Syntheses, Coordination, Spectroscopy and Electropolymerisation Studies of New Alkynyl and Vinyl Linked Benzo- and Aza-crown Ether–Bipyridyl Ruthenium(II) Complexes. Spectrochemical Recognition of Group IA/IIA Metal Cations

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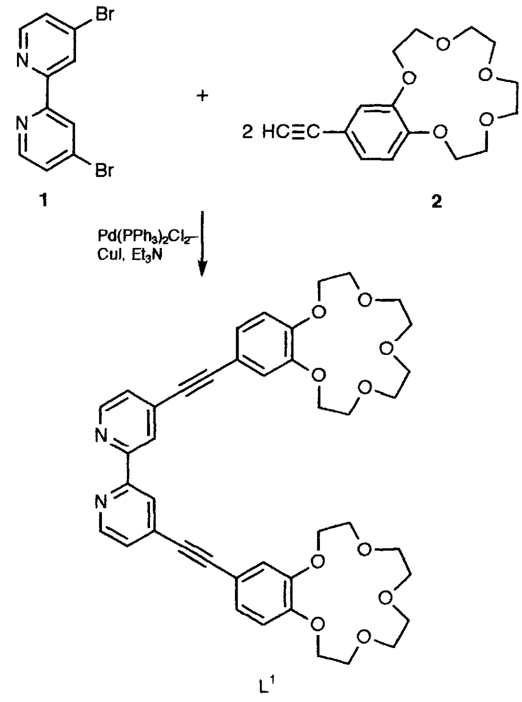
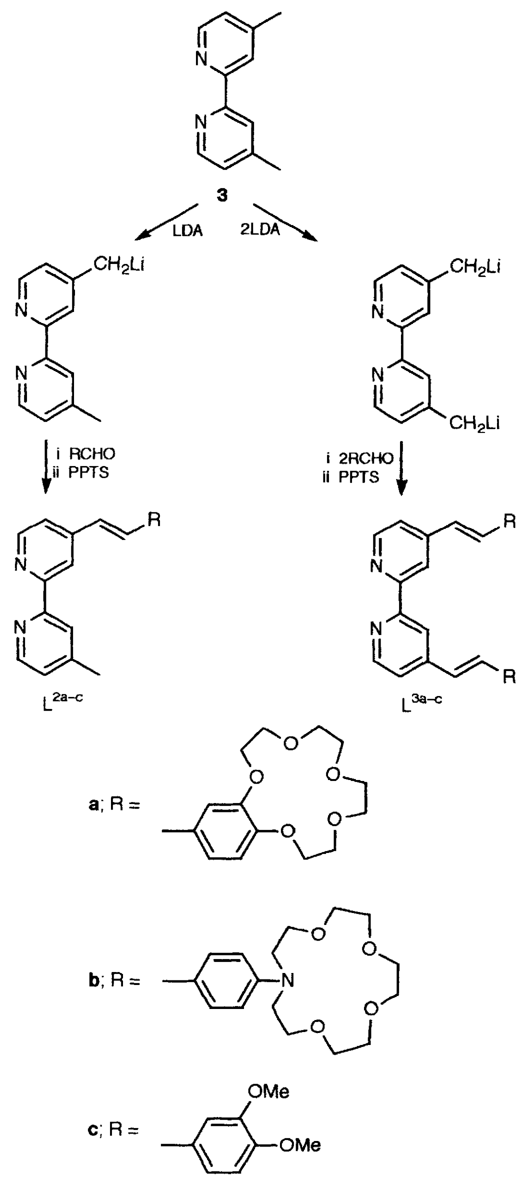
New alkynyl and vinyl linked benzo- and aza-crown ether–bipyridyl ruthenium(II) complexes have been prepared and electropolymerised onto platinum and optically transparent conducting glass electrodes to produce novel films capable of spectrochemically recognising alkali and alkaline earth metal guest cations.

The prospect of modelling electron-transfer processes in biological systems, producing new electro- and photo-active catalysts and developing new materials of relevance to the emerging field of molecular electronics 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 to our knowledge been fully exploited.[4] This communication reports the syntheses, coordination and electropolymerisation studies of new alkynyl and vinyl linked benzo- and aza-crown ether–bipyridyl ruthenium(II) complexes and demonstrates that these novel systems spectrochemically recognise group IA and IIA metal cations.

The reaction of 4,4′-dibromo-2,2′-bipyridine **1**[5] with two moles of 4-ethynylbenzo-15-crown-5 **2**[6] in the presence of $Pd(PPh_3)_2Cl_2$ and CuI gave L^1 in 85% yield, Scheme 1. The new *trans* vinyl linked benzo-crown ether–, aza-crown ether– and bismethoxyphenyl–bipyridyl ligands L^2 and L^3 were prepared in excellent yields (70–95%) *via* mono- or di-lithiation of 4,4′-dimethyl-2,2′-bipyridine **3**[7] followed by addition of the appropriate 4-formyl substituted compound and dehydration,[8] Scheme 2. The structures of all these new compounds were characterised on the basis of spectroscopic



Scheme 1



Scheme 2 LDA = lithium diisopropylamide, PPTS = pyridinium toluene-*p*-sulphonate

and analytical evidence.† The monoligand ruthenium(II) complexes $[RuL^{1-3}(bipy)_2][PF_6]_2$ and corresponding tris(ligand) ruthenium(II) complexes $[RuL^{1-3}{}_3][PF_6]_2$ were obtained by refluxing the appropriate ligand with $[RuCl_2(bipy)_2]\cdot 2H_2O$[9] (bipy = bipyridyl) and $RuCl_3\cdot 3H_2O$, respectively in dimethylformamide, followed by purification on Sephadex LH-20 and precipitation of the complexes on addition of ammonium hexafluorophosphate.‡

Heteropolymetallic ruthenium(II)–sodium complexes such as **4** and **5** were isolated from complexation reactions of $[RuL^{1-3}(bipy)_2][PF_6]_2$ and $[RuL^{1-3}{}_3][PF_6]_2$ with excess amounts of sodium hexafluorophosphate.‡ Subsequent solution ^{13}C NMR titration studies with these ruthenium(II) complexes and sodium perchlorate suggested the same alkali metal stoichiometries as those found in the isolated complexes in which each benzo-crown ether moiety binds one sodium cation.

Evidence for the spectrochemical recognition of metal ions by the monomeric vinyl linked benzo-crown ether and aza-crown ether complexes is provided upon examination of their optical emission spectra in acetonitrile. The metal-to-ligand charge transfer (MLCT) emission maxima for the complexes $[RuL^{2a,b}(bipy)_2][PF_6]_2$, $[RuL^{2a,b}{}_3][PF_6]_2$, $[RuL^{3a,b}(bipy)_2][PF_6]_2$ and $[RuL^{3a,b}{}_3][PF_6]_2$ are shifted to significantly lower wavelengths and increase in intensity in the presence of Li^+, Na^+ or Mg^{2+}. For example with $[RuL^{3b}(bipy)_2][PF_6]_2$ addition of an excess amount of sodium ions gave a 16 nm blue shift (from 686 to 670 nm) (Fig. 1). No corresponding shift is observed for the complex $[RuL^{3c}{}_3][PF_6]_2$ or the prototype $[Ru(bipy)_3][PF_6]_2$, suggesting that alkali or alkaline earth metal cation coordination at the respective crown ether recognition site is responsible for this effect. Valeur and coworkers have recently reported similar group IA and IIA metal cation induced blue shifts in the emission spectra of fluorophores linked to crown ethers.[10]

Cathodic electropolymerisation reactions have been noted for a variety of tris(2,2′-bipyridyl) transition metal complexes that have vinylic substituents on one or more ligands.[11] It was

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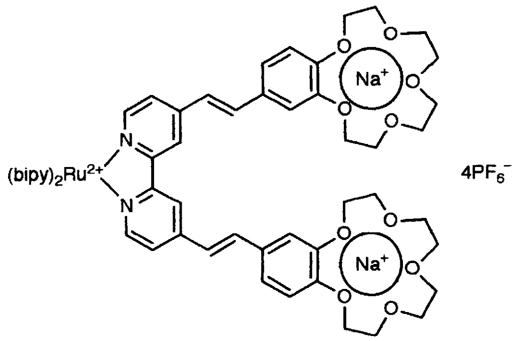
† All new compounds gave spectroscopic and analytical data in accordance with assigned structures. Data are quoted for a selection of the ligands.

For L^1; m.p. 224–225 °C. ν_{max} 2220 (C≡C) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 3.78 (s, 16H, OCH_2), 3.92–3.95 (m, 8H, OCH_2), 4.16–4.18 (m, 8H, OCH_2), 6.83–7.18 (m, 6H, ArH), 7.39 (d, 2H, *J* 4.95 Hz, 5,5′-PyH), 8.51 (s, 2H, 3,3′-PyH), 8.66 (d, 2H, *J* 4.95 Hz, 6,6′-PyH); *m/z* (FAB) 727 (M + H$^+$).

For L^{3a}: m.p. 219–220 °C. ν_{max} 1625 (C=C), 960 (=CH) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 3.78 (s, 16H, OCH_2), 3.94–3.97 (m, 8H, OCH_2), 4.15–4.21 (m, 8H, OCH_2), 6.86–7.37 (m, 8H, ArH and 5,5′-PyH), 6.98 (d, 2H, *J* 16.3 Hz, =CH), 7.38 (d, 2H, *J* 16.3 Hz, =CH), 8.52 (s, 2H, 3,3′-PyH), 8.64 (d, 2H, *J* 5.1 Hz, 6,6′-PyH); *m/z* (FAB) 741 (M + H$^+$).

For L^{3b}: m.p. 216–218 °C. ν_{max} 960 (=CH) cm^{-1}; δ_H (270 MHz, $CDCl_3$) 3.48–3.80 (m, 40H, OCH_2 and NCH_2), 6.66, 6.69, 7.42 and 7.45 (s, 8H, ArH, AB system), 6.90 (d, 2H, *J* 16.5 Hz, =CH), 7.30 (d, 2H, *J* 16.5 Hz, =CH), 7.34 (d, 2H, *J* 5.2 Hz, 5,5′-PyH), 8.48 (s, 2H, 3,3′-PyH), 8.61 (d, 2H, *J* 5.2 Hz, 6,6′-PyH); *m/z* (FAB) 795 (M + H$^+$).

‡ For example. $[RuL^{2a}(bipy)_2][PF_6]$, 81% yield; $[RuL^{3a}{}_3][PF_6]_2$, 70% yield; **4** quantitative yield; **5** quantitative yield. Satisfactory C, H, N analyses were obtained for the ruthenium complexes.



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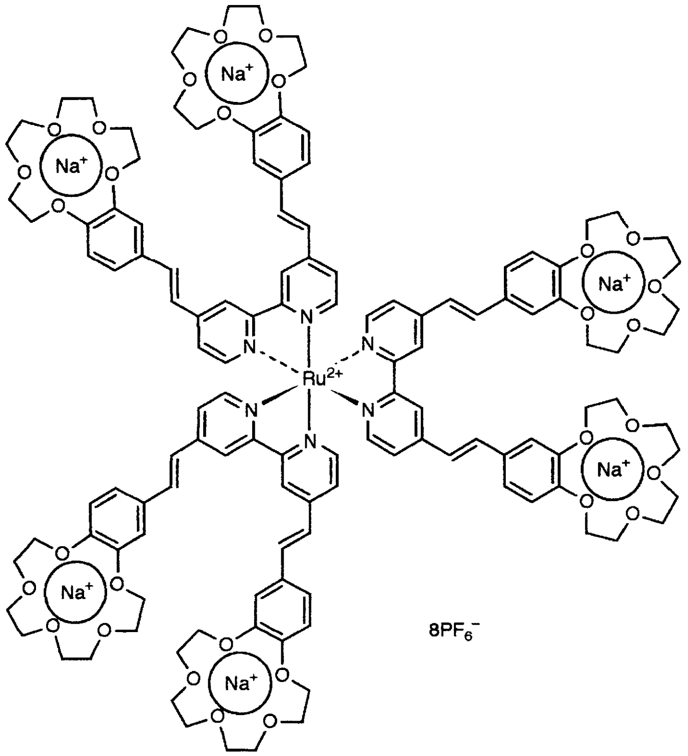

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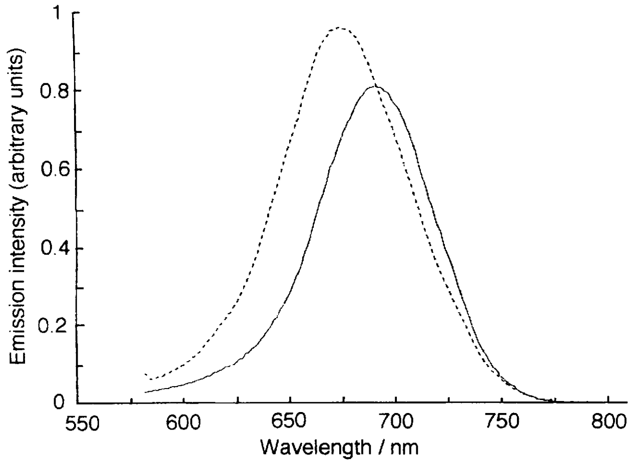

Fig. 1 Emission spectrum (solid line) of 1 × 10^{-4} mol dm^{-3} $[RuL^{3b}(bipy)_2][PF_6]_2$ in deoxygenated MeCN solution at 25 °C. Broken line shows emission spectrum after addition of excess Na^+ (as $NaClO_4$–MeCN solution) (excitation wavelength = 550 nm).

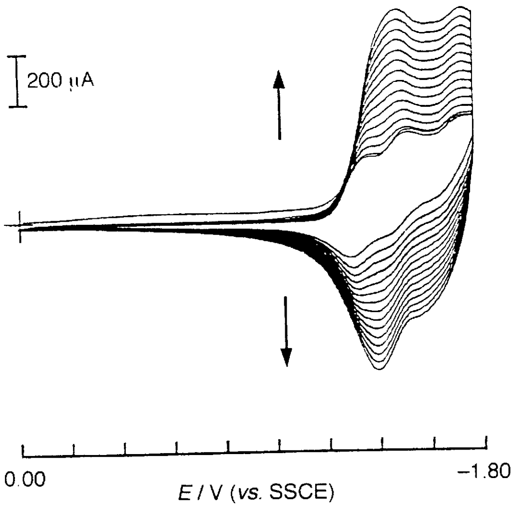

Fig. 2 Sequential cyclic voltammograms for an acetonitrile solution containing 1.33 mmol dm^{-3} $[RuL^{2a}{}_3][PF_6]_2$ in 0.1 mol dm^{-3} NBu_4BF_4 at 100 mV s^{-1}. The arrows indicate current increase.

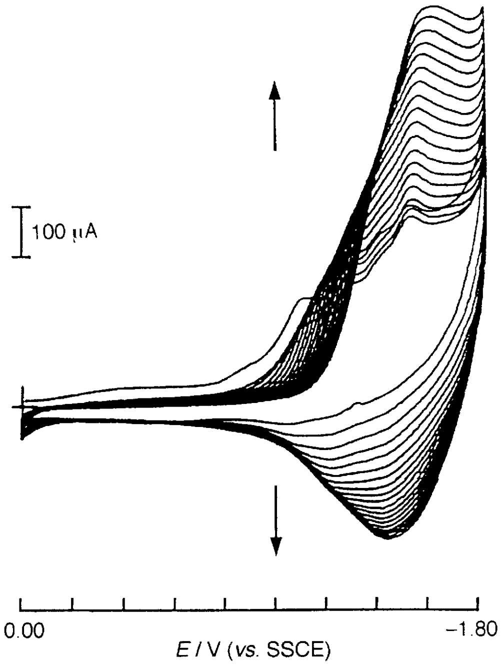

Fig. 3 Sequential cyclic voltammograms for an acetonitrile solution containing 0.67 mmol dm^{-3} $[RuL^1{}_3][PF_6]_2$ in 0.1 mol dm^{-3} NBu_4BF_4 at 100 mV s^{-1}. The arrows indicate current increase.

anticipated that sequential potential scanning of solutions of the $[RuL^{2-3}(bipy)_2][PF_6]_2$ and $[RuL^{2-3}{}_3][PF_6]_2$ complexes to the series of ligand-centred reductions would activate the vinylic linkages and initiate electropolymerisation. All $[RuL^{2a-c}{}_3][PF_6]_2$ complexes were indeed electropolymerised onto platinum electodes to form smooth, adherent orange films, as exemplified by Fig. 2 which shows the steady increase in current attributable to the combined electroactivity of the polymeric film and that of the inward-diffusing complex. Complexes $[RuL^{3a-c}{}_3][PF_6]_2$ were also electropolymerised although less efficiently (lower rate of current increase on sequential scanning), possibly due to steric crowding of the 4,4′ substituents, and complexes $[RuL^{2-3}(bipy)_2][PF_6]_2$ only exhibited solution redox processes analogous to the prototype $[Ru(bipy)_3][PF_6]_2$. Tris(2,2′-bipyridyl) transition metal complexes with alkynyl substituents were successfully electropolymerised, Fig. 3, with higher efficiencies than the analogous

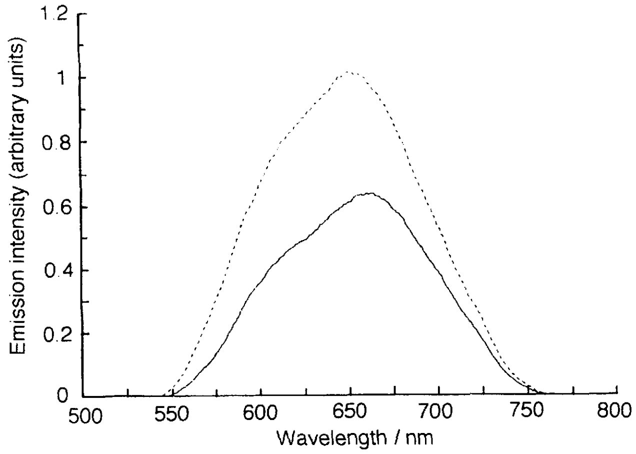

Fig. 4 Emission spectrum (solid line) of a film of poly-[RuL^{2a}]$_3^{2+}$ coated onto an optically transparent conducting glass electrode in deoxygenated MeCN solution at 25 °C. Broken line shows emission spectrum after addition of excess of Mg^{2+} (as $Mg(ClO_4)_2$–MeCN solution). (Excitation wavelength = 450 nm).

vinyl linked complexes. All poly-[RuL$^{1-3}_3$]$^{2+}$ modified electrodes in complex-free supporting electrolyte revealed current for the Ru^{III-II} and ligand-centred redox processes.

To investigate further the nature of these crown ether polymer films the absorption spectrum of poly-[RuL$^{2a}_3$]$^{2+}$ was obtained *via* electropolymerisation onto an optically transparent conducting glass electrode. In addition to exhibiting a MLCT band (470 nm) corresponding to that of the monomeric precursor [RuL$^{2a}_3$][PF_6]$_2$ (475 nm), an absorption maximum corresponding to the ligand-centred π–π* transition in the monomer (366 nm) is observed (360 nm). It is likely that the low energy nature of this ligand-centred transition in the monomeric complex is a result of the extended conjugation due to the presence of the vinyl and benzo-crown ether groups. The presence of a band at similar wavelength in the polymer suggests therefore that not all the vinyl groups are removed by the electropolymerisation process and also that the benzo-crown ether substituent remains attached after polymerisation. As for the monomeric complex, the ligand centred absorption band and the MLCT emission maximum of the polymer was shifted to lower wavelengths in the presence of alkali and alkaline earth 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 displaying no shifts with alkali and alkaline earth metal cations. In conclusion these preliminary results have shown that these crown ether polymer film materials represent a new class of spectrochemical sensing device for alkali and alkaline earth metal cations.

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