Resonance Raman Investigation of $Ru(phen)_2(dppz)^{2+}$ and Related Complexes in Water and in the Presence of DNA

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Resonance Raman (rR) spectroscopy was utilized to gain insight into the electronic structure of dppz (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) complexes of Ru(II) and Os(II). The time-resolved resonance Raman (TR^3) spectrum of $Ru(phen)_2(dppz)^{2+}$ (phen = 1,10-phenanthroline) collected under 355 nm (fwhm ≈ 10 ns) excitation is consistent with the population of a ligand-centered (LC) $^3\pi\pi^*$ state of the dppz ligand. Since emission from the Ru(II) → (dppz) metal-to-ligand charge transfer (MLCT) excited state is observed, both states must possess similar energies. Lowering of the MLCT state energy in $Ru(phen)_2(F_2\text{-}dppz)^{2+}$ and $Os(phen)_2(dppz)^{2+}$ with respect to that of the $^3\pi\pi^*$ state results in the disappearance of the LC $^3\pi\pi^*$ excited-state peaks in the rR spectrum, indicative of its fast deactivation to the lower MLCT state in these complexes. Addition of DNA to the samples containing $Ru(phen)_2(dppz)^{2+}$ and $Ru(phen)_2(F_2\text{-}dppz)^{2+}$ leads to a decrease in intensity of the peaks associated with the intercalating phenazine part of the dppz ligand. Further increase in the DNA:Ru ratio causes broadening of the spectrum. This broadening has been interpreted in terms of strong $\pi\pi$ interaction between the intercalated dppz ligand and the DNA bases.

Introduction

The binding of Ru(II) complexes to DNA has recently been the subject of intense investigation.[1−5] One of the most interesting classes of complexes are those that contain the dppz ligand (dppz = dipyrido[3,2-*a*:2′,3′-*c*]phenazine) owing to their high binding affinity for DNA ($K_b \geq 10^6\ M^{-1}$), the ligand's ability to intercalate between the bases, as well as the observed rapid electron transfer mediated by the DNA π-stack.[6−11] The structure of $Ru(phen)_2(dppz)^{2+}$ (phen = 1,10-phenanthroline) is shown in Figure 1. The strong binding of $Ru(L)_2(dppz)^{2+}$ (L = phen, bpy = 2,2′-bipyridine, dip = 4,7-diphenyl-1,10-phenanthroline) complexes to DNA gives rise to the "molecular light switch effect", where the nearly undetectable emission from the triplet metal-to-ligand charge transfer (MLCT) excited state of $Ru(L)_2(dppz)^{2+}$ in water becomes strongly enhanced upon DNA binding, owing to the intercalation of the planar dppz ligand between the base pairs of DNA.[6−9]

The understanding of the electronic structure of the $Ru(L)_2(dppz)^{2+}$ complexes in solution and bound to DNA is important in the assessment of the factors that govern fast electron transfer (ET) through DNA, which is related to dppz intercalation.[10] In addition, to be able to quantitatively explain the observed ET results, it is necessary to assess the magnitude of the $\pi\pi$ interaction between the dppz ligand and the DNA bases. Resonance Raman (rR) spectroscopy provides a tool for the investigation of the molecular conformation of both ground and excited states in homogeneous solvents and microheterogeneous environments. The interaction of the dppz ligand with the DNA π-stack may be probed by monitoring the changes in the spectral profiles of $Ru(L)_2(dppz)^{2+}$ upon addition of DNA.

In the present work rR was utilized to obtain information about the electronic structure of $Ru(L)_2(dppz)^{2+}$ (L = phen, bpy, dip, dppz), $Ru(phen)_2(F_2\text{-}dppz)^{2+}$ (F_2-dppz = 7,8-difluorodipyridophenanzine), and $Os(phen)_2(dppz)^{2+}$ as well as their interaction with DNA. The rR spectra were collected with pulsed excitation (354.7 nm, fwhm ≈ 10 ns) at low and high energies to obtain ground-state and excited-state spectra. The observed changes in the spectral profile upon addition of DNA provide information on the $\pi\pi$ interaction between the intercalated dppz ligand and the DNA bases.

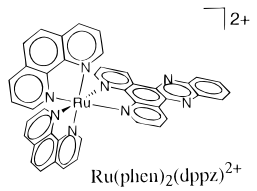

Figure 1. Structure of $Ru(phen)_2(dppz)^{2+}$.

Experimental Methods

Materials. $Ru(L)_2(dppz)^{2+}$ complexes, where L = phen, bpy, dip, were synthesized by literature methods from the corresponding $Ru(L)_2(phendione)^{2+}$ precursors.[12] The preparation of $Os(phen)_2(dppz)^{2+}$ and $Ru(phen)_2(F_2\text{-}dppz)^{2+}$ (F_2-dppz = 7,8-difluorodipyridophenanzine) has been previously reported.[12,13] Calf-thymus DNA was purchased from Sigma and was purified by a method previously described.[14] All the experiments utilizing DNA were performed in 5 mM Trizma buffer (pH = 7, 50 mM NaCl), and the DNA concentration is expressed as the concentration of bases.

Instrumentation. The rR spectra were obtained utilizing the third harmonic (354.7 nm) of a Spectra-Physics GCR-150-30 Nd:YAG laser operating at 30 Hz as the excitation source and were recorded utilizing a Spex Triplemate monochromator with a EG&G PAR OMA II diode array detector. The Raman signal backscattered with a ∼11° geometry from the sample contained in Suprasil quartz NMR tubes purchased from Wilmad (unless otherwise stated) was collected into the monochromator equipped with a 2400 grooves/mm grating with two 600 grooves/mm filter

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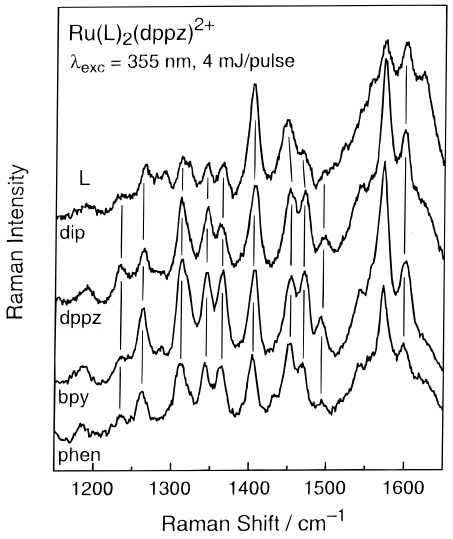

Figure 2. Resonance Raman spectra of $Ru(L)_2(dppz)^{2+}$ complexes in water obtained with 355 nm (4 mJ/pulse, ~10 ns) excitation (L = dip, dppz, bpy, phen).

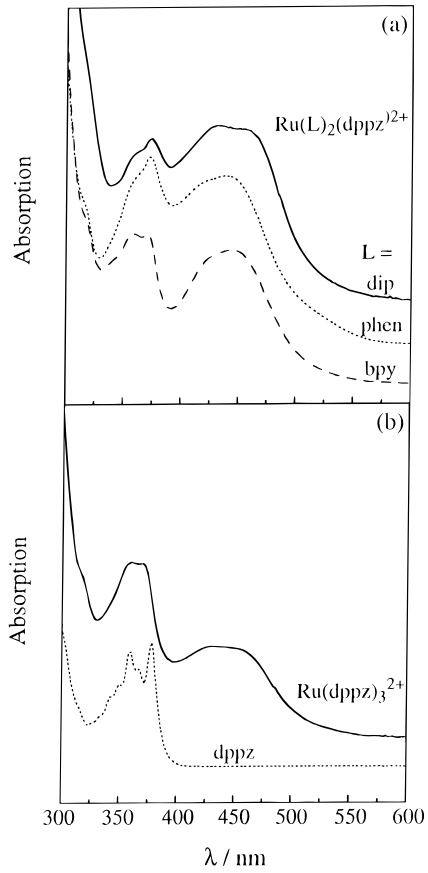

Figure 3. Electronic absorption spectra of (a) $Ru(L)_2(dppz)^{2+}$ complexes in water (L = dip, phen, bpy) and (b) $Ru(dppz)_3^{2+}$ in water and free dppz ligand CH_3CN. The spectra were arbitrarily scaled for display.

stage gratings. Absorption measurements to determine sample concentrations and to ensure sample integrity following each Raman experiment were performed in a Hewlett-Packard diode array spectrometer (HP 8452A) with HP8452Win System software installed in an HP Vectra VL2 4/50 desktop computer.

Results and Discussion

Water. The resonance Raman spectra of $Ru(L)_2(dppz)^{2+}$ complexes are shown in Figure 2 (L = phen, bpy, dip, dppz).

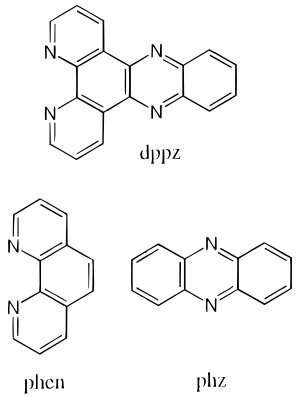

Figure 4. Structure of the dppz ligand and its two structural components, phen and phz.

TABLE 1: Peak Postions and Molecular Contributions to Each Mode for the Low-Power Spectrum of $Ru(phen)_2(dppz)^{2+}$ in Water

peak position/cm^{-1}	assignment
1262	phz part of dppz ligand[a]
1310	phen part of dppz ligand[b]
1342	*c*
1365	see text
1403	phz part of dppz ligand[a]
1453	phen part of dppz ligand + other phen ligands[b]
1469	phen part of dppz ligand[b]
1493	phz part of dppz ligand[a]
1572	phz part of dppz ligand[a]
1599	phen part of dppz ligand[b]

[a] Reference 20. [b] Reference 19. [c] This dppz mode cannot be identified in terms of the phen and phz parts of the ligand.

The spectra of all the complexes shown in Figure 2 exhibit similar peak positions and relative intensities, which indicates that in all cases the resonance enhancement stems from the same electronic state. Inspection of the electronic absorption spectra of these complexes and that of the dppz ligand (Figure 3) reveals a dppz-based absorption in the 350−370 nm region, assigned to a $^1\pi\pi^*$ transition.[12] The peak at 378 nm observed in the spectrum of the free ligand has been assigned to the $^1n\pi^*$ transition of the phenazine (phz) part of the dppz ligand (Figure 4).[15] Therefore, the observed rR spectra upon low-power 355 nm excitation would be expected to be dominated by vibrational modes characteristic of the ground-state dppz ligand in resonance with the $^1\pi\pi^*$ state.

As suggested in a previous report, the rR spectrum of the dppz ligand obtained under 355 nm excitation can be separated into contributions from the phen and the phz (phz = phenazine) parts of the ligand (Figure 4).[16] The ground-state peaks of $Ru(phen)_2(dppz)^{2+}$ shown in Figure 2 correspond to vibrational modes of dppz in resonance with the ligand-localized $^1\pi\pi^*$ state, which possess a spectral profile consistent with the superposition of the rR spectra of the phz and phen fragments.[17−19] The peak positions observed under 355 nm low-energy excitation for $Ru(phen)_2(dppz)^{2+}$ and their corresponding assignments are listed in Table 1. The ancillary phen ligands in the complex contribute to the spectral profile with a peak at 1453 cm^{-1}, which is the strongest band in the ground-state 355 nm spectrum of $Ru(phen)_3^{2+}$.[18] This is evident from the intensity of the 1453 cm^{-1} peak relative to that at 1469 cm^{-1} in $Ru(phen)_2(dppz)^{2+}$ compared to the same bands in the spectra of $Ru(dppz)_3^{2+}$ and $Ru(bpy)_2(dppz)^{2+}$ (Figure 2). In addition, the 1453 cm^{-1} band becomes broader and shifts to 1449 cm^{-1} in $Ru(dip)_2(dppz)^{2+}$, corresponding to the largest peak in the $Ru(dip)_3^{2+}$ spectrum obtained with 355 nm excitation.[18] Clearly, since the 1453 cm^{-1}

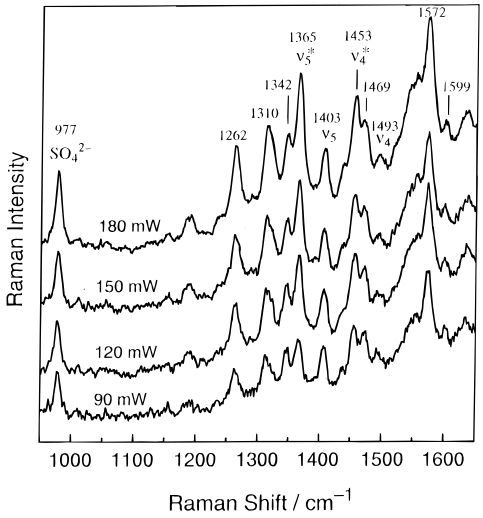

Figure 5. Power dependence of the rR spectrum of Ru(phen)$_2$(dppz)$^{2+}$ in water (λ_{exc} = 355 nm, ~10 ns) collected from a flowing liquid stream. The labels ν_4 and ν_5 are associated with the phz part of the dppz ligand (see text). The concentration of Na_2SO_4 used as an intensity standard was 0.2 M.

band is also present in the spectrum of Ru(dppz)$_3^{2+}$, some of its intensity must arise from the phen part of the dppz ligand. The peak at 1469 cm^{-1} is also present in all the spectra containing the dppz ligand, and by comparison to the rR spectrum of phz, it cannot be associated with the phz part of the dppz ligand. It is likely that the 1451 cm^{-1} vibrational mode of phen in the rR spectrum of Ru(phen)$_3^{2+}$ is split into dppz to give rise to the 1453 and 1469 cm^{-1} modes.[19] All the other peaks in Table 1 were assigned by comparison to the rR spectra of phz and Ru(phen)$_3^{2+}$.[19,20]

In the rR spectrum of Ru(bpy)$_2$(dppz)$^{2+}$ no contributions from the Ru(bpy) chromophore were observed. The ground-state spectrum of Ru(bpy)$_3^{2+}$ can only be obtained under CW excitation, since pulsed laser light (and even focused CW excitation) gives rise to the vibrations associated with the MLCT excited state of the complex.[21] Ru(bpy)$_3^{2+}$ possesses a very weak absorption in the 350−360 nm range. Therefore, it is not surprising that resonance enhancement of the Ru(bpy)$_3^{2+}$ ground-state Raman signal is weak with 355 nm excitation. The strong $\pi\pi^*$ absorption of the dppz ligand in conjunction with the weak enhancement of the Ru(bpy)$_3^{2+}$ ground state leads to the observation of only dppz peaks in the rR spectrum of Ru(bpy)$_2$(dppz)$^{2+}$ under 355 nm excitation. Since the Ru(II) → (bpy) MLCT state is expected to be higher in energy than both the Ru(II) → (dppz) MLCT state and $^3\pi\pi^*$ state of dppz, observation of the vibrations associated with bpy$^{\bullet-}$ is not likely.[22]

The power dependence of the rR spectrum of Ru(phen)$_2$dppz^{2+} is shown in Figure 5. It is evident from a comparison of the spectra collected under the lowest and highest power conditions that at high excitation energies the relative height of the peaks at 1365 cm^{-1} (ν_5*) and 1453 cm^{-1} (ν_4*) increases with respect to the other spectral peaks, as well as that of the SO_4^{2-} standard, and have therefore been assigned to the excited state of the complex. These two peaks are not due to photodecomposition products, since the low-power spectrum is restored following collection of the spectra under high laser power. In addition, the spectra in Figure 5 were collected utilizing a liquid stream (pumped with a Micropump, Barish Co.) to avoid signals from decomposition products, especially at high laser powers.

The long-lived excited states of Ru(II) diimine complexes are typically MLCT in nature.[22] The Ru(L)$_2$(dppz)$^{2+}$ complexes

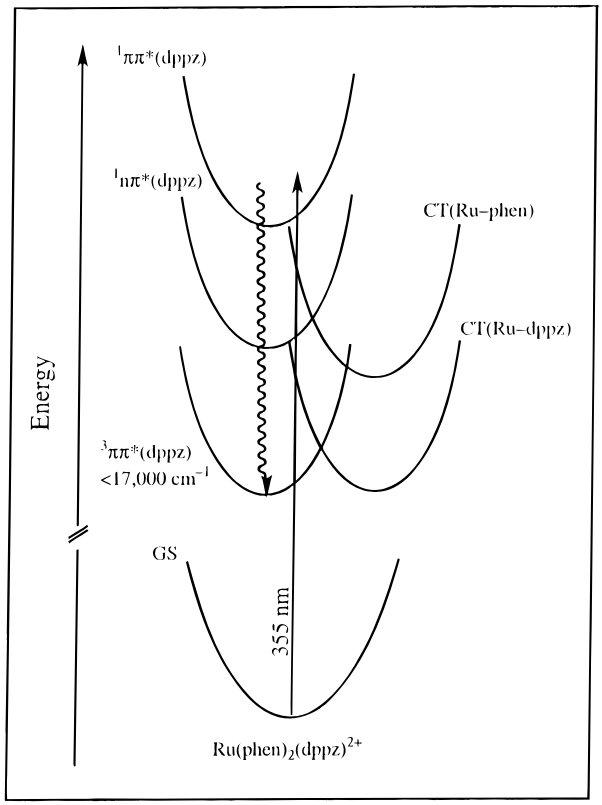

Figure 6. Schematic representation of the potential energy surfaces of Ru(phen)$_2$(dppz)$^{2+}$ showing the LC dppz states and the MLCT states.

presented here also possess a low-lying Ru(II) → (dppz) MLCT state with a strong emission centered at 620 nm in acetonitrile.[23] If the observed excited-state rR peaks are due to the MLCT state, then the largest bands in the spectrum should be at similar positions as those measured in the independently prepared dppz$^{\bullet-}$.[24] Comparison of the position of the two excited-state peaks with those obtained from the rR spectra of electrochemically reduced phz and chemically reduced phen under similar excitation wavelengths reveals that the largest peaks in those spectra do not correspond to those observed in the Ru(phen)$_2$(dppz)$^{2+}$ excited state.[16,25,26] In addition, Schoonover and co-workers reported that the rR spectrum of dppz$^{\bullet-}$ is a superposition of the spectra of phz$^{\bullet-}$ and phen$^{\bullet-}$.[16] Neither of the two observed excited-state peaks corresponds to those reported for dppz$^{\bullet-}$. Therefore, these peaks must be assigned to another transient species or excited state.[16]

Another possible source of the peaks observed under high-energy conditions is an excited state localized on the dppz ligand. It has been shown that phz possesses a low-lying $^3\pi\pi^*$ state ($E(^3\pi\pi^*)$ = 17 000 cm^{-1}), which may be lower than or similar in energy to the Ru(II) → (dppz) MLCT excited state. This behavior has been reported for the Re(I) complex of dppz, where the dppz-centered $^3\pi\pi^*$ state lies lower in energy than the MLCT state.[16] If this is the case, direct excitation of the LC $^1\pi\pi^*$ state of the dppz ligand with 355 nm could lead to rapid deactivation to the LC $^3\pi\pi^*$ state with some crossover into the MLCT, as shown in Figure 6. Population of the $^3\pi\pi^*$ state in this manner, in conjunction with a significant extinction coefficient for an electronic transition from the lowest $^3\pi\pi^*$ state to higher states, would lead to a TR^3 signal of the ligand-localized $^3\pi\pi^*$ state. Indeed the strongest peaks observed in the high-power spectrum of Ru(phen)$_2$(dppz)$^{2+}$ (Figure 5) correspond to those observed in the TR^3 spectrum of the $^3\pi\pi^*$ excited-state phz under 355 nm excitation.[20] The peaks observed at 1453 and 1365 cm^{-1} correspond to the ν_4 and ν_5

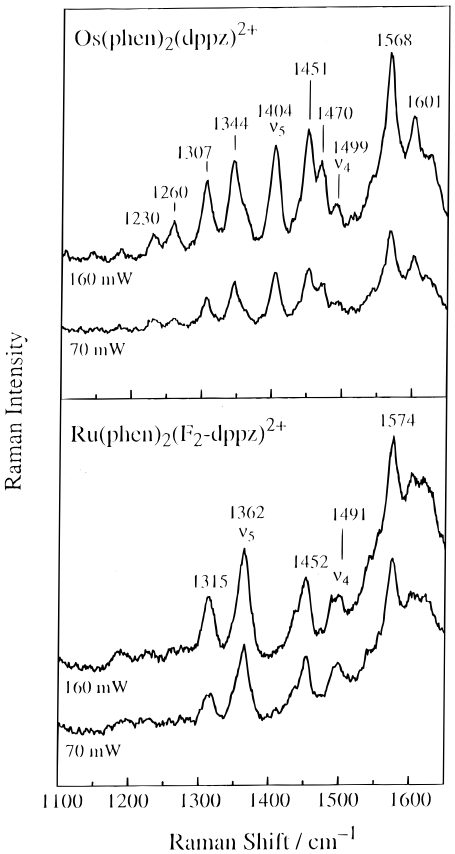

Figure 7. Resonace Raman spectra of $Os(phen)_2(dppz)^{2+}$ (top panel) and $Ru(phen)_2(F_2\text{-}dppz)^{2+}$ (bottom panel) with $\lambda_{exc} = 355$ nm (~10 ns) under low- and high-energy excitation conditions.

vibrational modes of *phz shifted to lower energies from their ground-state positions at 1493 and 1404 cm^{-1}, respectively.[20] The peak at 1453 cm^{-1}, however, also contains contributions from the Ru(phen) chromophore.[19]

To test this hypothesis, complexes for which the MLCT states are expected to be lower in energy than that of $Ru(phen)_2(dppz)^{2+}$ have been utilized. These are $Ru(phen)_2(F_2\text{-}dppz)^{2+}$ and $Os(phen)_2(dppz)^{2+}$, where both the Ru(II) → (F_2-dppz) and Os(II) → (dppz) transitions lie at energies lower than that of Ru(II) → (dppz) owing to a more easily reduced ligand and more easily oxidized metal center, respectively. The rR spectra collected under 355 nm pulsed excitation at low and high pulse energies are shown in Figure 7 for $Os(phen)_2(dppz)^{2+}$ and $Ru(phen)_2(F_2\text{-}dppz)^{2+}$. In both cases there is no change in the relative intensities of the bands as the power of the excitation beam is increased. This suggests that the spectral features observed correspond to those of the ground state of the dppz ligand in resonance with its $^1\pi\pi^*$ state in $Os(phen)_2(dppz)^{2+}$ and F_2-dppz in $Ru(phen)_2(F_2\text{-}dppz)^{2+}$. For these complexes the $^3\pi\pi^*$ excited state spectrum is not observed owing to its fast deactivation to populate the lower-lying MLCT state. The fact that the rR spectrum of the MLCT excited state is not observed can be explained by its low extinction coefficient relative to that of the ground state at 355 nm. Transient absorption experiments on these complexes are currently underway.

Interactions with DNA. Interaction of $Ru(L)_2(dppz)^{2+}$ complexes with DNA leads to increased emission from the MLCT state with a slight blue-shift in the emission maximum.[12] However, as explained above the ground-state rR spectra of all the dppz complexes presented here are in resonance with the dppz ligand's $^1\pi\pi^*$ state, and the observed excited-state peaks in $Ru(phen)_2(dppz)^{2+}$ are due to the $^3\pi\pi^*$ excited state of dppz in resonance with higher electronic states. Therefore, the MLCT excited state need not be considered in the discussion of the rR and TR[3] spectra collected utilizing 355 nm excitation.

Addition of small amounts of DNA to solutions containing $Ru(phen)_2(dppz)^{2+}$ (Figure 8a) leads to the decrease in the intensity of the rR peaks in the spectrum relative to those at 1310 and 1453 cm^{-1} (labeled P in the figure), which are the two peaks that possess large contributions from the phen part of the dppz ligand. The other dppz modes decrease in intensity, especially those associated with the phz moiety (Figure 8a). Since the phz part of the dppz ligand intercalates between the DNA bases, the decrease in intensity of the vibrational modes associated with this part of the molecule can be explained by a strong $\pi\pi$ stacking interaction. Further addition of DNA leads to a broad featureless spectral profile. Similar results were obtained for $Ru(phen)_2(F_2\text{-}dppz)^{2+}$, where the spectra as a function of DNA concentration are shown in Figure 8b. Again, the intensity of the dppz peaks decrease relative to the bands at

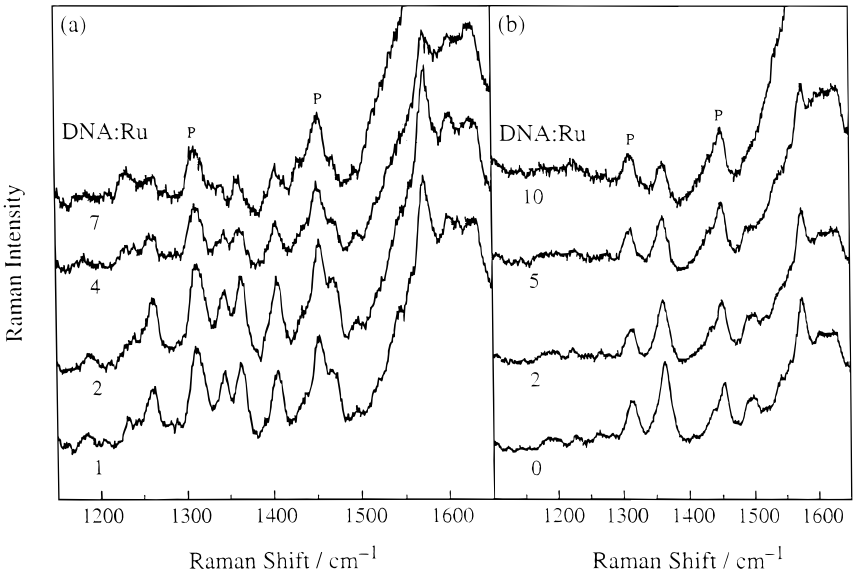

Figure 8. Resonance Raman spectra ($\lambda_{exc} = 355$ nm, ~10 ns) at various DNA:complex ratios (5 mM tris, 50 mM NaCl, pH = 7) of (a) $Ru(phen)_2(dppz)^{2+}$ and (b) $Ru(phen)_2(F_2\text{-}dppz)^{2+}$. The peaks labeled with a P are those that possess a large contribution from the phen part of the dppz ligand.

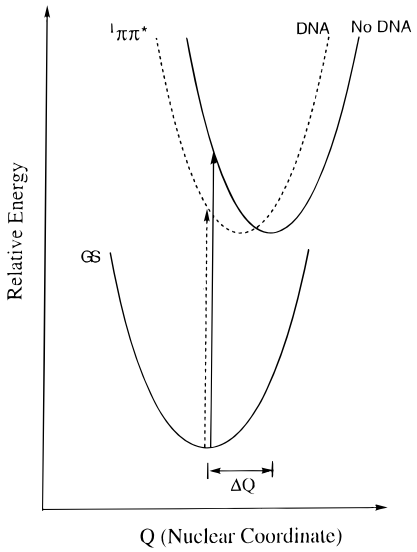

Figure 9. Schematic representation of the ground state (GS) and dppz LC $^1\pi\pi^*$ excited-state potential energy surfaces of Ru(phen)$_2$(dppz)$^{2+}$ free in solution (solid curve) and bound to DNA (dashed curve). The positions of maximum vibronic overlap for the absorption of the free and DNA-bound complex are drawn as a solid and a dashed arrow, respectively.

1313 and 1452 cm^{-1} (labeled P in the figure), which correspond to those that possess a large contribution from the phen part of the dppz ligand.

The decrease in signal intensity and broadening of the spectral profile as a greater fraction of the dppz ligand intercalates between the DNA bases is not unexpected. There have been several reports of rR spectra of molecules intercalated in DNA, and in all cases a marked decrease in the signal intensity is observed upon addition of DNA.[27−29] Although this phenomenon is often used to support intercalation arguments, there have been various descriptions of its origin. These will be discussed separately below.

Hypochromicity and red-shift of the electronic absorption band assigned to the dppz $^1\pi\pi^*$ transition upon addition of DNA lead to a decrease of the extinction coefficient at 355 nm relative to that of the free Ru(phen)$_2$(dppz)$^{2+}$ complex.[7,8,12] These spectral changes are pronounced in DNA:Ru ratios ranging from 0 to 4. However, for ratios greater than 4 a slight increase in the absorption at 355 nm is observed.[7] The initial decrease in the extinction coefficient at the excitation wavelength will lead to a decrease in the resonance enhancement, thus leading to a decrease in intensity of the observed signal. However, the rR signal continues to decrease for DNA:Ru ratios greater than 4, indicating that changes in the extinction coefficient alone cannot account for the decresing signal intensity at all DNA concentrations.

Another possible explanation is a shift in the nuclear coordinate (Q) of the LC dppz $^1\pi\pi^*$ excited-state potential energy surface upon DNA intercalation relative to the free ligand (Figure 9). This explanation is consistent with both the lower energy of the absorption maximum for the $^1\pi\pi^*$ transition in the presence of DNA as well as the lower rR signal intensity. The intensity of Raman bands are dependent on the nuclear displacement (ΔQ) between the ground and resonant excited-state potential energy surfaces. Thus, Franck−Condon resonance Raman scattering from a molecule with little change in nuclear coordinates between the states in resonance is expected to be very weak.[30,31]

A third explanation stems from similar results observed in the rR spectra of π-stacked porphyrin dimers and trimers, where a greater $\pi\pi$ interaction, determined from the interporphyrin distance, leads to the broadening and disappearance of the rR spectrum.[32] In the porphyrin systems the observations were explained as homogeneous broadening owing to the contribution from a number of modes to the absorption contour.[32] A similar argument can be utilized for the strong $\pi\pi$ interaction of the dppz ligand with DNA bases both above and below the ligand plane. Such strong interaction is known to cause a broadening and decrease in the rR intensity of other intercalated molecules.[27−29] These interactions can provide strong electronic coupling between the intercalator's $\pi\pi^*$ excited state and the electronic states of the stacked base pairs.

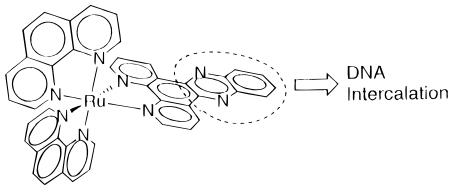

Figure 10. Structure of Ru(phen)$_2$ddpz^{2+} showing the phz part of the dppz ligand (dashed circle) and the direction of DNA intercalation of the dppz ligand.

It is likely that more that one, or even all three, of the above explanations for the signal decrease is operative in this case. However, it is important to note that the loss in signal intensity is an indication of intercalative binding of the dppz ligand. In fact, broadening of the rR spectrum in the presence of DNA is not observed for other Ru(II) diimine complexes, such as Ru(phen)$_3^{2+}$ and Ru(bpy)$_2$(dip)$^{2+}$, since dppz exhibits classical intercalation between the DNA bases whereas phen, bpy, and dip do not.[9]

There have been two previous reports of the rR and TR^3 spectra of Ru(II) complexes of dppz.[16,33] The spectra reported by Schoonover and co-workers are in good agreement with the ones presented in Figures 2 and 5. However, those obtained by Coates and co-workers appear different from those collected in the present work.[16,33] It is clear from the spectra and the text that the pulse energies utilized by Coates and co-workers to obtain the spectra are quite high.[33] Under such high-power conditions it is not unlikely that the complex is undergoing multiphoton photochemical change and that some of the observed signals are due to resonance enhancement of the products. The authors also collected spectra at these high powers in the presence of DNA and observed a new peak at 1525 cm^{-1}. However, since it is not clear that the spectral profile at very high energy is that of the intact complex, conclusions regarding this new peak cannot be made at this time. In our experimental setup the photon intensities utilized by Coates cannot be reached owing to shattering of our sample holder. However, such high energies are uncommon and impractical when making assignments of the resulting spectra.

Conclusions

The ground-state rR spectra of Ru(L)$_2$(dppz)$^{2+}$ complexes under 355 nm excitation is consistent with resonance with the LC $^1\pi\pi^*$ state of the dppz ligand, which is known to absorb strongly at the excitation wavelength. The excited-state signal of Ru(phen)$_2$(dppz)$^{2+}$ observed at high pulse energies is consistent with the population of the LC dppz $^3\pi\pi^*$ excited state, which is believed to lie at energies similar to those of the Ru(II) → (dppz) MLCT state. The observed excited-state signal is consistent with that previously observed for phz; the phz part of the dppz ligand is circled (dashed curves) in Figure 10. Upon lowering the MLCT energy through the utilization of a more easily reduced dppz derivative, F$_2$-dppz or Os(II) as the metal

center, the excited-state spectrum due to the dppz $^3\pi\pi^*$ state disappears. The TR[3] spectrum of the MLCT excited state in these complexes is not observed presumably because the extinction coefficient of the MLCT excited state is much smaller than that of the ground state at 355 nm. Transient absorption experiments on these complexes are currently underway.

Upon addition of limited amounts of DNA to dppz complexes of Ru(II), the rR peaks that correspond to the phz part of the ligand decrease in intensity. Further addition of DNA leads to a broadening of the spectrum. This phenomenon can be explained in terms of the intercalation between the phz part of the dppz ligand (Figure 10), which leads to a strong $\pi\pi$ interaction between the dppz ligand and the DNA bases. This strong interaction between the π system of the ligand and that of the confacial DNA bases can lead to an electronic coupling between the complex and the DNA π-stack that is greater than that expected for intermolecular donor−acceptor systems.

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References and Notes

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