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TRANSIENT RESONANCE RAMAN STUDIES OF Ru(II) COMPLEXES IN DNA AND IN HOMOGENEOUS MEDIA

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Transient resonance Raman (TR^2) spectroscopy has been used to investigate the metal-ligand charge-transfer (MLCT) excited states of Ru(II) polypyridyl complexes in DNA and in homogeneous solution. In DNA, complexes of the type $[Ru(L)_2(L')]^{2+}$ were studied, where L = 2, 2'-bipyridyl (bpy), 1, 4, 5, 8-tetraazaphenanthrene (tap), and L' = dipyrido [3,2:a-2',3':c]-phenazine (dppz) or 1,4,5,8,9,12-hexaazatriphenylene (HAT). For $[Ru(bpy)_2(HAT)]^{2+}$, the enhancement pattern of vibrational modes in the TR^2 spectra attributable to reduced $HAT^{\cdot-}$ in the triplet MLCT state suggest perturbations to the intraligand transition of $HAT^{\cdot-}$ in the presence of DNA. Transient RR spectra for $[Ru(tap)_2(dppz)]^{2+}$ are indicative of formation of the species $Ru^{II}(tap^{\cdot-})(tap)(dppz)$ by electron transfer from DNA to the triplet MLCT state of the complex.

TR^2 spectra for complexes of the type, $[(Ru(bpy)_2)_n(L)]^{2+}$, $n = 1, 2$ where L = a triazole bridging ligand, illustrate the use of the technique as a probe of the response of MLCT states to the electronic environment.

Keywords: Resonance Raman; Ru(II) complexes; DNA

INTRODUCTION

Transient resonance Raman (TR^2) spectroscopy is an effective and versatile technique for probing the excited state vibrational structure

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of transition metal and organometallic complexes. The photophysics and photochemistry of metal polypyridyl complexes have provided a fruitful proving ground for the technique, especially to probe the nature of the lowest energy metal-ligand charge-transfer (MLCT) excited states of such species. This paper aims to illustrate how TR^2 spectroscopy can be used: (i) to study the effect of a DNA environment on the MLCT excited states of Ru(II) polypyridyl complexes; (ii) to investigate changes to the MLCT excited states of metal complexes brought about by small modifications to the electronic environment.

RESULTS AND DISCUSSION

The experimental techniques employed have been described elsewhere [3]. The excitation source used for the TR^2 experiments was a Q-switched Nd/YAG laser, with additional wavelengths provided by means of either a dye laser or a Raman wavelength-shifting cell containing H_2 or CH_4. Samples were contained in spinning cells with [complex] = *ca* 10^{-4} mol dm^{-3}. For DNA studies, a DNA: complex ratio of 20 was generally used.

Among species which exhibit high affinity towards DNA are mixed-ligand complexes of the type $[Ru(L)_2(L')]^{2+}$, where L = 1, 10-phenanthroline (phen), 2,2′-bipyridyl (bpy), 1,4,5,8-tetraazaphenanthrene (tap) and L′ = dipyrido [3, 2:a-2′,3′:c]-phenazine (dppz) or 1,4,5,8,9,12-hexaazatriphenylene (HAT). The structures of dppz and HAT are shown in Figure 1. In the complexes with L′ = dppz and L = phen (**1**) or bpy (**2**), intercalative binding of the planar dppz ligand with the base pairs of DNA is now considered to be well-established [2].

We have studied [1] the interaction of racemic forms of (**1**) and (**2**) with DNA using both TR^2 and excited state absorption (ESA) spectroscopy. Recently, the work has been extended [3] to probe the interactions of the enantiomers (Δ- and Λ-) of (**1**) with DNA. Spectra recorded at probe wavelengths within the region of strong excited state absorption show clear changes to the enhancement patterns associated with the modes of the $dppz^{\cdot-}$ radical anion in the ^{3}MLCT state. This is indicative of perturbation of the $\pi^*-\pi^*$ intraligand transition of the intercalating dppz ligand. Figure 2 compares the TR^2 spectra of the

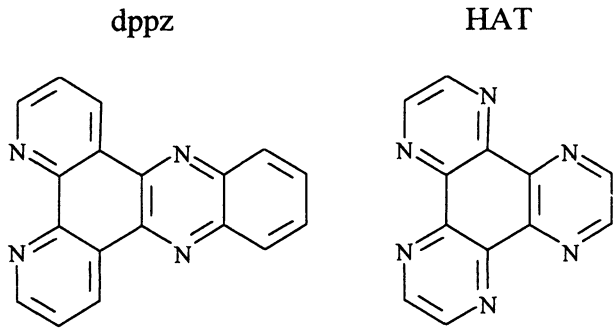

FIGURE 1 Structures of dppz and HAT ligands.

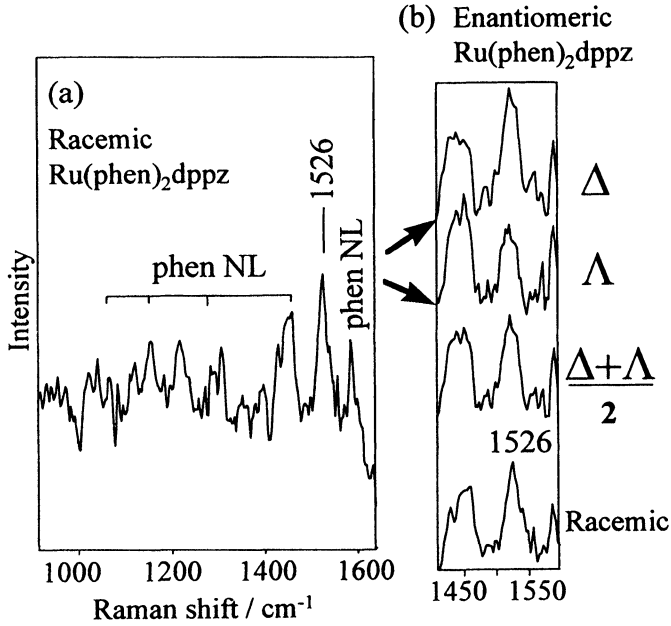

FIGURE 2 Scaled subtractions of excited state RR spectra of $[Ru(phen)_2dppz]^{2+}$ at an excitation wavelength of 355 nm. [Spectra recorded in presence of DNA]−[spectra recorded in buffer alone]: (a) racemic complex; (b) Δ and Λ enantiomers, displaying only the region surrounding the 1526 cm^{-1} feature. (The (Δ + Λ)/2 and the racemic spectra are shown for comparison).

enantiomers and the racemic form and shows changes in the intensity of a feature at 1526 cm^{-1}, a marker band for intercalation. This has been interpreted as reflecting the distinctive response of the enantiomers to the chiral environment of the DNA binding sites. Although the photophysics of the lowest MLCT excited state of the 'paradigm' polypyridyl complex, $[Ru(bpy)_3]^{2+}$, are altered in the presence of DNA, the species is known to bind non-intercalatively. Consistent with this, TR^2 measurements carried out during the present work confirm that the spectral features characteristic of the ^{3}MLCT excited of this complex are identical in aqueous buffer and in DNA.

Since the above results establish that TR^2 spectroscopy can clearly distinguish between intercalative and non-intercalative DNA-binding, the technique was applied to the complex $[Ru(bpy)_2HAT]^{2+}$, which has also shown significant photophysical perturbation upon binding [4]. The HAT ligand, on which the electron resides in the ^{3}MLCT state, has a planar aromatic skeleton which is less extended than that of dppz (Fig. 1), and thus the extent of the association with DNA is less obvious.

Point-by-point absorbance difference spectra recorded of the photoexcited complex in H_2O, CH_3CN and DNA environments are essentially indistinguishable. However, transient RR spectra recorded at 355 nm of the complex in presence and absence of DNA showed changes in both the relative intensity and the positions of several bands, as shown in Figure 3. While the changes are small, due to the similarity in position of many $HAT^{\cdot-}$ modes compared with both HAT and bpy ground state features, it is clear that the enhancement pattern in DNA of the reduced $HAT^{\cdot-}$ modes is different from that in aqueous solution. In parallel with the conclusions reached for complexes (**1**) and (**2**) above, this difference in enhancement pattern suggests a perturbation to the intraligand $\pi^* - \pi^*$ transition of $HAT^{\cdot-}$ in the presence of DNA.

Investigations were also performed on the complex $[Ru(tap)_2dppz]^{2+}$ bound to DNA. Intercalation of the dppz ligand persists but electron localisation is now on the tap ligand in the ^{3}MLCT state. When DNA-bound, a 60% reduction in the intensity of the ^{3}MLCT luminescence was observed. This is tentatively ascribed to a photo-induced electron transfer to the ^{3}MLCT state, $Ru^{III}(tap^{\cdot-})$ (tap)(dppz), from a nearby guanine base of the DNA-helix [5], to give the species Ru^{II}

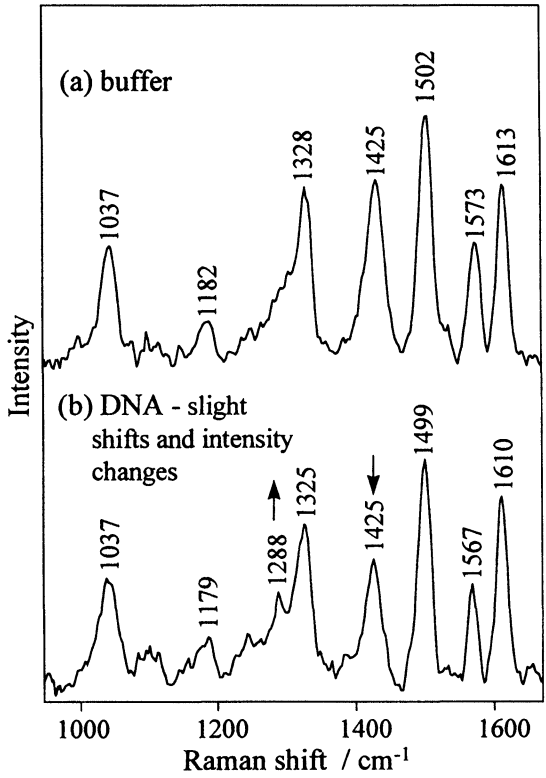

FIGURE 3 Excited state resonance Raman spectra of $[Ru(bpy)_2HAT]^{2+}$ recorded at an excitation wavelength of 355 nm in the presence and absence of DNA.

$(tap^{\cdot-})(tap)(dppz)$, in which the presence of the $tap^{\cdot-}$ entity is thought to destabilise Ru(dπ) orbitals, resulting in a red shift of the $Ru^{II} \rightarrow$ tap and $Ru^{II} \rightarrow$ dppz MLCT transitions. Transient RR spectra at 480 nm and other excitation wavelengths show that, in DNA, significant enhancement of modes due to tap and dppz ligands arises, consistent with the proposed electron transfer quenching.

To study the influence on MLCT states, of changes to the electronic environment, TR^2 spectra were recorded of the dinuclear complex $(Ru(bpy)_2)_2bpt)^{3+}$ (bpt = 3, 5-*bis*(pyridin-2-yl)-1,2,4-triazole), at probe wavelengths within the excited state absorption region.

These indicate clearly that the promoted electron is localised on the bpy ligand in the ^{3}MLCT state. However, corresponding spectra of the

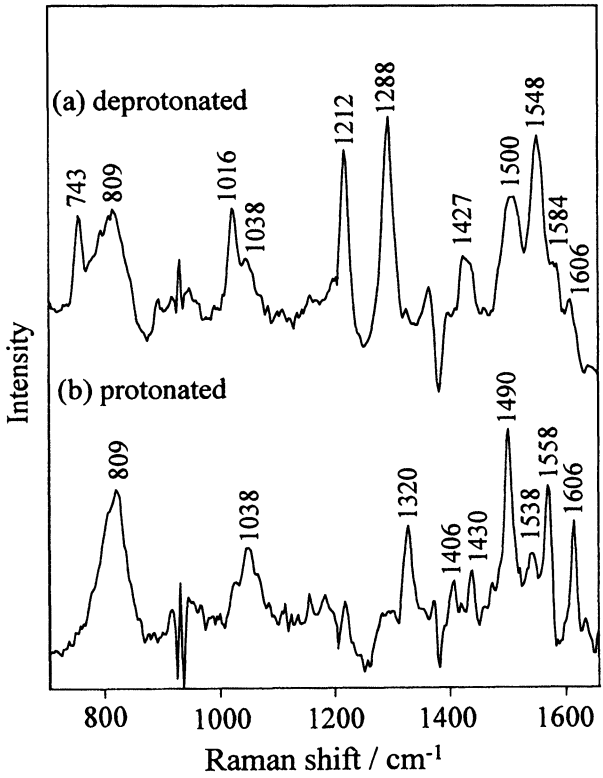

FIGURE 4 Excited state resonance Raman spectra of $[Ru(bpy)_2bpzt]^+$ in acetonitrile recorded at an excitation wavelength of 355 nm (solvent bands subtracted): (a) deprotonated; (b) protonated.

closely related complex $(Ru(bpy)_2)_2bpzt)^{3+}$ (bpzt = 3, 5-*bis*(pyrazin-2-yl)-1,2,4-triazole) indicate that in the lowest excited MLCT state the electron resides on the bridging ligand. Hence, replacing pyridine by pyrazine rings in this case results in stabilisation of the π^* accepting-orbital of this ligand below that of bpy.

Figure 4 shows further examples of the sensitivity of the MLCT states of these metal polypyridyl systems to the electronic environment. The transient RR spectrum in Figure 4a of the mononuclear complex $(Ru(bpy)_2bpzt)^+$, indicates that the ^{3}MLCT state is *bpy-based* unlike the above dinuclear complex. Thus removal of a $Ru(bpy)_2$ unit results in destabilisation of the π^* orbital of the bridging bpzt

ligand. It is evident from Figure 4b however, that protonation of the triazole moiety of the bridging ligand results in a switch back to a Hbpzt-based lowest excited state.

Acknowledgments

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