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Synthesis, emission, electrochemistry and cation-binding studies of ruthenium(II)–diimine–crown and –terpyridine–crown complexes

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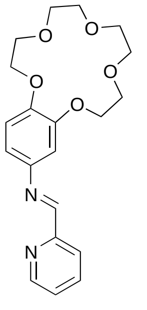
A series of ruthenium(II) complexes with crown-containing ligands of the types $[\mathrm{Ru}(\overset{\frown}{\mathrm{NN}})_2(\mathrm{L}')]^{2+}$ {$\overset{\frown}{\mathrm{NN}}$ = 2,2′-bipyridine (bipy), L′ = *N*-(2-pyridinylmethylene)-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclononadecin-16-ylamine (dic); $\overset{\frown}{\mathrm{NN}}$ = 1,10-phenanthroline (phen), L′ = dic} and $[\mathrm{Ru}(\overset{\frown}{\mathrm{NN}})(\mathrm{L}')]^{2+}$ {$\overset{\frown}{\mathrm{NN}}$ = L′ = *N*-[4-{4′-(2,2′ : 6′,2″-terpyridyl)}benzyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane (L^1); $\overset{\frown}{\mathrm{NN}}$ = 2,2′ : 6′,2″-terpyridine (terpy), L′ = L^1} have been synthesized and their emission, electrochemical and cation-binding properties studied.

Design and synthesis of organic host molecules which could selectively accommodate a metal ion at its co-ordination site/cavity and undergo a concurrent colour or redox change have been considered as a worthwhile subject in host–guest chemistry.[1] Recently, increasing attention has been paid to the design of inorganic hosts[2] with the awareness of the interesting photochemical and photophysical properties involved in the metal to ligand charge-transfer (MLCT) state of many inorganic systems. However, most of these studies focus on the synthesis and preliminary changes that occur upon cation binding, with relatively few systems subject to intensive binding studies.[3,4]

As an extension of our previous work on transition-metal complexes with crown ether pendants,[3,4] we report herein the synthesis of two species of ruthenium(II) polypyridine complexes with crown ether pendants: ruthenium(II)–terpyridine complexes with an azacrown pendant and ruthenium(II)–diimine complexes with a benzocrown moiety. The emission, electrochemistry and cation-binding properties of these ruthenium(II) complexes are also reported.



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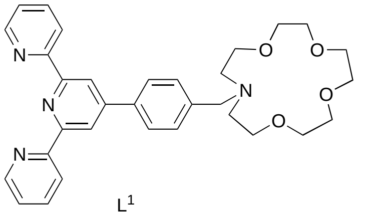
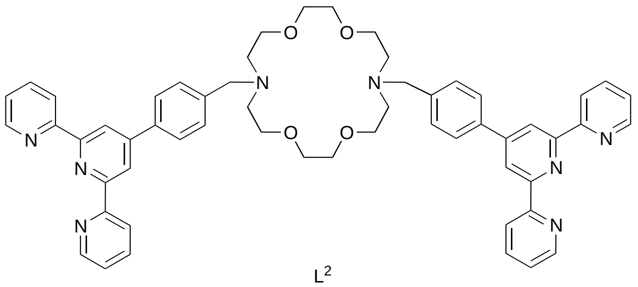


L^1



L^2

Experimental

Ruthenium trichloride was obtained from Johnson Matthey Chemical Company. 2,2′-Bipyridine (bipy), 1,10-phenanthroline (phen), 2,2′ : 6′,2″-terpyridine (terpy), 2-pyridinecarboxaldehyde, 2-acetylpyridine, 4-formyltoluene, 1-aza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane), 1-aza-18-crown-6 (1,4,7,10,13-pentaoxa-16-azacyclooctadecane) and 4,13-diaza-18-crown-6 (1,4,7,10-tetraoxa-13,16-diazacyclooctadecane) were obtained from Aldrich Chemical Company. 4′-(4-Tolyl)(2,2′ : 6′,2″-terpyridine) (tterpy),[5,6] 4′-[(4-bromomethyl)-phenyl]-2,2′ : 6′,2″-terpyridine (bmpterpy),[7] *N*-(2-pyridylmethylene)phenylamine (di),[8] *N*-(2-pyridinylmethylene)-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclononadecin-16-ylamine (dic),[3,4] $[\mathrm{Ru(terpy)Cl_3}]$,[9] *cis*-$[\mathrm{Ru(bipy)_2Cl_2}]\cdot 2\mathrm{H_2O}$,[10] *cis*-$[\mathrm{Ru(phen)_2Cl_2}]\cdot 2\mathrm{H_2O}$,[10] $[\mathrm{Ru(phen)_2(di)}]^{2+}$,[8] $[\mathrm{Ru(terpy)(tterpy)}]^{2+}$,[6] $[\mathrm{Ru(terpy)(L^1)}]^{2+}$ (L^1 = *N*-[4-{4′-(2,2′ : 6′,2″-terpyridyl)}benzyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane) and $[\{\mathrm{Ru(terpy)}\}_2(\mathrm{L}^2)]^{4+}$ (L^2 = *N*,*N*′-bis[4-{4′-(2,2′ : 6′,2″-terpyridyl}benzyl]-1,4,7,10-tetraoxa-13,16-diazacyclooctadecane)[11] were synthesized according to literature procedures. All other reagents were of analytical grade and were used as received.

Syntheses

***N*-[4-{4′-(2,2′ : 6′,2″-terpyridyl)}benzyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane L^1.** A mixture of bmpterpy (247 mg, 0.60 mmol), 1-aza-15-crown-5 (145 mg, 0.66 mmol) and *N*,*N*-diisopropylethylamine (50 µl) in ethanol (15 $\mathrm{cm^3}$) was refluxed for 24 h. The solvent was then removed and the residue dissolved in dichloromethane (2 $\mathrm{cm^3}$) and purified by column chromatography on alumina using diethyl ether–acetone as eluent. A pale yellow oil was obtained. Yield: 162 mg, 50%. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, 298 K): δ 2.84 (m, 4 H, $\mathrm{CH_2N}$), 3.64–3.72 (m, 16 H, $\mathrm{CH_2O}$), 3.76 (s, 2 H, $\mathrm{C_6H_4C}H_2\mathrm{N}$), 7.33–7.38 (m, 2 H, pyridyl H), 7.49 (d, *J* = 8, 2 H, aryl H), 7.83–7.91 (m, 2 H, pyridyl H; 2 H, aryl H), 8.67 (dt, *J* = 8 and 1 Hz, 2 H, pyridyl H) and 8.75 (m, 4 H, pyridyl H).

$[\mathrm{Ru(bipy)_2(dic)}][\mathrm{PF_6}]_2$ 1. The compounds *cis*-$[\mathrm{Ru(bipy)_2Cl_2}]\cdot 2\mathrm{H_2O}$ (52 mg, 0.10 mmol) and AgOTf (OTf = $\mathrm{O_3SCF_3}$) (51 mg, 0.20 mmol) were suspended in $\mathrm{N_2}$-deaerated acetone (25 $\mathrm{cm^3}$). The mixture was stirred for 3 h at room temperature and filtered by gravity. To the clear red-brown solution was added 1.5 equivalents of dic (56 mg, 0.15 mmol). The solution was then deaerated by N_2 bubbling, and refluxed for 12 h with vigorous stirring. The brownish red solution was then evaporated to dryness. The brown residue was then taken up in ethanol, filtered and precipitated with a saturated aqueous solution of NH_4PF_6. The precipitate was collected by filtration and washed with diethyl ether to remove any unreacted dic ligand. The crude product was recrystallized from acetonitrile–diethyl ether to give pure brown plates of compound **1**. Yield: 50 mg, 47%. ^{1}H NMR (300 MHz, CD_3CN, 298 K): δ 3.55–3.98 (m, 16 H, CH_2O), 6.08–6.17 (m, 2 H, aryl H), 6.49 (d, $J = 8$, 1 H, aryl H), 7.24 (m, 1 H, pyridyl H), 7.35–7.67 (m, 6 H, pyridyl H), 7.76 (d, $J = 6$, 2 H, pyridyl H), 7.84 (td, $J = 8$ and 1, 1 H, pyridyl H), 8.03–8.17 (m, 5 H, pyridyl H), 8.28 (t, $J = 8$ Hz, 2 H, pyridyl H), 8.55 (m, 3 H, pyridyl H) and 8.99 (s, 1 H, N=CH). Positive-ion fast atom bombardment (FAB) mass spectrum: m/z 787 $\{M\}^+$ and 629 $\{M - \text{bipy}\}^+$ (Found: C, 46.24; H, 3.47; N, 7.58. Calc. for the triflate salt $C_{42}H_{40}F_6N_6O_{11}RuS_2$: C, 46.54; H, 3.69; N, 7.75%).

[Ru(phen)$_2$(dic)][PF$_6$]$_2$ 2. The synthesis of [Ru(phen)$_2$(dic)][PF$_6$]$_2$ was similar to that of [Ru(bipy)$_2$(dic)][PF$_6$]$_2$ except [Ru(phen)$_2$Cl$_2$]·2H$_2$O was used instead of [Ru(bipy)$_2$Cl$_2$]·2H$_2$O. The red solid was recrystallized from dichloromethane–diethyl ether. Yield: 43 mg, 38%. ^{1}H NMR (300 MHz, CD_3CN, 298 K): δ 3.55–3.98 (m, 16 H, CH_2O), 5.86 (d, $J = 2$, 1 H, aryl H), 6.12 (dd, $J = 8$ and 2, 1 H, aryl H), 6.30 (d, $J = 8$, 1 H, aryl H), 7.31–7.41 (m, 2 H, phen H), 7.67 (d, $J = 5$, 1 H, pyridyl H), 7.75 (d, $J = 5$ Hz, 1 H, pyridyl H), 7.88–8.07 (m, 4 H, phen H; 1 H, pyridyl H), 8.14–8.18 (m, 2 H, phen H), 8.24–8.32 (m, 4 H, phen H), 8.56–8.75 (m, 2 H, phen H; 1 H, pyridyl H), 9.00 (s, 1 H, C=NH) and 9.02 (s, 2 H, phen H). Positive-ion FAB mass spectrum: m/z 833 $\{M\}^+$ and 653 $\{M - \text{phen}\}^+$ (Found: C, 44.53; H, 3.67; N, 7.22. Calc. for $C_{44}H_{40}F_{12}N_6O_5P_2Ru \cdot CH_2Cl_2$: C, 44.70; H, 3.50; N, 6.95%).

[Ru(L^1)$_2$][PF$_6$]$_2$ 3. The compounds $RuCl_3 \cdot 2H_2O$ (100 mg, 0.48 mmol) and L^1 (540 mg, 1.00 mmol) were dissolved in ethanol–H$_2$O (15 cm^3, 1:1, v/v) and allowed to reflux for 24 h. The orange solution was then filtered and rotary evaporated to about 5 cm^3. Addition of a saturated aqueous solution of NH_4PF_6 to the concentrated solution of the complex precipitated a bright orange solid. The solid was collected by filtration and recrystallized by vapour diffusion of diethyl ether into a concentrated acetonitrile solution of the complex to give bright orange plates of compound **3**. Yield: 459 mg, 65%. ^{1}H NMR (300 MHz, CD_3CN, 298 K): δ 3.38–4.00 (m, 40 H, CH_2CH_2), 4.64 (s, 4 H, $C_6H_4CH_2N$), 7.17–7.22 (m, 4 H, pyridyl H), 7.44 (d, $J = 7$, 4 H, aryl H), 7.91–8.00 (m, 4 H, aryl H; 4 H, pyridyl H), 8.30 (d, $J = 8$, 2 H, pyridyl H), 8.36 (t, $J = 8$ Hz, 2 H, pyridyl H), 8.65–8.96 (m, 4 H, pyridyl H) and 9.03 (s, 4 H, pyridyl H). Positive-ion FAB mass spectrum: m/z 1326 $\{M + PF_6\}^+$ and 1181 $\{M\}^+$ (Found: C, 52.18; H, 5.10; N, 7.57. Calc. for $C_{64}H_{72}F_{12}N_8O_8P_2Ru$: C, 52.21; H, 4.93; N, 7.61%).

[Ru(terpy)(L^1)][PF$_6$]$_2$ 4. A mixture of [Ru(terpy)Cl$_3$] (85 mg, 0.19 mmol) and L^1 (110 mg, 0.2 mmol) in ethanol (15 cm^3) with a few drops of triethylamine as reductant was refluxed for 24 h. The brown suspension turned reddish orange. The solution was then concentrated to about 5 cm^3 and filtered to remove any unreacted [Ru(terpy)Cl$_3$]. To the filtrate, a saturated aqueous solution of NH_4PF_6 was added dropwise until no further precipitation occurred. The solid was collected and recrystallized from dichloromethane–diethyl ether to give red-orange needles of compound **4**. Yield: 122 mg, 55%. ^{1}H NMR (300 MHz, CD_3CN, 298 K) δ 3.38–4.00 (m, 20 H, CH_2CH_2), 4.63 (s, 2 H, $C_6H_4CH_2N$), 7.13–7.21 (m, 4 H, pyridyl H), 7.35–7.39 (m, 2 H, aryl H; 2 H, pyridyl H), 7.89–7.95 (m, 2 H, aryl H; 4 H, pyridyl H), 8.30 (d, $J = 8$, 2 H, pyridyl H), 8.43 (t, $J = 8$, 1 H, pyridyl H), 8.50 (d, $J = 8$, 2 H, pyridyl H), 8.65 (d, $J = 8$, 2 H, pyridyl H), 8.76 (d, $J = 8$ Hz, 2 H, pyridyl H) and 9.00 (s, 2 H, pyridyl H). Positive-ion FAB mass spectrum: m/z 1019 $\{M + PF_6\}^+$ and 874 $\{M\}^+$ (Found: C, 42.31; H, 3.53; N, 6.96. Calc. for $C_{47}H_{47}F_{12}N_7O_4P_2Ru \cdot 3CH_2Cl_2$: C, 42.30; H, 3.76; N, 6.91%).

Physical measurements and instrumentation

The UV/VIS spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorometer. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. Proton NMR spectra were recorded on a Bruker DPX-300 Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane. Positive-ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new complexes were performed by Butterworth Laboratories Ltd.

Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150-10 pulsed Nd:YAG laser. Luminescence decay signals were recorded on a Tektronix Model TDS 620 A digital oscilloscope and analyzed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a round-bottomed flask (10 cm^3) equipped with a side-arm fluorescence cuvette (pathlength 1 cm) and sealed from the atmosphere with a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

Cyclic voltammetric measurements were carried out with a PAR model 175 universal programmer and a model 173 potentiostat. Cyclic voltammograms were recorded with a Kipp & Zonen BD90 X−Y recorder at scan rates 50–500 mV s^{-1}. The electrolytic cell used was a conventional two-compartment cell. The reference electrode is the Ag–AgNO$_3$ (0.1 M in acetonitrile) electrode with a vycor glass interfacing the working electrode compartment. Electrochemical studies were performed in non-aqueous medium (0.1 M NBu_4PF_6 in acetonitrile) with the glassy carbon (Atomergic Chemetal V25) electrode as working electrode and a piece of platinum gauze as counter electrode which was separated from the working electrode by a sintered glass frit. The ferrocenium–ferrocene couple was used as the internal reference.

Electronic absorption titrations for binding constant determination were performed with a Hewlett-Packard 8452A diode array spectrophotometer at 25 °C controlled by the Lauda RM6 compact low-temperature thermostat. A supporting electrolyte (0.1 M NBu_4PF_6) was added to maintain constant ionic strength of the sample solution during the titration. This is especially important for MLCT transitions which are usually rather sensitive to the nature of the solution medium.

Results and Discussion

The synthesis of the dic ligand was a simple Schiff-base formation from the condensation of 2-pyridinecarboxaldehyde and 4′-aminobenzo-15-crown-5 (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylamine). Complexes **1** and **2** were prepared in reasonable yields from the reaction of dic and the respective precursor complexes [Ru(bipy)$_2$(Me$_2$CO)$_2$]$^{2+}$ and [Ru(phen)$_2$(Me$_2$CO)$_2$]$^{2+}$ in ethanol. The procedure is similar to those reported for other heteroleptic ruthenium(II) polypyridine complexes.[10]

The terpyridine moiety of the terpyridine–crown ligands L^1 and L^2 are connected to the crown moiety through a benzyl bridge. In order to obtain a reasonable amount of the terpyridine precursor, the one-step Hantzsch synthesis developed by Case and Kaspen[12] and later by Spahni and Calzaferri[7] was applied. The bromination step of ttерpy can easily be achieved by a radical reaction with N-bromosuccinimide (NBS) accord-

Table 1 Electrochemical data for complexes **1**–**4** in CH_3CN (0.1 M $NBu^n_4PF_6$)[a]

Complex	Reduction $E_{\frac{1}{2}}$ *vs.* SCE[b]/V ($E_{\frac{1}{2}}$ in Na^+)[c]	ΔE_{red}/mV anodic shift upon Na^+ addition	Oxidation $E_{\frac{1}{2}}$ *vs.* SCE[b]/V ($E_{\frac{1}{2}}$ in Na^+)[c]
1	−1.09 (−1.04),	45	+1.30
	−1.56 (−1.56)	0	(+1.30)
2	−1.11 (−1.05),	56	+1.37
	−1.51 (−1.50)	6	(+1.37)
$[Ru(phen)_2(di)]^{2+}$	−1.05 (−1.05),	0	+1.34
	−1.51 (−1.51)	0	(+1.34)
3	−1.30 (−1.30),	0	+1.29
	−1.54 (−1.54)	0	(+1.29)
4	−1.29 (−1.29),	0	+1.27
	−1.54 (−1.54)	0	(+1.27)

[a] Working electrode, glassy carbon; scan rate, 100 mV s^{-1}. [b] SCE = saturated calomel electrode. [c] Measurements made in CH_3CN (0.1 M $NaClO_4$).

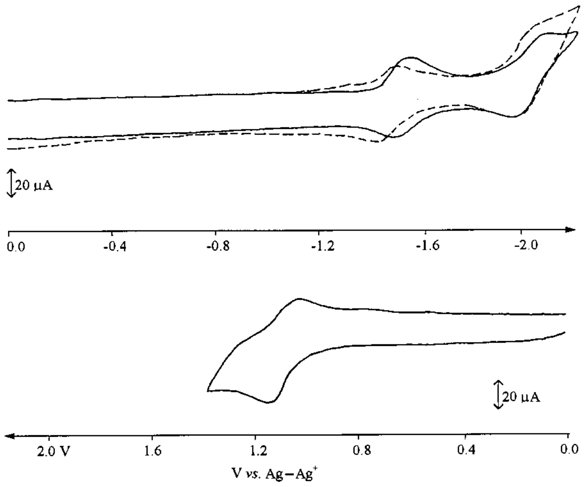


Fig. 1 Cyclic voltammograms of $[Ru(bipy)_2(dic)]^{2+}$ in 0.1 M $NBu^n_4PF_6$ (——) and in 0.1 M $NaClO_4$ in acetonitrile (– – –). Scan rate 100 mV s^{-1}

ing to the procedure reported by Spahni and Calzaferri.[7] The incorporation of the crown pendant is straightforward, involving the reaction between secondary amines and alkyl halides. Similar ligands with crown ether pendants were synthesized by Ward and co-workers recently.[11]

The homoleptic complex $[Ru(L^1)_2][PF_6]_2$ **3** was prepared in good yield from $RuCl_3 \cdot 2H_2O$ and L^1 in ethanol.The heteroleptic complex $[Ru(terpy)(L^1)][PF_6]_2$ **4** was obtained in two steps which involve the initial preparation of $[Ru(terpy)Cl_3]$ and the subsequent reaction of the terpyridine–crown ligand with $[Ru(terpy)Cl_3]$ in ethanol under reflux in the presence of a mild reducing agent such as triethylamine. All the newly synthesized complexes gave satisfactory elemental analyses and have been characterized by positive-ion FAB mass spectrometry and ^1H NMR spectroscopy.

The electrochemical data of the complexes together with that of a related uncrowned analogue are in Table 1. The cyclic voltammogram of **1** is shown in Fig. 1. The cyclic voltammograms of complexes **1**, **2** and $[Ru(phen)_2(di)]^{2+}$ all exhibit two quasi-reversible reduction couples and a reversible oxidation couple, with $\Delta(E_{pa} - E_{pc})$ of the reduction couples of *ca.* 60–90 mV. The oxidation couples for these complexes are typical of those observed in other ruthenium(II)–diimine complexes and are assigned as the $Ru^{3+/2+}$ couples. The first reduction couple of the complexes are assigned as reductions of the dic or di ligands.

Upon addition of Na^+ ions, complexes **1** and **2** experienced an anodic shift in the first reduction couple, while the oxidation and second reduction waves remained more or less unperturbed (Fig. 1). Control experiments using the uncrowned ruthenium(II) complexes showed no shifts in the redox couples upon addition of cations, indicative of the authentic binding nature of the crown analogues rather than an ionic effect. The bound Na^+ ion introduces a positive charge on the crown ligand and hence facilitates the reduction. Moreover, the electron-donating effect of the polyether group on the benzocrown could be considered as being diminished in the presence of Na^+. Such an anodic shift has also been observed in many other crown-linked systems. For example, 1,1′-dimethyl-3,3′-bis[*N*-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylcarbamoyl]-4,4′-bipyridinium displayed a 45 mV anodic shift upon cation inclusion.[13] However, for many neutral redox-active organic compounds with a crown pendant, such as nitrobenzo substituted lariat crown ethers,[14,15] a substoichiometric amount of the guest metal cation results in two well resolved redox couples corresponding to the free molecule and the sodium cation-bound species. The observation of the coexistence of the two waves rather than a shift in the potential alone was attributed to the much larger binding constant, K_s, of these neutral compounds. The presence of positive charges on the crowned ruthenium(II) complexes would inevitably lead to a smaller binding constant, K_s, and hence, an anodic shift in the first reduction couple was observed instead.

The shifts of the first reduction wave of **1** upon addition of Li^+, Na^+ and K^+ ions are 30, 45 and 25 mV, respectively. No further shifts were observed in the presence of an excess of alkali-metal cations. The anodic shifts of the first reduction potentials of complexes **1** and **2** upon binding of the alkali-metal cations decrease in the order: $Na^+ > Li^+ > K^+$, indicative of the larger effects of sodium and lithium ions in comparison to that of potassium ions. These findings are consistent with the stronger binding of sodium and lithium ions to the 15-crown-5 moiety as well as the lowest charge density of potassium ions among the three cations studied. Similar results were obtained in the electrochemical studies of the crown ether benzodithiolene complexes reported by Lowe and Garner.[16] Similar magnitudes of the anodic shifts have also been observed in other quinone and nitrobenzene redox-active macrocycles.[14,15]

Both complexes **3** and **4** exhibit similar cyclic voltammograms, with two reversible reduction couples and a reversible oxidation couple. The oxidation couples are assigned as the $Ru^{3+/2+}$ couple with the reduction couples as the terpyridine ligand-based reductions. No remarkable changes were observed in the cyclic voltammograms of complexes **3** and **4** upon addition of Na^+ ions. This may possibly be due to an insignificant communication between the crown pendant and the Ru(II)–terpy moiety. As commonly observed in other host systems with pendants attached through methylene bridges,[17] the electronic communication is negligible since the methylene bridge functions as an insulatory linkage between the receptor and the reporter. Similar findings were reported for the related aza-18-crown-6 complexes.[11]

The electronic absorption spectral data of the complexes are summarized in Table 2. The electronic absorption spectra of

Table 2 Photophysical and electronic absorption spectral data for complexes **1**–**4** at 298 K

Complex	Medium	Emission maximum/nm (τ_o/μs)	λ_{abs}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})
1	CH_3CN	797 (0.10)	286 (48), 388 (8.3), 424 (10), 474 (8.6)
	0.1 M $NaClO_4$ in CH_3CN	807 (0.25)	
2	CH_3CN	780 (0.16)	264 (53), 382 (10), 420 (9.3), 480 (7.2)
	0.1 M $NaClO_4$ in CH_3CN	788 (0.26)	
$[Ru(phen)_2(di)]^{2+}$	CH_3CN	760 (0.49)	264 (85), 382 (9.7), 438 (14), 476 (13)
3	CH_3OH	642	
	CH_3CN	644	274 (83), 284 (82), 312 (81), 330 (sh) (53), 490 (35)
4	CH_3OH	646	
	CH_3CN	653	274 (45), 282 (46), 310 (62), 330 (sh) (32), 484 (21)
$[Ru(terpy)(L)]^{2+}$	CH_3OH	645	
	CH_3CN	648	283 (24), 308 (30), 484 (10)*
$[\{Ru(terpy)\}_2(L^2)]^{4+}$	CH_3CN	641	283 (46), 308 (55), 484 (18)*

* From ref. 11.

complexes **1** and **2** are dominated by intense absorptions in the UV region and two broad bands in the visible region. The high-energy absorptions are typical of ligand-centred transitions. The lowest energy band at *ca*. 474–480 nm was tentatively assigned as a dπ(Ru)→π*(dic) MLCT transition, while the adjacent band at *ca*. 420–424 nm was tentatively assigned as an admixture of MLCT dπ(Ru)→π*(bipy) or dπ(Ru)→π*(phen) transitions and an intraligand π→π*/n→π* transition of the dic ligand. Upon addition of alkali-metal ions at a constant ionic strength, a blue shift in the absorption energies is observed. These shifts were ascribed to the binding of the cations to the polyether cavity, as similar effects were absent in the uncrowned complex $[Ru(phen)_2(di)]^{2+}$. Similar findings have also been observed in related copper(I)[3] and rhenium(I) systems.[4] The electronic absorption spectra of complexes **3** and **4** are also characterized by intense bands in the UV and visible region. The high energy absorptions in the UV region are typical of ligand-centred (LC) transitions. The intense absorption in the visible region at *ca*. 484–490 nm is assigned as a metal to ligand charge-transfer (MLCT) transition. It is likely that the absorption band at *ca*. 484 nm in complex **4** corresponds to an admixture of dπ(Ru)→π*(terpy) and dπ(Ru)→π*(L^1) MLCT transitions. The MLCT absorptions at similar wavelengths have also been observed in the crowned analogues of different ring size, $[Ru(terpy)(L)]^{2+}$ and $[\{Ru(terpy)\}_2(L^2)]^{4+}$ [11] and uncrowned $[Ru(tterpy)_2]^{2+}$, $[Ru(terpy)_2]^{2+}$ and $[Ru(terpy)(tterpy)]^{2+}$.[5,18]

The absorption energies of complexes **3**, **4** and the related $[Ru(terpy)(L)]^{2+}$ and $[\{Ru(terpy)\}_2(L^2)]^{4+}$ were found to be rather insensitive to the presence of alkali-metal ions. This probably arises as a result of the presence of the insulating methylene bridge between the crown pendant and the ruthenium(II)–terpyridine chromophore.

The photophysical data of the complexes are summarized in Table 2. Acetonitrile solutions of complexes **1** and **2** produced red emission with a maxima at *ca*. 780–790 nm upon excitation at $\lambda > 350$ nm. The origin of the emission is possibly derived from the lowest triplet MLCT state as commonly observed in other ruthenium(II)–diimine systems. The emission has also been found to undergo a red shift in energy with slightly increased intensity upon Na^+ ion inclusion. The red shift in emission energies could be rationalized by the lowering of the π*(dic) orbital energy upon cation binding, resulting in a lower ^{3}MLCT emission energy. The enhancement in the emission intensity is likely to be the consequence of the blocking of the intramolecular electron-transfer quenching mechanism since the unbound crown could be viewed as a dialkoxybenzene moiety capable of acting as a good electron donor. Upon cation binding, its donor properties are destroyed and the photoinduced electron transfer no longer represents a substantial quenching pathway.

An alternative explanation could be the result of the change in the energy difference between the ^{3}MLCT and triplet ligand field (^{3}LF) states. The emission decay processes could be envisaged as consisting of two channels: a temperature-independent radiative deactivation to ground state and a thermally-activated pathway from ^{3}MLCT to ^{3}LF of the ruthenium(II) center. The latter decay process was highly sensitive to the energy difference between the ^{3}MLCT and ^{3}LF states. The energy difference between the ^{3}MLCT state and ^{3}LF state would increase upon inclusion of cation. Therefore, an increase in emission intensity and a shift of emission energy to the red would occur upon cation binding.

On the other hand, excitation of solutions of complexes **3**, **4** and the related 18-membered crown analogues $[Ru(terpy)(L)]^{2+}$ and $[\{Ru(terpy)\}_2(L^2)]^{4+}$ in acetonitrile[11] at $\lambda > 350$ nm produced a very weak red emission at *ca*. 650 nm. Similar emissive properties have also been reported for the uncrowned analogues.[18] Furthermore, it is likely that the presence of the azacrown moiety, which is in fact, a tertiary amine and commonly acts as a reductive quencher, would quench the MLCT emission *via* an intramolecular reductive electron-transfer mechanism, resulting in a low luminiscence quantum yield. Such a photoinduced electron transfer (PET) quenching mechanism has also been reported by de Silva and co-workers.[19]

The emission of complexes **3**, **4** and the related $[Ru(terpy)(L)]^{2+}$ and $[\{Ru(terpy)\}_2(L^2)]^{4+}$ cations has been found to exhibit a pH dependence. The pH titration curve of complex **4** is shown in Fig. 2. Upon protonation, an enhancement in the emission intensity is observed. It is likely that the azacrown no longer functions as a good electron donor. The blocking of such a photoinduced electron transfer quenching pathway would lead to an enhancement of the luminescence quantum yield at low pH values as depicted in Scheme 1. Similar observations have also been reported in other related complexes.[20]

In the case of complex **3**, there was a slight drop in emission intensity upon lowering the pH at the very early stage and then the intensity grew again as the pH value was further decreased.

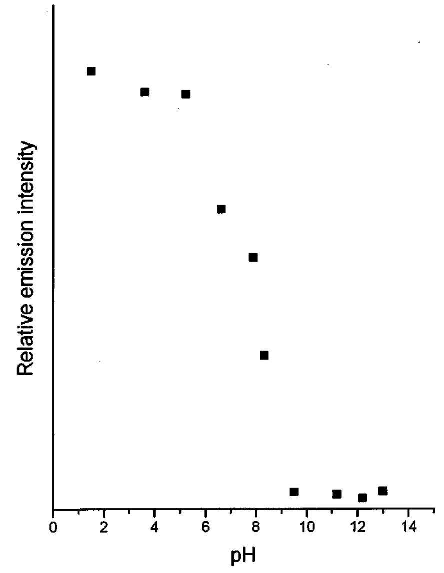
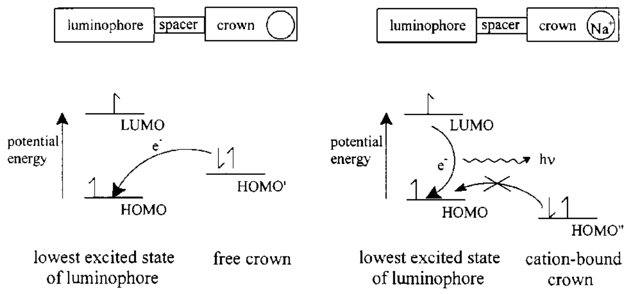


Fig. 2 The pH titration curve for complex **4**. The emission intensity was monitored at 650 nm



Scheme 1

This phenomenon may probably be attributed to the stepwise protonation of the two distant amino groups. Upon protonation of the first amino group, the remaining unprotonated amino group should still be capable of acting as a reductive quencher while the protonated one rendered the ruthenium(II) terpyridine component more electron deficient and hence a better electron acceptor. As a result, the first protonation did not inhibit the quenching process, but instead enhanced it, resulting in a drop in emission intensity at the early stage of increasing acidity of the media. Further increase in acidity ensured protonation of both azacrown moieties and blocked the quenching pathway, leading to the enhanced intensity. Similar observations have been reported in the pH dependence studies of $[Ru(bipy)_2(L^3)]^{2+}$ (L^3 = 5,5′-diaminomethyl-2,2′-bipyridine) by Grigg and Norbert.[20]

It has been well documented that azacrowns selectively bind alkali and alkaline-earth metal ions. In light of this, studies on the change of luminescent properties upon metal ion inclusion were carried out. A representative titration curve for the emission intensity of **4** at different concentration of Na^+ ions is shown in Fig. 3. Similar to the pH dependence studies, upon addition of Na^+ ions, the emission intensity increases with increasing concentration. It is likely that upon binding of the cation, which could be considered to act as an electron-withdrawing group, the azacrown moiety became a poorer electron donor and the quenching effect would be greatly reduced. Near the saturation region, there was a slight drop in I/I_0 upon further increase in the Na^+ ion concentration. It is likely that the slight drop in emission intensity is a result of ion-pairing effect. Similar observations have also been reported in other organic ion probes.[21] However, the increase in the emission intensity of **4** upon addition of cations was not significant, resulting in a large uncertainty in the determination of the binding constants using luminescence studies.

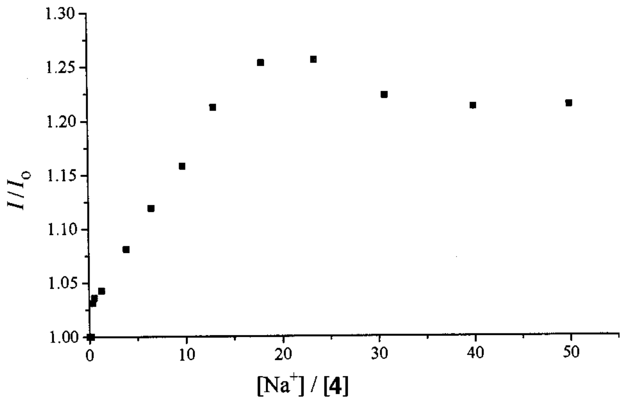


Fig. 3 Titration curve for the emission intensity of complex **4** at different concentrations of Na^+ ion

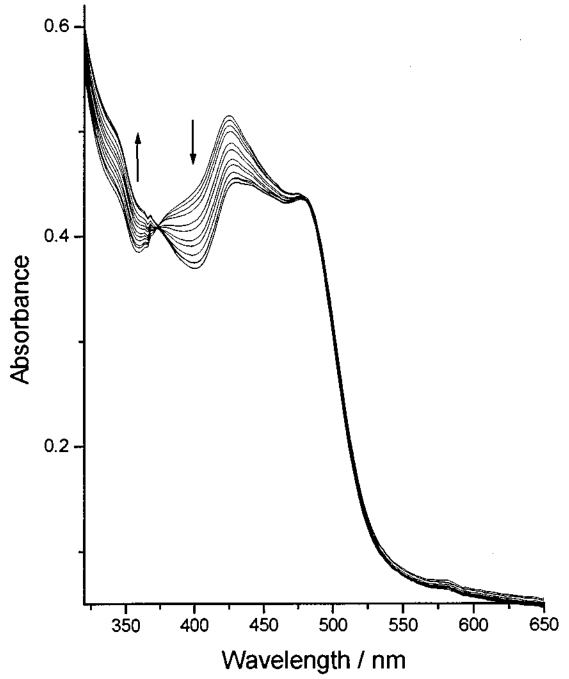


Fig. 4 The electronic absorption spectrum of complex **1** in acetonitrile upon addition of Na^+ at 298 K

The cation binding studies of complexes **1** and **2** have been pursued further using UV/VIS spectrophotometric measurements. The UV/VIS absorption spectral traces upon sequential addition of sodium ions to a solution of **1** in acetonitrile are shown in Fig. 4. A summary of the titration curves monitoring the changes in absorbance of an acetonitrile solution of **1** at 410 nm *versus* the concentration of sodium, potassium and lithium salts is depicted in Fig. 5. The curves show a gradual decrease in absorbance at 410 nm upon increasing the cation concentration, reaching saturation at higher cation concentrations. With such absorption information, the binding constants could be determined with equation (1) where A_0 is the

$$\frac{A_0}{A_0 - A} = \left(\frac{\varepsilon_f}{\varepsilon_f - \varepsilon_b}\right)\left(1 + \frac{1}{K_s[M]}\right) \qquad (1)$$

initial absorbance in the absence of metal cations, A is the absorbance of the solution mixture at an alkali-metal ion concentration [M], ε_f and ε_b are the molar absorption coefficients of the host complex $[Ru(\overset{\frown}{NN})_2(dic)]^{2+}$ ($\overset{\frown}{NN}$ = bipy **1** or phen **2**) and the bound species $[Ru(\overset{\frown}{NN})_2(dic)\cdot M]^{3+}$, respectively, and K_s is the binding constant.

A plot of $A_0/(A_0 - A)$ *versus* $[M^+]^{-1}$ gave a satisfactory straight line and the binding constant can be determined from

Table 3 Binding constants of complexes **1** and **2** with alkali-metal cations in CH_3CN at 298 K

Cation	log K_s for complex **1**	log K_s for complex **3**
Li^+	3.48	3.47
Na^+	3.35	3.25
K^+	2.72	2.58

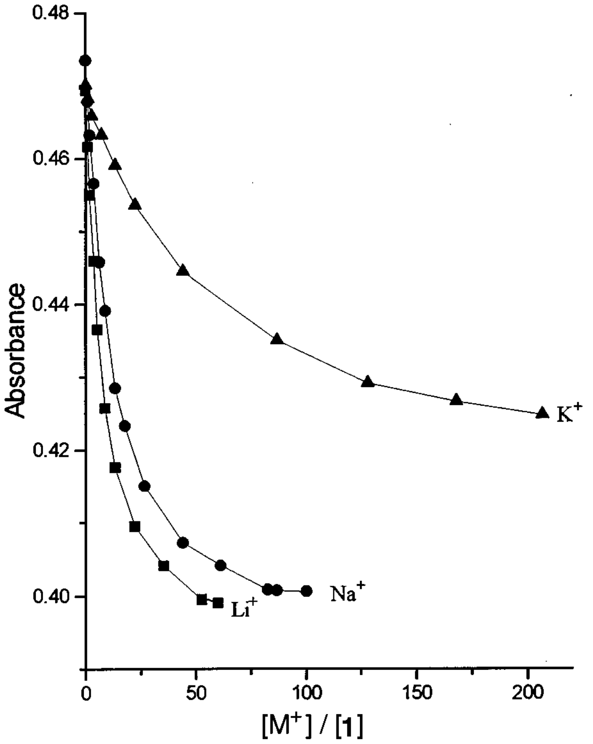


Fig. 5 The electronic absorption titration curves for complex **1** with alkali-metal cations in acetonitrile at 298 K. The absorbance was monitored at 410 nm

the ratio of the *y*-intercept/slope.[22] The binding constants for complexes **1** and **2** are collected in Table 3.

Inspection of Table 3 reveals that the binding constants of complexes **1** and **2** towards the respective ions in acetonitrile are fairly similar in magnitude. This suggests that the spectator ligands would have negligible effects on the crown ligand and would not significantly alter the binding ability of the complexes. In general, the affinity for K^+ ions is the lowest for both complexes **1** and **2**, in line with the lower selectivity of benzo-15-crown-5 (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine) for K^+ ions. It is interesting to note that the binding constants for metal ions in a series of related complexes with the dic ligand follow the order: **1** < $[Cu(dic)(PPh_3)_2]^+$ [3] < $[Re(dic)(CO)_3Cl]$,[4] suggestive of the importance of the effect of overall positive charge on the host complexes in the design of the cation probe.

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