nm cannot be resolved from solvent cut-off. [b] Ref. 15. Data for 4-methyl-4′-vinyl-2,2′-bipyridine would be more relevant, however none are given in the literature references to its synthesis. It has been stated that it is a white solid indicating that it does not absorb visible radiation.[12a,16]

Table 2 Substituent constants (from. ref. 19)

Substituent	σ_M	σ_p	σ_R ($=\sigma_p - \sigma_m$)
NMe$_2$	−0.21	−0.83	−0.62
OMe	0.12	−0.27	−0.39

conjugation to the benzo- or aza-15-crown-5 ethers. Comparison of ε values demonstrates that the localized benzo-or aza-15-crown-5 ether absorbance will be submerged by the bipyridine-localized π–π*(1) band. Introduction of the second vinyl-linked benzocrown ether substituent in L^{3a} induces a shift in λ_{max} to lower energy, an effect not produced on introduction of the first substituent. The π–π*(1) and π–π*(2) absorbances of L^{2a} and L^{3a} correlate with the number of substituents. Comparison of π–π*(1) and π–π*(2) transitions in L^{2b} and L^{3b} is not possible due to poor resolution of these bands in the spectrum of L^{3b} in this region. In all four ligands the extended conjugation is shown to provide an additional lower-energy intraligand π–π* band which explains their colours. The λ_{max} and ε values of this band are seen to correlate with the number of substituents. The presence of a similar low-energy intraligand π–π* band has been noted for the ligands 1,4-bis[2-(4′-methyl-2,2′-bipyridin-4-yl)-ethenyl]benzene at 360 nm[17] and 4,4′-bis[*p*-(diethylamino)-α-styryl]-2,2′-bipyridine at 394 nm.[18]

Consideration of Hammett substituent parameters (Table 2) offers an explanation for the longer λ_{max} values of the low-energy intraligand π–π* band in the azacrown ether-bipyridyl ligands as compared to the benzocrown ether-bipyridyl ligands. The NMe$_2$ substituent can be considered as a model for the phenyl substituent in *N*-phenylaza-15-crown-5 ether, and 3,4-disubstituted OMe as a model for the benzo group in benzo-15-crown-5-ether. The literature agreement between σ_{found} and the sum of the σ_m and σ_p values has been found to be satisfactory for 3,4-dimethoxy substitution (in 3-R^1-4-R^2-C$_6$H$_3$Y)[20] and hence

Table 3 Electronic absorption and emission (in bold) data (298 K) in acetonitrile (with salt present as indicated) for $[Ru(bipy)_3]^{2+}$ and the vinyl-linked benzocrown ether-bipyridyl ruthenium(II) complexes[a]

		λ_{max}/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})			
Complex	Band	None	0.002 mol dm^{-3} NBu_4ClO_4	0.001 mol dm^{-3} $NaClO_4$	0.001 mol dm^{-3} $Mg(ClO_4)_2$
$[Ru(bipy)_3]^{2+}$	π–π*(2)	243 (2.81)	243 (3.35)	244 (3.00)	243 (3.24)
	π–π*(1)	286 (9.13)	286 (10.75)	286 (10.70)	287 (10.58)
	m.l.c.t.	450 (1.56)	450 (1.83)	450 (1.90)	450 (1.80)
	{π–π*(2):π–π*(1)}	0.31:1	0.31:1	0.28:1	0.31:1
	m.l.c.t.	**605**	**605**	**605**	**605**
$[RuL^{2a}(bipy)_2]^{2+}$	π–π*(2)	245 (4.88)	244 (5.01)	244 (4.79)	244 (4.77)
	π–π*(1)	288 (9.93)	288 (10.11)	288 (10.22)	288 (10.26)
	π–π*	348 (2.76)	352 (2.70)	343 (3.21)	335 (3.98)
	m.l.c.t.	457 (2.46)	457 (2.53)	457 (2.47)	457 (2.40)
	{π–π*(2):π–π*(1)}	0.49:1	0.50:1	0.47:1	0.47:1
	m.l.c.t.	**630**	**630**	**630**	**630**
$[RuL^{3a}(bipy)_2]^{2+}$	π–π*(2)	245 (4.78)	245 (4.53)	244 (4.18)	245 (4.08)
	π–π*(1)	290 (7.63)	290 (7.57)	290 (7.46)	289 (8.04)
	π–π*	370 (4.63)	367 (4.66)	356 (4.48)	344 (4.89)
	m.l.c.t.	465 (2.67)	465 (2.69)	464 (2.47)	467 (2.24)
	{π–π*(2):π–π*(1)}	0.63:1	0.60:1	0.56:1	0.51:1
	m.l.c.t.	**659**	**659**	**658**	**657**
$[RuL^{2a}{}_3]^{2+}$	π–π*(2)	246 (6.58)	246 (5.81)	244 (7.76)	246 (7.81)
	π–π*(1)	296 (8.06)	296 (7.21)	294 (9.38)	293 (10.56)
	π–π*	366 (7.64)	364 (6.72)	356 (7.64)	345 (11.16)
	m.l.c.t.	475 (3.71)	474 (3.25)	476 (3.40)	474 (4.11)
	{π–π*(2):π–π*(1)}	0.82:1	0.81:1	0.83:1	0.74:1
	m.l.c.t.	**670**	**670**	**668**	**666**
$[RuL^{3a}{}_3]^{2+}$	π–π*(2)	246 (9.43)	248 (7.06)	245 (8.75)	237 (6.80)
	π–π*(1)	310 (11.21)	308 (8.26)	307 (11.08)	303 (9.24)
	π–π*	377 (13.43)	378 (10.48)	369 (13.47)	344 (12.70)
	m.l.c.t.	491 (4.93)	491 (4.32)	491 (5.43)	491 (3.98)
	{π–π*(2):π–π*(1)}	0.84:1	0.85:1	0.79:1	0.74:1
	m.l.c.t.	**672**	**672**	**669**	**665**

[a] Error in λ is ± 2 nm; absorption bands below 220 nm cannot be resolved from solvent cut-off.

$\Sigma\sigma = -0.15$ is applicable for the combined effect of the 3,4-disubstituted OMe. The more negative σ_R parameters for NMe_2 giving rise to a larger resonance effect therefore explains the longer λ_{max} values.

Electronic Absorption and Fluorescence Emission Spectra of the Vinyl-linked Benzocrown ether-bipyridyl Ruthenium(II) *Complexes*.—Ruthenium(II) polypyridyl complexes exhibit both intraligand and low-energy metal-to-ligand charge transfer (m.l.c.t.) bands.[1,21] Electronic absorption λ_{max} and ε data for the vinyl-linked benzocrown ether-bipyridyl ruthenium(II) complexes are summarized and contrasted with those of the prototype $[Ru(bipy)_3]^{2+}$ in Table 3. Complexation with ruthenium(II) causes all the π–π*(1) and π–π*(2) transitions to move to lower energy, a shift expected for π-conjugated systems and ascribed to the effect of the positive charge on the energy levels of bipyridine.[21] Consideration of the data for pure acetonitrile solutions reveals that absorption in the ultraviolet region is sensitive to the number of vinyl linkages in the complexes. Thus the π–π*(1) transition shifts to lower energies with an increase in the number of vinyl linkages as has been observed for the free ligands. Table 3 shows that the ratio of the ε values [π–π*(2):π–π*(1)] correlates with the number of vinyl linkages. Decrease in this ratio has been related to the consumption of vinyl groups during solution polymerization of tris(4-methyl-4′-vinyl-2,2′-bipyridine) transition-metal complexes in order to study the relationship between relative polymer size and the proportion of vinyl groups consumed.[22]

The low-energy intraligand π–π* band observed for L^{2a} (at 338 nm) and L^{3a} (at 344 nm) is also observed for the complexes, with shifts to lower energies due to the polarizing power of the ruthenium(II) centre and good correlation between ε values and the number of vinyl substituents. Examination of Table 3, with Fig. 2 as an example, reveals that the presence in solution of an excess of sodium or magnesium perchlorate shifts this band to significantly higher energies, with increases in absorbance values. Spectrochemical recognition of sodium and magnesium cations is confirmed by the absence of changes in this band for the complexes in the presence of an excess of tetrabutylammonium perchlorate. For all complexes, magnesium cations produced a larger effect, demonstrating the importance of the polarizing power of the guest metal cation in determining the magnitude of the shift to higher energies. Thus the higher charge:radius ratio of magnesium cations produces

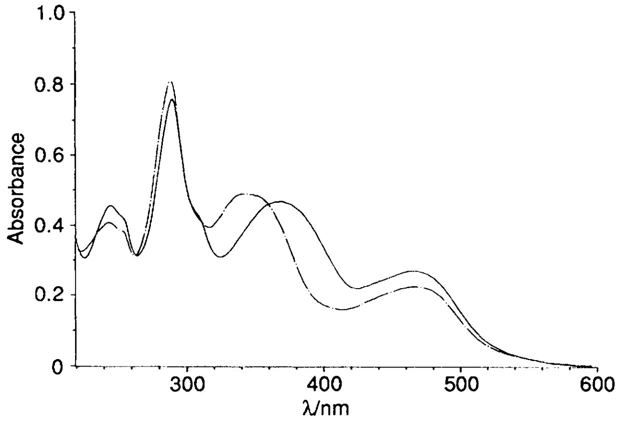


Fig. 2 Electronic absorption spectra (220–600 nm) of 0.000 01 mol dm^{-3} $[RuL^{3a}(bipy)_2][PF_6]_2$, 0.0002 mol dm^{-3} NBu_4ClO_4 (——) and 0.000 01 mol dm^{-3} $[RuL^{3a}(bipy)_2][PF_6]_2$, 0.0001 mol dm^{-3} $Mg(ClO_4)_2$ (— · —), each in acetonitrile at 298 K

Table 4 Electronic absorption and emission (in bold) data (298 K) in acetonitrile (with salt present as indicated) for $[RuL^{3c}{}_3][PF_6]_2$[a]

	λ_{max}/nm (10^{-4} ε/dm^3 mol^{-1} cm^{-1})			
Band	None	0.002 mol dm^{-3} NBu_4ClO_4	0.001 mol dm^{-3} $NaClO_4$	0.001 mol dm^{-3} $Mg(ClO_4)_2$
π–π*(2)	243 (9.42)	243 (8.36)	244 (9.32)	246 (6.42)
π–π*(1)	312 (10.21)	309 (9.45)	312 (10.54)	306 (7.64)
π–π*	349 (13.57)	351 (12.50)	348 (15.66)	376 (10.86)
m.l.c.t.	491 (3.21)	490 (3.47)	490 (2.82)	491 (3.83)
{π–π*(2) : π–π*(1)}	0.92 : 1	0.89 : 1	0.88 : 1	0.84 : 1
m.l.c.t.	**673**	**673**	**673**	**673**

[a] Error in λ is ± 2 nm; absorption bands below 220 nm cannot be resolved from solvent cut-off.

the larger effect. Interestingly, Table 4 shows that the presence of magnesium cations in a solution of the dimethoxyphenyl-containing 'model' complex $[RuL^{3c}{}_3]^{2+}$ produced an opposite effect, a shift to a lower energy with decrease in absorbance being observed.

A broad low-energy m.l.c.t. absorption band is observed for the complexes analogous to that for the prototype $[Ru(bipy)_3]^{2+}$ (λ_{max} = 450 nm) and $[Ru(mvbipy)(bipy)_2]^{2+}$ (λ_{max} = 452 nm).[12a] With an increase in the number of vinyl-linked benzocrown ethers the m.l.c.t. band of the complexes progressively shifts to lower energies, coupled with an increase in absorbance. Extended conjugation of 2,2′-bipyridine ligands is known to produce such effects such as in the literature data[23] for tris(4,4′-disubstituted-2,2′-bipyridine)ruthenium(II) complexes in EtOH–MeOH (4:1 v/v) solution at 293 K; (*i*) substituent = benzyl (λ_{max} = 460 nm, 10^{-4}ε = 1.61 dm^3 mol^{-1} cm^{-1}), (*ii*) substituent = phenyl (λ_{max} = 473 nm, 10^{-4}ε = 2.80 dm^3 mol^{-1} cm^{-1}) and (*iii*) substituent = styryl (λ_{max} = 487 nm, 10^{-4}ε = 3.30 dm^3 mol^{-1} cm^{-1}). It is of note that the m.l.c.t. band of the vinyl-linked benzocrown ether-bipyridyl ruthenium(II) complexes shows similar trends to those of the π–π*(1) band, an effect to be expected owing to the similarity in structure of the two bands.[21] Measurement of the corresponding fluorescence emission maxima of the m.l.c.t. bands offered an alternative method for assessing the effect of ligand variation and also metal–cation binding on excited-state energies. Table 3 shows that the m.l.c.t. emission maxima of the complexes progressively shift to lower energies with increase in the number of vinyl-linked benzocrown ethers, as observed for the m.l.c.t. absorption maxima. The m.l.c.t. energies have likewise been correlated to the degree of polymerization (*via* proportion of vinyl groups remaining) for the solution polymerization of tris(4-methyl-4′-vinyl-2,2′-bipyridine) transition-metal complexes.[22] The m.l.c.t. absorption and emission data for $[RuL^{3a}{}_3]^{2+}$ in pure acetonitrile correlate with those for $[RuL^{3c}{}_3]^{2+}$ (Table 4) indicating that the mesomeric/inductive effects of the benzocrown ether are controlled by the α-OCH_2 substituents, the remainder of the macrocycle having little effect. That the m.l.c.t. absorption and emission maxima move to *lower* energies with increase in the number of electron-donating substituents on the bipyridine ligands can be explained by analogy to spectral measurements on the series $[RuL_nL'_{3-n}]^{2+}$ (L = 2,2′-bipyridine, L′ = 4,4′-dimethyl-2,2′-bipyridine), where destabilization of the d–π highest occupied molecular orbital (HOMO) by the two ligands not involved as charge acceptors in the m.l.c.t. excited state is the controlling factor.[24] The addition of excess amounts of the salts, shown in Table 3, then provides evidence that in addition to spectrochemical recognition of metal cations by the low-energy intraligand π–π* absorption bands, the m.l.c.t. emission maxima of the complexes are also sensitive to metal cation binding. No corresponding shifts to higher energies are observed for the dimethoxyphenyl-containing 'model' complex $[RuL^{3c}{}_3]^{2+}$ (Table 4) or for the prototype $[Ru(bipy)_3]^{2+}$ (Table 3), suggesting that metal cation co-ordination, causing lowering of the electron-donating strength of the α-OCH_2 substituents, is responsible for this effect. That the vinyl linkage is necessary for such spectrochemical recognition is demonstrated by the similarity of the electronic absorption/emission spectra for acetonitrile solutions of $[RuL(bipy)_2]^{2+}$ and $[RuL_3]$ (L = **6a**) containing the various salts to those of $[Ru(bipy)_3]^{2+}$. Furthermore, as for $[Ru(bipy)_3]^{2+}$, the low-energy intraligand π–π* band is absent for the ruthenium(II) complexes of the alcohols. Valeur and co-workers[25,26] have recently reported similar Group IA and IIA metal cation-induced blue shifts in the emission spectra of fluorophores linked to crown ethers.

Electronic Absorption and Fluorescence-emission Spectra of the Vinyl-linked Azacrown ether-bipyridyl Ruthenium(II) *Complexes*.—Electronic absorption λ_{max} and ε data for the vinyl-linked azacrown ether-bipyridyl ruthenium(II) complexes are given in Table 5. Absorption in the ultraviolet region is sensitive to the number of vinyl-linked azacrown ethers as found for the vinyl-linked benzocrown ether-bipyridyl ruthenium(II) complexes. Thus the π–π*(1) transition decreases in energy with the number of vinyl linkages and the ratio of the ε values [π–π*(2) : π–π*(1)] correlates with the number of vinyl linkages.

The low-energy intraligand π–π* band observed for L^{2b} (at 380 nm) and L^{3b} (at 394 nm) is also observed for the complexes, with shifts to lower energies due to the polarizing power of the ruthenium(II) centre and good correlation between ε values and the number of vinyl substituents. Significant overlap between the low-energy intraligand π–π* and the m.l.c.t. bands makes assignment difficult for a number of cases. However, consideration of the data in Table 5 reveals that the presence of an excess of sodium perchlorate in solution shifts the intraligand π–π* band to significantly higher energies providing resolution of the λ_{max} from the m.l.c.t. band. Observations concerning trends in absorbance values are difficult to make because ε values will incorporate a contribution from the m.l.c.t. band. Spectrochemical recognition of sodium cations is confirmed by the absence of changes in the presence of an excess of tetrabutylammonium perchlorate. Interestingly, the trend on addition of an excess of magnesium perchlorate is to shift the intraligand π–π* band to lower energies, however it must be emphasized that the overlap of this band with the m.l.c.t. makes judgement difficult.

Table 5 shows that the m.l.c.t. band absorbance values increase with the number of vinyl-linked azacrown ethers as has been observed for the vinyl-linked benzocrown ether-bipyridyl ruthenium(II) complexes. Although difficult to assess due to overlap with the intraligand π–π* band, the m.l.c.t. emission maxima appear to shift to lower energies with increase in the number of vinyl-linked azacrown ethers. Measurement of the corresponding fluorescence emission maxima of the m.l.c.t. bands avoided the problem of overlap with the intraligand π–π* absorption band. Table 5 shows that the m.l.c.t. energies from the emission maxima do indeed progressively shift to lower energies with increase in the number of vinyl-linked azacrown ethers. Higher shifts away from the m.l.c.t. fluorescence emission

Table 5 Electronic absorption and emission (in bold) data (298 K) in acetonitrile (with salt present as indicated) for the vinyl-linked azacrown ether-bipyridyl ruthenium(II) complexes[a]

		λ_{max}/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})			
Complex	Band	None	0.002 mol dm^{-3} NBu_4ClO_4	0.001 mol dm^{-3} $NaClO_4$	0.001 mol dm^{-3} $Mg(ClO_4)_2$
$[RuL^{2b}(bipy)_2]^{2+}$	$\pi-\pi^*(2)$	246 (4.01)	246 (4.06)	245 (4.24)	247 (3.91)
	$\pi-\pi^*(1)$	288 (7.28)	288 (7.37)	289 (7.42)	288 (7.37)
	$\pi-\pi^*$	not resolved	not resolved	not resolved	not resolved
	m.l.c.t.	464 (2.66)	464 (2.66)	458 (2.21)	460 (2.86)
	$\{\pi-\pi^*(2):\pi-\pi^*(1)\}$	0.55:1	0.55:1	0.57:1	0.53:1
	m.l.c.t.	**620**	**620**	**610**	**620**
$[RuL^{3b}(bipy)_2]^{2+}$	$\pi-\pi^*(2)$	246 (4.95)	247 (4.94)	246 (4.94)	246 (4.94)
	$\pi-\pi^*(1)$	289 (7.33)	289 (7.19)	290 (8.02)	289 (7.48)
	$\pi-\pi^*$	406 (5.61)	404 (5.69)	379 (4.97)	437 (5.86)
	m.l.c.t.	450 (5.31)	*449 (5.41)*	not resolved	not resolved
	$\{\pi-\pi^*(2):\pi-\pi^*(1)\}$	0.68:1	0.69:1	0.66:1	0.66:1
	m.l.c.t.	**686**	**686**	**670**	**683**
$[RuL^{2b}{}_3]^{2+}$	$\pi-\pi^*(2)$	254 (6.25)	254 (6.29)	252 (6.27)	255 (6.63)
	$\pi-\pi^*(1)$	297 (6.25)	294 (6.67)	297 (6.67)	299 (7.34)
	$\pi-\pi^*$	*438 (6.71)*	*430 (6.95)*	400 (5.47)	431 (6.45)
	m.l.c.t.	466 (6.88)	466 (7.01)	453 (5.02)	459 (6.28)
	$\{\pi-\pi^*(2):\pi-\pi^*(1)\}$	1.00:1	0.94:1	0.94:1	0.90:1
	m.l.c.t.	**691**	**691**	**677**[b]	**689**
$[RuL^{3b}{}_3]^{2+}$	$\pi-\pi^*(2)$	254 (9.21)	251 (5.44)	248 (7.70)	256 (9.30)
	$\pi-\pi^*(1)$	314 (7.73)	315 (5.02)	313 (8.70)	314 (8.90)
	$\pi-\pi^*$	400 (15.63)	399 (7.60)	378 (9.90)	428 (17.60)
	m.l.c.t.	*477 (9.95)*	not resolved	not resolved	not resolved
	$\{\pi-\pi^*(2):\pi-\pi^*(1)\}$	1.19:1	1.08:1	0.89:1	1.05:1
	m.l.c.t.	**696**	**696**	**682**[c]	**694**

[a] Error in λ is ± 2 nm; absorption bands below 220 nm cannot be resolved from solvent cut-off. For italicized data peaks are broad and error in λ is ± 10 nm. [b] A separate experiment with addition of lithium perchlorate to 0.001 mol dm^{-3} yielded a value of 683 nm. [c] A separate experiment with addition of lithium perchlorate to 0.001 mol dm^{-3} yielded a value of 686 nm.

maximum of the prototype $[Ru(bipy)_3]^{2+}$ are observed for the vinyl-linked azacrown ether-bipyridyl ruthenium(II) complexes than for the vinyl-linked benzocrown ether-bipyridyl ruthenium(II) complexes. The more negative σ_R value of the aza-15-crown-5 ether that has been suggested above will again be the reason for the greater effect. Addition of excess amounts of the salts (data in Table 5) also shows that in addition to spectrochemical recognition of sodium cations by the low-energy intraligand π–π* absorption bands, the m.l.c.t. emission maxima of the complexes are sensitive to binding of sodium and magnesium cations. Binding of metal cations in the azacrown ethers will prevent electron donation to the phenyl group, thus producing a shift of the m.l.c.t. band back to higher energies. This effect will again be greater for the aza-15-crown-5-ether.

Fluorescence-emission Quenching.—A further feature of the m.l.c.t. spectra is that emission intensities are lower for the complexes in comparison to $[Ru(bipy)_3]^{2+}$. A likely mechanism for such fluorescence quenching is photoinduced electron transfer (p.e.t.) from the benzocrown ether or azacrown ether to the excited $[Ru(bipy)_3]^{2+}$ moiety.[5,27] This mechanism is particularly favourable for the azacrown ether complexes. For 1 mmol dm^{-3} $[RuL^{2b}(bipy)_2]^{2+}$ in 0.1 mol dm^{-3} NBu_4BF_4–acetonitrile we have measured E_{ox}(azacrown ether) = +0.72 V and $E_{red}[RuL^{2b}(bipy)_2{}^{2+}]$ = −1.36 V by cyclic voltammetry. A value of −0.14 eV for the Gibbs free energy of the electron transfer, ΔG(e.t.), is obtained from the Weller equation[5,28] using 2.12 eV[1] {the value for $[Ru(bipy)_3]^{2+}$} as the excited state energy, E_s, of the complex and 0.1 eV as the ion-pairing energy, $E_{i.p}$; ΔG(e.t.)/eV = $-E_s + E_{ox}$(azacrown ether) − $E_{red}[RuL^{2b}(bipy)_2{}^{2+}] - E_{i.p}$). Fig. 3 illustrates the retrieval of the fluorescence intensity on addition of sodium perchlorate to a solution of $[RuL^{3b}(bipy)_2]^{2+}$. The binding of sodium cations by the azacrown ether will induce an anodic shift in E_{ox}(azacrown ether), thereby making p.e.t. less favourable.

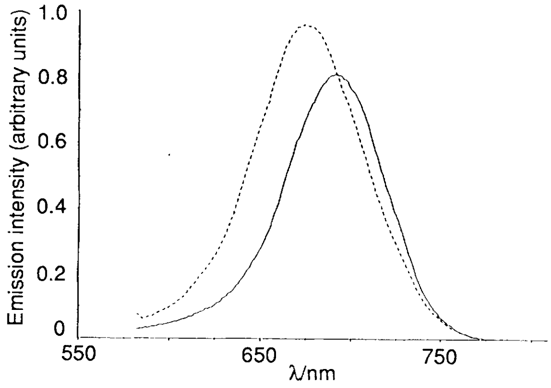


Fig. 3 Fluorescence-emission spectrum (——) of 0.0001 mol dm^{-3} $[RuL^{3b}(bipy)_2][PF_6]_2$ in acetonitrile at 298 K. The broken line shows the emission spectrum after addition of an excess of Na^+ (as $NaClO_4$–acetonitrile solution). Excitation wavelength = 550 nm

Electronic Absorption and Fluorescence-emission Spectra of the Polymeric vinyl-linked Benzocrown ether-bipyridyl Ruthenium(II) *Complexes*.—To investigate the nature of the electropolymerized crown ether polymer films prepared above the absorption spectrum of poly-$[RuL^{2a}{}_3]^{2+}$ on an optically transparent conducting glass electrode was obtained. In addition to exhibiting a m.l.c.t. band (470 nm) corresponding to that of the monomeric precursor $[RuL^{2a}{}_3]^{2+}$ (475 nm), an absorption maximum corresponding to the low-energy intraligand π–π* transition in the monomer (366 nm) is observed (360 nm). The presence of a band at similar wavelength for the polymer shows that not all the vinyl groups are removed by the electropolymerization process and also that the benzocrown ether remains attached after polymerization. As for the monomeric complex, the ligand-centred absorption band and the m.l.c.t. emission maximum of the polymer was

Table 6 Electronic absorption and emission (in bold) data (298 K) in acetonitrile (with salt present as indicated) for the alkynyl-linked bipyridyl ruthenium(II) complexes[a]

		λ_{max}/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})			
Complex	Band	None	0.002 mol dm^{-3} NBu_4ClO_4	0.001 mol dm^{-3} $NaClO_4$	0.001 mol dm^{-3} $Mg(ClO_4)_2$
$[RuL^1(bipy)_2]^{2+}$	π–π*(2)	244 (5.62)	244 (5.79)	244 (7.03)	244 (6.50)
	π–π*(1)	288 (10.95)	288 (10.93)	288 (14.01)	288 (12.01)
	π–π*	350 (3.39)	350 (3.46)	344 (4.64)	338 (4.45)
	m.l.c.t.	456 (2.27)	456 (2.28)	456 (2.78)	458 (2.33)
	{π–π*(2):π–π*(1)}	0.51:1	0.53:1	0.50:1	0.54:1
	m.l.c.t.	**635**	**638**	**640**	**641**
$[RuL^1_3]^{2+}$	π–π*(2)	250 (11.96)	250 (11.25)	250 (10.81)	252 (10.63)
	π–π*(1)	308 (12.51)	308 (11.83)	300 (11.67)	296 (11.65)
	π–π*	348 (11.06)	348 (10.55)	344 (12.12)	338 (13.82)
	m.l.c.t.	486 (2.94)	484 (2.93)	vbr[b]	vbr[b]
	{π–π*(2):π–π*(1)}	0.96:1	0.95:1	0.93:1	0.92:1
	m.l.c.t.	**636**	**635**	**635**	**636**

[a] Error in λ is ± 2 nm; absorption bands below 220 nm cannot be resolved from solvent cut-off. [b] Peaks are broad and error in λ is ± 10 nm.

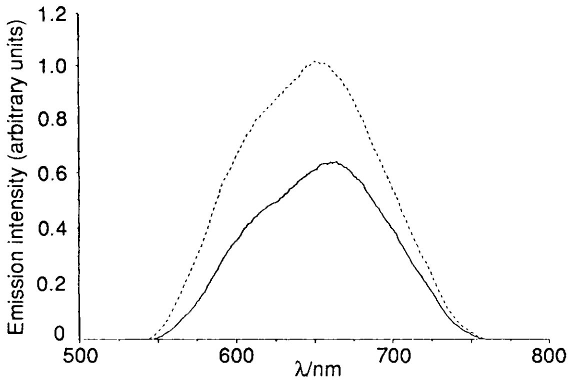


Fig. 4 Fluorescence-emission spectrum (——) of a film of poly-$[RuL^{2a}_3]^{2+}$ coated onto an optically transparent conducting glass electrode in acetonitrile at 298 K. The broken line shows the emission spectrum after addition of an excess of Mg^{2+} [as $Mg(ClO_4)_2$–acetonitrile solution]. Excitation wavelength = 450 nm

shifted to higher energies in the presence of Group IA/IIA metal cations (Fig. 4). Further confirmation of the retention of the crown ether moiety in the polymer came from the absorption and emission spectra of poly-$[RuL^{2c}_3]^{2+}$ containing no crown ether groups which displayed no shifts with Group IA/IIA metal cations.

Electronic Absorption and Fluorescence-emission Spectra of the Alkynyl-linked Benzocrown ether-bipyridyl Ruthenium(II) *Complexes.*—Electronic absorption λ_{max} and ε data for the alkynyl-linked benzocrown ether-bipyridyl ruthenium(II) complexes are given in Table 6. Absorption in the ultraviolet region is sensitive to the number of alkynyl-linked benzocrown ethers as found for the vinyl-linked ruthenium(II) complexes. Both the π–π*(1) and π–π*(2) transitions decrease in energy with the number of alkynyl linkages and the ratio of the ε values [π–π*(2):π–π*(1)] correlates with the number of alkynyl linkages.

The low-energy intraligand π–π* band observed for the vinyl-linked ruthenium(II) complexes is also present, with an increase in the ε value from the mono to the tris complex. Presence of an excess of sodium or magnesium perchlorate in solution shifts the intraligand π–π* band to significantly higher energies. Spectrochemical recognition of sodium and magnesium cations is confirmed by the absence of changes in the presence of an excess of tetrabutylammonium perchlorate.

On going from the mono to the tris complex the m.l.c.t. band absorbance increases, with a shift to lower energy. A similar trend is not observed for the fluorescence-emission maxima of the m.l.c.t. bands. The shifts away from the m.l.c.t. fluorescence-emission maximum of the prototype $[Ru(bipy)_3]^{2+}$ are observed to be lower for the alkynyl- than for the vinyl-linked ruthenium(II) complexes {contrast the values in pure acetonitrile for $[RuL^1_3]^{2+}$ (636 nm) with $[RuL^{3a}_3]^{2+}$ (672 nm) and $[RuL^{3b}_3]^{2+}$ (696 nm)}. This observation is correlated by the effect of unsaturated groups on the ultraviolet absorption bands of benzene, the effect of the ethynyl group being less than that of a vinyl group.[29] Addition of excess amounts of the salts (data in Table 6) shows that, unlike the low-energy intraligand π–π* absorption bands, the m.l.c.t. emission maxima of the complexes are not sensitive to binding of sodium and magnesium cations.

Conclusion

Electronic absorption and fluorescence-emission measurements have demonstrated spectrochemical recognition of Group IA/IIA metal cations by the novel functionalized crown ethers both as solution complexes and as polymeric films. Thus the λ_{max} and ε values for the low-energy ligand-based π–π* transition observed in the $[RuL(bipy)_2]^{2+}$ and $[RuL_3]^{2+}$ ($L = L^1$, L^{2a}, L^{2b}, L^{3a} or L^{3b}) complexes are sensitive to the binding of sodium and magnesium cations. These spectral observations corroborate recent electrochemical studies[7] where we have shown that the benzo-15-crown-5 ether units of the solution $[RuL(bipy)_2]^{2+}$ ($L = L^{2a}$ or L^{3a}) complexes are more difficult to electrooxidize on binding of sodium or magnesium cations. The spectroscopic results further demonstrate that the λ_{max} and ε values of the m.l.c.t. band of the vinyl-linked ruthenium(II) complexes are also sensitive to binding of sodium and magnesium cations. By contrast, the metal-based Ru^{III}–Ru^{II} redox potentials for benzo-15-crown-5 ether-containing complexes both in solution and as polymer films had been shown not to be perturbed by changes in the supporting electrolyte.[7] The spectral measurements demonstrated the presence of residual unsaturated linkages in the electropolymerized films, providing a technique that could be applied to probe the mechanisms and efficiencies of such electropolymerizations.

Experimental

Melting points were recorded on a Gallenkamp apparatus in open capillaries and are uncorrected. Mass spectra (electron impact and fast atom bombardment) were obtained on a Kratos MS80 RF instrument and also at the SERC mass spectrometry service, University College Swansea. Infrared spectra were recorded on a Perkin Elmer 297 instrument (4000–600 cm^{-1}). Solid samples were run in the form of KBr discs or as a Nujol mull and liquid samples neat between NaCl plates. Nuclear magnetic resonance spectra were obtained on JEOL FX90Q, GX270 and Bruker WH400 (University of Warwick) instruments using tetramethylsilane as an internal standard.

Electrochemical studies were performed using an EG & G Princeton Applied Research model 273 potentiostat. A three-electrode system was employed with platinum flag or indium–tin oxide optically transparent glass (30 Ω 'per square' from Balzers) working electrodes and a platinum-mesh counter electrode. Electrode potentials were measured and are quoted with respect to a Radiometer sodium chloride saturated calomel electrode (SSCE) at 22 ± 2 °C. No *iR* compensation was employed. Both counter and reference electrodes were separated from the working-electrode compartment of the electrochemical cell by glass frits. Measurements were carried out in deoxygenated acetonitrile solutions containing 0.1 mol dm^{-3} supporting electrolyte. Platinum working electrodes were pretreated before an investigation of a given complex by immersion in concentrated sulfuric acid:anodization, then cathodization (1 min each at 50 mA in 0.5 mol dm^{-3} sulfuric acid) followed by washing with deionized water, then acetonitrile and finally drying in air.

A Perkin Elmer model 3000 fluorescence spectrophotometer controlled by an Elonex 386 computer was used for recording the uncorrected fluorescence-emission spectra. Interference filters provided either 450 or 550 nm excitation wavelengths [the latter for the vinyl-linked azacrown ether-bipyridyl ruthenium(II) complexes owing to overlap of the m.l.c.t. and the low-energy intraligand π–π^* bands], with an absorption filter being used to cut off radiation below 490 nm reaching the emission monochromator. The Perkin Elmer front-surface accessory (5212–3130) was used for measurements on the polymer films. A Hewlett-Packard HP 8451A diode-array spectrophotometer controlled by a Vectra QS/16S computer was employed for recording the electronic absorption spectra. All spectral measurements were conducted at 25 °C using a 1 × 1 cm rectangular quartz cuvette and deoxygenated solutions. Data reported are for 0.000 01 mol dm^{-3} solutions, Beer's law being found to apply for the range tested, 0.000 0025–0.000 02 mol dm^{-3}.

Materials.—Where necessary, solvents were purified prior to use and stored under nitrogen. Tetrahydrofuran and toluene were distilled from sodium using benzophenone as indicator, diisopropylamine, triethylamine and acetonitrile from calcium hydride. All other solvents employed were of reagent grade. Unless stated to the contrary, commercial grade chemicals were used without further purification. The following compounds were prepared according to literature procedures: 4,4′-dibromo-2,2′-bipyridine **1**,[10] 4-ethynylbenzo-15-crown-5 **2**,[11] 4-formylbenzo-15-crown-5,[30] 4-formylphenylaza-15-crown-5[31] and $[RuCl_2(bipy)_2]\cdot 2H_2O$.[13]

Syntheses.—4,4′-*Bis*(2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxaethynylcyclopentadecin*-15-*yl*)-2,2′-*bipyridine* (L^1). A deaerated and stirred mixture of 4,4′-dibromo-2,2′-bipyridine **1** (1.0 g, 3.2 mmol), 4′-ethynylbenzo-15-crown-5 (2.0 g, 6.86 mmol), bis(triphenylphosphine)palladium(II) chloride (96 mg, 0.14 mmol), copper(I) iodide (52 mg, 0.27 mmol) in dry thf (45 cm^3) and triethylamine (15 cm^3) was heated at 65 °C for 4 h and then at room temperature overnight, under N_2. The solvent was removed *in vacuo* and the resulting residue was dissolved in chloroform, washed with water, dried ($MgSO_4$), the solvent removed *in vacuo* and the crude product purified by flash column chromatography (FCC) [silica gel, eluent CH_2Cl_2–MeOH–NH_4OH (100:8:1.5)] to yield 4-bromo-4′-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylethynyl)-2,2′-bipyridine (0.20 g, 12%), m.p. 142 °C (CH_2Cl_2–MeOH) (Found: C, 59.6; H, 4.6; N, 5.4. $C_{26}H_{25}BrN_2O_5$ requires C, 59.45; H, 4.80; N, 5.35%); ν_{max}(KBr) 2200 (C≡C) cm^{-1}; δ_H(270 MHz, $CDCl_3$) 3.77 (s, 8 H, OCH_2), 3.91–3.94 (m, 4 H, OCH_2), 4.15–4.18 (m, 4 H, OCH_2 bonded to benzo), 6.82–7.18 (m, 3 H, benzo H), 7.39 (d, 1 H, *J* 4.9, $H^{5'}$ of bipy), 7.50 (d, 1 H, *J* 5.0 Hz, H^5 of bipy), 8.49 and 8.51 (s, 2 H, $H^{3,3'}$ of bipy) and 8.62–8.65 (m, 2 H, $H^{6,6'}$ of bipy); *m/z* 524 (M^+, 4), 526 (M + 2, 4), 395 (5), 366 (21), 257 (13), 236 (18), 200 (12), 152 (18), 129 (24), 111 (35), 98 (85) and 55 (100%). A second fraction, after recrystallization from CH_2Cl_2–MeOH, gave L^1 (2.0 g, 85%), m.p. 224–225 °C (Found: C, 67.7; H, 6.4; N, 3.7. $C_{42}H_{44}N_2O_{10}\cdot 0.5H_2O$ requires C, 67.65; H, 6.10; N, 3.75%); ν_{max}(KBr) 2200 (C≡C) cm^{-1}; δ_H(270 MHz, $CDCl_3$) 3.78 (s, 16 H, OCH_2), 3.92–3.95 (m, 8 H, OCH_2), 4.16–4.18 (m, 8 H, OCH_2), 6.83–7.18 (m, 6 H, benzo H), 7.39 (d, 2 H, *J* 4.9, $H^{5,5'}$ of bipy), 8.51 (s, 2 H, $H^{3,3'}$ of bipy) and 8.66 (d, 2 H, *J* 4.9 Hz, $H^{6,6'}$ of bipy); δ_C(67.8 MHz, $CDCl_3$) 155.46, 150.41, 149.11, 148.74, 132.92, 125.93, 125.31, 123.17, 116.97, 114.57, 113.27, 94.67, 85.86, 71.16, 70.42, 70.40, 69.42, 69.40, 68.97 and 68.76; *m/z* (FAB) 737 ($M + H^+$, 8), 307 (8), 289 (7), 154 (100), 89 (49) and 77 (57%).

Alcohols **5a**–**5c**. *n*-Butyllithium (17.5 cm^3, 28.0 mmol) in hexane was added to a solution of diisopropylamine (4.0 cm^3, 28.5 mmol) in dry thf (130 cm^3) at −77 °C, under N_2. The pale yellow solution was stirred at −77 °C for 30 min and then a solution of 4,4′-dimethyl-2,2′-bipyridine **3** (5.0 g, 27.0 mmol) in dry thf (150 cm^3) was added *via* a dropping funnel to produce a dark orange-red solution. The acetone–solid CO_2 bath was replaced with an ice–water bath and the mixture was stirred at 0 °C for 1 h; then a solution of the appropriate aldehyde (30.0 mmol) in dry thf (30 cm^3) was added in one portion *via* a syringe. Stirring was continued at 0 °C for 1 h and then at ambient temperature. The reaction was quenched with methanol (3 cm^3), poured into water, and extracted with several portions of chloroform. The combined extracts were washed with brine, dried over $MgSO_4$, and the solvent removed *in vacuo*. The crude product was purified by crystallization or subjected to FCC using the column material and solvents specified.

4-[2-*Hydroxy*-2-(2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecan*-15-*yl*)*ethyl*]-4′-*methyl*-2,2′-*bipyridine* **5a**. FCC [silica gel, eluent CH_2Cl_2–MeOH–NH_4OH (100:10:2)], yield 76%, yellow viscous oil [Found (compound +0.5 H_2O): C, 66.0; H, 6.7; N, 5.4. $C_{27}H_{32}N_2O_6$ requires C, 67.45; H, 6.70; N, 5.85%]; δ_H(270 MHz, $CDCl_3$) 2.40 (s, 3 H, CH_3), 2.94–3.11 (m, 2 H, CH_2 of Et), 3.60 (br s, 1 H, OH), 3.72 (s, 8 H, OCH_2), 3.82–3.88 (m, 4 H, OCH_2), 4.02–4.08 (m, 4 H, OCH_2), 4.89 (t, *J* 7.9, 1 H, CHOH), 6.73–6.85 (m, 3 H, benzo H), 7.02 (d, 1 H, *J* 5.0, $H^{5'}$ of bipy), 7.09 (d, 1 H, *J* 4.9, H^5 of bipy), 8.17 (s, 1 H, $H^{3'}$ of bipy), 8.24 (s, 1 H, H^3 of bipy), 8.43 (d, 1 H, *J* 5.3, $H^{6'}$ of bipy) and 8.45 (d, 1 H, *J* 5.4 Hz, H^6 of bipy); *m/z* 480 (M^+, 9), 462 (3), 296 (74), 183 (100), 169 (29), 163 (91), 149 (60), 143 (16), 137 (15) and 91 (15%).

4-[2-*Hydroxy*-2-(p-1,4,7,10-*tetraoxa*-13-*azacyclopentadecan*-13-*ylphenyl*)*ethyl*]-4′-*methyl*-2,2′-*bipyridine* **5b**. FCC [silica gel, eluent CH_2Cl_2–MeOH–NH_4OH (100:5:1)], yield 53%, yellow viscous oil (Found: (compound +0.5 H_2O): C, 67.3; H, 7.5; N, 8.1. $C_{29}H_{37}N_3O_5$ requires C, 68.60; H, 7.35; N, 8.30%); δ_H(270 MHz, $CDCl_3$) 2.19 (s, 1 H, OH), 2.43 (s, 3 H, CH_3), 3.06–3.12 (m, 2 H, CH_2 of Et), 3.56–3.77 (m, 20 H, CH_2O and CH_2N), 4.91 (t, 1 H, CHOH), 6.61, 6.64, 7.20, 7.23 (AB, 4 H, phenyl H), 7.12 (d, 1 H, *J* 5, $H^{5'}$ of bipy), 7.14 (d, 1 H, *J* 5, H^5 of bipy), 8.21 (s, 1 H, $H^{3'}$ of bipy), 8.30 (s, 1 H, H^3 of bipy), 8.52 (d, 1 H, *J* 5.3, $H^{6'}$ of bipy) and 8.54 (d, 1 H, *J* 5.3 Hz, H^6 of bipy); *m/z* (FAB) 508 ($M + H^+$, 72), 490 (29), 460 (6), 391 (4), 324 (25), 273 (10), 242 (5), 213 (6), 185 (100) and 165 (17%).

4-[2-(3,4-*Dimethoxyphenyl*)-2-*hydroxyethyl*]-4′-*methyl*-2,2′-*bipyridine* **5c**. FCC [alumina, eluent $CHCl_3$–MeOH (100:2)], yield 95%, m.p. 79–81 °C (Found: C, 72.3: H, 6.6; N, 7.7. $C_{21}H_{22}N_2O_3$ requires C, 72.00; H, 6.35; N, 8.00%); δ_H(270 MHz, $CDCl_3$) 2.40 (s, 3 H, CH_3), 3.02–3.07 (m, 2 H, CH_2 of Et), 3.50 (br s, 1 H, OH), 3.82 and 3.84 (s, 6 H, OCH_3), 4.93 (t, 1 H, CHOH), 6.76–6.88 (m, 3 H, phenyl H), 7.05 (d, 1 H, J 5.1, H^5 of bipy), 7.09 (d, 1 H, J 4.9, H^5 of bipy), 8.16 (s, 1 H, H$^{3'}$ of bipy), 8.25 (s, 1 H, H^3 of bipy), 8.41 (d, J 4.9, H$^{6'}$ of bipy) and 8.46 (d, 1 H, J 5.1 Hz, H^6 of bipy); m/z 350 (M^+, 7), 332 (19), 184 (100), 168 (57), 166 (26), 152 (14), 139 (16), 85 (38) and 83 (58%).

Diols **6a–6c**. To a solution of diisopropylamine (5.0 cm^3, 35.7 mmol) in dry thf (30 cm^3) at −77 °C, under nitrogen, was added 1.6 mol dm^{-3} LiBu^n in hexane (22 cm^3, 35.0 mmol). The pale yellow solution was stirred at −77 °C for 45 min and a solution of compound **3** (2.5 g, 13.5 mmol) in dry thf (75 cm^3) was added dropwise to produce a dark orange-red solution. On warming to 0 °C the mixture became bright orange and was stirred for 1 h before the appropriate aldehyde (27 mmol) in thf (40 cm^3) was added over a 5 min period. The mixture was stirred at 0 °C for 1 h and then for 5 h at room temperature. It was quenched with MeOH (2.5 cm^3), poured into water (170 cm^3) and extracted with CHCl$_3$ (3 × 100 cm^3). The combined extracts were washed with water, brine, dried (MgSO$_4$) and concentrated *in vacuo* to give the crude product which was purified by FCC.

4,4′-*Bis*[2-*hydroxy*-2-(2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*-15-*yl*)*ethyl*]-2,2′-*bipyridine* **6a**. FCC [silica gel, eluent CH$_2$Cl$_2$–MeOH–NH$_4$OH (100:10:2)], yield 7.3 g (70%), m.p. 180–181 °C (EtOH–CH$_2$Cl$_2$) (Found: C, 63.4; H, 6.6; N, 3.7. C$_{42}$H$_{52}$N$_2$O$_{12}$·H$_2$O requires C, 63.45; H, 6.85; N, 3.50%); δ_H[270 MHz, (CD$_3$)$_2$SO] 2.95–2.97 (m, 4 H, CH$_2$), 3.60 (br s, 16 H, OCH$_2$), 3.74 (br s, 8 H, OCH$_2$), 4.01 (br s, 8 H, OCH$_2$), 3.74 (br s, 8 H, OCH$_2$), 4.01 (br s, 8 H, OCH$_2$), 4.78 (m, 2 H, CH), 5.32 (d, 2 H, J 4.7, OH), 6.86 (s, 4 H, benzo H), 6.98 (s, 2 H, benzo H), 7.24 (d, 2 H, J 5.0, H$^{5,5'}$ of bipy), 8.25 (s, 2 H, H$^{3,3'}$ of bipy) and 8.51 (d, 2 H, J 5.0 Hz, H$^{6,6'}$ of bipy); m/z (FAB) 815 (M + K$^+$), 799 (M + Na$^+$), 777 (M + H$^+$) other major fragmentations at 758, 479, 349, 297 and 185.

4,4′-*Bis*[2-*hydroxy*-2-p-(1,4,7,10-*tetraoxa*-13-*azacyclopentadecan*-13-*ylphenyl*)*ethyl*]-2,2′-*bipyridine* **6b**. FCC [silica gel, eluent CH$_2$Cl$_2$–MeOH–NH$_4$OH (100:5:1)], yield 58% (Found: C, 64.5; H, 7.3; N, 6.6. C$_{46}$H$_{62}$N$_4$O$_{10}$·1.5H$_2$O requires C, 64.40; H, 7.65; N, 6.55%); δ_H(270 MHz, CDCl$_3$) 2.22 (br s, 2 H, OH), 3.0–3.17 (m, 4 H, CH$_2$), 3.56–3.77 (m, 40 H, OCH$_2$ and NCH$_2$), 4.88–4.93 (m, 2 H, CH), 6.61, 6.64, 7.20, 7.23 (AB, 8 H, phenyl H), 7.14 (d, 2 H, J 5 H$^{5,5'}$ of bipy), 8.29 (s, 2 H, H$^{3,3'}$ of bipy) and 8.53 (d, 2 H, J 5 Hz, H$^{6,6'}$ of bipy); m/z (FAB) 854 (M + Na$^+$), 831 (M + H$^+$), other major fragmentations at 814, 490, 324, 220, 206 and 185.

4,4′-*Bis*[2-(3,4-*Dimethoxyphenyl*)-2-*hydroxyethyl*]-2,2′-*bipyridine* **6c**. FCC [alumina, eluent CH$_2$Cl$_2$–MeOH (100:2)], yield 82%, m.p. 174–175 °C (toluene–MeOH) (Found: C, 69.5; H, 6.3; N, 5.1. C$_{30}$H$_{32}$N$_2$O$_6$ requires C, 69.75; H, 6.25; N, 5.40%); δ_H[270 MHz, (CD$_3$)$_2$SO] 2.95–2.98 (m, 4 H, CH$_2$), 3.72 (s, 6 H, OCH$_3$), 3.73 (s, 6 H, OCH$_3$), 4.80 (m, 2 H, CH), 5.33 (d, 2 H, J 4.7, OH), 6.88 (s, 4 H, phenyl H), 7.00 (d, 2 H, J 5, H$^{5,5'}$ of bipy), 8.30 (s, 2 H, H$^{3,3'}$ of bipy) and 8.52 (d, 2 H, J 5 Hz, H$^{6,6'}$ of bipy); m/z (FAB) 517 (M + H$^+$), other major fragmentations at 499, 350, 333, 213 and 185.

(E)-*Alkenes* L^2 *and* (E,E)-*dienes* L^3. A mixture of the appropriate alcohol (5 mmol) or diol (2.5 mmol), pyridinium toluene-*p*-sulfonate (1 mmol), and dry toluene (160 cm^3) was refluxed overnight using a Dean–Stark trap, then cooled to room temperature and the toluene removed *in vacuo*. The residue was dissolved in CHCl$_3$, washed with water, brine and dried (MgSO$_4$). The solvent was removed *in vacuo* to give the crude product which was purified by crystallization or by FCC using the column material and solvents specified.

4-*Methyl*-4′-(2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*-15-*ylvinyl*)-2,2′-*bipyridine* L^{2a}. Yield 95%, m.p. 143–144 °C (propan-2-ol) (Found: C, 69.0; H, 6.5; N, 5.8. C$_{27}$H$_{30}$N$_2$O$_5$·0.5H$_2$O requires C, 68.75; H, 6.65; N, 5.95%); ν_{max}(KBr) 1625 (C=C) and 960 (=CH) cm^{-1}; δ_H(270 MHz, CDCl$_3$) 2.45 (s, 3 H, CH$_3$), 3.77 (s, 8 H, OCH$_2$), 3.91–3.97 (m, 4 H, OCH$_2$), 4.15–4.22 (m, 4 H, OCH$_2$), 6.85–7.35 (m, 5 H, benzo H and H$^{5,5'}$ of bipy), 6.96 (d, 1 H, J 16.3, CH=), 7.38 (d, 1 H, J 16.3, CH=), 8.26 (s, 1 H, H^3 of bipy), 8.49 (s, 1 H, H$^{3'}$ of bipy), 8.57 (d, 1 H, J 4.9, H^6 of bipy) and 8.61 (d, 1 H, J 5.1 Hz, H$^{6'}$ of bipy); m/z 462 (M^+, 100), 331 (81) and 304 (51%).

4-*Methyl*-4′-(p-1,4,7,10-*tetraoxa*-13-*azacyclopentadecan*-13-*ylstyryl*)-2,2′-*bipyridine* L^{2b}. FCC [silica gel, eluent CH$_2$Cl$_2$–MeOH–NH$_4$OH (100:2.5:0.5)], yield 96% (Found: C, 70.3; H, 7.4; N, 8.3. C$_{29}$H$_{35}$N$_3$O$_4$·0.5H$_2$O requires C, 69.85; H, 7.30; N, 8.45%); ν_{max}(Nujol) 960 (=CH) cm^{-1}; δ_H(270 MHz, CDCl$_3$) 2.44 (s, 3 H, CH$_3$), 3.57–3.80 (m, 20 H, CH$_2$O and CH$_2$N), 6.66, 6.69, 7.41, 7.44 (AB, 4 H, phenyl H), 6.89 (d, 1 H, J 16.3, =CH), 7.13 (m, 1 H, H^5 of bipy), 7.29 (d, 1 H, J 16.3 Hz, =CH), 7.33 (m, 1 H, H$^{5'}$ of bipy), 8.25 (s, 1 H, H^3 of bipy), 8.45 (s, 1 H, H$^{3'}$ of bipy) and 8.56–8.59 (m, 2 H, H$^{6,6'}$ of bipy); m/z 489 (M^+, 36), 323 (16), 273 (9), 198 (14), 184 (14), 170 (19), 91 (20), 71 (23), 56 (67) and 43 (100%).

4-(3,4-*Dimethoxystyryl*)-4′-*methyl*-2,2′-*bipyridine* L^{2c}. Yield 86%, m.p. 119–120 °C (ethyl acetate–hexane) (Found: C, 76.0; H, 5.8; N, 8.3. C$_{21}$H$_{20}$N$_2$O$_2$ requires C, 75.90; H, 6.05; N, 8.45%); ν_{max}(KBr) 1625 (C=C) and 960 (=CH) cm^{-1}; δ_H(270 MHz, CDCl$_3$) 2.45 (s, 3 H, CH$_3$), 3.92 (s, 3 H, OCH$_3$), 3.96 (s, 3 H, OCH$_3$), 6.87–7.36 (m, 5 H, phenyl H and H$^{5,5'}$ of bipy), 6.99 (d, 1 H, J 16.3, CH=), 7.40 (d, 1 H, J 16.3, CH=), 8.26 (s, 1 H, H$^{3'}$ of bipy), 8.50 (s, 1 H, H^3 of bipy), 8.57 (d, 1 H, J 4.9 Hz, H$^{6'}$ of bipy) and 8.62 (d, 1 H, H^6 of bipy); m/z 332 (M^+, 97), 331 (100), 317 (34), 301 (26), 286 (15), 257 (6), 240 (5) and 219 (4%).

4,4′-*Bis*(2,3,5,6,8,9,11,12-*octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecin*-15-*ylvinyl*)-2,2′-*bipyridine* L^{3a}. Yield 88%, m.p. 219–220 °C (CH$_2$Cl$_2$–MeOH (Found: C, 67.8; H, 6.7; N, 3.7. C$_{42}$H$_{48}$N$_2$O$_{10}$ requires C, 68.10; H, 6.55; N, 3.80%); ν_{max}(KBr) 1625 (C=C) and 960 (=CH) cm^{-1}; δ_H(270 MHz, CDCl$_3$) 3.78 (s, 16 H, OCH$_2$), 3.94–3.97 (m, 8 H, OCH$_2$), 4.15–4.21 (m, 8 H, OCH$_2$), 6.86–7.37 (m, 8 H, benzo H and H$^{5,5'}$ of bipy), 6.98 (d, 2 H, J 16.3, =CH), 7.38 (d, 2 H, J 16.3, =CH), 8.52 (s, 2 H, H$^{3,3'}$ of bipy) and 8.64 (d, 2 H, J 5.1 Hz, H$^{6,6'}$ of bipy); δ_C(67.8 MHz, CDCl$_3$) 156.23, 149.98, 149.38, 149.24, 146.06, 133.20, 129.69, 124.16, 121.29, 120.88, 118.06, 113.60, 111.94, 71.15, 71.12, 70.48, 70.42, 69.55, 69.47, 69.09 and 68.87; m/z (FAB) 741 (M + H$^+$), other major fragmentations at 653, 609, 463, 365, 314, 281 and 217.

4,4′-*Bis*(p-1,4,7,10-*tetraoxa*-13-*azacyclopentadecan*-13-*ylstyryl*)-2,2′-*bipyridine* L^{3b}. Yield 98%, m.p. 217–218 °C (CH$_2$Cl$_2$–MeOH) (Found: C, 64.4; H, 6.6; N, 6.5. C$_{46}$H$_{58}$N$_4$O$_8$·CH$_2$Cl$_2$ requires C, 64.15; H, 6.85; N, 6.35%); ν_{max}(KBr) 960 (=CH) cm^{-1}; δ_H(270 MHz, CDCl$_3$) 3.48–3.80 (m, 40 H, OCH$_2$ and NCH$_2$), 6.66, 6.69, 7.42, 7.45 (AB, 8 H, phenyl H), 6.90 (d, 2 H, J 16.5, =CH), 7.30 (d, 2 H, J 16.5, =CH), 7.34 (d, 2 H, J 5.2, H$^{5,5'}$ of bipy), 8.48 (s, 2 H, H$^{3,3'}$ of bipy) and 8.61 (d, 2 H, J 5.2 Hz, H$^{6,6'}$ of bipy); δ_C(67.8 MHz, CDCl$_3$), 156.14, 149.15, 148.04, 146.84, 133.58, 128.58, 124.01, 121.09, 120.52, 117.84, 111.52, 71.34, 70.22, 70.11, 68.41 and 52.63; m/z (FAB) 795 (M + H$^+$).

4,4′-*Bis*(3,4-*dimethoxystyryl*)-2,2′-*bipyridine* L^{3c}. Yield 83%, m.p. 235–236 °C (CH$_2$Cl$_2$–MeOH) (Found: C, 74.8; H, 5.9; N, 5.5. C$_{30}$H$_{28}$N$_2$O$_4$ requires C, 75.00; H, 5.85; N, 5.85%); ν_{max}(KBr) 1625 (C=C) and 960 (=CH) cm^{-1}; δ_H(270 MHz, CDCl$_3$), 3.92 (s, 6 H, OCH$_3$), 3.96 (s, 6 H, OCH$_3$), 6.78–7.38 (m, 8 H, phenyl H and H$^{5,5'}$ of bipy), 7.00 (d, 2 H, J 16.3, =CH), 7.41 (d, 2 H, J 16.3, =CH), 8.55 (s, 2 H, H$^{3,3'}$ of bipy) and 8.65 (d, 2 H, J 5.2 Hz, H$^{6,6'}$ of bipy); m/z 480 (M^+, 100), 465 (29), 449 (28), 433 (12), 421 (11), 405 (7), 331 (9), 240 (29) and 44 (29%).

[RuL(bipy)$_2$][PF$_6$]$_2$. A stirred mixture of 1 equivalent of [RuCl$_2$(bipy)$_2$]·2H$_2$O and 1.2 equivalents of the appropriate ligand in 2-methoxyethanol was refluxed under nitrogen for 24 h. After removing the solvent *in vacuo*, water was added and the mixture filtered. The filtrate was concentrated and passed down a Sephadex LH-20 column using methanol as eluent. Addition of aqueous ammonium hexafluorophosphate to a methanolic solution of the complex, followed by slow removal of the methanol *in vacuo* afforded the hexafluorophosphate salt (Table 7).

[RuL$_3$][PF$_6$]$_2$. A stirred mixture of 1 equivalent of RuCl$_3$·3H$_2$O and 3.0 equivalents of the appropriate ligand in

Table 7 Yields and elemental analyses of the ruthenium(II) complexes

Compound	Yield (%)	Analysis (%) C	H	N
$[RuL^1(bipy)_2][PF_6]_2 \cdot H_2O$	75	50.8	3.9	6.0
		(51.1)	(4.3)	(5.8)
$[RuL^{2a}(bipy)_2][PF_6]_2 \cdot 2H_2O$	81	47.9	3.9	6.9
		(47.7)	(4.1)	(7.1)
$[RuL^{2b}(bipy)_2][PF_6]_2 \cdot 3H_2O$	56	46.8	5.0	8.0
		(47.2)	(4.6)	(7.9)
$[RuL^{2c}(bipy)_2][PF_6]_2 \cdot H_2O$	71	46.0	3.6	8.0
		(46.0)	(3.8)	(7.8)
$[RuL^{3a}(bipy)_2][PF_6]_2 \cdot H_2O$	72	48.3	4.8	5.2
		(48.5)	(4.9)	(5.5)
$[RuL^{3b}(bipy)_2][PF_6]_2$	71	49.6	5.6	7.3
		(49.9)	(5.3)	(7.1)
$[RuL^{3c}(bipy)_2][PF_6]_2 \cdot H_2O$	73	49.6	4.2	6.8
		(50.0)	(3.9)	(7.0)
$[RuL^1{}_3][PF_6]_2$	83	58.3	5.1	3.5
		(58.2)	(5.1)	(3.2)
$[RuL^{2a}{}_3][PF_6]_2$	68	53.9	5.2	4.2
		(53.6)	(5.2)	(4.6)
$[RuL^{2b}{}_3][PF_6]_2 \cdot 3H_2O$	86	54.8	6.1	6.8
		(54.6)	(5.9)	(6.6)
$[RuL^{2c}{}_3][PF_6]_2$	86	54.6	4.2	5.9
		(54.5)	(4.4)	(6.1)
$[RuL^{3a}{}_3][PF_6]_2$	68	57.9	5.8	3.4
		(57.9)	(5.6)	(3.2)
$[RuL^{3b}{}_3][PF_6]_2 \cdot 3H_2O$	86	58.4	6.3	6.3
		(58.6)	(6.4)	(5.9)
$[RuL^{3c}{}_3][PF_6]_2$	52	58.6	4.5	4.7
		(59.0)	(4.6)	(4.6)

* Calculated values in parentheses.

dmf was refluxed for 24 h and complexes isolated as above (Table 7).

Heteropolymetallic complexes. To a stirred solution of $[RuL^{3a}(bipy)_2][PF_6]_2$ (103 mg, 0.07 mmol) in acetone (20 cm^3) was added an excess amount of sodium hexafluorophosphate (60 mg, 0.35 mmol) in methanol (10 cm^3). The resulting solution was refluxed for 30 min under a nitrogen atmosphere, then allowed to cool to room temperature. The solvent was partially evaporated to precipitate the crude product, which was filtered off, washed several times with methanol (to remove the excess of sodium hexafluorophosphate), and dried to yield $[(bipy)_2RuL^{3a}Na_2][PF_6]_4$ (Found: C, 42.3; H, 3.6; N, 4.5. $C_{62}H_{64}F_{24}N_6Na_2O_{10}P_4Ru$ requires C, 41.85; H, 3.60; N, 4.70%); m/z (FAB) 1634 ($M + H^+ - PF_6$), 1466 [$M - (Na + 2PF_6)$], and other major fragmentations at 1299, 1155, 741, 577 and 460. An analogous procedure using $[RuL^{3a}{}_3][PF_6]_2$ was used to prepare $[RuL^{3a}{}_3Na_6][PF_6]_8$ (Found: C, 43.0; H, 4.4; N, 2.7. $C_{126}H_{144}F_{48}N_6Na_6O_{30}P_8Ru$ requires C, 43.3; H, 4.1; N, 2.4%).

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