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Time-resolved spectroscopic studies of the influence of the electronic environment on the charge-transfer excited states of mono- and di-nuclear Ru(II) complexes

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Contents

Abstract

Resonance Raman (RR) spectroscopic studies, supplemented by excited state absorption techniques, were used to probe the effect of modifications to the electronic environment on the excited states of mono- and di-nuclear Ru(II) polypyridyl complexes containing triazole-based bridging ligands. Ground state RR spectroscopy showed that coordination of the σ-donating bridging ligands to a second $Ru(bpy)_2$ moiety resulted in stabilization of the metal d(π)-orbitals, whereas excited state RR spectroscopy revealed a concomitant stabilization of the π^*-level of the bridging ligand. With 3,5-bis(pyrazin-2-yl)-1,2,4-triazole) as bridging ligand (BL), the latter effect was sufficient to cause a switching from a bpy-based to a BL-based ^{3}MLCT state, with evidence suggesting charge polarisation towards a pyrazine fragment. Further, for pyrazine-containing bridging ligands, protonation of the triazole fragment resulted in a switching of the lowest excited state to a BL-based excited state. © 1998 Elsevier Science S.A.

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1. Introduction

The incorporation of metal complexes as useful building blocks in light-driven supramolecular systems relies to a considerable degree on a knowledge of their photophysics and redox characteristics. Furthermore, the influence of one metal centre on the electronic environment of a neighbouring centre may exert a significant effect on the photophysics, making parallel study of mono- and counterpart di-nuclear complexes highly desirable. Through the development of versatile synthetic strategies a substantial number of mixed-ligand complexes of the type $[Ru(L_1)_{n-3}(L_2)_n]^{2+}$ and the corresponding dinuclear complexes have been prepared, with the aim of tuning the excited state properties. One such class of Ru(II) polypyridyl complexes are those with bridging ligands containing strong σ-donating triazolate fragments, the role of the bridging ligand with respect to the excited state properties being one of the issues of central interest [1].

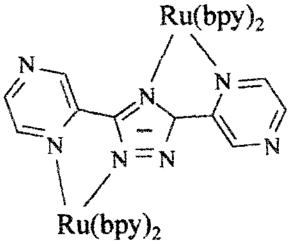
Resonance Raman (RR) spectroscopy is well established as an effective method for characterisation of the charge-transfer excited states of metal complexes [2]. Time-resolved excited state absorption (ESA), and in some cases spectroelectrochemical (thin layer electrode) methods, provide a valuable complement to the RR studies [3].

In the work reported in this article, these techniques have been applied to the triazole-containing complexes, $[Ru(bpy)_2(bpzt)]^+$ [A], $[(Ru(bpy)_2)_2(bpzt)]^{3+}$ **[B]** and $[Ru(bpy)_2(pztr)]$ [C]. As the structures below indicate, the pztr ligand can only coordinate to one $Ru(bpy)_2$ unit, whereas the bpzt ligand is capable of bridging two of these moieties. A primary, general aim of the study was to utilize these complexes as examples of well-characterised systems in which the selective capabilities of transient resonance Raman spectroscopy in particular could be exploited to probe changes in excited state character engendered by alterations to the electronic environment.

2. Experimental

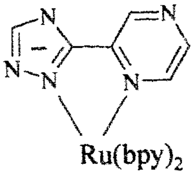
Ground state resonance Raman spectra were recorded using a CCD detector (Princeton Instruments Model LN/UV 1152) coupled to a Jobin–Yvon HR640 spectrometer. The excitation source was an Ar^+ laser, (Spectra Physics Model 2025) with outputs at 351 nm, 363.8 nm and in the visible range (450–528 nm) [3].

A Q-switched Nd:YAG pulsed laser was used in conjunction with an H_2-filled Raman-shifting cell as the excitation source for both laser flash photolysis and transient resonance Raman scattering studies [4]. The latter work generally used the single-colour pump and probe method [1,4], in which the leading edge of the laser



$[(Ru(bpy)_2)_2bpzt]^{3+}$

[B]



$[Ru(bpy)_2pztr]^+$

[C]

pulse incident on the sample pumps the molecules into the excited state and the trailing edge probes the Raman scattering. Incident pulse energies for the excited state RR experiments were typically *ca.* 3 mJ, and for flash photolysis and excited state absorption (ESA) measurements, somewhat higher, in the region of 10 mJ. The sample concentration used for both resonance Raman and flash photolysis studies was typically 10^{-4} mol dm^{-3}.

3. Results and discussion

The ground state electronic absorption spectra of [A] and [**B**] both show a strong MLCT absorption band with λ_{max} at *ca.* 450 and 442 nm, respectively. Both complexes exhibit transient formation and monoexponential return to the ground state upon pulsed laser excitation, evidently corresponding to the formation and decay of the thermally equilibrated, lowest energy triplet metal–ligand charge-transfer (^{3}MLCT) states of the mono- and di-nuclear complexes. The ^{3}MLCT lifetimes were in the region of 250 ns (measured in degassed acetonitrile) for both complexes, but the corresponding excited state absorption (ESA) spectra show some differences (Fig. 1). In particular, both the main absorption band below 400 nm and the weaker one near 500 nm lie at somewhat higher energy for the dinuclear species and the latter shows a further weak feature near 430 nm. The ESA spectrum for [**C**] (not shown) is very similar to that for [A], though the ^{3}MLCT lifetime is somewhat shorter, *ca.* 200 ns.

Ground state RR spectra were recorded of [A] and [**B**] using 457.9 nm as the excitation wavelength. The RR spectrum for the dinuclear complex [**B**], in acetonitrile solution is shown in Fig. 2. A series of characteristic bpy features are present, alongside some smaller bands at 1509, 1367 and 1198 cm^{-1} assignable to the bpzt ligand, enhanced through resonance with Ru(II)→bpy and Ru(II)→bpzt MLCT transitions, respectively. The same bpzt features appear in the spectrum of the mononuclear complex, [**A**], also in acetonitrile, but are significantly weaker with respect to neighbouring bpy features. This observation may be interpreted in terms of a shift towards the blue of the Ru(II)→bpzt transition, caused by the second

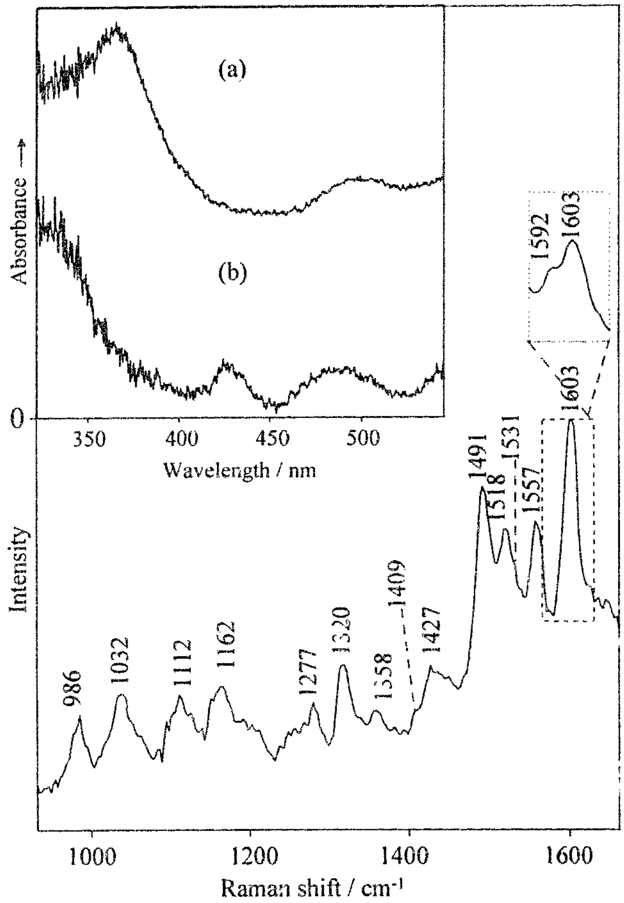


Fig. 1. Excited state RR spectra at $\lambda_{ex} = 355$ nm using the single-colour pulse technique (laser pulse duration *ca.* 8 ns) of $[(Ru(bpy)_2)_2bpzt]^{3+}$ in water; inset shows excited state absorption spectra recorded with $\lambda_{ex} = 416$ nm of (a) $[Ru(bpy)_2bpzt]^+$ and (b) $[(Ru(bpy)_2)_2bpzt]^{3+}$, recorded using a gated multichannel diode array, 20 ns after laser excitation; the absorbance scale (arbitrary units) has been corrected for ground state depletion.

metal centre. This transition evidently contributes more to the lower energy side of the 440 nm-centred absorption band of [**B**] and the blue shift therefore brings the transition more into resonance with the 457.9 nm excitation wavelength. Excitation profiles for bpzt modes of [**B**] provide additional evidence that the bpzt-based MLCT transition does lie to the low energy side of the MLCT absorption [5]. The blue-shift appears to be a result of the sharing of the σ-donor strength of the triazole-based bridging ligand between two $Ru(bpy)_2$ moieties, resulting in a relative stabilization of the Ru(dπ)-orbitals. The bpzt features also become significantly stronger with respect to bpy modes, in aqueous solution as compared to acetonitrile. Similar solvent effects were found for [**C**].

Transient resonance Raman (RR) spectra have been recorded at several wave-

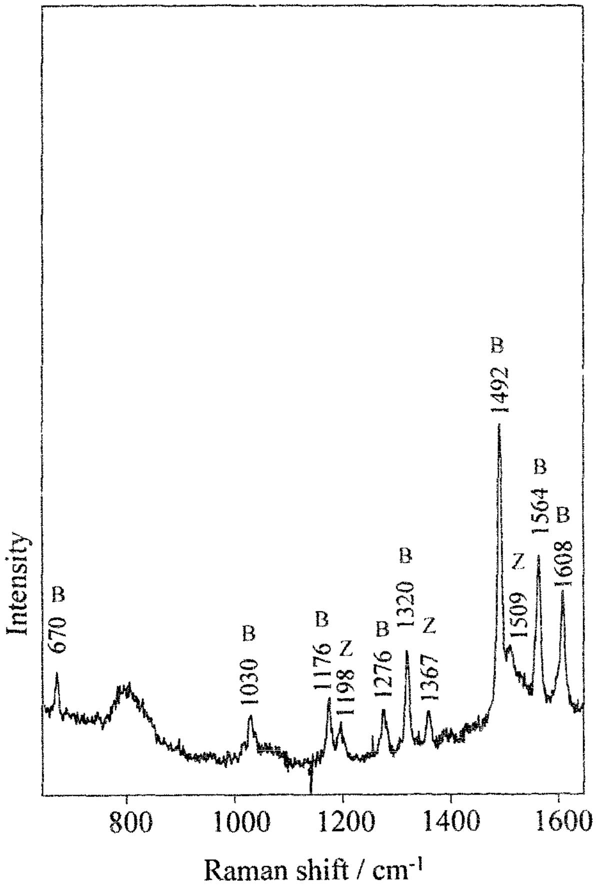


Fig. 2. Ground state RR spectra recorded at λ_{ex}=457.9 nm of [(Ru(bpy)$_2$)$_2$bpzt]$^{3+}$ in acetonitrile (solvent bands subtracted): B, Z denote vibrational modes of bpy and bpzt ligands, respectively.

lengths for all three complexes. Under the conditions of high irradiance available using pulsed excitation at 355 nm substantial conversion to the excited state can be achieved for any of the complexes [A–C]. For instance, the 355 nm pulsed RR spectrum of the mononuclear complex [A] showed three types of vibrational feature: (i) modes characteristic of the $bpy^{\bullet -}$ radical anion, (ii) modes of the neutral bpy ligand and (iii) modes of the neutral bpzt ligand. The clear implication is that the ^{3}MLCT state of [A] generated by the leading edge of the laser pulse can be formulated as $Ru^{III}(bpy^{\bullet -})(bpy)(bpzt)$, i.e. a "bpy-localised" excited state.

The spectrum recorded of [**B**] in aqueous solution under similar conditions of pulsed laser excitation at 355 nm as used for [A] exhibited a markedly different enhancement pattern, shown in Fig. 1. (The same spectrum was observed in acetonitrile but the spectral signal:noise ratio in the aqueous medium was superior.) The features assignable to $bpy^{\bullet -}$ which were observed for [A] are absent. Modes associated with neutral bpy ligand are still present but are stronger than those seen for

[A]. The latter finding alone points towards electron localisation on the bpzt *bridging* ligand in the ^{3}MLCT state of the dinuclear complex, with *two* neutral bpy ligands now remaining attached to the oxidised metal centre and thus accounting for the observed increase in the intensity of bpy modes. More definitive evidence that electron localization in the ^{3}MLCT state is on the bpzt ligand is demonstrated by the appearance in Fig. 1 of several new bands attributable to the $bpzt^{\cdot -}$ anion. Importantly, many of these are nearly coincident in position with modes of the bipyrazine radical anion ($bpz^{\cdot -}$) reported by Kincaid et al. [6] in the RR spectrum of the localised ^{3}MLCT state of the homoleptic complex $Ru(bpz)_3^{2+}$, suggesting that in the localised ^{3}MLCT state, $(bpy)_2Ru^{(III)}(bpzt^{\cdot -})Ru^{(II)}(bpy)_2$, there is significant charge polarisation towards the pyrazine end of the reduced bpzt ligand. Hence, complexation to a second metal centre has resulted in a lowering of the energy of the π*-accepting level of the bpzt ligand below that of bpy. Interestingly, bands associated with *neutral* bpzt ligand are also evident in the spectrum, and are close in position to known bands of neutral bipyrazine. Thus the ^{3}MLCT excited state of [**B**] can be described as a localised mixed-valence entity on the vibrational timescale with modes due to both negatively charged and neutral pyrazine components of the asymmetric bridging ligand. These conclusions are reinforced by resonance Raman probing of the less intense region of the ESA spectrum of [**B**] near 500 nm (Fig. 1(b), inset). Spectra generated by pulsed 532 nm excitation revealed $bpzt^{\cdot -}$ features enhanced via resonance with a lower energy π*–π* transition of the reduced ligand, as well as a series of bands identifiable as modes of neutral pyrazine. These results and those exhibited in Fig. 1 demonstrate the rather unique ability of transient RR spectroscopy to probe the interesting phenomenon of charge polarisation in the CT excited states of metal complexes, an effect first reported in metal polypyridyls by Kincaid et al. [6].

The excited state RR spectrum of [C] generated by pulsed excitation at 355 nm is very similar to that observed for [A], indicating electron localization on the bpy ligand in the ^{3}MLCT state of this complex also. Vibrational mode assignments in support of this conclusion were made on the basis of comparisons with spectra of the deuterated analogues [7] of [C], $[Ru(\mathbf{d}_8\text{-}bpy)_2(pztr)]^+$ and $[Ru(bpy)_2(\mathbf{d}_4\text{-}pztr)]^+$.

As a second example of the response of excited state character to changes in the immediate electronic environment, the influence of protonation of the complexes was investigated. Resonance Raman spectra of the ^{3}MLCT states of the mononuclear complexes [A] and [C] and of the dinuclear species [**B**] were generated, as already illustrated, by the single-colour pump–probe technique, using 355 nm pulsed excitation, in acetonitrile solutions in the presence of added diethylamine or trifluoroacetic acid as deprotonating or protonating agents, respectively. The observed effects are illustrated in Fig. 3 for the case of [C]. It is clear that protonation of the pztr ligand results in lowering of the energy of the π*-level of this ligand below that of bpy, switching the nature of the ^{3}MLCT excited state from being bpy-based to being pyrazine-based. Analogous results were obtained, *mutatis mutandis*, for complex [A]. Protonation of the triazole ring in the dinuclear complex [**B**] is not possible and in this case therefore, not unexpectedly, the 355 nm pulse-generated RR spectra were

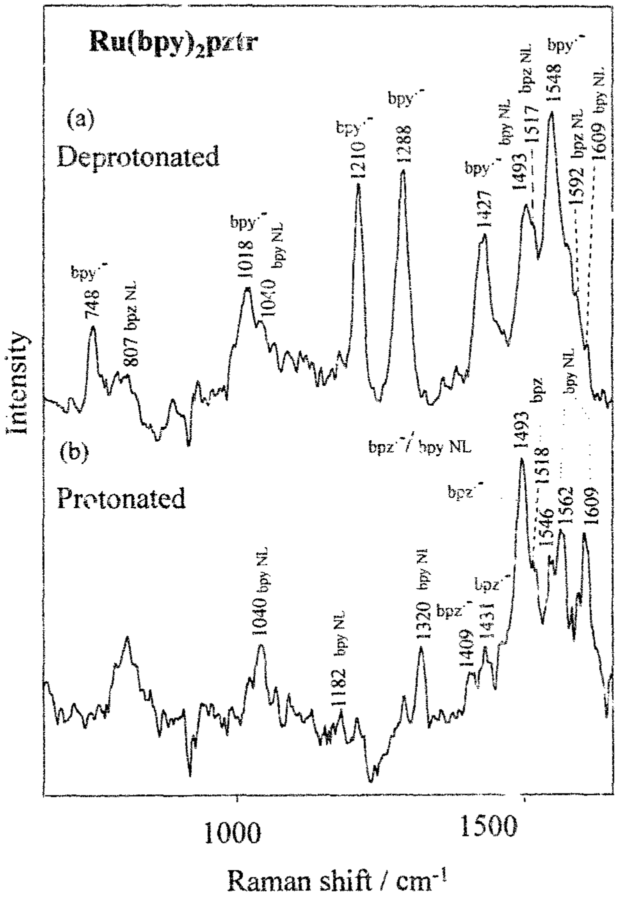


Fig. 3. Excited state RR spectra recorded at $\lambda_{ex} = 355$ nm using the single-colour pulse technique (laser pulse duration *ca.* 8 ns), of $[Ru(bpy)_2(pztr)]^+$ in acetonitrile (solvent bands subtracted) with dropwise additions of: (a) diethylamine, (b) trifluoroacetic acid.

identical in the protonating and deprotonating environments, both spectra being indicative of a bpzt-localised ^{3}MLCT state, as established in the investigations described earlier.

4. Conclusions

While it could be argued that the *broad* features of the response of the excited states of metal complexes, of the type under investigation here, to changes in the electronic environment are already understood or are in a general sense "predictable" on the basis of spectral and electrochemical properties, unequivocal characterisation of excited state changes in response to electronic or other influences require the more precise, selective probing possible through the methods of transient resonance

Raman spectroscopy. The studies presented here give some indication of the potential of the technique. The ability to "map" vectorial distribution of charge consequent on photoexcitation is important in a number of respects. In particular, the photophysical sensitivity of complexes to small changes of the electronic environment, imposed, for example, either through introduction of additional metal centre(s) or changes in pH, clearly has significance with respect to their potential use in light-driven systems, where tunability of excited state properties is generally part of the strategy to be used in the design of useful supramolecular devices.

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