Preparation, Photophysical, Electrochemical, and Ion-Binding Properties of Ru(II) Polypyridyl Complexes Containing a Crown Ether Unit

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Two polypyridyl ligands, 4′-(4,5-diazafluoren-9-ylimino)benzo-15-crown-5 (L^1) and 4′-(4,5-diazafluoren-9-ylimino)benzo-12-crown-4 (L^2), and their Ru(II) complexes $[(bpy)_2RuL^1](PF_6)_2$ and $[(bpy)_2RuL^2](PF_6)_2$, respectively, have been synthesized and characterized. The two complexes display metal-to-ligand charge transfer absorptions at around 444 nm in CH_3CN solution at r. t. and emission at around 573 nm in an EtOH-MeOH (4 : 1, v/v) glassy matrix at 77 K. Electrochemical studies of the complexes show one Ru(II)-centered oxidation at around 1.33 V and three ligand-centered reductions. The binding ability of the complexes with Na^+ and Li^+ has been investigated by UV/Vis absorption and emission spectroscopy and electrochemical titrations. Addition of Na^+ and Li^+ to solutions of the complexes results in a progressive quenching of the emission, a hyperchromic effect of the UV/Vis absorption, and a progressive cathodal shift of the Ru(II)-centered $E_{1/2}$ potential. The stability constants for the stoichiometric 1 : 1 ratio of the complexes and the cations have been obtained by UV/Vis absorption titration.

Key words: Ru(II) Complex, Crown Ether, Photophysics, Electrochemistry, Ion Binding

Introduction

Transition metal complexes have been widely employed as sensors because their photophysical and electrochemical properties are readily influenced by altering the electronic environment of the metal center [1 – 7]. The polypyridyl complexes of d^6 metals, with their strong metal-to-ligand charge transfer absorptions and emitting excited states, are good candidates as signaling subunits [8 – 11]. Ligands with a macrocyclic unit attached to a metal polypyridyl core are potentially useful in the preparation of luminescent or electrochemical sensors, in which the macroscopic properties of the core are modified by molecular level interactions between the recognition center and the substrate [12 – 15]. The metal polypyridyl complex most widely used as a fluorophore is probably $Ru(bpy)_3{}^{2+}$. Considerable effort has been devoted to the design and synthesis of Ru(II) polypyridyl complexes acting as chemical sensors. Ru(II) polypyridyl complexes have proved to be particularly versatile in sensor applications, because their outstanding photophysical and electrochemical properties are quite sensitive to variations of external stimuli [16 – 19]. The sodium ion is the most abundant metal ion in living cells and plays vital roles in many cellular processes. The lithium ion plays an important therapeutic role in the treatment of manic depressive behavior, but an excessive dose of lithium can cause adverse physiological effects such as nausea and vomiting. So, monitoring of Na^+ and Li^+ levels in biological systems is desirable [20 – 22]. Herein, we report on the synthesis and characterization of two Ru(II) polypyridyl complexes with a benzocrown ether attached *via* a C=N moiety to a 4,5-diazafluorene unit acting as a substrate binding site. The photophysical and electrochemical properties of the two complexes in response to Na^+ or Li^+ binding are also presented and discussed.

Experimental Section

Materials and physical measurements

2,2′-Bipyridine, 1,10-phenanthroline, benzo-15-crown-5, benzo-12-crown-4, NH_4PF_6, ruthenium trichloride hydrate, ethyl acetate, toluene, CH_3CN, $CHCl_3$, EtOH, MeOH, Et_2O, and DMF were purchased from the Tianji Chemical Reagent

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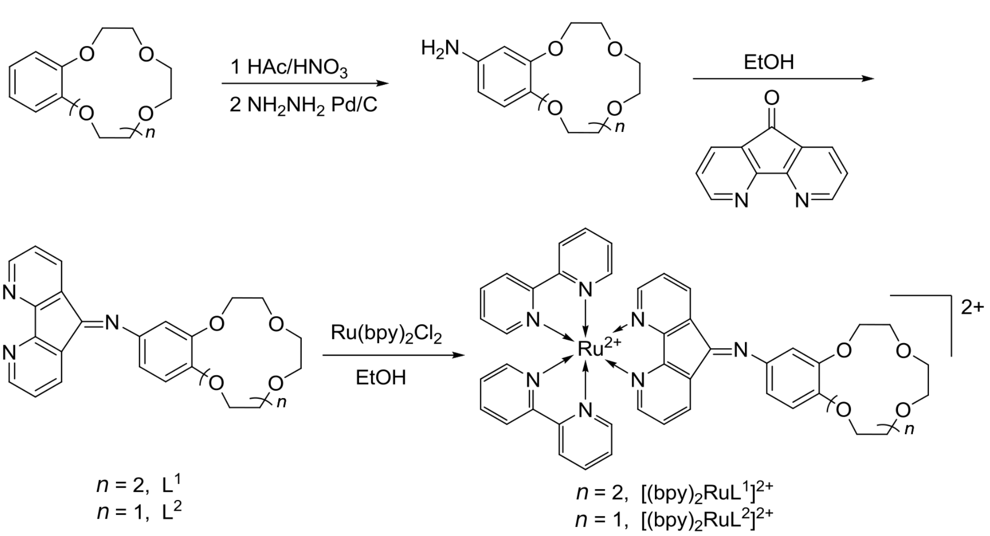

Scheme 1. Synthesis of ligands L^1/L^2 and the corresponding complexes $[(bpy)_2RuL^1]^{2+}$ and $[(bpy)_2RuL^2]^{2+}$.

Factory. All solvents and raw materials were of analytical grade and were used as received, with the exception of CH_3CN, which was filtered over activated alumina and distilled from P_2O_5 immediately prior to use. Tetrabutylammonium perchlorate (TBAP) [23], 4,5-diazafluoren-9-one (dafo) [24], 4′-aminobenzo-15-crown-5, 4′-aminobenzo-12-crown-4 [25], and $Ru(bpy)_2Cl_2 \cdot 2H_2O$ [26] were synthesized according to literature procedures.

^1H NMR spectra were performed on a Mercury Plus 400 spectrometer using TMS as an internal standard. EI-MS data were obtained using a Thermo Electron Corporation Trace DSQ mass spectrometer. ESI-TOF spectra were performed on a Mariner Biospectrometry Workstation. LC-MS data were recorded on a Bruker Daltonics Esquire 6000 mass spectrometer. Elemental analyses were obtained using a Perkin-Elmer 240C analytical instrument, absorption spectra on a Varian Cary-100 UV/Visible spectrophotometer, and emission spectra with a Hitachi F-4500 spectrophotometer. Emission quantum yields were calculated relative to $Ru(bpy)_3{}^{2+}$ (Φ_{std} = 0.376) in an EtOH-MeOH (4 : 1, v/v) glassy matrix [27]. Electrochemical measurements were carried out at r. t. using a CHI 660B electrochemical workstation. Cyclic voltammetry and differential pulse voltammetry were performed in CH_3CN and DMF solutions by using a micro cell equipped with a platinum disk working electrode, a platinum auxiliary electrode and a saturated potassium chloride calomel reference electrode with 0.1 mol L^{-1} TBAP as supporting electrolyte. All samples were purged with nitrogen prior to measurement.

Preparations

The outline of the preparation of ligands L^1/L^2 and the corresponding Ru(II) complexes $[(bpy)_2RuL^1](PF_6)_2$ and $[(bpy)_2RuL^2](PF_6)_2$, shortly called Ru-L^1 and Ru-L^2, respectively, is presented in Scheme 1.

4′-(4,5-diazafluoren-9-ylimino)benzo-15-crown-5 (L^1)

4,5-diazafluoren-9-one (208 mg, 1.1 mmol) and 4′-aminobenzo-15-crown-5 (286 mg, 1 mmol) were heated to reflux for 6 h in EtOH (30 mL) containing a catalytic amount of acetic acid under nitrogen atmosphere. Then the solvent was removed under reduced pressure. The resulting mixture was chromatographed on silica, eluted first with $CHCl_3$/ethyl acetate (1 : 1, v/v) to recover the starting material 4,5-diazafluoren-9-one (dafo), then with $CHCl_3$/EtOH (35 : 1, v/v) affording the desired product as a red solid. Yield: 384 mg (85 %). – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.82 (t, 8H, J = 4.4 Hz), 3.91 (t, 2H, J = 4.4 Hz), 3.97 (t, 2H, J = 4.4 Hz), 4.10 (t, 2H, J = 4.4 Hz), 4.21 (t, 2H, J = 4.4 Hz), 6.53 (dd, 1H, J = 8.2, 1.6 Hz), 6.58 (d, 1H, J = 2.4 Hz), 6.95 (d, 1H, J = 8.4 Hz), 7.02 – 7.08 (m, 2H), 7.39 (dd, 1H, J = 7.6, 1.2 Hz), 8.23 (d, 1H, J = 8.0 Hz), 8.66 (dd, 1H, J = 4.8, 1.6 Hz), 8.80 (d, 1H, J = 3.6 Hz). – MS ((+)-EI): m/z = 447 (calcd. 447 for $C_{25}H_{25}N_3O_5$, $[M]^+$).

4′-(4,5-diazafluoren-9-ylimino)benzo-12-crown-4 (L^2)

Ligand L^2 was prepared by the same procedure as described for ligand L^1, except that 4′-aminobenzo-12-crown-4 (182 mg, 0.76 mmol) was used instead of 4′-aminobenzo-15-crown-5 to react with 4,5-diazafluoren-9-one (159 mg, 0.87 mmol) affording a red solid. Yield: 239 mg (78 %). – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.88 – 3.98 (m, 6H), 4.02 (t, 2H, J = 4.0 Hz), 4.19 (t, 2H, J = 4.2 Hz), 4.29 (t, 2H, J = 4.0 Hz), 6.59 (d, 1H, J = 2.4 Hz), 6.64 (t, 1H, J = 2.8 Hz), 6.99 (dd, 1H, J = 5.4, 2.2 Hz), 7.04 – 7.08 (m, 1H), 7.13 (d,

Table 1. Photophysical and electrochemical data of Ru(II) polypyridyl complexes.

	Absorption	Emission[a]		$E_{1/2}$, V (ΔE_p, mV)[b]	
Complex	λ_{max}, nm (10^4 ε, mol^{-1} cm^{-1})	λ_{max}, nm	Φ	Oxidation	Reduction
	444 (1.71)				−0.86 (72)
Ru-L^1	286 (6.97)	573	0.023	1.33 (68)	−1.42 (140)
	237 (5.59)				−1.66 (88)
	444 (1.99)				−0.87 (76)
Ru-L^2	286 (7.59)	573	0.026	1.33 (72)	−1.42 (132)
	237 (5.68)				−1.67 (82)

[a] In an EtOH-MeOH (4 : 1, v/v) glassy matrix; the uncertainty in quantum yield is 15 %; [b] oxidation potentials are recorded in 0.1 mol L^{-1} TBAP/CH$_3$CN, reduction potentials are recorded in 0.1 mol L^{-1} TBAP/DMF, and potentials are given *vs.* SCE; scan rate = 200 mV S^{-1}; ΔE_p is the difference between the anodic and cathodic waves.

1H, J = 6.8 Hz), 7.44 (dd, 1H, J = 5.2, 1.2 Hz), 8.27 (dd, 1H, J = 6.0, 1.6 Hz), 8.70 (dd, 1H, J = 3.6, 1.2 Hz), 8.85 (dd, 1H, J = 5.0, 1.4 Hz). – MS ((+)-EI): m/z = 403 (calcd. 403 for $C_{23}H_{21}N_3O_4$, [M]$^+$).

[(bpy)$_2$RuL^1](PF$_6$)$_2$ (Ru-L^1)

A mixture of ligand L^1 (116 mg, 0.26 mmol) and Ru(bpy)$_2$Cl$_2$ · 2H$_2$O (121 mg, 0.23 mmol) in EtOH (15 mL) was heated to reflux for 8 h under a nitrogen atmosphere. After cooling to r. t., the product was precipitated by dropwise addition of saturated aqueous NH$_4$PF$_6$ until no more precipitate formed. The precipitate was collected by filtration and washed with water, ethanol and diethyl ether, then purified twice by column chromatography on alumina using CH$_3$CN/toluene (2 : 1, v/v) as eluent, followed by recrystallization from a CH$_3$CN/Et$_2$O mixture (vapor diffusion method) affording a red solid. Yield: 135 mg (50 %). – ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.61 (s, 8H), 3.74 (s, 2H), 3.79 (s, 2H), 4.01 (s, 2H), 4.08 (s, 2H), 6.71 (dd, 1H, J = 8.6, 2.4 Hz), 6.85 (d, 1H, J = 2.4 Hz), 7.04 (d, 1H, J = 8.4 Hz), 7.36 – 7.38 (m, 2H), 7.49 – 7.54 (m, 2H), 7.56 – 7.63 (m, 4H), 7.73 (d, 1H, J = 5.2 Hz), 7.82 (dd, 2H, J = 8.1, 6.0 Hz), 8.08 (d, 1H, J = 5.2 Hz), 8.11 – 8.21 (m, 5H), 8.42 (d, 1H, J = 8.0 Hz), 8.83 (d, 2H, J = 7.6 Hz), 8.79 (d, 2H, J = 7.6 Hz). – MS (ESI-TOF): m/z = 430.7 [M–2PF$_6$]$^{2+}$, 1007.4 [M–PF$_6$]$^+$. – Analysis for $C_{45}H_{41}F_{12}N_7O_5P_2Ru$: calcd. C 46.96, H 3.59, N 8.52; found C 46.83, H 3.45, N 8.34.

[(bpy)$_2$RuL^2](PF$_6$)$_2$ (Ru-L^2)

Complex Ru-L^2 was prepared by the same procedure as described for Ru-L^1, except that L^2 (78 mg, 0.19 mmol) was used instead of L^1 to react with Ru(bpy)$_2$Cl$_2$ · 2H$_2$O (86 mg, 0.17 mmol) affording a red solid. Yield: 103 mg (56 %). – ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.69 (t, 4H), 3.77 (d, 2H, J = 2.8 Hz), 3.82 (s, 2H), 4.08 (d, 2H, J = 2.8 Hz), 4.15 (s, 2H), 6.74 (d, 1H, J = 8.8 Hz), 6.89 (d, 1H, J = 2.0 Hz), 7.09 (dd, 1H, J = 8.2, 2.6 Hz), 7.38 – 7.41 (m, 2H), 7.55 (dd, 2H, J = 7.2, 2.4 Hz), 7.58 – 7.66 (m, 4H), 7.76 (d, 1H, J = 4.8 Hz), 7.86 (dd, 2H, J = 8.0, 5.2 Hz), 8.11 (d, 1H, J = 4.8 Hz), 8.14 – 8.24 (m, 5H), 8.44 (d, 1H, J = 8.0 Hz), 8.81 (d, 2H, J = 8.0 Hz), 8.85 (d, 2H, J = 8.0 Hz). – MS (LC): m/z = 408.5 [M–2PF$_6$]$^{2+}$, 962.1 [M–PF$_6$]$^+$. – Analysis for $C_{43}H_{37}F_{12}N_7O_4P_2Ru$: calcd. C 46.66, H 3.37, N 8.86; found C 46.52, H 3.21, N 8.63.

Results and Discussion

Absorption spectra

The absorption spectra of the complexes Ru-L^1 and Ru-L^2 have been studied in CH$_3$CN solution. The working concentration of the complexes was 10^{-5} mol L^{-1}. The spectra are shown in Fig. 1. The data for the energy maxima and the absorption coefficients are summarized in Table 1. Assignments of the absorption bands were made on the basis of the well-documented optical transitions of analogous Ru(II) polypyridyl complexes [28 – 31]. The absorption spectra of the complexes Ru-L^1 and Ru-L^2 com-

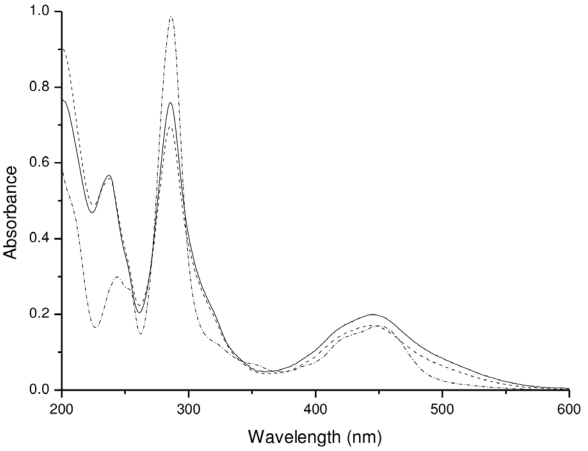

Fig. 1. Absorption spectra of complexes Ru-L^1 (dash), Ru-L^2 (solid) and Ru(bpy)$_3$$^{2+}$ (dash dot) in CH$_3$CN solution at r. t.

prise three distinct regions. The bands at around 286 and 237 nm are attributed to the intraligand $\pi \rightarrow \pi*$ transitions centered on 2,2′-bipyridine. The lowest energy band at around 444 nm is assigned to metal-to-ligand charge transfer (MLCT) transitions, which consist of $d\pi$(Ru)→ $\pi*$(bpy) and $d\pi$(Ru)→ $\pi*$(L) components. The lowered symmetry removes the degeneracy of the $\pi*$ levels, which results in the appearance of a non-symmetrical MLCT band. The MLCT absorption maxima of the complexes are blue-shifted by about 6 nm compared with that of $Ru(bpy)_3^{2+}$ [32], suggesting that the donor properties of the ligands L^1 and L^2 are weaker than that of 2,2′-bipyridine.

Emission

Complexes Ru-L^1 and Ru-L^2 display no emission at all in CH_3CN solution at r. t. upon excitation into the MLCT band. The emission properties of Ru(II) polypyridyl complexes generally follow the energy gap law [33–35]. The ^{3}MLCT state is reasonably long-lived and is thought to be deactivated by three processes: radiative decay k_r, radiationless decay k_{nr}, and thermal population of a higher-lying excited state $k^{-\Delta E/RT}$. For the last process, the thermally accessible excited state has been designated as a ligand field excited state. The energy of this presumed ligand field state should depend on the ligand field strength. The emission intensities follow the model shown in Fig. 2 originally proposed by Crosby, Meyer and others [36–40]. 4,5-diazafluoren-9-one derivatives are known to be lower than 2,2′-bipyridine in the spectrochemical series [41, 42]. Therefore, the ligand field excited state energy will be lowered if 2,2′-bipyridines are replaced by 4,5-diazafluoren-9-one derivatives. The values of ΔE for the such Ru(II) complexes are substantially lower than the value for $Ru(bpy)_3^{2+}$. Consequently, the population of the ligand field state is very efficient for these complexes at r. t., and they are essentially non-emissive. The emission spectra of such Ru(II) complexes are similar to that of $Ru(bpy)_3^{2+}$ in an EtOH-MeOH (4 : 1, v/v) glassy matrix at 77 K (Fig. 3) [43] because the energy transfer is inhibited in this case. Complexes Ru-L^1 and Ru-L^2 exhibit a characteristic emission at around 573 nm in an EtOH-MeOH (4 : 1, v/v) glassy matrix with an excitation wavelength at 436 nm (Table 1).

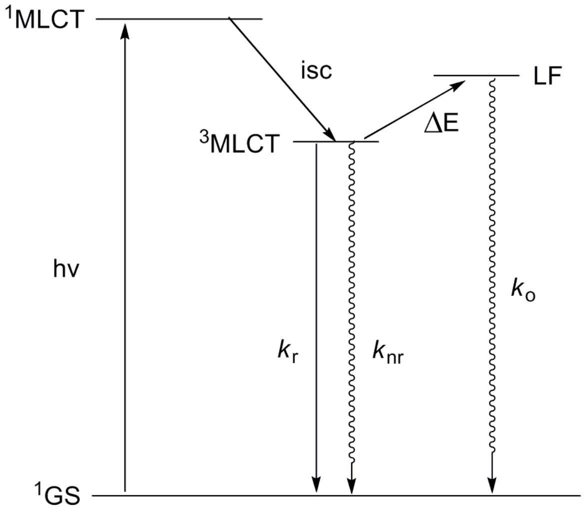

Fig. 2. Energy state diagram as based on the Crosby-Meyer model.

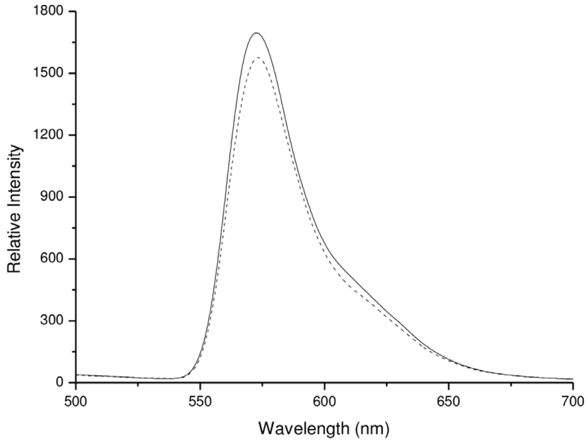

Fig. 3. Emission spectra of Ru-L^1 (dash) and Ru-L^2 (solid) in an EtOH-MeOH (4 : 1, v/v) glassy matrix at 77 K.

Electrochemistry

The electrochemical behavior of the complexes Ru-L^1 and Ru-L^2 were studied in CH_3CN and DMF solutions with 0.1 mol L^{-1} TBAP as supporting electrolyte. In CH_3CN solution, the reductions are not well-behaved due to the adsorption of the reduced species onto the surface of the platinum electrode. In DMF solution, the complexes display three clear reduction processes, but do not show the oxidative waves due to the limitation by the solvent. Therefore, the oxidation potentials were recorded in CH_3CN solution, but the reduction potentials were recorded in DMF solution (Table 1).

Complex Ru-L^1 exhibits a Ru(II)-centered reversible oxidation at 1.33 V. This potential is slightly

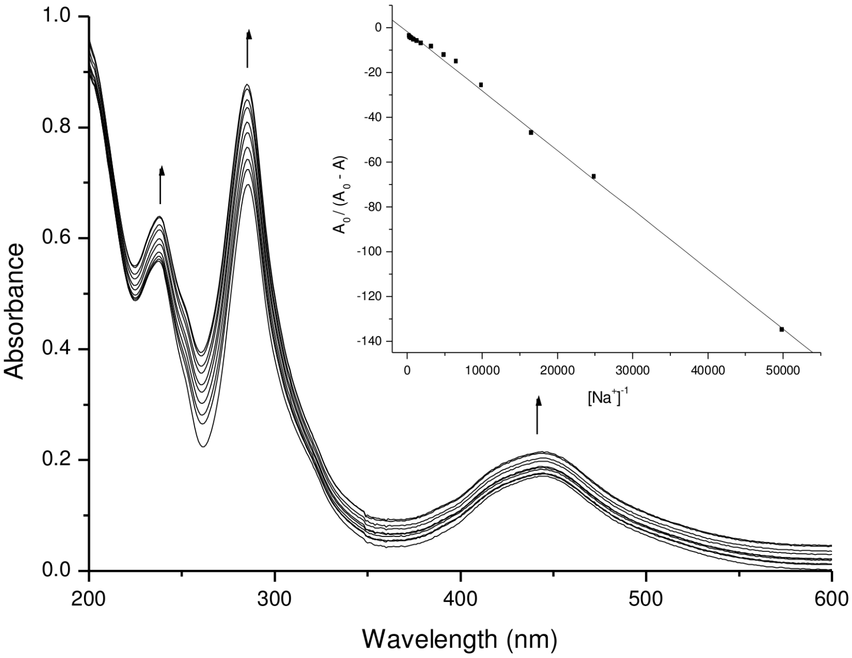

Fig. 4. UV/Vis absorption titration spectra of complex Ru-L^1 (10^{-5} mol L^{-1}) with added NaClO$_4$ (0 – 3 × 10^{-3} mol L^{-1}) in CH$_3$CN at r. t.; plotting of $A_0/(A_0–A)$ *versus* [Na$^+$]$^{-1}$ at 286 nm (inset).

more positive (50 mV) than that of Ru(bpy)$_3^{2+}$, but slightly more negative (by about 60 mV) than that of the parent complex [(bpy)$_2$Ru(dafo)]$^{2+}$ (dafo = 4,5-diazafluoren-9-one) [41, 42]. The oxidation indicates that ligand L^1 is a stronger π acceptor than 2,2′-bipyridine, but a weaker π acceptor than dafo. The first reduction of complex Ru-L^1 at -0.86 V is a reversible process, which is consistent with the addition of an electron to the LUMO localized on L^1 giving the species [(bpy)$_2$Ru$^{\mathrm{II}}$L$^{\bar{\cdot}}$]$^+$. It appears that ligand L^1 is more easily reduced than 2,2′-bipyridine, so complex Ru-L^1 should possess an excited state lower in energy than the Ru(II)→bpy charge transfer states. 4,5-diazafluoren-9-one derivatives are known to be lower than 2,2′-bipyridine in the spectrochemical series [41, 42], and the absorption spectra of complex Ru-L^1 do not show any particular band significantly lower in energy than Ru(bpy)$_3$]$^{2+}$. Therefore the easy reduction probably involves an orbital which does not receive a significant contribution from the chelating nitrogen atoms of the ligand L^1, and the promoted electron is most likely associated with the C=N moiety of ligand L^1 [41, 42]. The second quasi-reversible reduction process at -1.42 V is located on one of the two 2,2′-bipyridine ligands of the Ru(II) center, adding an electron to the 2,2′-bipyridine localized LUMO+1 orbital yielding the species [(bpy)(bpy$^{\bar{\cdot}}$)Ru$^{\mathrm{II}}$L$^{\bar{\cdot}}$]. The third reduction at -1.66 V is reversible and affords the species [(bpy$^{\bar{\cdot}}$)(bpy$^{\bar{\cdot}}$)Ru$^{\mathrm{II}}$L$^{\bar{\cdot}}$]$^-$. The electrochemical behavior of complex Ru-L^2 is similar to that of complex Ru-L^1.

Cation Binding

The cation binding properties of the two complexes were investigated by UV/Vis absorption and emission spectroscopy and electrochemistry. A tracing of the UV/Vis absorption spectra upon a sequential addition of Na$^+$ ($0–3\times10^{-3}$ mol L^{-1}) to the CH$_3$CN solution of complex Ru-L^1 (10^{-5} mol L^{-1}) is shown in Fig. 4, which shows a gradual increase in absorbance intensities upon increasing Na$^+$ concentration, reaching a saturation at high Na$^+$ concentration. With such absorption information, the binding constant could be determined with the equation $A_0/(A_0-A) = [\varepsilon_\mathrm{f}/(\varepsilon_\mathrm{f}-\varepsilon_\mathrm{b})]$ $(1+1/K_\mathrm{s}[\mathrm{M}])$. A_0 is the initial absorbance in the absence of Na$^+$, A is the absorbance of the solution at a Na$^+$ concentration [Na$^+$], ε_f and ε_b are the molar absorption coefficients of the host complex and the bound species, respectively, and K_s is the binding constant. Plotting $A_0/(A_0-A)$ *versus* [Na$^+$]$^{-1}$ at 286 nm gives a satisfactory straight line, and the binding constant determined from the ratio of the *y* intercept/slope is 595 M^{-1} [44]. The satisfactory linearity of the fit ($R = 0.9988$) supports a stoichiometry of 1 : 1. This is in

Fig. 5 (color online). Color changes are seen by naked eye for the complex Ru-L^1 (10^{-3} mol L^{-1}) in 0.1 mol L^{-1} TBAP/CH_3CN solution upon increasing [Na^+] from 0 to 0.1 mol L^{-1} (from right to left).

accordance with the well-known preference of benzo-15-crown-5 for the sodium ion due to its appropriate cavity size. Furthermore, color changes of complex Ru-L^1 (10^{-3} mol L^{-1}) in 0.3 mol L^{-1} TBAP/CH_3CN solution as a function of [Na^+] are shown in Fig. 5. Upon increasing [Na^+] from 0 to 0.1 mol L^{-1}, the color of the solution gradually changes from orange to deep red. Complex Ru-L^2 has a similar absorption behavior with Li^+ and the binding constant is 398 M^{-1}.

Fig. 6 shows the emission spectra of complex Ru-L^1 as a function of [Na^+]. The emission intensity of the EtOH-MeOH (4 : 1, v/v) glassy matrices of complex Ru-L^1 (10^{-5} mol L^{-1}) undergoes a progressive decrease that is [Na^+]-dependent. After complete complexation, the emission intensity declines to a minimum value of $I/I_0 = 0.34$ at [Na^+] = 3×10^{-3} mol L^{-1}. The system shows an effective on/off response to the interaction with the sodium ion. Addition of Li^+ to the solution of complex Ru-L^2 also causes a progressive decrease in emission intensity to $I/I_0 = 0.42$ at [Li^+] = 3×10^{-3} mol L^{-1}. Emission quenching can be ascribed to binding of the cation to the polyether cavity, by which the environment around the Ru(II) polypyridyl complex chromophore is perturbed.

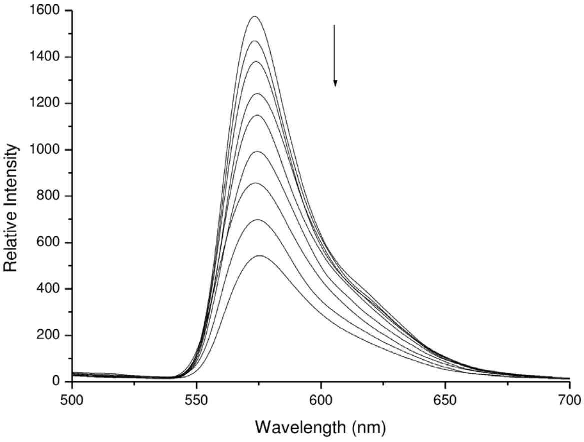

Fig. 6. Emission titration spectra of complex Ru-L^1 (1×10^{-5} mol L^{-1}) with added $NaClO_4$ ($0-3 \times 10^{-3}$ mol L^{-1}) in an EtOH-MeOH (4 : 1, v/v) glassy matrix.

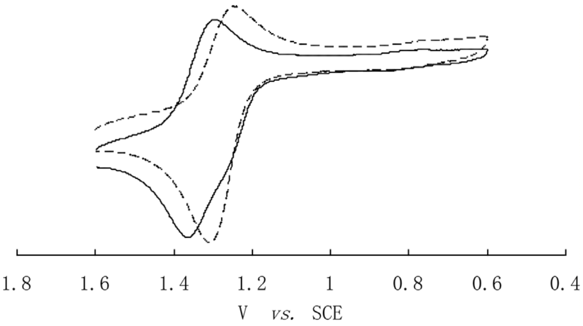

Fig. 7. Cyclic voltammetry of complex Ru-L^1 (5×10^{-4} mol L^{-1}) in CH_3CN (0.1 mol L^{-1} TBAP) in the absence (solid) and presence (dash) of $NaClO_4$.

The oxidation couple of complex Ru-L^1 experiences a progressive cathodal shift upon addition of Na^+ to the CH_3CN solution with 0.1 mol L^{-1} TBAP as supporting electrolyte. After complete interaction, the Ru(II)-centered $E_{1/2}$ shifts from 1.328 to 1.274 V (Fig. 7). Binding of the cation introduces a positive charge on the polyether cavity. The positive charge may be partly delocalized over the whole ligand framework, which increases the σ-donor and decreases the π-acceptor capacity of the ligand, resulting in a destabilization of the $d\pi$ orbital of Ru(II). This facilitates the oxidation of Ru(II) by removal of an electron from the $d\pi$ orbital of Ru(II). The electrochemical behavior of complex Ru-L^2 is the same as that of complex Ru-L^1, the Ru(II)-centered $E_{1/2}$ of complex Ru-L^2 also having a 42 mV cathodal shift after complete complexation with Li^+.

Conclusion

In an attempt to take advantage of the activity of benzocrown ethers to selectively bind metal ions, two polypyridyl ligands containing the macrocyclic units benzo-12-crown-4 or benzo-15-crown-5, and their corresponding Ru(II) complexes have been prepared. The two complexes exhibit conventional electrochemical and spectroscopic properties. They exhibit specific sequestering ability for Na^+ or Li^+, respectively, according to the results of UV/Vis absorption and emission spectroscopy and electrochemistry titrations, and therefore are potential candidates as chemical sensor for Na^+ or Li^+ probing.

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