Ligand-Specific Charge Localization in the MLCT Excited State of $Ru(bpy)_2(dpphen)^{2+}$ Monitored by Time-Resolved Resonance Raman Spectroscopy

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Time-resolved resonance Raman spectroscopy has been employed to examine the location of the promoted electron in the metal-to-ligand charge-transfer (MLCT) excited state of $Ru(bpy)_2(dpphen)^{2+}$ (bpy = 2,2′-bipyridine; dpphen = 4,7-diphenyl-1,10-phenanthroline). Variations in the environment about $Ru(bpy)_2(dpphen)^{2+}$ shift the localization of charge in the MLCT excited state from bpy in neutral micelles (Brij 35) to dpphen in the presence of DNA and anionic surfactants ($C_{12}H_{25}OSO_3Na$, $C_{10}H_{23}OSO_3Na$, and $C_8H_{21}OSO_3Na$), whereas in water the electron is localized on both ligands. The shifts in the electronic absorption spectrum and the dependence of the ground-state resonance Raman (rR) signal with excitation wavelengths coincident with the high- and low-energy sides of the MLCT absorption band are consistent with a lowering of the energy of the Ru(II)–dpphen transition with respect to that of bpy in anionic micelles.

Introduction

Molecular probes whose photophysical properties are sensitive to their immediate environment are of great interest, since their interactions with microheterogeneous systems can provide dynamic and static information concerning the organized medium.[1-4] Heterogeneous microenvironments, such as those in micelles, cyclodextrins, and DNA,[1] may possess hydrophobic and hydrophilic spaces and may be ionic or neutral. It has been demonstrated that micelles and DNA are able to increase the luminescence quantum yield and lifetimes of many Ru(II) complexes,[5-7] and in the case of DNA stereoselective interaction may be operative.[7] A potential probe of stereoselective interactions with DNA is $Ru(bpy)_2(dpphen)^{2+}$ (bpy = 2,2′-bipyridine; dpphen = 4,7-diphenyl-1,10-phenanthroline), which has been shown by time-resolved resonance Raman (TR^3) spectroscopy to exhibit localization of the promoted electron on both bpy and dpphen in water owing to the similar energies of the two ligands.[8]

It was recently established that localization in the metal-to-ligand charge-transfer (MLCT) excited state of $Ru(bpy)_3^{2+}$ and other bpy-containing chromophores is intrinsic to the complex and is not a solvent-driven phenomenon.[9,10] The mechanism for localization has been explained by utilizing Raman data.[11] However, we report here the selective localization of the excited electron in $Ru(bpy)_2(dpphen)^{2+}$ on either bpy or dpphen, dictated by distinct solvation environments about each ligand. The perturbations of the MLCT excited state of $Ru(bpy)_2(dpphen)^{2+}$ were observed in the presence of DNA as well as anionic and neutral surfactants and may be attributed to the difference in hydrophobicity between bpy and dpphen.

Since the initial determination of the localized nature of the lowest MLCT excited state of $Ru(bpy)_3^{2+}$,[12,13] numerous studies have been conducted on this and related systems.[14-16] Time-resolved resonance Raman (TR^3) spectroscopy has proven to be a powerful tool in the characterization of electron localization in the MLCT excited state of Ru(II) diimine complexes.[17-24] As

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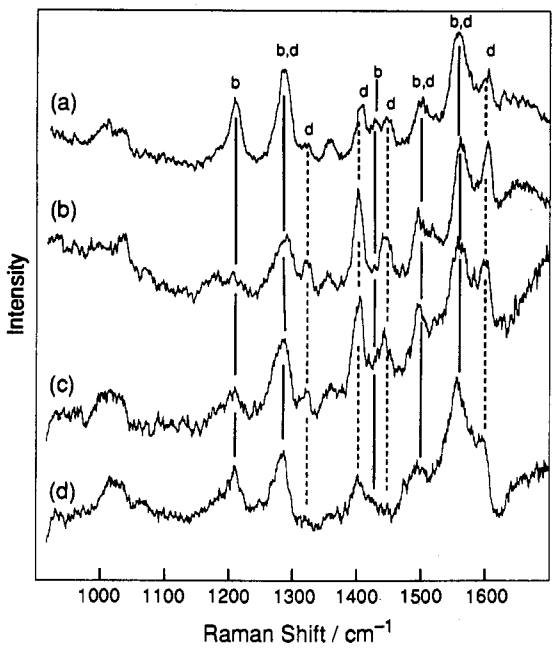

Figure 1. TR^3 spectra of ~5 × 10^{-4} M Ru(bpy)$_2$(dpphen)$^{2+}$ in (a) water, (b) 3 mM SDS, (c) 1.7 mM calf thymus DNA in Tris buffer (5 mM Tris, 50 mM NaCl, pH = 6.7), and (d) 3 mM Brij 35. The parentage of the strongest peaks is denoted by b (bpy) or d (dpphen); b,d represents contributions from both ligands.

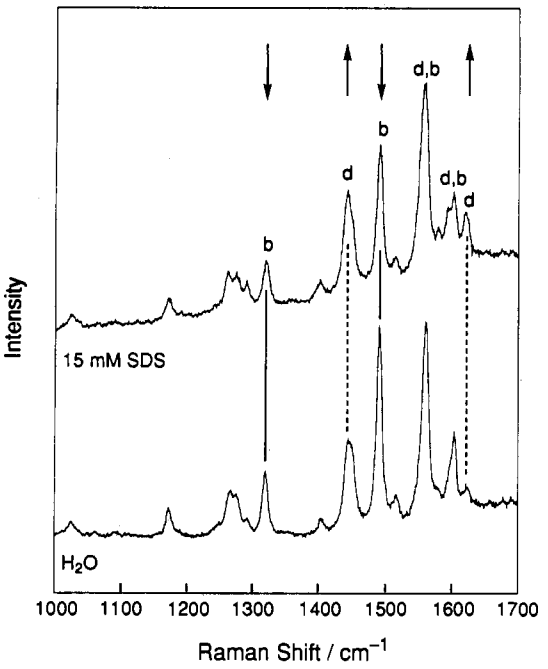

Figure 2. Ground-state resonance Raman spectra of ~5 × 10^{-4} M Ru(bpy)$_2$(dpphen)$^{2+}$ in water and 15 mM SDS recorded under 457.9-nm excitation. The parentage of the strongest peaks is denoted by b (bpy) or d (dpphen); b,d represents contributions from both ligands. The arrows indicate the changes in relative intensities of the peaks due to bpy and dpphen in the presence of SDS with respect to water.

reported previously, in water the TR^3 spectrum of Ru(bpy)$_2$(dpphen)$^{2+}$ contains contributions from both reduced bpy and dpphen,[8] indicating that on the vibrational time scale the promoted electron is localized on the π^* orbital of either bpy or dpphen ligands. Typically a small energy difference between ligands leads to localization on both ligands,[8,24] whereas localization on only the lowest-energy ligand is observed when the energy gap is large.[24]

Experimental Methods

The ground-state rR and excited-state TR^3 spectra were collected with two different instruments, each consisting of a Spex Triplemate monochromator equipped with a diode array detector (EG&G PAR OMA III). The filter stage gratings in both cases were 600 gr/mm, but different main stage gratings, with 1800 and 2400 gr/mm, were utilized for the rR and TR^3 experiments, respectively. The CW excitation sources were a Liconix HeCd laser (λ_{ex} = 441.6 nm, 20 mW) and a Coherent Innova 100 Ar$^+$ (λ_{ex} = 457.9 nm, 30 mW); the scattered Raman signal was collected in a 90° geometry from a 1 cm × 1 cm quartz cell. The TR^3 spectra were obtained following excitation by the third harmonic (354.7 nm, ~2.5 mJ) of a Quanta Ray DCR2 Nd:YAG laser operating at 20 Hz, and a backscattering detection geometry (~11° between pump and collection optics) was utilized. The samples for the TR^3 experiments were contained in a Suprasil quartz NMR tube (purchased from Wilmad), or the scattering was directly detected from a liquid stream, pumped with a Micropump (Barish Pump Co). Absorption measurements were performed in a Perkin-Elmer 3840 diode array spectrometer.

The chloride salt of Ru(bpy)$_2$(dpphen)$^{2+}$ was synthesized by refluxing Ru(bpy)$_2$Cl$_2$ with excess dpphen (both reagents purchased from Aldrich) in DMF and was purified by passing the reaction mixture through a Sephadex G-50 column.[15] The PF_6^- salt of Ru(bpy)$_2$(dpphen)$^{2+}$ was obtained from the Cl^- salt by filtering out the precipitate formed by the addition of ammonium hexafluorophosphate (purchased from Aldrich) in water. The anionic surfactants were purchased from Lancaster Synthesis or Kodak, and Brij 35 was purchased from Aldrich. Calf-thymus DNA was purchased from Sigma and was purified by the method previously described.[25]

Results

Parts a–c of Figure 1 show the TR^3 spectra of Ru(bpy)$_2$(dpphen)$^{2+}$ in water, in the presence of 15 mM $C_{12}H_{25}OSO_3Na$ (SDS), and with calf-thymus DNA, respectively, recorded following 354.7 nm, ~2.5 mJ (fwhm = 10 ns) excitation. In the presence of anionic surfactants of varying chain lengths, $C_{12}H_{25}OSO_3Na$, $C_{10}H_{23}OSO_3Na$, and $C_8H_{21}OSO_3Na$, the signal in the TR^3 spectrum arising from bpy$^{\bullet-}$ (labeled b in the figure) disappears, and only the contributions from dpphen$^{\bullet-}$ (labeled d in the figure) are observed. The spectral features were assigned to each ligand by comparison to the TR^3 spectra of the parent tris complexes, Ru(bpy)$_3^{2+}$ and Ru(dpphen)$_3^{2+}$.[8,12,17] The TR^3 spectrum in the presence of DNA, shown in Figure 1c, exhibits exclusively the excited-state signal from dpphen, as was suggested in an earlier paper.[26] The reverse trend is observed in neutral micelles (3 mM Brij 35), where the greatest contribution to the TR^3 signal arises from bpy$^{\bullet-}$ (Figure 1d), and only the largest peak in the dpphen$^{\bullet-}$ spectrum (at 1404 cm^{-1}) is evident. The presence of a simple electrolyte (Na_2SO_4) does not alter the TR^3 spectrum relative to that of pure water. The observed effect is not due to shifts in the electronic absorption spectrum, since transient absorption spectra of Ru(bpy)$_2$(dpphen)$^{2+}$ do not shift significantly upon addition of either SDS or Brij 35.[27] These observations suggest that it is the presence of an anionic medium, coupled to a hydrophobic area, that leads to the relative stabilization of dpphen with respect to bpy in Ru(bpy)$_2$(dpphen)$^{2+}$. The absence of the negative charge on the surfactant, however, has a reverse effect, destabilizing dpphen with respect to bpy.

This conclusion is supported by the ground-state resonance Raman (rR) spectra of Ru(bpy)$_2$(dpphen)$^{2+}$, in the presence and

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(27) The transient absorption spectrum was recorded 20 ns after a Nd:YAG laser pulse (λ_{exc} = 532 nm, fwhm ~ 10 ns) by utilizing a pulsed Xe arc lamp (150 W) with the standard pump–probe technique.

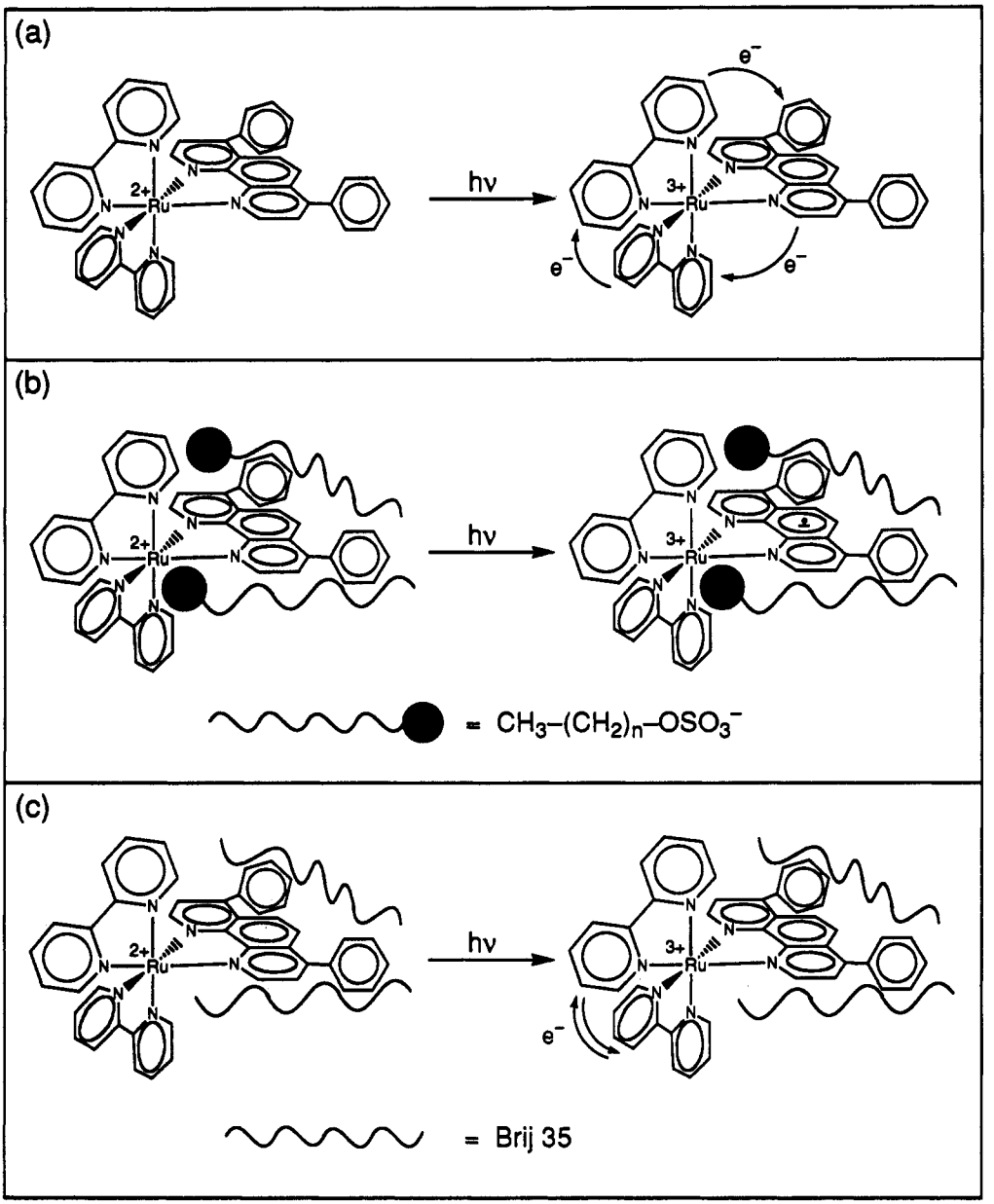

Figure 3. Schematic representation of $Ru(bpy)_2(dpphen)^{2+}$ in (a) water, (b) anionic surfactants, and (c) neutral Brij 35, showing the localization of the electron upon excitation. In water the electron resides on both bpy and dpphen, in anionic surfactants only on dpphen, and in Brij 35 on bpy.

absence of anionic micelles, with excitation wavelengths coincident with the low- (457.9 nm) and high-energy (441.6 nm) sides of the broad MLCT absorption band.[28] In the presence of anionic surfactants, such as SDS, the relative resonance enhancement of bpy to dpphen varies depending on the excitation energy. With 457.9-nm excitation, addition of SDS results in enhancement of dpphen signal in the 1000–1700-cm^{-1} region (Figure 2), whereas the observed relative contributions to the spectrum are reversed upon 441.6-nm excitation. In Figure 2 the arrows indicate the enhancement of the strongest peak in the dpphen spectrum relative to those of bpy. These results indicate that addition of SDS lowers the Ru(II)–dpphen MLCT transition energy with respect to that of bpy. In agreement with the rR excitation profile of the MLCT electronic absorption band, a red shift of the low-energy side of the MLCT absorption is observed in the electronic spectrum of $Ru(bpy)_2(dpphen)^{2+}$ in the presence of SDS. A similar shift is also evident in the absorption spectrum of $Ru(dpphen)_3^{2+}$ upon addition of SDS, whereas that of $Ru(bpy)_3^{2+}$ remains unchanged.

Discussion

A schematic representation of the charge localization in the MLCT excited state of $Ru(bpy)_2(dpphen)^{2+}$ as a function of solvent environment is shown in Figure 3. In water, localization of the excited electron on both bpy and dpphen is observed. In the presence of anionic surfactants and DNA, the charge is localized only on dpphen, but with the neutral Brij 35, the electron resides only on the bpy ligands. It should be noted that the formation of micelles is not necessary to observe this phenomenon, and therefore it must arise from a premicellar adduct of the complex. Such complexation is known to take place with anionic surfactants with moderate binding constants and to affect the emissive behavior of Ru(II) diimine complexes.[29]

In the presence of the nonionic surfactant Brij 35, the TR^3 spectra show mostly bpy signals. It is has been shown that Triton X-100, another nonionic surfactant, does not affect the lifetime or spectral characteristics of $Ru(bpy)_3^{2+}$ or $Ru(phen)_3^{2+}$.[30] Although the absorption and emission spectra of $Ru(phen)_2$-

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$(dpphen)^{2+}$ are not appreciably perturbed upon addition of Triton X-100, the MLCT state lifetime increases.[29] These findings indicate that Triton X-100 and possibly other nonionic surfactants interact only with the hydrophobic dpphen ligand in $Ru(phen)_2(dpphen)^{2+}$ and $Ru(bpy)_2(dpphen)^{2+}$ complexes. It is possible that this interaction raises the Ru–dpphen transition with respect to the Ru–bpy in $Ru(bpy)_2(dpphen)^{2+}$, therefore inducing localization of charge on bpy. This hypothesis is reasonable since it has been shown for $Re(CO)_3(bpy(CH_2)_nCH_3)^+$ complexes that the Re–bpy MLCT transition shifts to higher energies with increasing intramolecular interactions as the alkyl side chain is lengthened.[31] In the case presented here, however, only the dpphen ligand interacts with Brij 35; therefore only the Ru–dpphen MLCT transition is expected to shift to higher energies.

It is apparent that there is a cooperative interaction between the negative charge and the hydrophobic regions about $Ru(bpy)_2(dpphen)^{2+}$, which results in a shift of the Ru–dpphen MLCT transition to lower energies. The exact nature of the perturbation on the MLCT excited state caused by these electrostatic and hydrophobic interactions with the long alkyl chain (surfactants) and major groove (DNA) is unknown; however there are several possible explanations of the observed results. The first, depicted in Figure 4a,b, is that the different solvation environment leads to a lowering of the Ru(II)–dpphen transition energy, thereby increasing the energy gap between bpy and dpphen. Since dpphen would in this case lie lower in energy than bpy, charge localization on dpphen would be expected. This explanation is consistent with the observed shifts in the absorption spectra of $Ru(dpphen)_3^{2+}$ and $Ru(bpy)_3^{2+}$ in surfactant media discussed above.

Another possibility is that the different solvation environments lead to changes in the solvent's reorganization energies about dpphen and bpy in the presence of anionic surfactants and DNA relative to those in water. Around bpy, the environment is likely to be more polar, near the negative charge, whereas in dpphen, the hydrophobic region provides a nonpolar surrounding. Since the polarities of the medium around bpy and dpphen change in opposite directions, the electron-transfer potential energy surfaces of each reduced ligand becomes displaced along the nuclear coordinate axis away from the other (Figure 4c). Such displacement is expected to decrease the interligand-electron-hopping rate by introducing a larger activation barrier to hopping. Since it is known from rR excitation profiles that the MLCT transition of dpphen lies just below that of bpy, the electron may populate dpphen and due to the large activation barrier may not be able to transfer to bpy.

A third scenario involves rotation about the C_2–$C_{2'}$ bond in bpy following its reduction, which is postulated to stabilize $bpy^{\bullet-}$ in the MLCT excited state of $Ru(bpy)_3^{2+}$ and therefore decrease the interligand-electron-hopping rate. The evidence for this rotation in the MLCT excited state arises from the intensity of the twisting marker bands (1212 and 1427 cm^{-1}) in the TR^3 spectrum of $Ru(bpy)_3^{2+}$, as was recently described in detail.[11] In the presence of SDS, the intensities of these bands diminish by 30–50% with respect to other $bpy^{\bullet-}$ peaks in the spectrum of $Ru(bpy)_3^{2+}$.[32] This change in relative intensities suggests that the stabilizing twisting motion in bpy is hindered in the presence of anionic surfactants in $Ru(bpy)_3^{2+}$. It may therefore be expected that in $Ru(bpy)_2(dpphen)^{2+}$ the energy gap between bpy dpphen would increase as $bpy^{\bullet-}$ is stabilized to a lesser extent. This is depicted in Figure 4b.

Further information on the localization of the MLCT excited state of $Ru(bpy)_2(dpphen)^{2+}$ may be obtained through the use of nonaqueous homogeneous solvents. To this end, the acquistion of a TR^3 spectrum of the PF_6^- salt of the complex in acetonitrile, rather that of than the Cl^- salt, was attempted with 354.7-nm excitation. However, emission from the sample at the monitoring wavelength precluded the observation of the weak Raman signal. The exploration of other counterions to examine the TR^3 spectra of $Ru(bpy)_2(dpphen)^{2+}$ in nonpolar homogeneous solvents, as well as transient absorption measurements, is currently underway. The specific solvation of ligands with different hydrophobicities can lead to tuning of the excited-state properties of a mixed-ligand transition metal diimine complex, shifting the localization of the electron from both ligands to only one. Thus, differences in the solvation about the ligation sphere of a single complex may be utilized to probe its microheterogeneous environment.

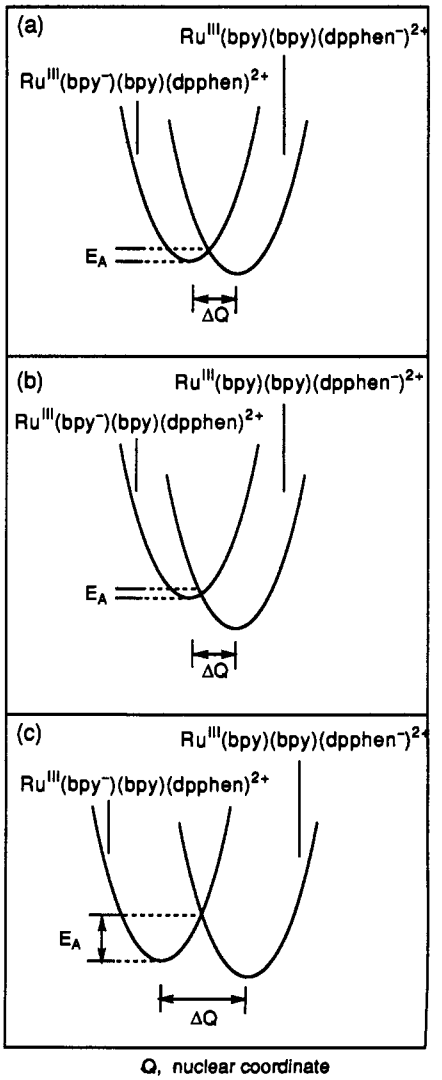

Figure 4. Schematic potential energy surfaces representing the electron hopping in the MLCT excited state of $Ru(bpy)_2(dpphen)^{2+}$. In water (a) the localization is on both bpy and dpphen owing to the small activation energy and driving force. Localization only on dpphen in the presence of anionic surfactants may occur because of an increase in the energy difference between bpy and dpphen (b) or due to differences in the solvent's reorganization energy which lead to displacement of the wells in opposite directions along the nuclear coordinate (c; see text). E_A and ΔQ refer to the activation energy for electron hopping and displacement of nucleii upon charge transfer, respectively.

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