Comparison of the Photophysical Properties of Osmium(II) Bis(2,2′:6′,2″-terpyridine) and the Corresponding Ethynylated Derivative

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The photophysical properties of osmium(II) bis(2,2′:6′,2″-terpyridine) have been recorded over a wide temperature range. An emission band is observed and attributed to radiative decay of the lowest-energy metal-to-ligand, charge-transfer (MLCT) triplet state. This triplet is coupled to two other triplet states that lie at higher energy. The second triplet, believed to be of MLCT character, is reached by crossing a barrier of only 640 cm^{-1}, but the highest-energy triplet, considered to be of metal-centered (MC) character, is separated from the lowest-energy MLCT triplet by a barrier of 3500 cm^{-1}. Analysis of the emission spectrum shows that both low- and high-frequency modes are involved in the decay process, while weak emission is seen from the second excited triplet state. The magnitude of the low- and high-frequency modes depends on temperature in fluid solution but not in a KBr disk. Apart from a substantial lowering of the triplet energy, the photophysical properties are relatively insensitive to the presence of an ethynylene substituent at the 4′ position of each terpyridine ligand. However, the barrier to reaching the MC triplet is markedly reduced, and the vibrational modes become less sensitive to changes in temperature.

Introduction

The photophysical properties of many transition-metal poly(pyridine) complexes are controlled by the Englman−Jortner energy-gap law.[1,2] However, it is recognized that in numerous cases the lifetime of the lowest-energy excited triplet state is affected by coupling to higher-energy excited states.[3] This is especially evident for ruthenium(II) poly(pyridine) complexes, where the lowest-energy metal-to-ligand, charge-transfer (MLCT) state couples to higher-energy MLCT states and also to metal-centered (MC) states.[4] These latter species are deactivated rapidly by way of internal conversion and serve to shorten the lifetime of the lowest-energy triplet at ambient temperature.[5,6] It is believed that the MC excited states lie at relatively high energy for the corresponding osmium(II) poly(pyridine) complexes.[7] This situation is seen clearly for the metal bis(2,2′:6′,2″-terpyridine) (terpy) complexes at room temperature because Ru-terpy is nonluminescent but Os-terpy emits with reasonable efficiency in the absence of molecular oxygen.[8] A further advantage of the Os-terpy chromophore is the availability of relatively strong absorption bands stretching across the far-red region of the spectrum.[9] This latter property is useful for the design of luminescent biolabels.[10]

Recent attention has concentrated on improving the emission probability of Ru-terpy by attaching substituents that promote extensive electron delocalization at the triplet level.[11,12] This strategy has resulted in the design of Ru-terpy derivatives that possess lowest-energy MLCT triplet states having lifetimes approaching 1 μs at room temperature.[13] Such prolongation of the triplet lifetime stems from a combination of decoupling the MC and MLCT states and by the general effects of increased electron delocalization. There still exists electronic coupling between nearby MLCT triplets. We now extend this approach to Os-terpy complexes in an effort to better understand their photophysical properties.

In the first instance, we compare the effects of attaching an ethynylene group at the 4′ position of the terpy ligand. To access the high energy MC state, it has been necessary to work at relatively high temperatures, but this is facilitated by the good thermal and photochemical stability of these materials. Prior work by Ohno and co-workers[4b,14] has shown that many transition-metal complexes emit in the solid state at high temperature, and we have built on this platform. In addition, compelling evidence has been reported for the participation of upper-lying MLCT excited states in both ruthenium(II)[15,16] and osmium(II)[17] poly(pyridine) complexes. Decay of these upper states contributes toward the measured luminescence lifetimes but appears to be dominated by nonradiative processes.

Experimental Procedures

All raw materials were purchased from Aldrich Chemicals Co. and were used as received. Solvents were dried by standard literature methods[18] before being distilled and stored under nitrogen over 4 Å molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL Lambda 500 spectrometer. Routine mass spectra and elemental analyses were obtained using in-house facilities. Samples of Os-terpy were prepared and purified by literature methods.[19] Preparation of the ethynylated derivative, Os-acet, will be reported elsewhere. The isolated compounds were converted to hexafluorophosphate salts and purified by repeated recrystallization. Analysis was made by ^{1}H and ^{13}C NMR, mass spectrometry, and elemental composition. The energy-minimized structures (Figure 1) were prepared with AMPAC.

Absorption spectra were recorded with a Hitachi U3310 spectrophotometer, while corrected luminescence spectra were

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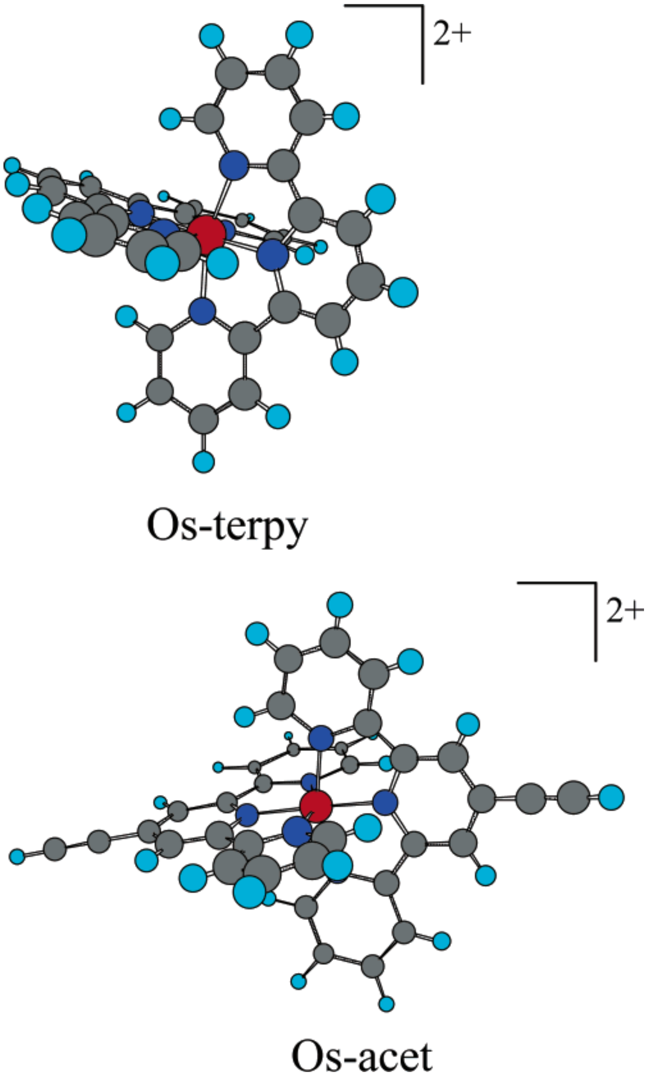

Figure 1. Energy-minimized structures for the compounds studied here.

recorded with a Spex Fluorolog tau-3 spectrophotometer. All luminescence measurements were made using optically dilute solutions and were corrected for spectral imperfections of the instrument by reference to a standard lamp. Emission quantum yields were measured relative to osmium(II) tris(2,2′-bipyridine).[20] Time-resolved luminescence measurements were made after excitation of the sample with a frequency-doubled, Q-switched Nd:YAG laser [full width at half-maximum (fwhm) = 4 ns and $\lambda = 532$ nm]. Approximately 512 individual laser shots were averaged prior to data analysis.

Temperature-dependent studies were made with either an Oxford Instruments Optistat DN cryostat or a Harrick Scientific demountable cell with a 1 mm path length. In each case, the sample was allowed to equilibrate at the new temperature before making a measurement. Luminescence studies were made with the sample dissolved in dried butyronitrile or ethylene glycol or dispersed in KBr and pressed into a pellet under high vacuum.

Results and Discussion

Photophysical Properties of Os-terpy. The absorption spectrum recorded for the parent complex, Os-terpy,[21] displays pronounced ligand-centered transitions in the UV region and MLCT transitions in the visible region (Figure 2). The spin-forbidden MLCT transitions stretch as far as 725 nm. Analysis of the latter spectral region in terms of Gaussian-shaped components places the 0,0 transition at 692 nm. Luminescence is readily observed at room temperature with a maximum at 710 nm (Figure 2). The magnitude of the Stokes shift suggests that the total reorganization energy accompanying decay of the triplet state is only ca. 200 cm^{-1}. The emission quantum yield (Φ_{LUM}) and lifetime (τ_{LUM}) in deoxygenated acetonitrile at 20 °C are 0.014 and 270 ns, respectively. Earlier work[22] has established that the emitting species is the lowest-energy MLCT triplet state. Both Φ_{LUM} and τ_{LUM} increase with decreasing temperature.[5a] In butyronitrile or ethylene glycol solution, the rate constant for deactivation of the lowest-energy MLCT triplet state ($k_D = 1/\tau_{LUM}$) depends on the temperature according to the following expression (Figure 3):[17a]

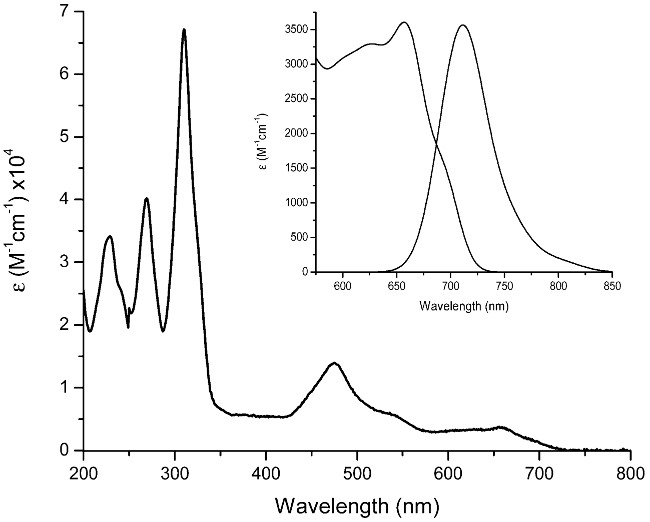

Figure 2. Absorption spectrum recorded for Os-terpy in butyronitrile solution. The inset shows the overlap between absorption and emission spectra as recorded at room temperature.

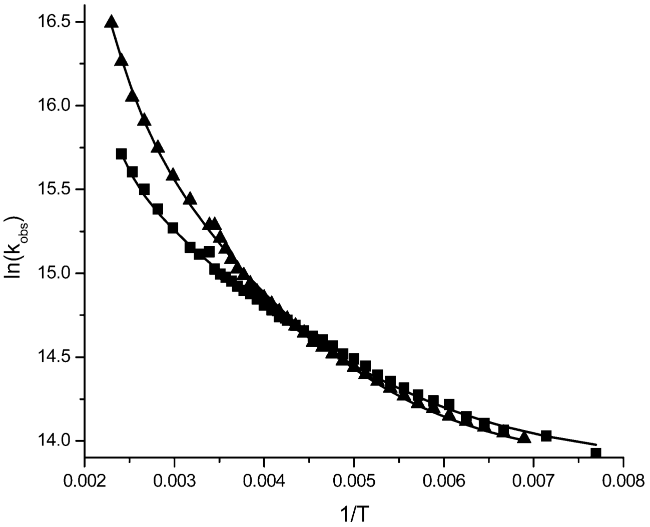

Figure 3. Effect of temperature on the decay rate constant for Os-terpy (■) and Os-acet (▲) measured in butyronitrile. The solid line drawn through the data points is a nonlinear, least-squares fit to eq 1.

$$k_D = \frac{k_0 + k_1 \exp\left(-\frac{E_A}{k_B T}\right) + k_P \exp\left(-\frac{E_B}{k_B T}\right)}{1 + \exp\left(-\frac{E_A}{k_B T}\right) + \exp\left(-\frac{E_B}{k_B T}\right)} \qquad (1)$$

Here, k_0 refers to the activationless rate constant that controls

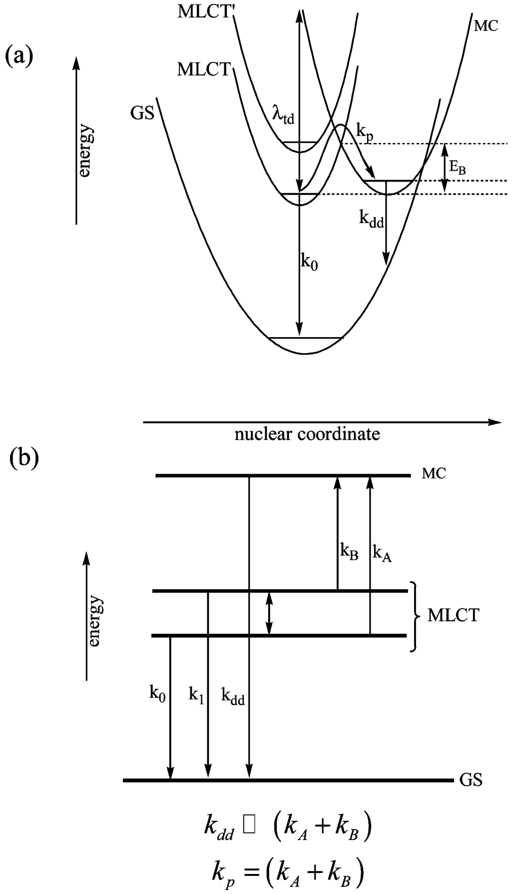

Figure 4. Energy level diagram proposed for the triplet manifold of **1**. Interconversion between the lowest-energy MLCT triplet state (MLCT) and the second triplet (MLCT′) is assumed to be reversible, but the population of the MC triplet state is followed by rapid decay to the ground state. Note that in the potential energy diagram (a) the position of the second MLCT triplet has been displaced to a higher energy for clarity of presentation.

triplet decay at low temperatures. The lowest-energy triplet state couples to a second triplet that lies at a slightly higher energy.[15−17] The barrier to reaching the upper triplet (E_A) is only 640 cm^{-1}, while the rate constant (k_1) for subsequent decay of this state is 5.2×10^7 s^{-1}. This latter triplet is most likely an MLCT state but possessing more pronounced singlet character than the lowest-energy triplet.[23] Both E_A and the ratio k_1/k_0 are closely comparable to values reported for other osmium(II) poly(pyridine) complexes. At elevated temperatures, both triplets couple to a high-energy excited state that is probably of MC character (Figure 4).[17] This model assumes that the energy gaps are independent of the temperature.

Reaching the MC state requires passage over a substantial barrier ($E_B = 3500$ cm^{-1}). This barrier can be compared to that reported earlier ($E_B = 1700$ cm^{-1}) for Ru-terpy.[8a] The experimental rate constant (k_P) for populating the MC state is 4.5×10^{10} s^{-1}, as calculated on the basis that deactivation of the MC triplet occurs faster than its formation.[24] In fact, k_P can be considered to represent the sum of the rate constants for reaching the MC state from each of the MLCT triplets (Figure 4).[17a] The barrier to reaching the MC triplet is greatly increased upon moving from solution to a KBr disk, and there is a corresponding increase in the rate constant for its formation (Table 1). This observation is in line with earlier studies made with Ru-terpy dispersed in a zeolite.[12c] These high-temperature studies do not permit estimation of the activationless rate constant, but fitting over the accessible temperature range in KBr does require inclusion of a second activated process.

TABLE 1: Parameters Extracted from the Temperature Dependence Observed for the Decay of the Lowest-Energy MLCT Triplet State and the Derived Triplet and Reorganization Energies

property	Os-terpy	Os-terpy	Os-acet	Os-acet
medium	BuCN	KBr	BuCN	KBr
k_0 (10^6 s^{-1})	1.4		1.1	
k_1 (10^7 s^{-1})	5.2	2.2	6.0	2.4
k_p (10^{10} s^{-1})	8.5	190	1.2	140
E_A (cm^{-1})	640	320	600	325
E_B (cm^{-1})	3500	4570	2520	4410
E_T (cm^{-1})[a]	14 310	14 280	13 760	13 710
λ_T (cm^{-1})	205	200	160	140
E_{BOLT} (cm^{-1})[b]	780		585	
k_{RAD} (10^4 s^{-1})[c]	5.2		2.4	

[a] The triplet energy, E_T, is calculated as $E_{00} + \lambda_T$. [b] This term is determined from $(N_1/N_0) = \exp(-E_{BOLT}/RT)$, where N_0 and N_1 refer, respectively, to the emission yields of the normal and hot emission. [c] The radiative rate constant, k_{RAD}, is calculated from $k_{RAD} = \Phi_{LUM}/\tau_{LUM}$.

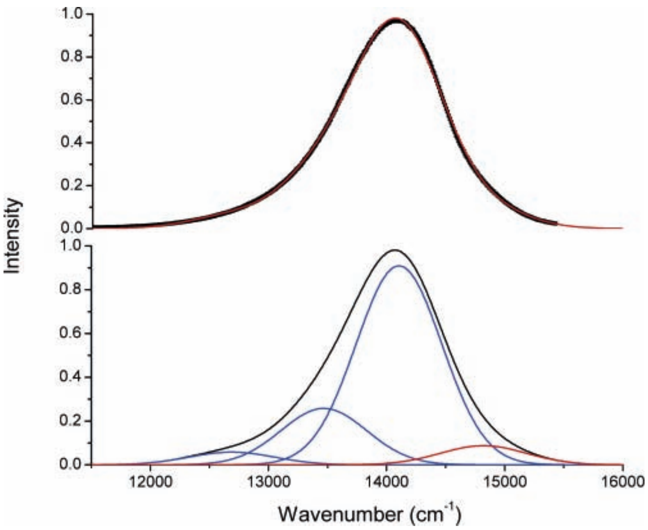

Figure 5. Deconvolution of the emission spectrum into the minimum number of Gaussian components (lower panel) and reconstitution of the entire emission spectrum (upper panel).

Analyzing the room-temperature emission spectrum in terms of a series of Gaussian profiles requires at least four bands of common half width (fwhm = 955 cm^{-1}).[25] The most intense band, which is located at 14 105 cm^{-1}, corresponds to the 0,0 transition (Figure 5). Two Gaussian bands are required at lower energy that correspond to the involvement of a medium-frequency vibrational mode of ca. 1420 cm^{-1} and a low-frequency vibration of ca. 640 cm^{-1}. In additional, there is a band corresponding to hot emission that lies about 715 cm^{-1} above the 0,0 transition.

The “normal” emission spectrum can be reconstituted in terms of eq 2.[26] Here, $I(\nu)$ is the ratio of the intensity of emission at energy ν in cm^{-1} to that at the peak maximum. The term E_{00} refers to the 0,0, energy gap while $h\omega_M$ and $h\omega_L$, respectively, are the medium- and low-frequency vibrational modes coupled to decay of the triplet state. Initial estimates for these latter parameters and also for the fwhm ($\Delta\nu_{1/2}$) were taken from the Gaussian analysis. The Huang−Rhys factors, S_M and S_L, reflect the extent of nuclear distortion along their respective quantum modes. The Laguerre polynomial and Boltzmann term allow for spectral broadening at higher temperatures. It should be

TABLE 2: Parameters Extracted from Fitting the Emission Spectra Recorded in Butyronitrile at Room Temperature to the Two-Mode Model given as eq 2

parameter	Os-terpy	Os-acet	parameter	Os-terpy	Os-acet
E_{00} (cm^{-1})	14 105	13 600	S_L	0.47	0.38
$h\omega_M$ (cm^{-1})	1420	1350	$\Delta\nu_{1/2}$ (cm^{-1})	855	780
$h\omega_L$ (cm^{-1})	640	555	$h\omega_H$ (cm^{-1})	715	835
S_M	0.31	0.28			

stressed that the emission spectrum cannot be described properly in terms of a single-mode analysis.[27]

$$I(\nu) = \sum_{m=0}^{5}\sum_{l=0}^{15}\left\{\left(\frac{E_{00} - m\hbar\omega_{\mathrm{M}} - l\hbar\omega_{\mathrm{L}}}{E_{00}}\right)^{3}\left(\frac{S_{\mathrm{M}}^{m}}{m!}\right)L(l)\exp(-Q)\right\}$$

$$Q = \left[-4\ln(2)\left(\frac{\nu - E_{00} + m\hbar\omega_{\mathrm{M}} + l\hbar\omega_{\mathrm{L}}}{\Delta\nu}\right)^{2}\right]$$

$$X = \frac{\hbar\omega_{\mathrm{L}}}{k_{\mathrm{B}}T}$$

$$L(l) = S_{\mathrm{L}}^{l}\sum_{p=0}^{\infty}\left(\frac{X^{p}p!}{(p+l)!}\right)\left[\sum_{q=0}^{p}\frac{(p+l)!(-S_{\mathrm{L}})^{q}}{(p-q)!(q+l)!p!}\right]^{2} \qquad (2)$$

The parameters derived on fitting the “normal” region of the room-temperature emission spectrum are collected in Table 2. The total reorganization accompanying triplet decay (λ_T) is ca. 205 cm^{-1}, while the triplet energy (E_T) is 14 310 cm^{-1}. The medium-frequency vibrational mode ($h\omega_M$ = 1400 cm^{-1}) can be attributed to C═C and/or C═N stretching vibrations associated with the slight change in structure.[28] The low-frequency mode ($h\omega_L$ = 630 cm^{-1}), which persists in a KBr disk and therefore is not associated with a specific solvent molecule,[29] is assigned to the Os−N bond. The Huang−Rhys factors are small and consistent with a modest structural change between the two states.

This spectral analysis was made over the full temperature range (see the Supporting Information). First, it was found that E_T and λ_T remained essentially independent of temperature. Both values are slightly lower in KBr compared to the fluid solution.[30] This finding suggests that the nuclear contribution to λ_T outweighs the solvent term and that there is little difference in polarity between the ground and triplet states. In reaching these conclusions it is assumed that lowering the temperature causes a substantial increase in effective polarity of butyronitrile[31] without affecting that of KBr. Both $h\omega_L$ and hw_M decrease progressively with decreasing temperature in fluid solution (see the Supporting Information) but are insensitive to temperature in KBr. There is a steady decrease in both S_M and S_L with increasing temperature that can be traced to changes in the vibrational frequencies. Again, these effects are attributed to changes in solvent polarity rather than temperature.

Close inspection of the emission spectrum, especially after fitting to eq 2, indicates that there is a small component situated at higher energy than the E_{00} band. This hot emission does not change with repeated purification of either sample or solvent, and its relative contribution to the total emission increases with increasing temperatures. From the Gaussian analysis, the peak position for hot emission lies ca. 710 cm^{-1} above the E_{00} band (Figure 5). This energy gap is slightly higher than that derived for $h\omega_L$ (=630 cm^{-1}). There are two possibilities for the origin of the hot emission: First, emission could take place from an upper vibrational level of the lowest-energy MLCT triplet. This is unlikely, however, because the upper vibrational level will be essentially isoenergetic with the second MLCT triplet. Internal conversion to the second MLCT state is expected to compete with radiative decay. An alternative assignment has the hot emission arising from radiative decay of the second MLCT triplet. This upper state possesses a lifetime some 35-fold shorter than the lower-energy state. Because this state is believed to retain more singlet character, it is not unreasonable to suppose that it might emit. As expected for emission from the second MLCT triplet, there is reasonable agreement between the energy gaps obtained from analysis of the kinetic data (E_A = 640 cm^{-1}) and the steady-state spectra (ΔE = 710 cm^{-1}).

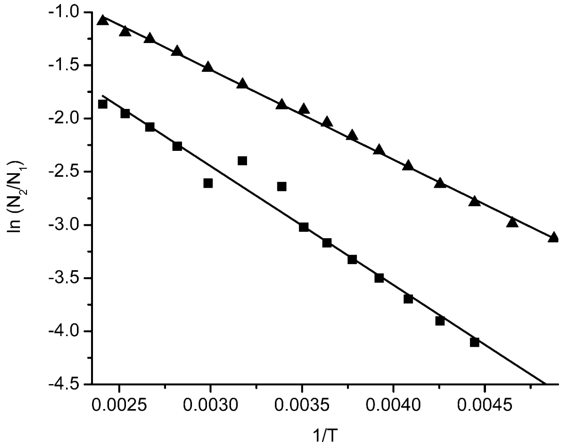

Figure 6. Effect of temperature on the ratio of upper and lower emission yields measured for Os-terpy (■) and Os-acet (▲) in butyronitrile. The solid line drawn through the data points is the best fit to the Boltzmann equation.

$$I(\nu) = \sum_{m=0}^{5}\sum_{l=0}^{15}\sum_{r=-5}^{0}\left\{\left(\frac{E_{00} - m\hbar\omega_{\mathrm{M}} - l\hbar\omega_{\mathrm{L}}}{E_{00}}\right)^{3}\left(\frac{S_{\mathrm{M}}^{m}}{m!}\right)YL(l)\exp(-Q)\right\}$$

$$Q = \left[-4\ln(2)\left(\frac{\nu - E_{00} + m\hbar\omega_{\mathrm{M}} + l\hbar\omega_{\mathrm{L}} + r\hbar\omega_{\mathrm{H}}}{\Delta\nu}\right)^{2}\right]$$

$$X = \frac{\hbar\omega_{\mathrm{L}}}{k_{\mathrm{B}}T}$$

$$Y = \exp\left(\frac{r\hbar\omega_{\mathrm{H}}}{k_{\mathrm{B}}T}\right)$$

$$L(l) = S_{\mathrm{L}}^{l}\sum_{p=0}^{\infty}\left(\frac{X^{p}p!}{(p+l)!}\right)\left[\sum_{q=0}^{p}\frac{(p+l)!(-S_{\mathrm{L}})^{q}}{(p-q)!(q+l)!p!}\right]^{2} \qquad (3)$$

Assuming the highest-energy Gaussian component arises from hot emission, a Boltzmann distribution for normal and hot emission gives an activation energy of 780 cm^{-1} (Figure 6).[32] This derived energy gap is close to the spectroscopic energy gap extracted from the curve-fitting routine and, within experimental limits, is fully consistent with the hot emission arising from the second MLCT triplet state. Equation 2 was modified so as to allow for hot emission from the second MLCT triplet, giving eq 3, and used to analyze the luminescence spectrum over the relevant temperature range (see the Supporting Information). It was found that the energy gap ($h\omega_H$) between the 0,0 bands for “hot” and “normal” emission has an average

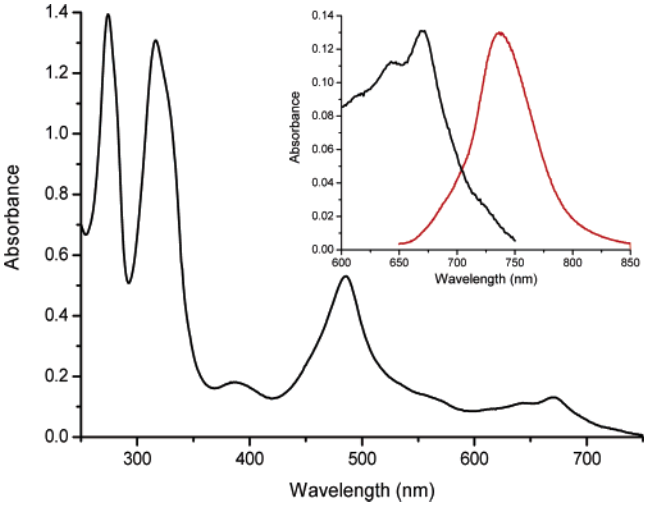

Figure 7. Absorption spectrum recorded for Os-acet in butyronitrile solution. The inset shows the overlap between absorption and emission spectra as recorded at room temperature.

value of 750 cm^{-1} over the full temperature range, including both solid and liquid phases.

Photophysical Properties of Os-acet. The absorption spectrum recorded for the substituted complex, Os-acet, remains similar to that of the parent, but the spin-forbidden MLCT transition stretches further into the near-IR region (Figure 7). There is an obvious shoulder at long wavelength ($\lambda_{max} = 720$ nm) that remains unaffected by extensive column chromatography or TLC. Also, the absorption spectrum indicates an additional transition centered around 390 nm that can be attributed to the ethynylated terpy ligand.[33] Luminescence is observed with a maximum at 737 nm (Figure 7), for which $\Phi_{LUM} = 0.0046$ and $\tau_{LUM} = 195$ ns in deoxygenated acetonitrile at room temperature. The Stokes shift corresponds to a reorganization energy (λ_T) of ca. 160 cm^{-1}. The corrected excitation spectrum agrees well with the absorption spectrum recorded over the entire visible range, and the emission decay profile is monoexponential at all monitoring wavelengths. As noted for the parent complex, the emission yield and lifetime increase with decreasing temperature. The rate constant for decay of the lowest-energy triplet state follows eq 1 with the parameters collected in Table 1.

The activationless rate constant k_0 found at low temperature is similar for both compounds, despite the fact that the triplet energy of Os-acet is considerably lower than that of the parent (Table 1). Likewise, both the barrier to reaching the upper MLCT triplet (E_A) and the rate constant for decay of this state (k_1) remain similar to those of the parent. There is a more obvious effect on the height of the barrier (E_B) for reaching the MC state and on the rate constant (k_P) for the population of this state (Table 1). Formation of the MC state corresponds to charge transfer from the terpy π-radical anion to a t_{2g} orbital localized on the Os^{3+} cation.[34] As such, the barrier can be described in terms of eq 4, where λ_{TD} is the reorganization energy and E_{TT} is the energy gap between the appropriate MLCT triplet and the MC state.[35] While it is clear that the substituent must decrease either the energy of the MC state or its reorganization energy, the present data do not allow partitioning of E_B into the individual terms.

$$E_B = \frac{(E_{TT} - \lambda_{TD})^2}{4\lambda_{TD}} \tag{4}$$

Confirmation that a high-energy MC state is involved was obtained by studying the temperature dependence of the luminescence properties in a transparent KBr disk. Over the range 300−450 K, the kinetic data could be fit to a simplified form of eq 1 having only two activated processes (Table 1). As observed for the parent complex, there is a substantial increase in both k_P and E_B under these conditions. The increase in E_B is due to an increase in the energy of the MC triplet state in KBr relative to the solution.[17a] However, 10-fold increase in k_P upon moving to the solid state is less easily explained. The most reasonable assumption is that the coupling element for intramolecular charge transfer increases in the solid state.[36]

The emission spectrum recorded for Os-acet in fluid solution is red-shifted with respect to that of the parent complex and shows a prominent shoulder on the high-energy side. The spectrum was unaffected by repeated purification of the sample and solvent. The relative emission yields for this hot emission and the normal emission followed the Boltzmann equation over a wide temperature range (Figure 6),[32] showing that the two states are in thermal equilibrium. The activation energy derived from the fit was 585 cm^{-1}, which is notably less than that found for the parent. This value remains in excellent agreement with both E_A ($=$590 cm^{-1}) and the spectroscopic energy gap ($\Delta E =$ 580 cm^{-1}) and is entirely consistent with hot emission arising from the second MLCT triplet state.

The room-temperature luminescence spectrum could be described in terms of eq 3, with the parameters collected in Table 2. Again, it is necessary to include both medium- and low-frequency vibrational modes, together with the hot emission. The derived parameters are comparable to those found for the parent complex, with $h\omega_M$ and $h\omega_L$ values of 1350 and 555 cm^{-1}, respectively. There is, however, a lowering of the triplet energy and a small reduction in the derived reorganization energy (Table 1). The variation in $h\omega_M$ and $h\omega_L$ with temperature is less than that found for the parent (see the Supporting Information).

Comparison of the Photophysical Properties in Fluid Solution. The most obvious effect of the ethynylene groups on the photophysical properties of these metal complexes concerns the lowering of the triplet energy (Table 1). This is a modest effect, corresponding to a decrease in E_T of ca. 550 cm^{-1}, compared to that found for Ru-terpy, where the decrease is 1400 cm^{-1}.[8a,16a] The decrease in triplet energy can be traced to a raising of the reduction potential for the ethynylated terpyridine ligand to a less negative value.[37] There is also a slight decrease in the reorganization energy accompanying decay of the lowest-energy triplet state (Table 1). Again, this effect mirrors that found earlier with Ru-terpy[16a] and can be attributed to the general effect of increased electron delocalization at the triplet level.[38] This latter situation arises because the promoted electron exists in an extended LUMO that encompasses part or all of the substituent.

The ethynylene group decreases the radiative rate constant, k_{RAD}, for both Os^{II} and Ru^{II} terpyridine complexes (Table 1). For Os^{II}, there is a 2-fold decrease in k_{RAD}. This effect cannot be explained simply in terms of the change in emission energy, and a quantitative assessment requires that the transition dipole moment undergoes a modest decrease upon substitution.[39] This is contrary to the situation found[16a] with Ru-terpy, where the transition moment increases upon ethynylation. In the event that electron delocalization is more significant for Os-acet than for Os-terpy, the separation between the metal center and the promoted electron will increase.[40] This should lead to an increase in the transition dipole moment, which happens with Ru-terpy.

Also, it is known that this term tends to increase with decreasing transition energy.[41] There is a small increase in the oscillator strength for Os-acet relative to the parent complex, which should also increase the cross-section for radiative decay.[42] However, it is likely that the extent of charge transfer changes upon ethynylation, while there is an accompanying increase in the singlet−triplet energy gap. These effects will tend to decrease k_{RAD}.[42] The difference in k_{RAD} values might also be associated with a modification of the spin−orbit coupling matrix element.[43]

It is notable that the rate constants for activationless decay of the triplet state, k_0, are closely comparable for Os-terpy and Os-acet despite the change in triplet energy. As found for Ru-terpy,[8a,16a] this behavior indicates that increased electron delocalization causes a small reduction in the electron-vibrational coupling constant. This effect is more significant for Ru-terpy, probably because the spin−orbit coupling properties are less than those associated with the Os^{II} cation. It is notable that k_1/k_0 remains similar for the two Os^{II} complexes, but ethynylation causes a marked increase in this ratio for the corresponding Ru^{II} complexes. This effect suggests that, whereas the upper MLCT state identified for Ru-terpy possesses increased singlet state character, there is little change for the corresponding Os-terpy system. Again, this relates to the increased spin−orbit coupling properties of the latter cation.[43]

For both Ru-terpy and Os-terpy, the substituent causes a modest decrease in both E_B and k_P. The process being examined here, which leads to the population of the MC state, can be considered in terms of an electron-transfer reaction for which k_2 refers to the activationless rate constant. In the event that the electronic coupling matrix element for intramolecular electron transfer remains independent of the substituent and medium, the change in k_2 indicates that ethynylation increases the reorganization energy (λ_{TD}).[44] There is a more substantial increase in λ_{TD} on moving from KBr to butyronitrile, which can be explained in terms of solvational effects.[45] Some support for a fixed coupling element is derived from the observation that there is a good semilogarithmic correlation between k_P and E_B (the so-called Barclay−Butler effect).[46] According to eq 4, the variation in E_B can also be explaned in terms of changes in λ_{TD}. This finding does not mean that there are no accompanying changes in the energy gap between MLCT and MC states, but it does suggest that the most important effects relate to induced changes in the reorganization energy. It should be noted that earlier work with $[Ru(bipy)_3]^{2+}$ has shown that the size of E_B depends on the nature of the solvent.[25,47]

Both Os-terpy and Os-acet require the inclusion of a low-frequency vibrational mode to properly reconstitute the luminescence spectra. As the precision of the instrument and the use of signal averaging and data analysis improves, it seems likely that this finding will become the norm for transition-metal complexes. The low-frequency mode is probably related to the Os−N bonds, although it is recognized that solvent modes become important in frozen glasses.[29] Surprisingly, both the medium- and low-frequency modes identified for Os-terpy show a marked temperature effect that is less apparent for Os-acet. The frequencies of both modes decrease with decreasing temperature in fluid solution (see the Supporting Information).[48] This effect is not observed in a KBr disk at higher temperatures. As such, the effect might be related to temperature-induced changes in solvent polarity[31] or refractive index.[49] Previous work with certain Re^{I} complexes has shown that $h\omega_M$ is affected by changes in the nature of the solvent,[50] but this was attributed to specific interactions with the solute. It should also be noted that the frequency of polar bonds can shift with varying solvent polarity even if there is no change in the electronic structure.[51]

For related complexes, it has been shown that the magnitude of both E_{00} and S_M depend on solvent polarity because of changes in the overlap of wave functions associated with excited and ground states.[52] In our work, it seems that temperature affects S_M and S_L but has little effect on E_{00}. The general effect is that S_M and S_L decrease with increasing temperature and that Os-terpy is more affected than Os-acet. The observed changes in the Huang−Rhys factors are due to systematic perturbations of the vibrational frequencies.[53] Other studies have also reported that changes in solvent polarity can affect certain vibrational frequencies for charge-transfer states.[54] In our case, the most important geometrical changes are associated with the C═C and C═N bonds and the Os−N bond. These are affected by changes in temperature to comparable degrees. The effect of increased electron delocalization, as induced by the ethynylene substituent, is to minimize these structural changes. Thus, the solvent effect might be expected to be less pronounced for Os-acet than for the parent. It should be mentioned that increasing temperature causes an increase in S_L for some conducting polymers because of thermal modification of the effective conjugation length.[55] This does not seem to be an option in our systems.

Hot emission is seen from both Os-terpy and Os-acet in fluid solution at ambient temperature; such emission has been reported previously for certain Os^{II} poly(pyridine) complexes but not in detail.[17a] For both compounds, the hot emission is associated with radiative decay of an upper MLCT triplet state that lies in thermal equilibrium with the lowest-energy triplet.[15−17] The fact that the two emitting states are in thermal equilibrium is shown by the data collected in Figure 6. The crude quantum yields for hot emission at room temperature are 0.0009 and 0.0006, respectively, for Os-terpy and Os-acet, as estimated by partitioning the total emission yield into “normal” and “hot” bands. When the Boltzmann distributions and the derived lifetimes for the upper state ($\tau = 1/k_2$) are taken into account, it appears that the radiative rate constant for Os-terpy is twice that of Os-acet. This effect mirrors that found for the lowest-energy triplets and confirms that the two MLCT triplets possess similar characteristics. Decay of the second MLCT triplet is dominated by nonradiative processes, however, for which the rate constants are roughly in line with the energy-gap law.[1]

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Supporting Information Available: Tables giving the various parameters extracted from spectral curve fitting over the full temperature range, figures showing reconstitution of the emission spectrum recorded for Os-acet in terms of the various equations, and a Barclay−Butler plot for the population of the MC state. This material is available free of charge via the Internet at http://pubs.acs.org.

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