

Excited-State Electronic Structure in Polypyridyl Complexes Containing Unsymmetrical Ligands

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Step-scan Fourier transform infrared absorption difference time-resolved (S^2 FTIR ΔA TRS) and time-resolved resonance Raman (TR^3) spectroscopies have been applied to a series of questions related to excited-state structure in the metal-to-ligand charge transfer (MLCT) excited states of $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^{2+}$, $[\text{Ru}(\text{bpy})_2(4-\text{CO}_2\text{Et}-4'-\text{CH}_3\text{bpy})]^{2+}$, $[\text{Ru}(\text{bpy})(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_2]^{2+}$, $[\text{Ru}(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_3]^{2+}$, $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CONEt}_2)_2-\text{bpy})]^{2+}$, $[\text{Ru}(\text{bpy})_2(4-\text{CONEt}_2-4'-\text{CH}_3\text{bpy})]^{2+}$, and $[\text{Ru}(4-\text{CONEt}_2-4'-\text{CH}_3\text{bpy})_3]^{2+}$ (bpy is 2,2'-bipyridine). These complexes contain bpy ligands which are either symmetrically or unsymmetrically derivatized with electron-withdrawing ester or amide substituents. Analysis of the vibrational data, largely based on the magnitudes of the $\bar{\nu}(\text{CO})$ shifts of the amide and ester substituents ($\Delta\bar{\nu}(\text{CO})$), reveals that the ester- or amide-derivatized ligands are the ultimate acceptors and that the excited electron is localized on one acceptor ligand on the nanosecond time scale. In the unsymmetrically substituted acceptor ligands, the excited electron is largely polarized toward the ester- or amide-derivatized pyridine rings. In the MLCT excited states of $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CONEt}_2)_2\text{bpy})]^{2+}$, $\Delta\bar{\nu}(\text{CO})$ is only 60–70% of that observed upon complete ligand reduction due to a strong polarization interaction in the excited state between the $d\pi^5$ Ru^{III} core and the excited electron.

Introduction

In photochemical and photophysical studies of polypyridyl complexes, mixed chelates and unsymmetrical polypyridyl ligands are frequently used to fine-tune excited-state properties and build molecular assemblies.^{1–33} As the symmetry of these

complexes is lowered, a number of important questions arise concerning electronic structure in the lowest-lying metal-to-ligand charge transfer (MLCT) excited states: (1) In multiple chelates, which ligand is the ultimate acceptor? (2) In complexes with two or more identical acceptor ligands, is the excited electron localized on one ligand or is it delocalized over both?

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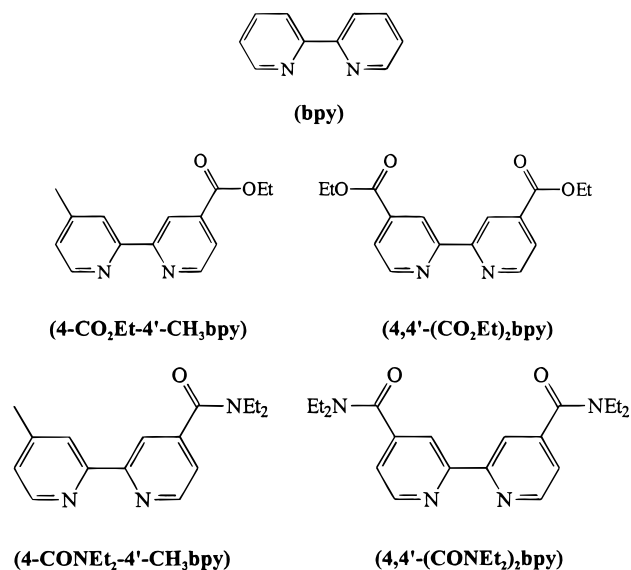
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- Damrauer, N. H.; Boussie, T. R.; Devenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8253–8268.
- Rutherford, T. J.; Keene, F. R. *Inorg. Chem.* **1997**, *36*, 2872–2878.
- Hage, R.; Lempers, H. E. B.; Haasnoot, J. G.; Reedijk, J.; Weldon, F. M.; Vos, J. G. *Inorg. Chem.* **1997**, *36*, 3139–3145.
- Gunde, K. E.; Credi, A.; Jandrasics, E.; von Zelewsky, A.; Richardson, F. S. *Inorg. Chem.* **1997**, *36*, 426–434.
- Jahng, Y.; Thummel, R. P.; Bott, S. G. *Inorg. Chem.* **1997**, *36*, 3133–3138.
- Dupray, L. M.; Meyer, T. J. *Inorg. Chem.* **1996**, *35*, 6299–6307.
- Kohle, O.; Ruile, S.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 4779–4787.
- Berg-Brennan, C.; Subramanian, P.; Absi, M.; Stern, C.; Hupp, J. T. *Inorg. Chem.* **1996**, *35*, 3719–3722.
- Dupau, P.; Renouard, T.; Le Bozec, H. *Tetrahedron Lett.* **1996**, *37*, 7503–7506.
- Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Treadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145–6157.
- Bardwell, D. A.; Barigelletti, F.; Cleary, R. L.; Flamigni, L.; Guardigli, M.; Jeffrey, J. C.; Ward, M. D. *Inorg. Chem.* **1995**, *34*, 2438.
- Anderson, P. A.; Strouse, G. F.; Treadway, J. A.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 3863–3864.
- Rutherford, T. J.; Reitsma, D. A.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1994**, 3659.
- Treffert-Ziemelis, S. M.; Golus, J.; Strommen, D. P.; Kincaid, J. R. *Inorg. Chem.* **1993**, *32*, 3890–3894.
- Danzer, G. D.; Golus, J. A.; Kincaid, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 8643–8648.
- Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1993**, 1321.

- Roffia, S.; Marcaccio, M.; Paradisi, C.; Paolucci, F.; Balzani, V.; Denti, G.; Serroni, S.; Campagna, S. *Inorg. Chem.* **1993**, *32*, 3003–3009.
- Strouse, G. F.; Anderson, P. A.; Schoonover, J. R.; Meyer, T. J.; Keene, F. R. *Inorg. Chem.* **1992**, *31*, 3004–3006.
- Rillema, D. P.; Blanton, C. B.; Shaver, R. J.; Jackman, D. C.; Boldaji, M.; Bundy, S.; Worl, L. A.; Meyer, T. J. *Inorg. Chem.* **1992**, *31*, 1600–1606.
- Chen, P.; Duesing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 5850–5858.
- Baiano, J. A.; Murphy, W. R. *Inorg. Chem.* **1991**, *30*, 4594–4598.
- Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Ellis Horwood: New York, 1991.
- Beley, M.; Collin, J. P.; Sauvage, J. P.; Sugihara, H.; Heisel, F.; Miehle, A. *J. Chem. Soc., Dalton Trans.* **1991**, 3157–3159.
- Yabe, T.; Orman, L. K.; Anderson, D. R.; You, S.-C.; Xu, X.; Hopkins, J. B. *J. Phys. Chem.* **1990**, *94*, 7128.
- Tapolsky, G.; Duesing, R.; Meyer, T. J. *J. Phys. Chem.* **1989**, *93*, 3885.
- Collin, J. P.; Guillerez, S.; Sauvage, J. P. *J. Chem. Soc. Chem. Commun.* **1989**, 776–778.
- Sahai, R.; Rillena, D. P.; Shaver, R.; Van Wallendael, S.; Jackman, D. C.; Boldaji, M. *Inorg. Chem.* **1989**, *28*, 1022–1028.
- Boyde, S.; Strouse, G. F.; Jones, W. E.; Meyer, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 7448–7494.
- Barqawi, K. R.; Llobet, A.; Meyer, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7751–7759.
- Brewer, K. J.; Murphy, W. R. J.; Petersen, J. D. *Inorg. Chem.* **1987**, *26*, 3376.
- Barigelletti, F.; Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *J. Phys. Chem.* **1986**, *90*, 5190–5193.
- McClanahan, S. F.; Dallinger, R. F.; Holler, F. J.; Kincaid, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 4853.
- Maerker, G.; Case, F. H. *J. Am. Chem. Soc.* **1958**, *80*, 2745–2748.

Chart 1



(3) What is the electronic distribution and polarization of the excited electron in unsymmetrically substituted acceptor ligands?
 (4) How do metal–ligand polarization and orbital overlap differ for different ligands?

In the symmetrically and unsymmetrically substituted ligands (4,4'-(CO₂Et)₂bpy), (4-CO₂Et-4'-CH₃bpy), (4,4'-(CONEt₂)₂bpy), and (4-CONEt₂-4'-CH₃bpy) shown in Chart 1, the electron-withdrawing ester, and amide substituents lower the energy of the lowest ligand π^* orbital relative to 2,2'-bipyridine (bpy).^{34,35} These ligands are widely used because ester and amide functional groups can be used for forming chemical links in molecular assemblies.^{6,7,13,22,35} The ester and amide C=O groups also provide useful spectroscopic “tags” for investigating excited-state electronic structure by step-scan Fourier transform infrared absorption difference time-resolved spectroscopy (S²FTIR ΔA TRS). Time-resolved resonance Raman (TR³) spectroscopy provides additional information about mid-energy, polypyridyl ring-stretching vibrations. We report here the application of both techniques to the elucidation of excited-state electronic and molecular structure in the mixed-ligand complexes [Ru(bpy)₂(4,4'-(CO₂Et)₂bpy)]²⁺, [Ru(bpy)₂(4-CO₂Et-4'-CH₃bpy)]²⁺, [Ru(bpy)(4,4'-(CO₂Et)₂bpy)]²⁺, [Ru(bpy)₂(4,4'-(CONEt₂)₂bpy)]²⁺, and [Ru(bpy)₂(4-CONEt₂-4'-CH₃bpy)]²⁺. Part of this work has appeared in a preliminary communication.³⁶

Experimental Section

Materials. All materials were used without further purification unless otherwise indicated. Acetonitrile was obtained from Burdick and Jackson. Acetonitrile-*d*₃ was obtained from Cambridge Isotope Labs. *N,N'*-Dimethyl-4,4'-bipyridinediium dication (methyl viologen, MV²⁺) was obtained from Acros Organics as the chloride salt, metathesized to the PF₆⁻ salt, and purified by recrystallizing twice from water. 10-Methylphenothiazine was obtained from Acros Organics and purified by sublimation. [Ru(bpy)₂(4,4'-(CO₂Et)₂bpy)](PF₆)₂, [Ru(bpy)₂(4-CO₂Et-4'-CH₃bpy)](PF₆)₂, [Ru(bpy)(4,4'-(CO₂Et)₂bpy)](PF₆)₂, [Ru(4,4'-(CO₂Et)₂bpy)₃](PF₆)₂, [Ru(bpy)₂(4,4'-(CONEt₂)₂bpy)](PF₆)₂, [Ru(bpy)₂(4-CONEt₂-4'-CH₃bpy)](PF₆)₂, and [Ru(4-CONEt₂-4'-CH₃bpy)₃](PF₆)₂ were prepared according to literature procedures.^{37,38}

(34) Worl, L. A.; Duesing, R.; Chem, P.; Della Ciana, L.; Meyer, T. J. *J. Chem. Soc., Dalton Trans.* **1991**, 849–858.

(35) Tapolsky, G.; Duesing, R.; Meyer, T. J. *Inorg. Chem.* **1990**, *29*, 2285–2297.

(36) Chen, P.; Omberg, K. M.; Kavaliunas, D. A.; Treadway, J. A.; Palmer, R. A.; Meyer, T. J. *Inorg. Chem.* **1997**, *36*, 954–955.

Raman Measurements. Time-resolved resonance Raman (TR³) spectra were measured by using the third harmonic (354.7 nm) of a Quanta-Ray DCR-2A pulsed Nd:YAG laser to both create the excited state and as a source for Raman scattering. Laser power was between 3 and 5 mJ per pulse. Resonance Raman (rR) spectra were acquired by 457.9 nm excitation from a Spectra-Physics 165-05 Ar⁺ laser. The scattered radiation was collected in a 135° backscattering geometry into a SPEX 1877 Triplemate spectrometer equipped with an 1800 grooves/mm grating. The Raman signal was detected by a Princeton Instruments IRY-700G optical multichannel analyzer operating in the gated mode with a ST-110 OSMA detector controller. Timing was controlled by a Princeton Instruments FG-100 pulse generator. The final spectra were the result of 9 min of total integration time. Data collection and storage were controlled by using an IBM AT computer and a Princeton Instruments SMA software package. All spectra were acquired in acetonitrile. Samples were ~4 mM in concentration, and were degassed by sparging with argon for 15 min.

Infrared Measurements. S²FTIR ΔA TR spectra were measured at Duke University on a step-scan modified Bruker IFS88 FTIR spectrometer with a standard globar source and dry air purge.³⁹ The ester-containing complexes were dissolved in acetonitrile to give an IR absorbance of 0.25 to 0.50 for the ester $\bar{\nu}(\text{C}=\text{O})$ band. The amide-containing complexes were dissolved in acetonitrile-*d*₃ to give an IR absorbance of 0.25–0.50 for the amide $\bar{\nu}(\text{C}=\text{O})$ band. All solutions were deoxygenated by sparging with argon for ~15 min. Spectra were measured under an inert atmosphere in a CaF₂ cell with a 250 μm Teflon spacer.

Laser flash excitation was provided by the third harmonic of a Quanta Ray DCR1A Nd:YAG laser (354.7 nm, ~3 mJ/pulse, 10 ns pulse width) operated at 10 Hz. Laser excitation and data acquisition were synchronized with a Stanford Research model DG535 pulse generator. An AC/DC-coupled photovoltaic Kolmar Technologies mercury cadmium telluride (PV MCT) detector with an effective rise time of 20 ns and a 50 MHz preamplifier was used to sample the transmitted IR probe beam. To eliminate extraneous energies and minimize data collection time, a germanium low-pass filter and the CaF₂ cell windows were used to limit the accessible spectral range to 2250–1150 cm⁻¹.

The detector's AC signal was further amplified by a Stanford Research model SR445 preamplifier (x25) before being directed to a 100/200 MHz PAD82a transient digitizer board in a 100 MHz Pentium computer. The DC signal was directed to the digitizer and used for phase correction of the AC signal. Bruker Instruments' Opus 2.2 and 3.0 software was used to process the recorded data.

The interferogram response before and after laser excitation was digitized in 10 ns time slices, with 75–150 laser shots averaged at each mirror position. S²FTIR ΔA TR spectra were calculated from the single beam ΔI transforms by the relationship, $\Delta A = -\log[1 + \Delta I(\bar{\nu}, t)/I(\bar{\nu})]$, where $I(\bar{\nu})$ is the static spectrum without excitation and $\Delta I(\bar{\nu}, t)$ is the change in intensity at time t after a laser flash. S²FTIR ΔA TR spectra shown were obtained from an average of 5–10 time slices, acquired from 0 to 100 ns after excitation. It is clear in all cases that the species observed in the first time slice is the same as the species observed in the averaged spectra. Ground-state spectra shown are an average of 32 (rapid) scans. Spectra were acquired with 6 cm⁻¹ resolution, and S²FTIR ΔA TRS data collection times were on average 30 min.

Results

Raman Measurements. TR³ band energies from 1000 to 1800 cm⁻¹ (354.7 nm excitation and scattering) and relative intensities for the MLCT excited states of the ester-substituted complexes, [Ru(4,4'-(CO₂Et)₂bpy)₃]²⁺, [Ru(bpy)(4,4'-(CO₂Et)₂bpy)]²⁺, [Ru(bpy)₂(4,4'-(CO₂Et)₂bpy)]²⁺, and [Ru(bpy)₂(4-CO₂Et-4'-CH₃bpy)]²⁺ in acetonitrile at 298 K are listed in

(37) Sasse, A. A. *Aust. J. Chem.* **1986**, *39*, 1053.

(38) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334–3341.

(39) Chen, P. Y.; Palmer, R. A. *Appl. Spectrosc.* **1997**, *51*, 580.

Table 1. TR³ and rR Band Energies (in cm⁻¹; 354.7 nm Excitation and Scattering for TR³; 457.9 nm Excitation for rR) and Relative Intensities^a from 1000 to 1800 cm⁻¹ in Acetonitrile at 298 K^b

[Ru(4,4'-(CO ₂ Et) ₂ bpy) ₃] ^{2+*}	[Ru(bpy)(4,4'-(CO ₂ Et) ₂ bpy) ₂] ^{2+*}	[Ru(bpy) ₂ (4,4'-(CO ₂ Et) ₂ bpy)] ^{2+*}	[Ru(bpy) ₂ (4-CO ₂ Et,4'-CH ₃ bpy)] ^{2+*}	[Ru(4,4'-(CO ₂ Et) ₂ bpy) ₃] ²⁺
1012 w	1013 m	1015 m	1015 m	1012 w
1211 w	1209 w	1210 w	1174 m	1175 w
1324 m	1322 m	1323 m	1323 m	1320 m
1428 m	1425 m	1425 m	1423 m	1432 m
1444 s	1445 s	1445 s	1443 s	1476 s
1492 m	1492 m	1494 m	1492 m	1492 m
1556 m	1556 m	1556 m	1547 w	1554 s
	1564 m	1564 m	1561 w	
1608 w	1606 w	1605 w	1600 m	1608 w
1712 w	1711 w	1710 w	1710 w	1733 m

^a Relative intensities are indicated as follows: s = strong; m = medium; w = weak. A solvent band appears in these spectra at 1378 cm⁻¹. ^b As the PF₆⁻ salts.

Table 2. TR³ and rR Band Energies (in cm⁻¹; 354.7 nm Excitation and Scattering for TR³; 457.9 nm Excitation for rR) and Relative Intensities^a from 1000 to 1800 cm⁻¹ in Acetonitrile at 298 K^b

[Ru(bpy) ₂ (4,4'-(CONEt ₂) ₂ bpy)] ^{2+*}	[Ru(bpy) ₂ (4-CONEt ₂ -4'-CH ₃ bpy)] ^{2+*}	[Ru(4-CONEt ₂ -4'-CH ₃ bpy) ₃] ^{2+*}	[Ru(4-CONEt ₂ -4'-CH ₃ bpy) ₃] ²⁺
1013 m	1013 w	1013 w	1015 w
1038 w	1038 w	1035 w	1028 m
1127 w	1129 w	1127 w	
1178 w	1194 m	1192 m	1174 m
1210 m	1207 m	1209 m	1261 m
1284 m	1282 m	1283 m	1274 m
1323 m	1320 m	1326 m	1320 m
1427 s	1425 s	1423 s	
1447 s	1440 s	1440 s	
1473 s	1455 s	1454 s	
1494 s	1490 s	1488 s	1489 s
1549 m	1548 m	1548 m	1548 m
1595 m	1595 m	1593 m	1562 m
1606 w	1605 m	1610 m	1607 m

^a Relative intensities are indicated as follows: s = strong; m = medium; w = weak. A solvent band appears in these spectra at 1378 cm⁻¹. ^b As the PF₆⁻ salts.

Table 1, along with resonance Raman (rR) band energies from 1000 to 1800 cm⁻¹ (457.9 nm excitation) and relative intensities for [Ru(4,4'-(CO₂Et)₂bpy)₃]²⁺. A solvent band appears in these spectra at 1378 cm⁻¹ and is not listed in the table.

The TR³ spectra of [Ru(4,4'-(CO₂Et)₂bpy)₃]^{2+*}, [Ru(bpy)-(4,4'-(CO₂Et)₂bpy)₂]^{2+*} and [Ru(bpy)₂(4,4'-(CO₂Et)₂bpy)]^{2+*} are dominated by bands arising from (4,4'-(CO₂Et)₂bpy) as the acceptor ligand. The energies of these bands are similar to those observed for 2,2'-bpy^{40,41} but can be differentiated since they are slightly shifted due to the ester and methyl substituents. In the spectra of [Ru(bpy)(4,4'-(CO₂Et)₂bpy)₂]^{2+*} and [Ru(bpy)₂(4,4'-(CO₂Et)₂bpy)]^{2+*}, a 2,2'-bpy band appears at 1564 cm⁻¹.^{40,41} This is not surprising since the excitation wavelength (354.7 nm) is in near-resonance with both bpy-based dπ → π* bands at ~400 nm and π → π*(bpy) bands at ~320 nm. The spectrum of [Ru(bpy)₂(4-CO₂Et-4'-CH₃bpy)]^{2+*} is dominated by bands arising from (4-CO₂Et-4'-CH₃bpy), and similar features appear. Subtle differences between the band energies for (4,4'-(CO₂Et)₂bpy) and (4-CO₂Et-4'-CH₃bpy) as acceptor ligand are evident. The ester ν(C=O) stretch (~1710 cm⁻¹) is not strongly enhanced in any of the TR³ spectra. It is somewhat enhanced in the rR spectrum, and appears at 1733 cm⁻¹.

TR³ band energies from 1000 to 1800 cm⁻¹ (354.7 nm excitation and scattering) and relative intensities for the MLCT excited states of [Ru(bpy)₂(4,4'-(CONEt₂)₂bpy)]²⁺, [Ru(bpy)₂(4-CONEt₂-4'-CH₃bpy)]²⁺, and [Ru(4-CONEt₂-4'-CH₃bpy)₃]²⁺ in acetonitrile at 298 K are listed in Table 2, along with rR band energies from 1000 to 1800 cm⁻¹ (457.9 nm excitation) and relative intensities for [Ru(4-CONEt₂-4'-CH₃bpy)₃]²⁺. A solvent band appears in these spectra at 1378 cm⁻¹ and is not listed in the table. The TR³ spectra of [Ru(bpy)₂(4-CONEt₂-4'-CH₃bpy)]^{2+*} and [Ru(4-CONEt₂-4'-CH₃bpy)₃]^{2+*} are dominated by bands arising from (4-CONEt₂-4'-CH₃bpy) as acceptor, and the spectrum of [Ru(bpy)₂(4,4'-(CONEt₂)₂bpy)]^{2+*} is dominated by bands from (4,4'-(CONEt₂)₂bpy) as acceptor. Subtle differences between (4,4'-(CONEt₂)₂bpy) and (4-CONEt₂-4'-CH₃bpy) as acceptor ligand can be discerned. The amide ν(C=O) stretch (expected to appear around 1630 cm⁻¹) is not strongly enhanced in any of the spectra.

Infrared Measurements. Ground- and excited-state ν(C=O) band energies (in cm⁻¹, 354.7 nm excitation) for [Ru(bpy)₂(4,4'-(CO₂Et)₂bpy)]²⁺, [Ru(bpy)(4,4'-(CO₂Et)₂bpy)₂]²⁺, [Ru(bpy)₂(4-CO₂Et-4'-CH₃bpy)]²⁺, [Ru(bpy)₂(4,4'-(CONEt₂)₂bpy)]²⁺, and [Ru(bpy)₂(4-CONEt₂-4'-CH₃bpy)]²⁺ are listed in Table 3 along with ν(C=O) shifts upon excitation (Δν̄, in cm⁻¹). Ground-state and excited-state ΔA spectra of [Ru(bpy)₂(4,4'-(CO₂Et)₂bpy)]²⁺, [Ru(bpy)(4,4'-(CO₂Et)₂bpy)₂]²⁺, and [Ru(bpy)₂(4-CO₂Et-4'-CH₃bpy)]²⁺ from 1625 to 1800 cm⁻¹ are shown in Figure 1, and of [Ru(bpy)₂(4,4'-(CONEt₂)₂bpy)]²⁺ and [Ru(bpy)₂(4-CONEt₂-4'-CH₃bpy)]²⁺ from 1550 to 1700 cm⁻¹ are shown in Figure 2. The band at 1610 cm⁻¹ in the amide spectra arises from a bipyridine-based ring-stretching mode.⁴¹⁻⁴³

(40) Strommen, D. P.; Mallick, P. K.; Danzer, G. D.; Lumpkin, R. S.; Kincaid, J. R. *J. Phys. Chem.* **1990**, *94*, 1357.

(41) Mallick, P. K.; Danzer, G. D.; Strommen, D. P.; Kincaid, J. R. *J. Phys. Chem.* **1988**, *92*, 5628.

(42) Omberg, K. M.; Schoonover, J. R.; Treadway, J. A.; Leasure, R. M.; Dyer, R. B.; Meyer, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 7013-7018.

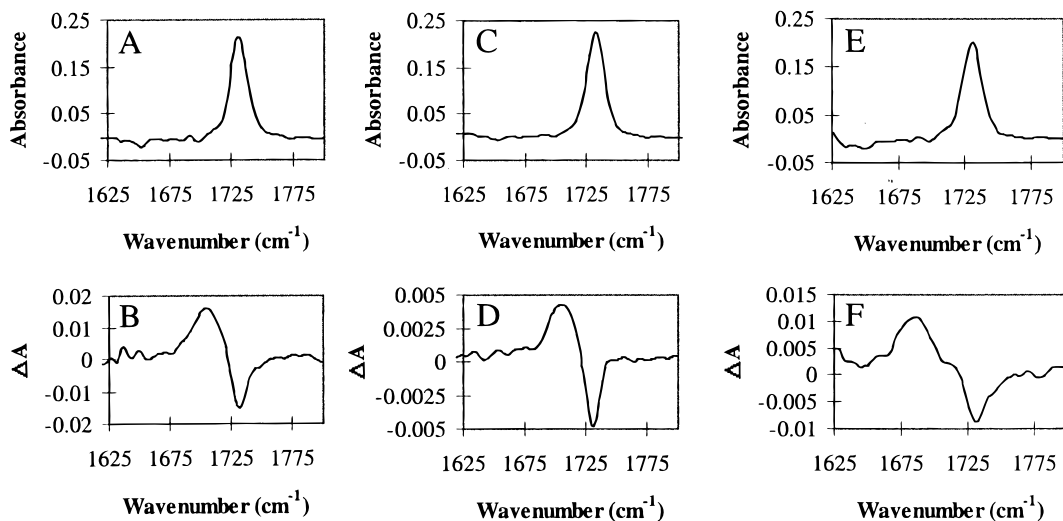


Figure 1. Ground-state (A, C, E) and S²FTIR ΔA TR (B, D, F) spectra of [Ru(bpy)₂(4,4'-(CO₂Et)₂bpy)](PF₆)₂ (A, B), [Ru(bpy)(4,4'-(CO₂Et)₂bpy)₂](PF₆)₂ (C, D), and [Ru(bpy)₂(4-CO₂Et-4'-CH₃bpy)](PF₆)₂ (E, F) from 1625 to 1800 cm⁻¹ in acetonitrile.

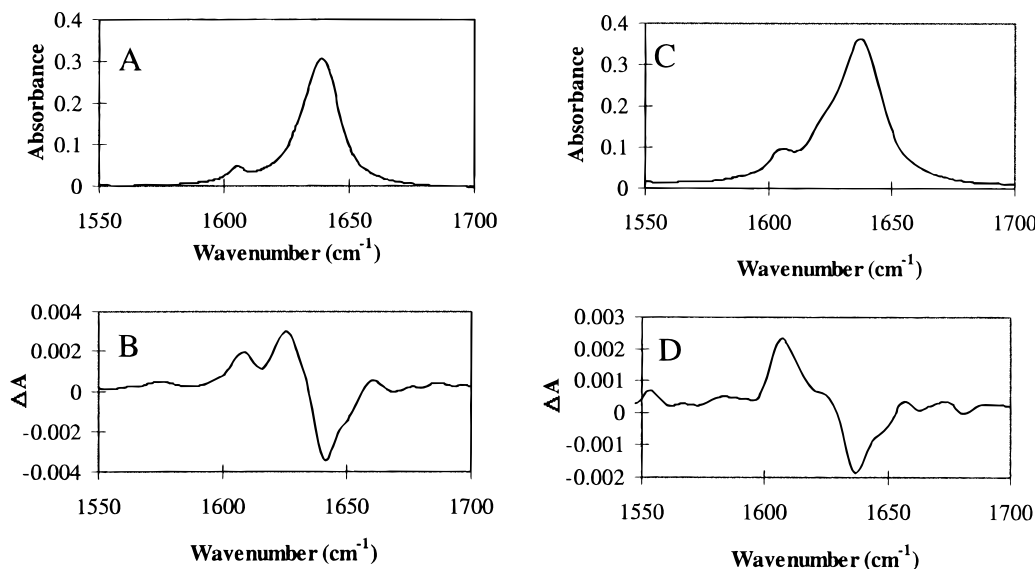


Figure 2. Ground-state (A, C) and S²FTIR ΔA TR (B, D) spectra of [Ru(bpy)₂(4,4'-(CONEt₂)₂bpy)](PF₆)₂ (A, B) and [Ru(bpy)₂(4-CONEt₂-4'-CH₃bpy)](PF₆)₂ (C, D) from 1550 to 1700 cm⁻¹ in acetonitrile.

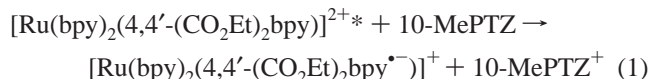
Table 3. Ground-State and S²FTIR ΔA TRS^a $\bar{\nu}(\text{C}=\text{O})$ Band Energies^a (in cm⁻¹) and Magnitude of the Shift Observed upon Excitation ($\Delta\bar{\nu}$) in cm⁻¹

complex ^b	ground-state energy	excited-state energy	$\Delta\bar{\nu}^c$
[Ru(bpy) ₂ (4,4'-(CO ₂ Et) ₂ bpy)] ²⁺ ^d	1731	1705	-26
[Ru(bpy)(4,4'-(CO ₂ Et) ₂ bpy) ₂] ²⁺ ^d	1731	1705	-26
[Ru(bpy) ₂ (4-CO ₂ Et-4'-CH ₃ bpy)] ²⁺ ^d	1731	1685	-46
[Ru(bpy) ₂ (4,4'-(CONEt ₂) ₂ bpy)] ²⁺ ^e	1638	1623	-15
[Ru(bpy) ₂ (4-CONEt ₂ -4'-CH ₃ bpy)] ²⁺ ^e	1637	1604	-33

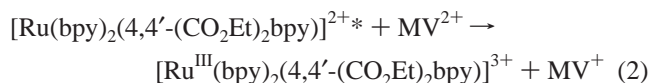
^a Average of 5–10 10-ns spectral slices acquired 0–100 ns after laser flash excitation at 354.7 nm. ^b As the PF₆⁻ salts. ^c $\Delta\bar{\nu}$ = excited-state energy – ground-state energy. ^d In acetonitrile at 298 K. ^e In acetonitrile-*d*₃ at 298 K.

Spectra of the fully reduced forms, [Ru^{II}(bpy)₂(4,4'-(CO₂Et)₂bpy⁻)]⁺, [Ru^{II}(bpy)(4,4'-(CO₂Et)₂bpy)(4,4'-(CO₂Et)₂bpy⁻)]⁺, [Ru^{II}(bpy)₂(4-CO₂Et-4'-CH₃bpy⁻)]⁺, and [Ru^{II}(bpy)₂(4,4'-(CONEt₂)₂bpy⁻)]⁺, and [Ru^{II}(bpy)₂(4-CONEt₂-4'-CH₃bpy⁻)]⁺

were obtained by reductive quenching of the excited states with added 10-methylphenothiazine (10-MePTZ) in acetonitrile at 298 K, as previously described (eq 1).³⁶



Spectra of [Ru^{III}(bpy)₂(4,4'-(CO₂Et)₂bpy)]³⁺, [Ru^{III}(bpy)₂(4-CO₂Et-4'-CH₃bpy)]³⁺, and [Ru^{III}(bpy)₂(4-CONEt₂-4'-CH₃bpy)]³⁺ were obtained by oxidative quenching of the excited state with added *N,N'*-dimethyl-4,4'-bipyridinium dication (methyl viologen, MV²⁺) in acetonitrile at 298 K, as previously described (eq 2).³⁶



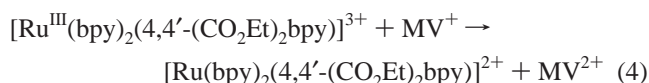
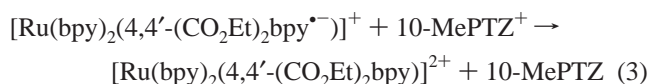
With a large excess of quencher, quenching occurs within the laser pulse. It is followed by back electron transfer, eq 3 or

Table 4. $\bar{\nu}(\text{C}=\text{O})$ Infrared Band Energies and Shifts Compared to the Ground State ($\Delta\bar{\nu}$) (in cm^{-1})^a

complex ^b	energy	$\Delta\bar{\nu}$ ^e
$[\text{Ru}^{\text{II}}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy}^{\ast-})]^+$ ^d	1688	-43
$[\text{Ru}^{\text{II}}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy}^{\ast-})]^+$ ^d	1695	-36
$[\text{Ru}^{\text{II}}(\text{bpy})_2(4-\text{CO}_2\text{Et}-4'-\text{CH}_3\text{bpy}^{\ast-})]^+$ ^d	1660	-71
$[\text{Ru}^{\text{III}}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^3+$ ^d	1734	<+3
$[\text{Ru}^{\text{III}}(\text{bpy})_2(4-\text{CO}_2\text{Et}-4'-\text{CH}_3\text{bpy})]^3+$ ^d	1741	<+10
$[\text{Ru}^{\text{II}}(\text{bpy})_2(4,4'-(\text{CONEt}_2)_2\text{bpy}^{\ast-})]^+$ ^e	1620	-18
$[\text{Ru}^{\text{II}}(\text{bpy})_2(4-\text{CH}_3,4'-\text{CONEt}_2\text{bpy}^{\ast-})]^+$ ^e	1596	-41

^a Average of 5–10 10-ns spectral slices acquired 0–100 ns after laser flash excitation at 354.7 nm in the presence of reductive or oxidative quenchers, see text. ^b As the PF_6^- salts. ^c $\Delta\bar{\nu}$ = band energy after quenching – initial band energy, in cm^{-1} . ^d In acetonitrile at 298 K. ^e In acetonitrile-*d*₃ at 298 K.

4, which occurs on the 10s of microseconds time scale, allowing observation of the reductively or oxidatively quenched complexes.



Infrared band energies and shifts upon oxidation or reduction are listed in Table 4. Additional ground-state and excited-state ΔA infrared spectra are available as Supporting Information.

Discussion

The vibrational data presented here address the four questions identified in the Introduction: (1) In multiple chelates, which ligand is the ultimate acceptor? (2) In complexes with two or more identical acceptor ligands, is the excited electron localized on one ligand or delocalized over two or more? (3) What is the extent of polarization of the excited electron in unsymmetrically substituted acceptor ligands? (4) How do metal–ligand polarization and orbital overlap differ for different ligands? There is also information about changes in molecular structure between the ground and excited states.

Identification of the Acceptor Ligand. The fingerprinting abilities of the TR³ technique are well established and have been frequently used to identify the acceptor ligand in mixed-chelates.^{14,15,32,44} In the ester-containing complexes, the TR³ spectra are dominated by bands arising from ring-stretching modes of the ester-substituted ligand, similar to those observed for $[\text{Ru}(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_2]^{2+}$. Absorption at the scattering wavelength (354.7 nm) is dominated by $\pi \rightarrow \pi^*$ transitions of the partly reduced acceptor ligand in the excited state. The TR³ data clearly establish that the ester-substituted ligand is the acceptor. Similarly, the TR³ spectra of the amide-containing complexes are dominated by bands arising from ring-stretching modes of the amide-substituted ligand, showing that it is the acceptor. These are expected results given the electron-withdrawing properties of the ester and amide substituents which lower the energies of the lowest π^* levels.^{34,35}

The acceptor ligand assignments are confirmed by the large negative shifts for $\bar{\nu}(\text{C}=\text{O})$ in the S²FTIR ΔA TR spectra (Table 3). In all cases, $\bar{\nu}(\text{C}=\text{O})$ is shifted to lower energy due to electron occupation and C=O mixing in the lowest π^* level, which decreases C=O bond order.

Localization versus Delocalization. In the MLCT excited states of multiple chelates containing equivalent ligands, there has been a long-standing debate over whether the excited electron is localized on a single ligand or delocalized over two or more.^{42,45,46} The ground-state and excited-state ΔA spectra of $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^{2+}$ and $[\text{Ru}(\text{bpy})(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_2]^{2+}$ in the $\bar{\nu}(\text{C}=\text{O})$ region address this issue directly, at least on the ~ 10 ns time scale. As shown in Figure 1, these spectra are identical, with a single $\bar{\nu}(\text{C}=\text{O})$ ground-state band appearing at 1731 cm^{-1} , and a single excited-state band appearing at 1705 cm^{-1} ($\Delta\bar{\nu} = -26 \text{ cm}^{-1}$). Since the excited electron must be localized on the ester-substituted ligand in $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^{2+}$, it must also be localized on one of the two ester-substituted ligands in $[\text{Ru}(\text{bpy})(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})_2]^{2+}$. If it were delocalized in the latter, the shift in $\bar{\nu}(\text{C}=\text{O})$ would be significantly less.

The situation is less clear for the singly reduced complexes, $[\text{Ru}^{\text{II}}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy}^{\ast-})]^+$ and $[\text{Ru}^{\text{II}}(\text{bpy})(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})(4,4'-(\text{CO}_2\text{Et})_2\text{bpy}^{\ast-})]^+$, where the $\bar{\nu}(\text{C}=\text{O})$ shifts are -43 and -36 cm^{-1} , respectively. This difference is probably within the uncertainty of the measurement. However, the smaller shift for $[\text{Ru}^{\text{II}}(\text{bpy})(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})(4,4'-(\text{CO}_2\text{Et})_2\text{bpy}^{\ast-})]^+$ may be real and arise from electronic coupling between the once-reduced and neutral (4,4'-(CO₂Et)₂bpy) ligands.

Polarization in Unsymmetrically Substituted Acceptor Ligands. A second, more subtle issue of localization versus delocalization in the same acceptor ligand is addressed by the excited-state ΔA spectra of $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^{2+}$ and $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CONEt}_2)_2\text{bpy})]^{2+}$ (Figure 1). In both cases, the appearance of a single $\bar{\nu}(\text{C}=\text{O})$ stretch in the excited-state spectra proves that the excited electron is delocalized over both pyridyl rings on the ~ 10 ns time scale. This is expected due to the symmetrical substitution of the (4,4'-(CO₂Et)₂bpy) and (4,4'-(CONEt₂)₂bpy) ligands.

For the acceptor ligands (4-CO₂Et-4'-CH₃bpy) and (4-CONEt₂-4'-CH₃bpy), there is considerable electronic asymmetry due to the electron-donating -CH₃ on one ring and electron-withdrawing -CO₂Et or -CONEt₂ on the other. The Hammett polar substituent constant, σ_I , for -CO₂Et is 0.30. For -CH₃, σ_I is -0.04.⁴⁷ The excited-state $\bar{\nu}(\text{C}=\text{O})$ shift for $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^{2+}$ is $\Delta\bar{\nu} = -26 \text{ cm}^{-1}$, while the shift for $[\text{Ru}(\text{bpy})_2(4-\text{CO}_2\text{Et}-4'-\text{CH}_3\text{bpy})]^{2+}$ is -46 cm^{-1} (Table 3). The near doubling of $\Delta\bar{\nu}$ for $[\text{Ru}(\text{bpy})_2(4-\text{CO}_2\text{Et}-4'-\text{CH}_3\text{bpy})]^{2+}$ is consistent with a high degree of polarization of the excited electron toward the ester-substituted pyridine, as expected. A related effect is observed for the amide-substituted bpy complexes. The shift in $\bar{\nu}(\text{C}=\text{O})$ for $[\text{Ru}(\text{bpy})_2(4-\text{CONEt}_2-4'-\text{CH}_3\text{bpy})]^{2+}$ is 33 cm^{-1} , compared to 15 cm^{-1} for $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CONEt}_2)_2\text{bpy})]^{2+}$, consistent with polarization of the excited electron toward the amide-substituted pyridine in (4-CONEt₂-4'-CH₃bpy). The Hammett polar substituent constant, σ_I , for -CONH₂ is 0.21.⁴⁷

Similar observations have been made by Kincaid and co-workers on Ru(II) complexes containing the unsymmetrical acceptor ligands 2-(2-pyridyl)pyrazine¹⁵ and 5-monomethyl-2,2'-bipyridine¹⁴ by resonance Raman and TR³. Their data were consistent with extensive polarization of the excited electron

(44) Schoonover, J. R.; Bignozzi, C. A.; Meyer, T. J. *Coord. Chem. Rev.* **1997**, *165*, 239–266.

(45) Riesen, H.; Wallace, L.; Krausz, E. *Inorg. Chem.* **1996**, *35*, 6908–6909.

(46) Turro, C.; Chung, Y. C.; Leventis, N.; Kuchenmeister, M. E.; Wagner, P. J.; Leroy, G. E. *Inorg. Chem.* **1996**, *35*, 5104–5106.

(47) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper Collins Publishers: New York, 1987.

toward the electron-deficient pyrazine fragment in 2-(2-pyridyl)pyrazine and toward the less electron-rich pyridine fragment in 5-monomethyl-2,2'-bipyridine.

Excited-State Electronic Distribution. Oxidation of $[\text{Ru}^{\text{II}}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^{2+}$ to $[\text{Ru}^{\text{III}}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^{3+}$ by excitation in the presence of oxidative quencher results in a shift of $<3 \text{ cm}^{-1}$. Oxidation of $[\text{Ru}^{\text{II}}(\text{bpy})_2(4-\text{CO}_2\text{Et}-4'-\text{CH}_3\text{bpy})]^{2+}$ to $[\text{Ru}^{\text{III}}(\text{bpy})_2(4-\text{CO}_2\text{Et}-4'-\text{CH}_3\text{bpy})]^{3+}$ by similar means results in a shift of $<10 \text{ cm}^{-1}$ (Table 4). The uncertainty in these shifts arises because they are within the bandwidth and difficult to quantify reliably. Both shifts are positive, consistent with a loss in $d\pi(\text{Ru})-\pi^*(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})$ or $\pi^*(4-\text{CO}_2\text{Et}-4'-\text{CH}_3\text{bpy})$ ground-state back-bonding upon oxidation to Ru^{III} , but the effect is small.

By contrast, reduction of $[\text{Ru}^{\text{II}}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^{2+}$ to $[\text{Ru}^{\text{I}}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy}^{\bullet-})]^{+}$ by excitation in the presence of reductive quencher results in a shift of -43 cm^{-1} . Reduction of $[\text{Ru}^{\text{II}}(\text{bpy})_2(4-\text{CO}_2\text{Et}-4'-\text{CH}_3\text{bpy})]^{2+}$ to $[\text{Ru}^{\text{I}}(\text{bpy})_2(4-\text{CO}_2\text{Et}-4'-\text{CH}_3\text{bpy}^{\bullet-})]^{+}$ by similar means results in a shift of -71 cm^{-1} (Table 4). These shifts are considerably larger than those in the excited states (Table 3).

The excited-state shift for $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CO}_2\text{Et})_2\text{bpy})]^{2+}$ (-26 cm^{-1}) is $\sim 60\%$ of the shift for fully reduced $[\text{Ru}^{\text{I}}(\text{bpy})_2-$

$(4,4'-(\text{CO}_2\text{Et})_2\text{bpy}^{\bullet-})]^{+}$ (-43 cm^{-1}). For $[\text{Ru}(\text{bpy})_2(4,4'-(\text{CO}-\text{NEt}_2)_2\text{bpy})]^{2+}$ (-15 cm^{-1}), it is $\sim 80\%$ of that for the fully reduced complex (-18 cm^{-1}). The smaller shifts in the absence of quencher are expected. Reductive quenching results in the electronic configuration $d\pi^6\pi^{*1}$ (ligand radical anions bound to $d\pi^6 \text{Ru}^{\text{I}}$). The excited-state configuration is $d\pi^5\pi^{*1}$, with a strong polarization interaction between the excited electron and the $d,^5 \text{Ru}^{\text{III}}$ core. The data suggest the interesting possibility that there may be a correlation between the excited-state $\bar{\nu}(\text{C}=\text{O})$ shifts and the extent of charge transfer, but this conclusion awaits an appropriate theoretical analysis.

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