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Intersystem-Crossing Dynamics in Heterodinuclear Polypyridyl-Bridged Complexes

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The excited-state properties of $[(L)_4M^{II}(dpp)Ru^{II}(bpy)_2](PF_6)_n$ (bpy = 2,2′-bipyridine; dpp = (2,3-bis(2-pyridyl)-pyrazine); $(L)_4M^{II} = (NH_3)_4Ru^{II}$ ($n = 4$) or $(CN)_4Fe^{II}$ ($n = 0$)) have been investigated by steady-state and time-resolved picosecond and nanosecond transient luminescence and absorption spectroscopic methods. The $[(NH_3)_4Ru^{II}(dpp)Ru^{II}(bpy)_2]^{4+}*$ complex is nonemissive in room-temperature H_2O solution. Picosecond laser flash photolysis of $[(NH_3)_4Ru^{II}(dpp)Ru^{II}(bpy)_2]^{4+}$ reveals the formation of a transient species that decays exponentially (τ = 290 (±80) ps) independent of excitation wavelength. The excited-state behavior of $[(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2]*$ display a complicated dependence on excitation wavelength. Following 591-nm pulsed laser excitation into the ${}^1[(d\pi)^5_{Fe}(\pi^*)^1_{dpp}] \leftarrow {}^1[(d\pi)^6_{Fe}]$ metal-to-ligand charge transfer (MLCT) band, a short-lived transient is formed with $\tau < 80$ ps. Laser excitation at 354.7 nm into the ${}^1[(d\pi)^5_{Ru}(\pi^*)^1_{bpy/dpp}] \leftarrow {}^1[(d\pi)^6_{Ru}]$ MLCT transition produces a transient species with $\tau > 200$ ns. One explanation for the wavelength-dependent photophysics of the $[(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2]$ is that the Fe^{II} metal center undergoes a low- to high-spin interconversion following ${}^1[(d\pi)^5_{Ru}(\pi^*)^1_{bpy/dpp}] \leftarrow {}^1[(d\pi)^6_{Ru}]$ excitation, a process not accessible via direct ${}^1[(d\pi)^5_{Fe}(\pi^*)^1_{dpp}] \leftarrow {}^1[(d\pi)^6_{Fe}]$ excitation.

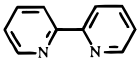
Introduction

The synthesis and ground- and excited-state properties of cyano- and polypyridyl-bridged homo- and heterobimetallic complexes have received considerable attention.[1] Recent studies have focused on issues such as (1) mechanisms for photoinitiated electron-transfer (E_LT) and energy-transfer (E_NT) processes,[2] (2) the strength of the electronic coupling between the metal centers mediated by the bridging ligand,[3] (3) vibrational trapping, (i.e., large amplitude changes in nuclear positions that occur upon E_LT),[4] and (4) the synthesis of designer systems for potential use as artificial photosynthetic devices.[1] A subset of these studies have focused on the spectroscopy and electrochemistry of multinuclear Fe^{II}-cyano/Ru^{II}-polypyridyl compounds,[5] linkage and distance dependence for E_NT processes in polypyridyl-bridged heterobimetallic Fe^{II}/Ru^{II} compounds,[6] and electron delocalization in polyene-bridged Fe^{II}/Ru^{II} compounds.[7]

Creutz and Sutin have demonstrated reductive quenching of $[Ru(bpy)_3]^{2+}*$ by $[Fe^{II}(CN)_6]^{4-}$ with a diffusion-controlled rate constant ($k_q = 3.5 \times 10^9$ M^{-1} s^{-1}) in H_2O, eq 1.[8]

$$[Fe^{II}(CN)_6]^{4-} + [Ru(bpy)_3]^{2+}* \xrightarrow{k_q} [Fe^{III}(CN)_6]^{3-} + [Ru(bpy)_3]^{+} \quad (1)$$

The photochemistry and photophysics of the monometallic $[Fe(CN)_4(bpy)]^{2-}$ and $[Ru(bpy)_3]^{2+}$ complexes have been studied extensively,[9,10] and the synthetic protocols to prepare heterobimetallic compounds are well developed.[11] Work in our laboratories has focused on the synthesis and characterization of the ground- and excited-state properties of heterobimetallic complexes of the form $[(NC)_4Fe^{II}(dpp)Ru^{II}(phen)_2]$, where the $[Fe^{II}(CN)_4]^{2-}$ fragment is an electron donor covalently bound to the $Ru^{II}(bpy)_2^{2+}$ with dpp as a bridging ligand (dpp = 2,3-(2-pyridyl)pyrazine). The luminescence properties of $[(NC)_4Fe^{II}(dpp)Ru^{II}(phen)_2]$ have been presented previously.[11a] Recent laser flash photolysis studies on the closely related $[(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2]$ complex, however, reveal profound excitation wavelength-dependent photophysics. Paradoxically, this behavior was not observed in $[(NH_3)_4Ru^{II}(dpp)Ru^{II}(bpy)_2]^{4+}*$, where the observed photophysics were found to be independent of excitation wavelength.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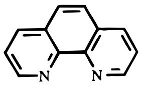
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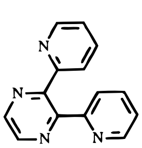
dpp

Experimental Section

Water was obtained by distillation of deionized water in alkaline permanganate in an all-glass apparatus. Spectrograde CH_3CN (Burdick and Jackson) was used without further purification for spectroscopic and electrochemical experiments.

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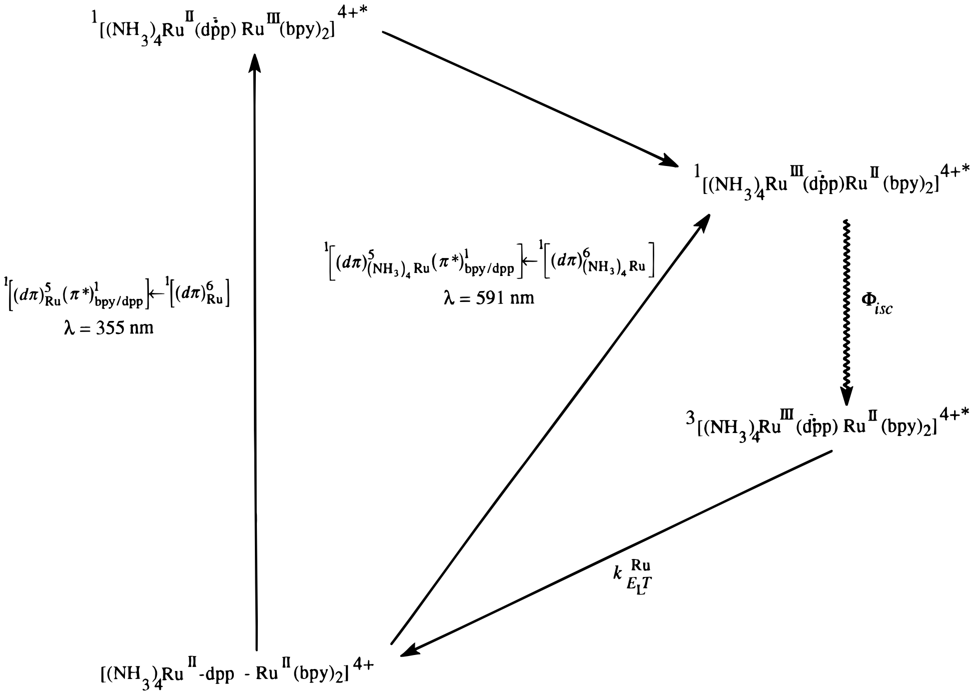
SCHEME 1



The synthesis of $[(CN)_4Fe(dpp)Ru(bpy)_2]$ and $[(NH_3)_4Ru(dpp)Ru(bpy)_2](PF_6)_4$ were performed using literature protocols.[11,12]

Absorption spectra and cyclic voltammograms were obtained using previously described instrumentation and protocols.[13] Details regarding the steady-state and time-resolved luminescence spectroscopic methods and the picosecond flash photolysis apparatus will be presented elsewhere.[12]

Results and Discussion

The UV–visible absorption spectra of $[(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2]$ and $[(NH_3)_4Ru^{II}(dpp)Ru^{II}(bpy)_2]^{4+}$ in room-temperature H_2O solution are dominated by high-energy intense ligand-centered $\pi^* \leftarrow \pi$ transitions (λ < 330 nm) and lower-energy, $^1[(d\pi)^5_M(\pi^*)^1_{dpp}] \leftarrow {}^1[(d\pi)^6_M]$, metal-to-ligand charge transfer (MLCT) bands. Two lower energy MLCT bands for $[(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2]$ were assigned to $^1[(d\pi)^5_{Ru}(\pi^*)^1_{bpy/dpp}] \leftarrow {}^1[(d\pi)^6_{Ru}]$ transitions ($\lambda^{abs}_{max} = 532$ nm ($\epsilon = 7100$ M^{-1} cm^{-1})) and $^1[(d\pi)^5_{Fe}(\pi^*)^1_{dpp}] \leftarrow {}^1[(d\pi)^6_{Fe}]$ ($\lambda^{abs}_{max} = 586$ nm ($\epsilon = 7400$ M^{-1} cm^{-1})), respectively. For $[(NH_3)_4Ru^{II}(dpp)Ru^{II}(bpy)_2]^{4+}$, $^1[(d\pi)^5_{Ru}(\pi^*)^1_{bpy/dpp}] \leftarrow {}^1[(d\pi)^6_{Ru}]$ transitions at $\lambda^{abs}_{max} = 433$ nm ($\epsilon = 6700$ M^{-1} cm^{-1}) and $^1[(d\pi)^5_{Ru(NH_3)_4}(\pi^*)^1_{dpp}] \leftarrow {}^1[(d\pi)^6_{Ru(NH_3)_4}]$ transitions at $\lambda^{abs}_{max} = 541$ nm ($\epsilon = 1.2 \times 10^4$ M^{-1} cm^{-1}) were similarly assigned.

The $M^{III/II}$ and ligand-based reduction potentials were determined by cyclic voltammetry. There is a significant redox asymmetry in $[(L)_4M^{II}(dpp)Ru^{II}(bpy)_2]^{n+}$, where the $(L)_4M^{II}$ ($(L)_4M^{II} = (NH_3)_4Ru$ ($n = 4$) or $(CN)_4Fe$ ($n = 0$)) metal centers are ≈0.4–0.5 V easier to oxidize than the $Ru^{II}(bpy)_2$ moiety. Therefore, the odd electron in the mixed-valent $[(L)_4M^{III}(dpp)Ru^{II}(bpy)_2]^{n+}$ and by inference the excited electron in $[(L)_4M^{III}(dpp^{\bullet-})Ru^{II}(bpy)_2]^{n+*}$ (Scheme 1), should be localized on the $Ru^{II}(bpy)_2$ portion of the heterobimetallic complex.

$[(NH_3)_4Ru^{II}(dpp)Ru^{II}(bpy)_2]^{4+*}$ in deoxygenated H_2O (λ_{excite} = 430 or 550 nm) was nonemissive in room-temperature fluid solution. A weak intrinsic emission in deoxygenated H_2O media at room temperature from $[(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2]^*$ (λ_{excite} = 430 nm) with λ^{em}_{max} (nm) = 718 nm, $\tau \leq 40$ ns ($k_{obsd} \geq 3 \times 10^7$ s^{-1}), and $\phi_{em} \leq 3 \times 10^{-4}$) was observed.[14]

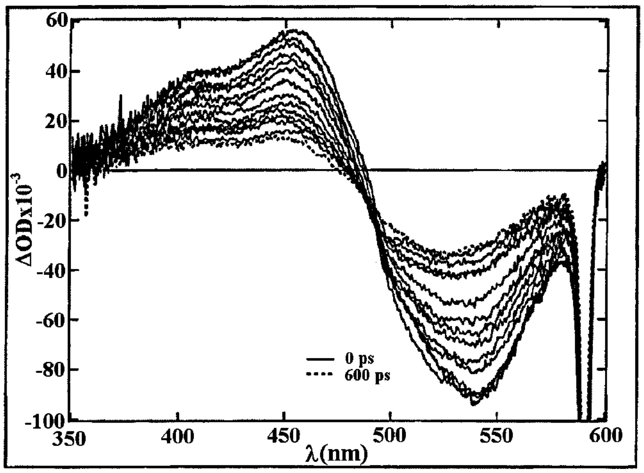


Figure 1. Picosecond transient absorption difference spectra of a ≈5 × 10^{-5} M solution of $[(NH_3)_4Ru(dpp)Ru(bpy)_2]^{4+}$ in H_2O with 591-nm pulsed laser excitation (2.5-ps pulse width). Each transient absorption difference spectrum is the result of ca. 1000 laser shots at 75 μJ/pulse. Each difference spectra were recorded in 43-ps intervals. The energy dependence of the signal intensity was linear in this energy regime.

Transient absorption difference spectra for $[(NH_3)_4Ru^{II}(dpp)Ru^{II}(bpy)_2]^{4+*}$ (≈10^{-5} M) following 2-ps, pulsed, 591-nm excitation are shown in Figure 1. The difference spectra are characteristic of an MLCT-based excited state with a strong positive signal at $\Delta\lambda^{abs}_{max} = 370$–440 nm due to $\pi^* \leftarrow \pi$ transitions in the polypyridyl radical anion and a strong bleach centered at $\Delta\lambda^{abs}_{max} = 540$ nm due to loss of the ground-state $^1[(d\pi)^5_{Ru(NH_3)_4}(\pi^*)^1_{dpp}] \leftarrow {}^1[(d\pi)^6_{Ru(NH_3)_4}]$ absorption band.[15] The transient absorption difference spectra evolve with time and return to preexcitation levels in 1–2 ns. The transient absorption data for excited-state decay were time-resolved and fit to a single, exponential decay function with $k_{obsd} = 3\ (\pm 1) \times 10^9$ s^{-1} ($\tau = 290\ (\pm 80)$ ps). Laser flash photolysis studies using 354.7-nm excitation gave similar transient absorption difference spectra and kinetic results ($k_{obsd} = 2.3\ (\pm 0.8) \times 10^9$ s^{-1} ($\tau = 230\ (\pm 70)$ ps)). The excited-state dynamics of $[(NH_3)_4Ru^{II}$-

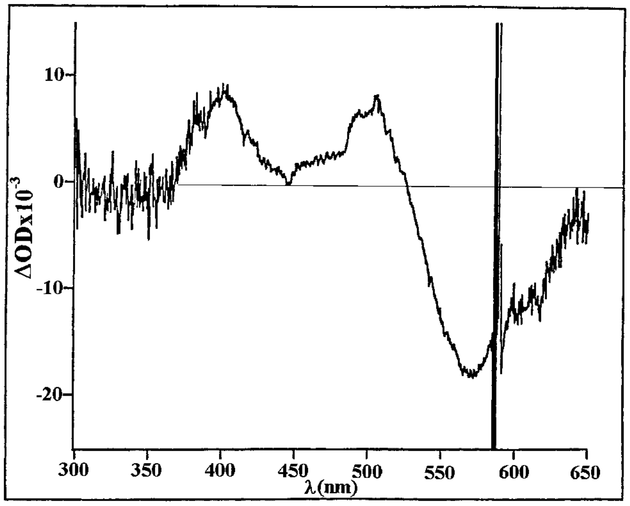
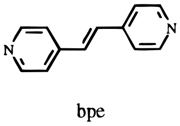
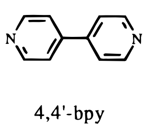
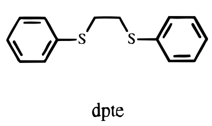


Figure 2. Picosecond transient absorption difference spectrum recorded of a ≈5 × 10^{-5} M solution [(CN)$_4$Fe(dpp)Ru(bpy)$_2$] in H$_2$O recorded 5 ps after 591-nm pulsed laser excitation (4-ps pulse width). The transient absorption difference spectrum is the result of ca. 500 laser shots at 75 μJ/pulse. The energy dependence of the signal intensity was linear in this energy regime.

(dpp)Ru$^{\mathrm{II}}$(bpy)$_2$]$^{4+*}$ were found to be similar to those reported for [(dpte)$_2$ClRu$^{\mathrm{II}}$(LL)Ru$^{\mathrm{II}}$Cl(bpy)$_2$]$^{2+*}$ (LL = bpe or 4,4′-bpy),[16] Scheme 1. Pulsed excitation at 355 or 591 nm results in the formation of the $^{1}[(\mathrm{NH_3})_4\mathrm{Ru^{II}(dpp^{\bullet-})Ru^{III}(bpy)_2}]^{4+*}$ and $^{1}[(\mathrm{NH_3})_4\mathrm{Ru^{III}(dpp^{\bullet-})Ru^{II}(bpy)_2}]^{4+*}$ Franck−Condon excited states, respectively, both of which decay within the 2-ps laser pulse to the $^{3}[(\mathrm{NH_3})_4\mathrm{Ru^{III}(dpp^{\bullet-})Ru^{II}(bpy)_2}]^{4+*}$ MLCT excited state. The $^{3}[(\mathrm{NH_3})_4\mathrm{Ru^{III}(dpp^{\bullet-})Ru^{II}(bpy)_2}]^{4+*}$ species then undergoes facile nonradiative relaxation to repopulate the ground state ($k^{\mathrm{Ru}}_{\mathrm{E_LT}}$ in Scheme 1).

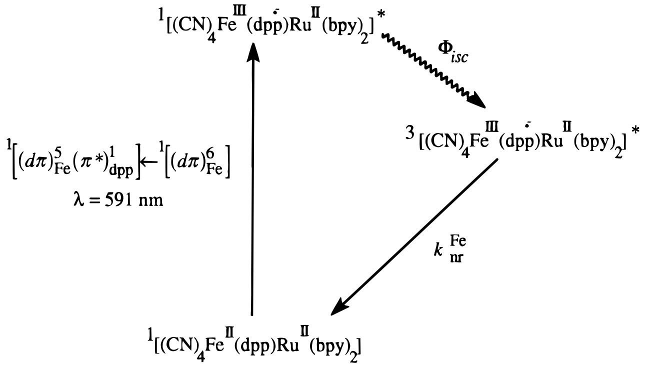

bpe


4,4′-bpy


dpte

Picosecond, laser-flash photolysis studies were conducted on aqueous solutions of [(NC)$_4$Fe$^{\mathrm{II}}$(dpp)Ru$^{\mathrm{II}}$(bpy)$_2$] (≈10^{-5} M) in the same manner described for [(NH$_3$)$_4$Ru$^{\mathrm{II}}$(dpp)Ru$^{\mathrm{II}}$(bpy)$_2$]$^{4+}$. Transient-absorption difference spectra for [(NC)$_4$Fe$^{\mathrm{II}}$(dpp)Ru$^{\mathrm{II}}$(bpy)$_2$]* measured following 2-ps pulsed, 591-nm excitation into the $^{1}[(\mathrm{d}\pi)^{5}_{\mathrm{Fe}}(\pi^*)^{1}_{\mathrm{dpp}}] \leftarrow {}^{1}[(\mathrm{d}\pi)^{6}_{\mathrm{Fe}}]$ MLCT band are shown in Figure 2. The difference spectra are characteristic of an MLCT-based excited state with a strong positive signals at $\Delta\lambda^{\mathrm{abs}}_{\mathrm{max}}$ = 400 nm and $\Delta\lambda^{\mathrm{abs}}_{\mathrm{max}}$ = 500 nm due to the polypyridyl radical anion and a strong bleach centered at $\Delta\lambda^{\mathrm{abs}}_{\mathrm{max}}$ = 580 nm due to loss of the ground state, $^{1}[(\mathrm{d}\pi)^{5}_{\mathrm{Fe}}(\pi^*)^{1}_{\mathrm{dpp}}] \leftarrow {}^{1}[(\mathrm{d}\pi)^{6}_{\mathrm{Fe}}]$, absorption band. The transient absorption signals at $\Delta\lambda^{\mathrm{abs}}_{\mathrm{max}}$ = 400, 500, and 580 nm evolve with time and reach preexcitation levels by 80 ps ($k_{\mathrm{obsd}} \geq 1.3 \times 10^{10}$ s^{-1}). The excited-state dynamics in [(NC)$_4$Fe$^{\mathrm{II}}$(dpp)Ru$^{\mathrm{II}}$(bpy)$_2$]* following $^{1}[(\mathrm{d}\pi)^{5}_{\mathrm{Fe}}(\pi^*)^{1}_{\mathrm{dpp}}] \leftarrow {}^{1}[(\mathrm{d}\pi)^{6}_{\mathrm{Fe}}]$ excitation can be accommodated by Scheme 2. The 591-nm excitation results in the formation of the $^{1}[(\mathrm{NC})_4\mathrm{Fe^{III}(dpp^{\bullet-})Ru^{II}(bpy)_2}]^*$ Franck−Condon excited state, which decays rapidly (within the 2-ps laser pulse) to the $^{3}[(\mathrm{NC})_4\mathrm{Fe^{III}(dpp^{\bullet-})Ru^{II}(bpy)_2}]^*$ based MLCT excited state. $^{3}[(\mathrm{NC})_4\mathrm{Fe^{III}(dpp^{\bullet-})Ru^{II}(bpy)_2}]^*$ then undergoes facile nonradiative relaxation (τ < 80 ps) to repopulate the ground state ($k^{\mathrm{Fe}}_{\mathrm{nr}}$ in Scheme 2).

SCHEME 2



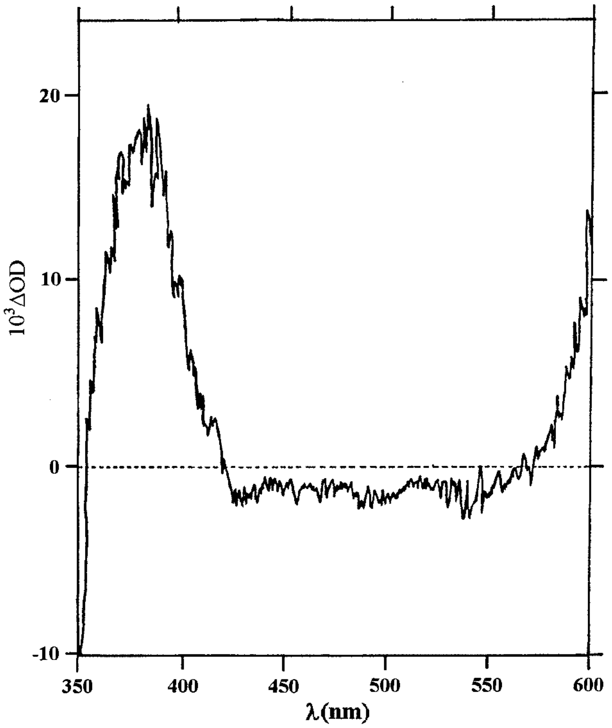
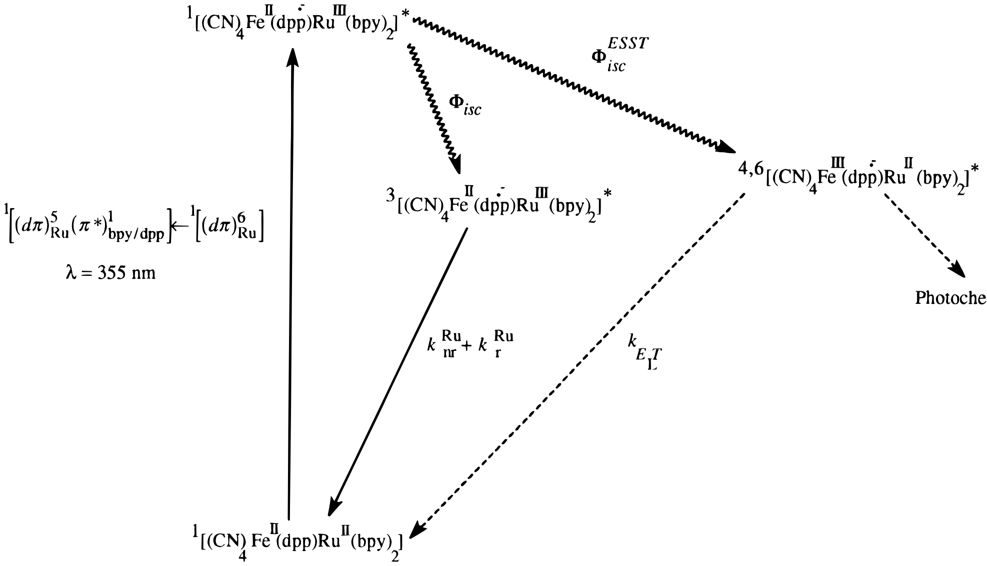


Figure 3. Picosecond transient absorption difference spectrum of a ≈5 × 10^{-5} M solution of [(CN)$_4$Fe(dpp)Ru(bpy)$_2$] in H$_2$O recorded 5 ps after 355-nm pulsed laser excitation (70-ps pulse width). The transient absorption difference spectrum is the result of 4000 laser shots at 300 μJ/pulse. The energy dependence of the signal intensity was linear in this energy regime.

Following 354.7-nm excitation into the $^{1}[(\mathrm{d}\pi)^{5}_{\mathrm{Ru}}(\pi^*)^{1}_{\mathrm{bpy/dpp}}] \leftarrow {}^{1}[(\mathrm{d}\pi)^{6}_{\mathrm{Ru}}]$ MLCT band for [(NC)$_4$Fe$^{\mathrm{II}}$(dpp)Ru$^{\mathrm{II}}$(bpy)$_2$], the prompt formation of a positive absorption at $\Delta\lambda^{\mathrm{abs}}_{\mathrm{max}}$ = 365 nm and $\Delta\lambda^{\mathrm{abs}}_{\mathrm{max}}$ > 600 nm are observed, Figure 3.[17a] These signals do not evolve appreciably on the picosecond time scale.[17b] The important observation here is that the [(NC)$_4$Fe$^{\mathrm{III}}$(dpp$^{\bullet-}$)Ru$^{\mathrm{II}}$(bpy)$_2$]* excited state obtained following 354.7-nm $^{1}[(\mathrm{d}\pi)^{5}_{\mathrm{Ru}}(\pi^*)^{1}_{\mathrm{bpy/dpp}}] \leftarrow {}^{1}[(\mathrm{d}\pi)^{6}_{\mathrm{Ru}}]$ excitation *is kinetically and spectrally distinct* from the excited state produced by 591-nm $^{1}[(\mathrm{d}\pi)^{5}_{\mathrm{Fe}}(\pi^*)^{1}_{\mathrm{dpp}}] \leftarrow {}^{1}[(\mathrm{d}\pi)^{6}_{\mathrm{Fe}}]$ excitation. The data are consistent with formation of an [(NC)$_4$Fe$^{\mathrm{III}}$(dpp$^{\bullet-}$)Ru$^{\mathrm{II}}$(bpy)$_2$]* excited state with a high-spin Fe$^{\mathrm{III}}$ configuration (denoted $^{4,6}[(\mathrm{NC})_4\mathrm{Fe^{III}(dpp^{\bullet-})Ru^{II}(bpy)_2}]$),[18] which can only be accessed via $^{1}[(\mathrm{d}\pi)^{5}_{\mathrm{Ru}}(\pi^*)^{1}_{\mathrm{bpy/dpp}}] \leftarrow {}^{1}[(\mathrm{d}\pi)^{6}_{\mathrm{Ru}}]$ excitation, Scheme 3.[19] Supporting evidence for this hypothesis comes from the [(NH$_3$)$_4$Ru$^{\mathrm{II}}$(dpp)Ru$^{\mathrm{II}}$(bpy)$_2$]$^{4+}$ system, where 10*Dq* in the Ru(NH$_3$)$_4$ fragment is much greater than 10*Dq* in the Fe(CN)$_4$ fragment. Therefore, the high-spin form of [(NH$_3$)$_4$Ru$^{\mathrm{III}}$ is not energetically accessible following 354.7-nm excitation, and the observed photophysics are wavelength independent. The observation of a weak intrinsic emission from [(NC)$_4$Fe$^{\mathrm{II}}$(dpp)Ru$^{\mathrm{II}}$(bpy)$_2$]* (see above) suggests that intersystem crossing from

SCHEME 3



$^1[(NC)_4Fe^{II}(dpp^{\bullet-})Ru^{III}(bpy)_2]^*$ to form $^3[(NC)_4Fe^{II}(dpp^{\bullet-})Ru^{III}(bpy)_2]^*$ (Φ_{isc} in Scheme 3) is competitive with excited-state spin trapping to form $^{4,6}[(NC)_4Fe^{III}(dpp^{\bullet-})Ru^{II}(bpy)_2]^*$ (Φ_{isc}^{ESST} in Scheme 3).[18,19]

The important conclusion is that spin selection rules do not play an appreciable role in the photophysical properties of the heterobimetallic bridged systems where spin−orbit coupling is present.[22] The apparent spin-forbidden nonradiative relaxation in

$$^{4,6}[(NC)_4Fe^{III}(dpp^{\bullet-})Ru^{II}(bpy)_2]^* \rightarrow\rightarrow {}^1[(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2] \qquad (2)$$

is not due to spin selection rules and can be accommodated using Marcus theory. In this argument, the nonradiative relaxation is treated as an electron-transfer process that involves a semiclassical surface crossing (strongly coupled region) where the rate constant (k_{E_LT}) is given by[3]

$$k_{E_LT} = \kappa_{el}\nu_{nu} \exp\left[\frac{-(\lambda + \Delta G^\circ)^2}{4\lambda k_B T}\right] \qquad (3)$$

where κ_{el} is the electronic transmission coefficient, ν_{nu} is the frequency of the correlated nuclear motions coupled to the electron-transfer event, λ is the reorganizational energy which includes both inner (λ_i) and outer sphere (λ_o) components, and ΔG° is the free energy change associated with the back electron transfer. It is expected that low-frequency Fe−C and Fe−N modes are involved in the back electron transfer since there should considerable changes in the Fe−C and Fe−N bond lengths upon going from a high- to low-spin configuration.[23] Therefore, there is an additional energetic component to λ_i that inhibits back electron transfer. New synthetic strategies as well as wavelength-dependent, resonance Raman, time-resolved Raman, and infrared studies are currently underway to further probe the excited properties of these remarkable systems.

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(14) (a) The emission maxima, emission quantum yield and rate constant for excited-state decay for $[\mathrm{Ru^{II}(bpy)_2(dpp)}]^{2+*}$ are $\lambda_{\max}^{\mathrm{em}}$ (nm) = 702 nm, $\phi_{\mathrm{em}} = 0.008\ (\pm 0.001)$, and $k_{\mathrm{obsd}} = 5.6 \times 10^6\ \mathrm{s^{-1}}$ ($\tau = 180$ ns), respectively. Comparative normalized emission spectra for $[\mathrm{Ru^{II}(bpy)_2(dpp)}]^{2+*}$ and $[\mathrm{(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2}]^*$ clearly show the emission band envelope for $[\mathrm{(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2}]^*$ is red-shifted by ≈15 nm relative to that observed for $[\mathrm{Ru^{II}(bpy)_2(dpp)}]^{2+*}$. (b) Emission spectra were uncorrected for instrument response.

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(17) (a) The $[\mathrm{(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2}]$ complex is strongly absorbing at 355 nm, as are the anologous $[\mathrm{(NH_3)_4Ru^{II}(dpp)Ru^{II}(bpy)_2}]$, $[\mathrm{(bpy)_2Ru^{II}(dpp)Ru^{II}(bpy)_2}]$ bimetallic complexes. Several overlapping ${}^1[(\mathrm{d}\pi)^5_{\mathrm{Ru}}(\pi^*)^1_{\mathrm{bpy/dpp}}] \leftarrow {}^1[(\mathrm{d}\pi)^6_{\mathrm{Ru}}]$ transitions and presumably contributions from ${}^1[(\mathrm{d}\pi)^5_{\mathrm{Fe}}(\pi^*)^1_{\mathrm{dpp}}] \leftarrow {}^1[(\mathrm{d}\pi)^6_{\mathrm{Fe}}]$ MLCT transitions contribute to the absorption spectrum of $[\mathrm{(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2}]$ in the near UV. The visible spectra have not been deconvoluted to quantitate the spectral contributions at 355 nm. We note that no detectable transient signals were observed following 355-nm, 10-ns, pulsed laser excitation on $[\mathrm{(NC)_4Fe^{II}(dpp)}]^{2-}$. Details will be presented elsewhere.[12] (b) Nanosecond laser flash photolysis experiments have been performed on $[\mathrm{(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2}]$ in aqueous media. The transient signals obtained following 355-nm, 10-ns, pulsed laser excitation displayed multiexponential kinetics. There is evidence for additional photochemically induced processes in the nanosecond laser flash photolysis experiments on $[\mathrm{(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2}]$. These processes presumably result in the formation of $[\mathrm{(NC)_4Fe^{II}(OH_2)(}\eta^1\mathrm{\text{-}dpp)Ru^{II}(bpy)_2}]$, where η^1-dpp is coordinated in a monodentate fashion to the $[\mathrm{(NC)_4Fe^{II}}]$ fragment. A first-order kinetic decay assigned to thermal recombination of $[\mathrm{(NC)_4Fe^{II}(OH_2)(}\eta^1\mathrm{\text{-}dpp)Ru^{II}(bpy)_2}]$ with concomitant loss of H_2O was observed on the microsecond time scale. Details will be presented elsewhere.[12]

$$[\mathrm{(NC)_4Fe^{II}(OH_2)(}\eta^1\mathrm{\text{-}dpp)Ru^{II}(bpy)_2}] \xrightarrow{k_{\mathrm{obsd}}} [\mathrm{(NC)_4Fe^{II}(dpp)Ru^{II}(bpy)_2}] + \mathrm{H_2O}$$

(18) The spin labels denote the possible electronic configurations at the Fe(III) center only. The exact spin state of the Fe(III) center in this complex cannot be deduced from the transient spectral data alone. However, the quartet configuration is favored because the strong field $\mathrm{CN^-}$ ligands probably place 10 *Dq* near the spin crossover point in O_h symmetry.

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(22) The relaxation of spin selection rules has been observed and discussed in other related Fe(II) polypyridyl complexes.[20a]

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