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Photophysical properties of binuclear ruthenium(II) bis(2,2′:6′,2″-terpyridine) complexes built around a central 2,2′-bipyrimidine receptor

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A binuclear complex has been synthesized having ruthenium(II) bis(2,2′:6′,2″-terpyridine) terminals attached to a central 2,2′-bipyrimidine unit *via* ethynylene groups. Cyclic voltammetry indicates that the substituted terpyridine is the most easily reduced subunit and the main chromophore involves charge transfer from the metal centre to this ligand. The resultant metal-to-ligand, charge-transfer (MLCT) triplet state is weakly emissive and has a lifetime of 60 ns in deoxygenated solution at room temperature. The luminescence yield and lifetime increase with decreasing temperature in a manner that indicates the lowest-energy MLCT triplet couples to at least two higher-energy triplets. Cations can bind to the central bipyrimidine unit, forming both 1 : 1 and 1 : 2 (ligand : metal) complexes as confirmed by electrospray MS analysis. The photophysical properties depend on the number of bound cations and on the nature of the cation. In the specific case of binding zinc(II) cations, the 1 : 1 complex has a triplet lifetime of 8.0 ns while that of the 1 : 2 complex is 1.8 ns. The 1 : 1 complexes formed with Ba^{2+} and Mg^{2+} are more luminescent than is the parent compound while the 1 : 2 complexes are much less luminescent. It is shown that the coordinated cations raise the reduction potential of the central bipyrimidine unit and thereby increase the activation energy for coupling with the metal-centred state. Complexation also introduces a non-emissive intramolecular charge-transfer (ICT) state that couples to the lowest-energy MLCT triplet and provides an additional non-radiative decay route. The triplet state of the 1 : 2 complex formed with added Zn^{2+} cations decays preferentially *via* this ICT state.

Introduction

The photophysical properties of numerous binuclear ruthenium(II) bis(2,2′:6′,2″-terpyridine) complexes have been reported in recent years.[1] Interest in these systems stems, in part, from the realization that whereas the parent complex, $[Ru(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2″-terpyridine), is essentially nonluminescent in fluid solution at ambient temperature[2] certain derivatives emit with reasonable efficiency under these conditions.[3] It has been recognised[4] that the emission lifetime of the binuclear complex is often substantially longer than that of the corresponding mononuclear species when the bridging ligand is highly conjugated. Examples of bridging ligands range from simple hydrocarbon chains, both saturated[5] and unsaturated,[6] to aromatic polycycles such as benzene,[7] naphthalene,[8] anthracene,[9] pyrene,[10] thiophene,[11] biphenyl,[12] 9,9-dimethylxanthene,[13] quinoxaline,[14] azobenzene[15] and 2,6-bis(benzimidazol-2-yl)pyridine.[16] Extended ligands have been reported[17] for which the metal–metal separation distance is increased progressively whilst a variety of heterotopic bridging ligands has been described.[18] In addition, the luminescence properties can be modified by replacing one of the Ru^{II} centres with other cations, such as Os^{II}, so that intramolecular triplet energy transfer becomes viable.[1] An interesting variant has been to include chelating functions within the bridging ligand that can coordinate added cations.[19] This strategy allows fine-tuning of the electronic properties of the bridging ligand by attachment of different analytes from solution. Examples of such secondary chelating groups include 1,10-phenanthroline,[20] 2,2′-bipyridine,[21] polyethers[22] and calixarenes.[23] We now seek to extend the range of such multifunctional supermolecules by describing the properties of a binuclear Ru-terpy complex built around a central 5,5′-diethynylene-2,2′-bipyrimidine bridging ligand. 2,2′-Bipyrimidine, which has often been used as a ligand for mono- and binuclear Ru^{II} complexes,[24] was selected for this work because it can bind two cations.[25]

The photophysical properties of mononuclear Ru-terpy derivatives are often dominated by the lowest-energy metal-to-ligand, charge-transfer (MLCT) triplet state. This species is short-lived in the parent complex (τ_{LUM} = 250 ps)[2] but can be much longer lived in certain substituted complexes (*e.g.*, τ_{LUM} = 1.2 μs).[6] Even for the parent complex, a proper description of the emissive state requires consideration of both an upper-lying MLCT state and a high-energy metal-centred (MC) state.[26] The situation is more intricate for many binuclear complexes where the effects of ligand-localised (LL) and intramolecular charge-transfer (ICT) states have to be taken into account.[27] Evidence has been presented to the effect that the triplet quantum yields for certain binuclear Ru-terpy complexes can be less than unity.[28] Furthermore, with mixed-metal binuclear complexes it is possible to observe intervalence charge transfer intermediates.[29] It is clear, therefore, that the triplet manifold is likely to be highly congested for those binuclear Ru-terpy complexes assembled around conjugated bridging ligands, especially those containing ancillary binding sites. In such cases, the luminescence properties might be sensitive to minor changes in the surrounding environment. For example, it has been reported that coordination of cations to the vacant bipyridine-based bridging ligand increases the emission quantum yield for appropriate binuclear Ru-terpy complexes.[21] Likewise, the solution pH has a marked influence on the various reduction potentials for certain binuclear Ru-terpy derivatives assembled around benzimidazole-based bridging ligands[16] whereas coordination of cations curtails electron transfer in some calixarene-bridged complexes.[23] Here, we examine in more detail the effects of cation binding to the bridging ligand and show that the emission yield

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can either increase or decrease according to the nature and number of bound cations.

Experimental

Nuclear magnetic resonance spectra were recorded at room temperature on a Bruker AC-200 instrument using 200.1 MHz for ^{1}H NMR and 50.3 MHz for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm) relative to residual protiated solvent (1.93 ppm d_3-acetonitrile) and the carbon resonance of the solvent. High-resolution mass spectral analysis (HRMS) was performed using a Mariner ESI-ToF instrument from Applied Bio-Systems/Perkin Elmer. All relevant patterns have the expected isotopic profiles, as compared with simulated profiles. Routine absorption spectra were measured in CH_3CN solution at room temperature with a Kontron Uvikon 941 spectrophotometer. FT-IR spectra were recorded in KBr pellets with an IFS 25 Bruker spectrometer. The identity of the final compounds, and all important precursors, was made on the basis of ^{1}H NMR, FAB$^+$-MS and elemental composition. Solvents were spectroscopic grade and were freshly distilled before use. The precursors [Ru(terpy)(terpy-Br)]$(PF_6)_2$[21a] and 5,5′-dibromo-2,2′-bipyrimidine[30] were prepared according to literature procedures.

Synthesis of 5,5′-di(trimethylsilylethynyl)-2,2′-bipyrimidine

5,5′-Dibromo-2,2′-bipyrimidine (0.108 g, 0.34 mmol), trimethylsilylacetylene (110 μl, 1.12 mmol), $[PdCl_2(PPh_3)_2]$ (0.024 g, 10 mol%), and CuI (0.013 g, 20 mol%) were added to an argon-degassed solution of ^{i}Pr$_2$NH (1 mL) and THF (10 mL). After 20 h, the solvent was evaporated under vacuum and the residue quenched with water (100 ml). The residual organic matter was extracted with CH_2Cl_2 (3 × 100 ml). The organic phase was dried over $MgSO_4$ and the target compound purified by column chromatography using flash silica as support and a mixture of CH_2Cl_2–1% MeOH as eluent. The pure compound was recovered as a white powder (0.097 g, 81%). ^{1}H NMR ($CDCl_3$) δ 9.0 ppm (s, 4H), 0,3 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 160.1, 159.3, 119.9, 105.1 (C≡C), 97.7 (C≡C), −0.3 ppm (TMS). FAB$^+$ (*m*-NBA) *m*/*z* (%) 351.3 ([M + H]$^+$, 100). IR (KBr, cm^{-1}) 3415, 2960, 2160 ($\nu_{C\equiv C}$), 1567, 1507, 1419, 1245, 863, 836, 757. UV-vis (CH_2Cl_2) λ (nm) (ε, M^{-1} cm^{-1}) 297 (45,900), 313 (46,000), 328 (sh, 33,600). Elemental analysis for $C_{18}H_{22}N_4Si_2$ (M = 350.57): C, 61.67; H, 6.33; N, 15.98; found: C, 61.44; H, 6.19; N, 15.65.

Synthesis of 5,5′-diethynyl-2,2′-bipyrimidine

5,5′-Bis-[2-(trimethylsilyl)-1-ethynyl]-2,2′-bipyrimidine (0.148 g, 0.42 mmol) and KF (0.060 g, 1.00 mmol) were added to a mixture of MeOH/THF (14 mL, 1/1) and reaction was allowed to proceed for 14 h. Afterwards the solvent was evaporated to dryness and the crude product purified by chromatography on flash silica with a mixture of CH_2Cl_2 and MeOH (0.5%) as eluent, affording a white powder (0.087 g, 99%). ^{1}H NMR($CDCl_3$) δ 9.0 ppm (s, 4H), 3.5 (s, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 160.4, 159.8, 119.0, 86.4. FAB$^+$ (*m*-NBA) *m*/*z* (%) 207.4 ([M + H]$^+$, 100%), 181.2 ([M–C≡C–H]$^+$, 20). IR (KBr, cm^{-1}) 3453, 3278 ($\nu_{C\equiv C-H}$), 2360, 1637, 1569, 1514, 1421, 1370, 1244, 1111, 939, 765. UV-vis (CH_2Cl_2) λ (nm) (ε, M^{-1} cm^{-1}) 291 (5920). Elemental analysis calculated for $C_{12}H_6N_4$ (M = 206.21): C, 69.90; H, 2.93; N, 27.17; found: C, 69.72; H, 2.75; N, 27.01.

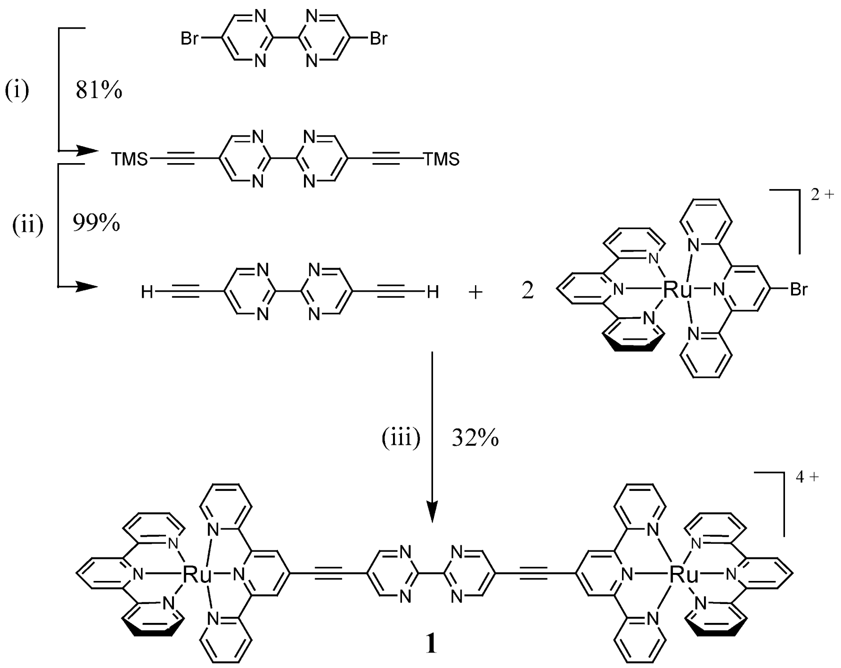
Synthesis of the dinuclear complex 1

A Schlenk flask was charged with 5,5′-diethynyl-2,2′-bipyrimidine (0.005 g, 0.025 mmol), [Ru(terpy)(terpy-Br)]$(PF_6)_2$ (0.046 g, 0.05 mmol), 10 ml degassed CH_3CN, $[Pd(PPh_3)_2Cl_2]$ (0.0011 g, 6 mol%) and CuI (0.0005 g, 10 mol%). After purging with argon, ^{i}Pr$_2$NH (0.5 mL) was added. The solution was stirred at room temperature for 6 days before KPF_6 (0.050 g, 5 eq.) in water (2 ml) was added and the solvent removed. The crude product was chromatographed on alumina, eluting with a mixture of CH_2Cl_2/CH_3CN 1/9 containing a gradient of CH_3CN/H_2O (10%). The analytically pure compound was obtained by recrystallization from CH_3CN/diethylether (0.016 g, 32%). ^{1}H NMR (CD_3CN) δ = 9.39 (s, 4H), 8.96 (s, 4H), 8.78 (d, 4H, ^3J = 8.0 Hz), 8.49 (m, 10H), 7.95 (m, 8H), 7.39 (m, 8H), 7.19 (m, 8H). ^{13}C{^{1}H} NMR (CD_3CN) δ = 161.3, 160.6, 158.3, 157.8, 156.1, 155.5, 153.0, 138.7, 136.8, 128.7, 128.2, 127.9, 125.8, 125.1, 125.0, 124.2, 118.8, 94.0, 90.1, 72.6, 61.4. MALDI-TOF *m*/*z* (nature of the peak, rel. inten.%) 494.4 ([M − 3PF$_6$]$^{3+}$, 23), 334.4 ([M − 4PF$_6$]$^{4+}$, 100). IR (KBr, cm^{-1}): 3421, 2924, 821, 558. UV-vis (CH_3CN) λ_{max}, nm (ε, M^{-1} cm^{-1}) 498 (68,600), 309 (141,700), 272 (92,600). Anal. calc. for $C_{72}H_{46}N_{16}P_4F_{24}Ru_2$ (M = 1917.27): C, 45.11; H, 2.42; N, 11.69. Found: C, 44.97; H, 2.33; N, 11.71.

Absorption spectra were recorded with a Hitachi U3310 spectrophotometer and luminescence studies were made with an Yvon-Jobin Fluorolog tau-3 spectrometer equipped with a cryogenic Ge photodetector. Emission spectra were fully corrected using a standard lamp. Luminescence spectra were recorded for optically dilute solutions after purging with dried N_2. The solution was sealed in the sample cell and cooled to the required temperature with an Oxford Instruments Optistat DN cryostat. Samples were equilibrated for at least 15 min at each temperature. Emission quantum yields were recorded with respect to ruthenium(II) tris(2,2′-bipyridine) in deoxygenated solution at room temperature.[31] Quantum yields were reproducible to within ±8% and temperatures were accurate to within ±0.2 K. Emission lifetimes were recorded after excitation of the sample with pulses delivered from either a frequency-doubled, Q-switched Nd-YAG laser (FWHM = 4 ns) or a frequency-doubled, mode-locked Nd-YAG laser (FWHM = 30 ps). Luminescence was isolated from scattered laser light with glass cut-off filters and focused onto the entrance slits of a high-radiance monochromator. The output was directed to a fast response PMT and then to a transient recorder for signal averaging. Laser flash photolysis studies were made with the Q-switched laser and with a pulsed Xe arc lamp as the monitoring source. Transient spectra were compiled point-by-point, with 5 individual laser shots being averaged at each wavelength. Kinetic measurements were made by averaging 25 individual records. Decay of the triplet excited state of **1** in the presence of excess $Zn(ClO_4)_2$ was measured after excitation with the mode-locked Nd-YAG laser and using a fast-response diode as detector. A total of 125 laser shots were averaged to obtain the required triplet lifetime.

Electrochemical studies employed cyclic voltammetry with a conventional 3-electrode system using a BAS CV-50 W voltammetric analyzer equipped with a Pt microdisk (2 mm^2) working electrode and a silver wire counter-electrode. Ferrocene was used as internal standard and was calibrated against a saturated calomel reference electrode (SSCE) separated from the electrolysis cell by a glass frit pre-soaked with electrolyte solution. Solutions contained the electrode-active substrate in deoxygenated anhydrous acetonitrile containing twice-recrystallized tetra-*N*-butylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The concentration of the solute was *ca.* 1.2 mM. The quoted half-wave potentials were reproducible to within ±15 mV.

Spectrophotometric titrations were made by adding small amounts of the required salt to a known solution of **1** in acetonitrile containing 0.1 M tetra-*N*-butylammonium hexafluorophosphate. Corrections were made for small changes in volume. The salts used were zinc(II) perchlorate, barium perchlorate, magnesium perchlorate, lithium perchlorate, potassium perchlorate or perchloric acid. The concentration of **1** was varied and at least 20 different concentrations of salt were used for each titration. Data analysis was made with SPECFIT after performing a statistical vector analysis to determine the number of significant components.



(i) [Pd(PPh$_3$)$_2$Cl$_2$] 10 mol %, CuI 20 mol %, THF, ^{i}Pr$_2$NH, rt; (ii) KF, CH$_3$OH, rt; (iii) [Pd(PPh$_3$)$_2$Cl$_2$] 6 mol %, CuI 10 mol %, CH$_3$CN, ^{i}Pr$_2$NH, rt . Conter-anions resulting from anion exchange are PF$_6^-$. TMS accounts for trimethylsilyl.

Fig. 1 Protocol used for the preparation of **1**.

Results and discussion

Synthesis

Preparation of the key 5,5′-diethynyl-2,2′-bipyrimidine platform was inspired by our previous synthesis of oligopyridine-based building blocks.[32] A Sonogashira protocol[33] was used to functionalise 5,5′-diethynyl-2,2′-bipyrimidine with trimethylsilylacetylene (Fig. 1). Quantitative deprotection was afforded with KF in protic media. A cross-coupling reaction was used to connect two [Ru(terpy)(terpy-Br)]$^{2+}$ fragments to the bipyrimidine core. This smooth reaction is promoted by palladium(0) generated *in situ* from palladium(II) and CuI. A secondary amine is required to quench the nascent acid. It is worth noting that the presence of CH$_3$CN, needed to dissolve the starting [Ru(terpy)(terpy-Br)](PF$_6$)$_2$ complex, does not significantly perturb the catalytic reaction. Similar observations were reported previously during the stepwise construction of ordered networks[34] and for certain copper-free aryl bromide cross-coupling reactions.[35] This strategy provides access to the target binuclear complex **1** without complications from side reactions or scrambling of the ruthenium centre.

Photophysical properties of the binuclear complex 1

The absorption spectrum recorded for **1** in acetonitrile solution shows a prominent metal-to-ligand, charge-transfer (MLCT) transition centred at 498 nm (Fig. 2). Weaker absorption stretching towards 630 nm can be attributed to the spin-forbidden MLCT transition while the capping terpy ligands absorb strongly around 280 nm. The bridging ligand displays several absorption bands within the 300–400 nm region. Overall, the spectrum is comparable to those noted for related alkynylene-substituted binuclear Ru-terpy complexes.[4] Luminescence could be observed in deoxygenated acetonitrile with a maximum at 705 nm (Fig. 2). The corrected excitation spectrum agrees well with the absorption spectrum across the entire visible and near-UV regions. However, the emission quantum yield was found to be very low (Φ_{LUM} = 0.0005 ± 0.0001) while the emission lifetime (τ_{LUM}) was measured as 60 ± 5 ns. Decay profiles were found to be mono-exponential at all monitoring wavelengths and independent of excitation wavelength. Both Φ_{LUM} and τ_{LUM} were highly reproducible among three different batches of **1**. Further purification by TLC immediately prior to making the photophysical measurements had no effect on either Φ_{LUM} or τ_{LUM}.

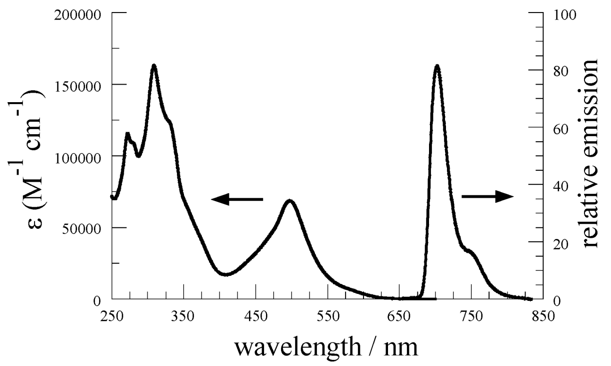


Fig. 2 Absorption and emission spectra recorded for **1** in deoxygenated acetonitrile at 20 °C.

Laser flash photolysis studies, made following excitation of **1** in deoxygenated acetonitrile at 532 nm, gave rise to a transient species that decayed with a lifetime of 60 ± 7 ns. The transient differential absorption spectrum shows strong bleaching of the MLCT band at 500 nm and of the absorption bands attributed to the bridging ligand around 300 nm (Fig. 3). There is significant absorption in the far-red region, as has been noted previously for alkynylene-substituted Ru-terpy complexes.[4] The measured decay kinetics were independent of excitation wavelength and of laser intensity. Addition of molecular oxygen caused a modest reduction in the lifetime of the transient.

In common with numerous other Ru-terpy complexes,[26,36] the emission yield and lifetime recorded for **1** in deoxygenated butyronitrile increased upon cooling the solution (Fig. 4). Following from earlier work,[37] the rate constant for non-radiative

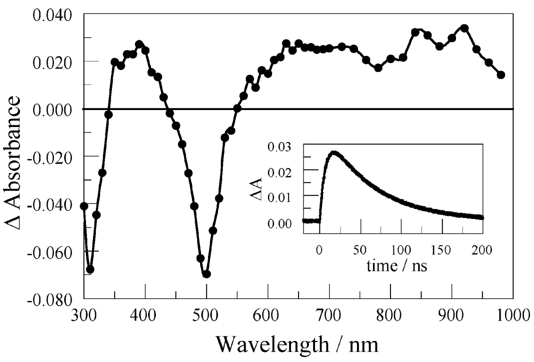


Fig. 3 Differential triplet absorption spectrum recorded after laser excitation of **1** in deoxygenated acetonitrile solution. The insert shows a decay kinetic trace recorded at 700 nm.

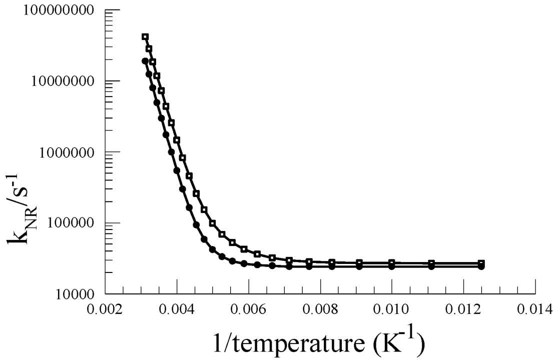


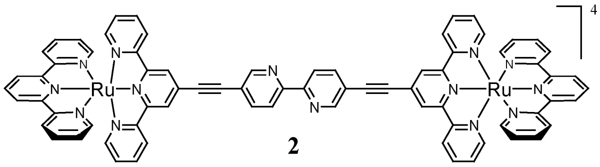
Fig. 4 Effect of temperature on the rate constant for nonradiative decay of **1** (☐) and the 1 : 1 complex (●) formed with $Mg(ClO_4)_2$ in deoxygenated butyronitrile.

decay of the triplet state ($k_{NR} = (1 - \Phi_{LUM})/\tau_{LUM}$) was found to follow a modified Arrhenius-type behaviour (eqn (1)) over a reasonable temperature range.

$$k_{NR} = k_0 + k_1 \exp\left(-\frac{E_A}{k_B T}\right) + k_2 \exp\left(-\frac{E_B}{k_B T}\right) \quad (1)$$

According to this expression, the lowest-energy triplet state decays *via* an activationless process with rate constant k_0 (= 2.7×10^4 s^{-1}) at low temperature to reform the ground state. This triplet state also couples to two higher-energy triplets, each of which is itself coupled to the ground state. The lower of these two upper-lying triplets is accessed by passing over a modest barrier (E_A = 950 cm^{-1}), while the rate constant for decay of this particular state is almost 2000-fold higher ($k_A = 4.5 \times 10^7$ s^{-1}) than k_0. This second triplet can be attributed to an MLCT state that possesses more singlet character.[37] Both these MLCT triplets couple to a higher-energy state that is reached by crossing a more substantive barrier (E_B = 2,780 cm^{-1}). The overall rate constant ($k_2 = 1.1 \times 10^{13}$ s^{-1}) associated with reaching this uppermost triplet is relatively high. Again, based on prior work,[26,38] the uppermost triplet is probably a metal-centred (MC) state. The derived values are in good accord with results observed for related Ru-terpy derivatives and are consistent with the emitting state being primarily of MLCT character. The radiative rate constant ($k_{RAD} = \Phi_{LUM}/\tau_{LUM} \approx 10^4$ s^{-1}) is low but not inconsistent with values determined for other Ru^{II} poly(pyridine) complexes.[26]

Cyclic voltammetry was carried out with **1** (*ca.* 1.2 mM) in deoxygenated acetonitrile containing 0.1 M tetra-*N*-butylammonium hexafluorophosphate. Upon anodic scans, a reversible, two-electron oxidation process was observed with a half-wave potential ($E_{1/2}$) of +1.27 V *vs.* SSCE. This electrode reaction corresponds to the one-electron oxidation of each metal centre. Analysis of the peak profile indicates that the two centres are oxidised at the same potential, thereby suggesting that they are not in strong electronic communication. No other oxidative process could be discerned in the cyclic voltammograms.



2

Three separate reductive steps could be discerned for **1** on cathodic scans, each process being *quasi*-reversible and having a well-defined half-wave potential (Table 1). To aid assignment, the measured reduction potentials are compared with those recorded for the parent complex,[3] $[Ru(terpy)_2]^{2+}$, and with the corresponding binuclear complex having 2,2′-bipyridine in place of bipyrimidine, **2**.[21a] The reductive pattern deduced for **2** has the first step corresponding to the one-electron reduction of each of the two ethynylated terpy ligands, followed by the one-electron reduction of each capping terpy ligand.[21a] The final step is due to the one-electron reduction of the central bipyridine unit (Table 1). On this basis, it seems likely that the least negative process found for **1** ($E_{1/2}$ = −1.11 V *vs.* SSCE) can be assigned to the one-electron reduction of the ethynylated terpy ligands. This assignment takes into account the realisation that this would be a two-electron step and that the presence of an ethynylene group at the 4′-position renders 2,2′:6′,2″-terpyridine much easier

Table 1 Comparison of the electrochemical properties of **1**, with and without added cation, with **2** and the parent complex. The value given in parentheses refers to the splitting between anodic and cathodic peaks (in mV) and the number of electrons accompanying the electrode process is reported as *n*e

Cmpd	Cation	$E_{1/2}^{OX}$ [c]/V *vs.* SSCE[a]	$E_{1/2}^{RED}$ [d]/V *vs.* SSCE	$E_{1/2}^{RED}$/V *vs.* SSCE	$E_{1/2}^{RED}$/V *vs.* SSCE
1	—	1.27 (60) 2e	−1.11 (60) 2e	−1.33 (70) 1e	−1.44 (84) 2e
	Zn^{2+}[a]	1.27 (60) 2e	−0.94 (60) 1e	−1.28 (65) 2e	−1.50 (90) 2e
	Zn^{2+}[b]	1.27 (60) 2e	−0.90 (60) 1e	−1.26 (65) 2e	−1.52 (90) 2e
	Ba^{2+}[a]	1.27 (60) 2e	−1.00 (60) 2e	−1.27 (65) 1e	−1.41 (90) 2e
	Ba^{2+}[b]	1.27 (60) 2e	−0.97 (60) 2e	−1.09 (65) 1e	−1.41 (90) 2e
	Mg^{2+}[a]	1.27 (60) 2e	−0.97 (60) 2e	−1.25 (65) 1e	−1.40 (80) 2e
	Mg^{2+}[b]	1.27 (60) 2e	−0.94 (60) 2e	−1.06 (65) 1e	−1.37 (80) 2e
	Li^{+}[a]	1.27 (60) 2e	−1.05 (70) 2e	−1.26 (65) 1e	−1.44 (85) 2e
	Li^{+}[b]	1.27 (60) 2e	−1.04 (70) 2e	−1.14 (65) 1e	−1.44 (85) 2e
	K^{+}[a]	1.27 (60) 2e	−1.06 (70) 2e	−1.27 (65) 1e	−1.48 (90) 2e
	K^{+}[b]	1.27 (60) 2e	−1.04 (70) 2e	−1.12 (65) 1e	−1.48 (90) 2e
2	—	1.31 (60) 2e	−1.06 (60) 2e	−1.42 (65) 2e	−1.57 (85) 1e
	Zn^{2+}[a]	1.31 (60) 2e	−0.99 (60) 2e	−1.23 (70) 1e	−1.43 (75) 2e
$[Ru(terpy)_2]^{2+}$	—	1.27 (60) 1e	−1.27 (60) 1e	−1.51 (70) 1e	—

[a] Perchlorate salt, molar ratio 1 : 2. [b] Excess salt. [c] Refers to oxidation of the metal center. [d] Refers to reduction of the ligand. [e] All potentials are reported in V *vs.* SSCE and using ferrocene as internal standard, +0.38 V *vs.* SSCE (ΔE_p = 60 mV).

to reduce.[39] There is a second two-electron reduction with $E_{1/2} = -1.44$ V *vs.* SSCE that can be assigned to the simultaneous reduction of the capping terpy ligands. The difference between these two $E_{1/2}$ values ($\Delta E_{1/2} = 0.33$ eV) is comparable to that found for **2** ($\Delta E_{1/2} = 0.36$ eV). A one-electron peak is situated between the terpy-based reductions and corresponds to $E_{1/2} = -1.33$ V *vs.* SSCE. This process is attributed to one-electron reduction of the central bipyrimidine fragment. This assignment allows for the fact that (i) bipyrimidine is easier to reduce than bipyridine, (ii) reduction would be a one-electron step, (iii) the ethynylene substituents would make reduction easier and (iv) no other reductive site is obvious.

On the basis of this interpretation, it becomes clear that the lowest-energy MLCT triplet state should be formed by selective charge injection from the Ru^{II} cation into the ethynylated terpy ligand. This would account for the red-shifted emission spectrum relative to the parent complex. It is possible that extensive electron delocalisation takes place at the triplet level since the reduction potentials of the terpy and bipyrimidine groups are not too dissimilar. Spectral analysis[40] of the emission spectrum recorded in fluid solution indicates that the reorganisation energy accompanying decay of the lowest-energy MLCT triplet state is *ca.* 600 cm^{-1} and that the triplet energy is *ca.* 14 800 cm^{-1}.

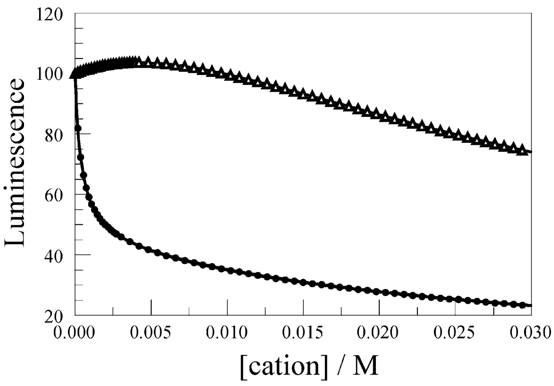


Fig. 5 Spectroluminescence titrations carried out for addition of zinc(II) perchlorate (●) and barium perchlorate (Δ) to **1** in acetonitrile containing background electrolyte (0.1 M). The solid line drawn through each data set corresponds to the best non-linear, least-squares fit to the model described by Table 2.

Complexation of zinc(II)

$$\beta_{11} = \frac{[\mathrm{ML}]}{[\mathrm{M}][\mathrm{L}]}$$
$$\beta_{12} = \frac{[\mathrm{M_2L}]}{[\mathrm{M}]^2[\mathrm{L}]} \quad (2)$$

Addition of a two-fold molar excess of zinc(II) perchlorate to a solution of **1** in acetonitrile results in a red shift of 4 nm and a small increase in absorptivity. Upon addition of excess $Zn(ClO_4)_2$, there was a further red shift of 4 nm and a modest loss of absorptivity. There is a corresponding decrease in the luminescence intensity. Spectroluminescence titrations carried out at constant ionic strength showed that the emission decreased non-linearly with increasing cation concentration (Fig. 5). A vector analysis[41] indicated that three species were needed to fit the entire data set. Taking into account the absorption spectral data, and allowing for the known complexes that form between bipyrimidine and zinc(II) cations,[42] it can be concluded that these species refer to **1** and the resultant 1 : 1 and 1 : 2 (ligand : metal) complexes.[25] Least-squares fitting of the titration data gave overall stability constants of $\log \beta_{11} = 3.41$ and $\log \beta_{12} = 4.88$ (Table 2). Further analysis of the luminescence data indicated that the relative Φ_{LUM} for the 1 : 1 complex was 15% that of **1** but the 1 : 2 species did not emit over the relevant spectral range. Emission from the 1 : 1 complex was red shifted by *ca.* 6 nm but otherwise retained similar spectral characteristics to that of **1**. Comparable stability constants were derived from analysis of the corresponding absorption spectral titrations.

The results of a time-resolved emission spectroscopic study were consistent with those derived from the above steady-state measurements. Thus, addition of low concentrations of zinc(II) perchlorate led to a gradual shortening of the lifetime of the emitting species from 60 to 8 ns. Once the shorter lifetime had been attained, the size of the signal decreased with increasing concentration of added cation but the lifetime remained constant. At high (>2 mM) concentrations of added cation, emission could not be separated from scattered laser light. Such behaviour indicates that the 1 : 1 complex has a luminescence lifetime of *ca.* 8 ns whilst no emission is apparent for the 1 : 2 (ligand : metal) complex. The precision of our set-up is insufficient to resolve individual lifetimes of 60 and 8 ns and we measure only the average value. The triplet lifetime of the 1 : 2 complex, measured by transient absorption spectroscopy with detection at 632 nm in the presence of 5 mM $Zn(ClO_4)_2$, was found to be 1.8 ± 0.2 ns at room temperature.

The effect of added Zn^{2+} cations on the cyclic voltammograms recorded for **1** in acetonitrile was also examined (Table 1). It was observed that, whilst the presence of Zn^{2+} did not affect $E_{1/2}$ for oxidation of the Ru^{II} centres, the first reduction process occurred at a less negative potential. In fact, the first step observed in the presence of a two-fold molar excess of $Zn(ClO_4)_2$ displayed the characteristic features[43] of a *quasi*-reversible, one-electron reduction process with $E_{1/2} = -0.94$ V *vs.* SSCE. There are two further reduction steps, each corresponding to a *quasi*-reversible two-electron reduction. On the basis of our earlier assignment, it is suggested that the first reduction process corresponds to addition of one electron to the coordinated bipyrimidine group. The second step can then be attributed to simultaneous reduction of the two ethynylated terpyridines with

Table 2 Parameters derived from analysis of the spectroluminescence titrations carried out with **1** in acetonitrile containing tetra-*N*-butylammonium hexafluorophosphate (0.1 M) as ionic strength mediator

Cation	$\log \beta_{11}$ [a]	$\log \beta_{12}$ [b]	$\Phi_{\mathrm{REL}}{}^{11}$ (%) [c]	τ_{11}/ns [d]	$\Phi_{\mathrm{REL}}{}^{12}$ (%) [e]	τ_{12}/ns [f]
Zn^{2+}	3.41	4.88	15	8	<2	1.8
Mg^{2+}	2.10	3.75	140	160	10	5
Ba^{2+}	1.74	3.34	135	140	10	8
Li^{+}	1.66	3.00	125	NA	35	20
K^{+}	1.55	2.85	115	NA	40	30
H^{+}	1.91	3.66	110	NA	45	32

[a] Overall stability constant for formation of the 1 : 1 complex, ±7%. [b] Overall stability constant for formation of the 1 : 2 complex, ±18%. [c] Luminescence yield for the 1 : 1 complex measured relative to **1** in the absence of added cation, ±10%. [d] Luminescence lifetime of the 1 : 1 complex measured in deoxygenated acetonitrile, ±10%. [e] Luminescence yield for the 1 : 2 complex measured relative to **1** in the absence of added cation, ±25%. [f] Luminescence lifetime of the 1 : 2 complex measured in deoxygenated acetonitrile, ±10%.

$E_{1/2} = -1.28$ V *vs.* SSCE while the final step corresponds to reduction of the capping ligands with $E_{1/2} = -1.50$ V *vs.* SSCE.

This interpretation requires that coordination of Zn^{2+} to the vacant bipyrimidine group renders $E_{1/2}$ some 0.4 eV more positive. A similar change was found earlier for bipyridine[21] (Table 1) and it is well established that reduction potentials of poly(pyridines) depend markedly on the nature of any bound cations. Prior reduction of the bipyrimidine ligand decreases the electron affinity for the ethynylated terpy groups and causes $E_{1/2}$ to shift towards more negative potentials. It is likely that reduction of these latter ligands will localise the added electron and this would push $E_{1/2}$ for the capping terpy ligands to a slightly more negative value (Table 1). In the presence of excess $Zn(ClO_4)_2$, the first reduction potential becomes slightly more negative, $E_{1/2} = -0.90$ V *vs.* SSCE, but the other processes remain essentially unaffected.

Complexation of other cations

Several other cations, namely Ba^{2+}, Mg^{2+}, Li^+, K^+ and H^+, were found to coordinate to **1** in acetonitrile solution. As noted above, **1** binds up to two cations in the form of 1 : 1 and 1 : 2 complexes and the derived stability constants are collected in Table 2. Binding is relatively weak but both steps are clearly resolved in the spectrophotometric titrations. Coordination of a cation causes a small (*e.g.*, 2 nm) red shift to both absorption and emission spectra. It was notable that for these cations the 1 : 1 complex is somewhat more luminescent than is **1** (Table 2). This effect is most evident for the addition of barium or magnesium perchlorate (Fig. 5). In all cases, the 1 : 2 species is less luminescent than the non-coordinated species. Attempts to follow the binding of Ba^{2+} cations to **1** by isothermal calorimetry and ^{13}C NMR were unsuccessful. Small shifts were observed for certain NMR peaks but these were insufficient for quantitative measurements. The calorimetry results were made irreproducible by the solvent attacking the rubber seals. It was noted, however, that **1** facilitates the entry of potassium picrate into CH_2Cl_2 from water. No such extraction occurs in the absence of **1**.

Time-resolved luminescence studies made in the presence of excess cation showed that complexation causes a modest decrease in the lifetime of the emitting state (Table 2). Under these conditions it is likely that the 1 : 2 species predominates. For both K^+ and Li^+, the triplet lifetime is essentially halved whereas a much shorter lifetime results from coordination of Ba^{2+} or Mg^{2+} cations. With the divalent cations, the time-resolved emission studies showed that the presence of low concentrations of cation causes a pronounced increase in τ_{LUM} (Table 2). At intermediate concentration of added cation, the time-resolved decay records are best analysed in terms of dual-exponential kinetics:

$$I(t) = A_{11}\exp\left(-\frac{t}{\tau_{11}}\right) + A_{12}\exp\left(-\frac{t}{\tau_{12}}\right) \qquad (3)$$

Here, τ_{11} and τ_{12} refer, respectively, to the emission lifetimes of the 1 : 1 and 1 : 2 complexes whilst A_{11} and A_{12} are their respective amplitudes. The averaged lifetimes derived for the 1 : 1 and 1 : 2 species are collected in Table 2. With increasing concentration of Ba^{2+} or Mg^{2+}, the significance of the shorter-lived component (A_{12}) increased but without affecting the measured lifetimes. This behaviour is a clear indication for the formation of complexes of different stoichiometry. It was not possible to make the same analysis for the univalent cations but, even so, the lifetimes of the 1 : 2 complexes could be obtained in the presence of excess salt (Table 2).

The presence of a two-fold molar excess of $Ba(ClO_4)_2$ affects the reductive processes seen in the cyclic voltammograms without perturbing $E_{1/2}$ for the Ru^{II} centres (Table 1). In particular, the first reduction step corresponds to a *quasi*-reversible two-electron process[43] with $E_{1/2} = -1.00$ V *vs.* SSCE. This electrode reaction is assigned to the simultaneous reduction of both ethynylated terpyridine ligands. It is seen that this step is made easier ($\Delta E_{1/2} = 0.11$ eV) by attachment of Ba^{2+} to the central bipyrimidine unit. The second reduction involves a *quasi*-reversible one-electron process for which $E_{1/2} = -1.27$ V *vs.* SSCE. This step can be assigned to reduction of the coordinated bipyrimidine group and, again, it is seen that this process is slightly assisted by cation binding ($\Delta E_{1/2} = 0.06$ eV). It is likely that the full effect of cation binding is not seen because of prior reduction of the appended terpyridine ligand. The capping terpy ligands are reduced with $E_{1/2} = -1.41$ V *vs.* SSCE. In the presence of excess $Ba(ClO_4)_2$, the reduction potential attributed to the coordinated bipyrimidine group moves to a less negative potential. The limiting value corresponds to $E_{1/2} = -1.09$ V *vs.* SSCE. We assign this latter process to the one-electron reduction of the corresponding 1 : 2 complex.

Electrospray mass spectral analysis

Electrospray mass spectra (ES-MS) were recorded in acetonitrile at low extraction cone voltage ($V_c = 40$V). This analysis indicates that the dinuclear Ru(II) complex **1** is weakly associated with its PF_6^- counteranion, exhibiting a major molecular peak at 334.4 corresponding to the $[\mathbf{1}–4PF_6]^{4+}$ cation and a minor peak at 495.4 due to the $[\mathbf{1}–3PF_6]^{3+}$ species. Upon decreasing the concentration from 0.15 mM to 0.015 mM, this latter peak disappeared, indicating dissolution of the ion pair. Addition of sub-stoichiometric amounts of $Zn(ClO_4)_2\cdot6H_2O$ to **1** in CH_3CN (0.15 mM; $\mathbf{1}/Zn < 1$) does not perturb significantly the spectra. Increasing the molar ratio of Zn forms a variety of polynuclear complexes that can be attributed to coordination of added cation to **1**. At high concentrations of cation ($Zn/\mathbf{1} > 5$), four additional peaks are clearly identified at 291.1, 308.5, 400.0, and 465.5 corresponding respectively to the $[\mathbf{1}–4PF_6 + 2Zn + 2ClO_4 + 2CH_3CN]^{6+}$, $[\mathbf{1}–4PF_6 + Zn + ClO_4 + CH_3CN]^{5+}$, $[\mathbf{1}–4PF_6 + Zn + 2ClO_4]^{4+}$, $[\mathbf{1}–4PF_6 + 2Zn + 4ClO_4]^{4+}$ species. Upon ten-fold dilution of the same solution, the situation becomes more complicated due to association of Zn with various anions present in the solution. In trying to identify the most likely assemblies, we note that addition of 10 equivalents of tetrabutylammonium chloride to an acetonitrile solution containing **1** and 5 equiv. of $Zn(ClO_4)_2$ at a concentration of 0.015 mM, the spectra gave a major peak at 368.1 corresponding probably to the $[\mathbf{1}–4PF_6 + Zn + 2Cl]^{4+}$ cation. This interesting observation can be understood in terms of the strong affinity of Zn cations for chloride under these conditions (high dilution and absence of supporting electrolyte) that stabilizes the complex in the form of a neutral $[ZnCl_2(bipyrimidine)]$ fragment. Under these conditions the di-zinc species is not observed.

For Ba^{2+} and Mg^{2+}, qualitative ES-MS studies also confirm the existence of complex **1** associated with these cations. However, the situation is complicated by kinetic problems and by hydrolysis of the PF_6^- anion imported by the starting Ru complex. At high concentration and high ratio of the salts (typically in CH_3CN/H_2O 4/1 v/v, 0.2 mM; Ba or $Mg/\mathbf{1} > 10$) the following peaks are clearly identified at 264.4 and 370.1, corresponding respectively to the $[\mathbf{1}–4PF_6 + 2Mg + ClO_4 + F + 2CH_3CN]^{6+}$ and $[\mathbf{1}–4PF_6 + Mg + ClO_4 + F]^{4+}$ cations and at 323.4 and 418.2, corresponding respectively to the $[\mathbf{1}–4PF_6 + Ba + ClO_4 + CH_3CN]^{5+}$, $[\mathbf{1}–4PF_6 + Ba + 2ClO_4]^{4+}$ cations. We notice that the di-Ba complex is not observed under these experimental conditions and that upon dilution by a factor of ten-fold the peaks corresponding to the supramolecular Ba complex vanish in favour of the starting complex **1**. These qualitative ES-MS studies are in keeping with the stability constants measured by spectrophotometric titrations (Table 2) which clearly highlight the higher affinity of complex **1** for Zn *versus* Mg and Ba. Calculated values corresponding to the monoisotopic *m*/*z* peak of the isotopic distribution and containing only the higher isotopes of each element are given in ref. 44.

Effect of the bound cation

This work has shown that cation binding affects the photophysical and electrochemical properties of the luminophore. Similar behaviour has been observed previously, notably with bipyridine as the bridging ligand where coordination leads to an increase in emission from the Ru-terpy based terminals.[21] The origin of this effect has not been explained in any detail. It is notable that whereas the 1 : 1 complex formed with Zn^{2+} is somewhat less luminescent than **1**, the 1 : 1 complexes formed with other cations are slightly more emissive. In all cases, the 1 : 2 complexes are less emissive than **1**. It is assumed that the added cations bind at the bipyrimidine N atoms, as is known from X-ray diffraction studies with simpler molecular fragments.[25] Clear experimental evidence for the stoichiometry of the resultant complexes was established by electrospray mass spectroscopy. Certain cations, such as Zn^{2+}, are likely to bind across the bipyrimidine group but other, notably Li^+, will bind to a single N atom. Cation binding raises the reduction potential for the bipyrimidine unit to a less negative value, according to the nature of the added cation. There are additional perturbations of the reduction potentials for the ethynylated terpy ligands.

Except for complexation with zinc perchlorate, there is no real change in the absorption spectrum upon coordination of the cation such that the radiative rate constant is unlikely to change significantly. Likewise, there are no obvious changes in the luminescence spectrum, other than slight spectral shifts of <10 nm. We can conclude, therefore, that cation binding does not induce a change in the nature of the emitting species, which is the lowest-energy MLCT triplet state associated with a Ru-terpy terminal. The modified luminescence yields and lifetimes, therefore, must reflect cation-induced changes in k_{NR}. Unfortunately, as is apparent from eqn (1), the magnitude of k_{NR} is set by a variety of kinetic and thermodynamic factors whilst k_0 is most likely determined by the energy-gap law.[45] In attempting to unravel the effects of bound cations on the photophysics of **1** we make three basic assumptions: (1) The main effect of the cation cannot be related to changes in k_0, since the triplet lifetimes vary at room temperature where the activated processes dominate.[46] (2) Cation binding induces an electronic effect, as observed for the change in reduction potential. (3) No single effect can be responsible for all the observations made across the range of complexes.

First, we consider the increase in Φ_{LUM} (and τ_{LUM}) found for most of the 1 : 1 complexes: Identical behaviour has been observed with bipyridine-based bridging ligands and seems to be the norm.[21] The general effect can easily be explained in terms of eqn (1), simply by raising one (or both) of the activation energies and/or decreasing one (or both) of the activated rate constants. Since cation binding has little obvious effect on the properties of the lowest-energy MLCT triplet state it is unreasonable to suppose that there is a significant perturbation of the upper-lying MLCT triplet. As such, we might expect both E_A and k_1 to remain fairly independent of the state of coordination around the bipyrimidine group. However, population of the MC state involves electron transfer from the ethynylated terpy π-radical anion to the e_g orbital of the Ru^{III} centre.[47] The activation energy for this process, E_B, can be expressed in terms of eqn (4)

$$E_B = \left\{ \frac{(\lambda + \Delta G^0)^2}{4\lambda} \right\} \tag{4}$$

where λ is the reorganization energy and ΔG° is the change in Gibbs free energy.[48] Because cation binding affects the reduction potential of the ethynylated terpy, there will be a decrease in ΔG° for intramolecular charge transfer. Provided ΔG° is positive, as seems most likely,[26] and ignoring any off-setting change in λ, cation binding will raise E_B and thereby decrease k_{NR} at ambient temperature. This situation will hold also for bipyridine-based bridging ligands and for the 1 : 1 complexes formed between **1** and cations such as Ba^{2+}, Mg^{2+}, Li^+, K^+ or H^+.

In an effort to justify this hypothesis, the triplet lifetime of the 1 : 1 complex formed between **1** and Mg^{2+} in butyronitrile was studied as a function of temperature. It was observed that k_{NR} decreased progressively with decreasing temperature in accordance with eqn (1). A non-linear least-squares fit of the experimental data (Fig. 4) gave $k_0 = 2.4 \times 10^4\ s^{-1}$; which is within the experimental error of the value found for **1**. Likewise, the barrier to reaching the upper-lying MLCT triplet (E_A = 1,180 cm^{-1}) and the rate constant for decay of this state ($k_A = 5.2 \times 10^7\ s^{-1}$) remain comparable to those determined for **1** under the same conditions. There is a more significant effect on the activation energy for reaching the MC state, where E_B = 2,935 cm^{-1}, although the combined rate constant for population of the MC state from the two MLCT triplets ($k_2 = 1.0 \times 10^{13}\ s^{-1}$) is not greatly affected by cation binding. The difference in activation energies between **1** and its Mg^{2+} complex (ΔE_B = 155 cm^{-1}) is sufficient to account for the change in triplet lifetime. However, since neither λ nor the actual energy gap between MC and MLCT triplets is known, it is not possible to attribute the alteration of E_B solely to a change in ΔG°.

In terms of the above explanation, attachment of Zn^{2+} cations to **1**, or formation of the corresponding 1 : 2 complexes, should cause a substantial prolongation of the triplet lifetime at room temperature. This is contrary to the experimental findings, where τ_{LUM} decreases in these cases. Under these conditions, cation binding must introduce a new quenching route. Since coordination raises the reduction potential for the bipyrimidine ligand to a less negative value, we suggest that this additional quenching process is associated with this phenomenon. The most likely possibility is that cation coordination lowers the energy of the intramolecular charge-transfer (ICT) state formed by charge injection from the Ru^{II} centre to the bipyrimidine unit. This ICT state lies at higher energy than the emitting MLCT triplet for **1** and is unlikely to figure in the overall photophysics. However, attaching a single Zn^{2+} cation reduces the energy of the ICT such that it lies slightly above that of the emitting triplet state. These two states will be in thermal equilibrium at room temperature such that the measured triplet lifetime (τ_{LUM} = 8 ns) refers to decay of the equilibrated mixture.[49] The ICT state appears to be non-emissive and, in order to affect the lifetime of the MLCT triplet, it must couple directly to the ground state. For the other 1 : 1 complexes, the energy gap between ICT and MLCT triplets lies between those evaluated for **1** and the 1 : 1 Zn^{2+} complex so that population of the ICT state will be relatively unimportant.

Formation of the ICT state can be considered in terms of an intramolecular charge-shift reaction and this process becomes highly favourable for the 1 : 2 complex formed with Zn^{2+}. The equilibrium mixture at room temperature will be dominated by the ICT state and the observed triplet lifetime of 1.8 ns can be attributed to this transient species. Decay of the ICT state must involve charge recombination to reform the ground state. The decay rate constant is insensitive to changes in temperature over a reasonable range (Fig. 4), in marked contrast to that of **1**. For the 1 : 2 complexes formed with other cations the MLCT and ICT states are expected to reside in thermal equilibrium at ambient temperature[48] and the measured triplet lifetime, therefore, corresponds to decay of the mixture. The actual distribution of triplet states, in any given case, depends on the stoichiometry, geometry and electronic properties of the complex.

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