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Photophysics of Re(I) and Ru(II) Diimine Complexes Covalently Linked to Pyrene: Contributions from Intra-Ligand Charge Transfer States

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The photophysical properties of Ru(II) and Re(I) polypyridyl complexes including a bis-bipyridyl pyrene ligand are presented. The complexes $\{[(bpy)_2Ru]_2bpb\}^{4+}$ and $[(CO)_3ReCl(bpb)]$ (bpy = 2,2′-bipyridine, bpb = 1,6-bis-(4-(2,2′-bipyrid-yl)-pyrene) were designed with the intent of examining intramolecular energy migration between MLCT states localized on the metal complexes and pyrene-localized $^3(\pi–\pi^*)$ states. Absorption spectroscopy of both complexes containing the bpb ligand reveals that in addition to the MLCT and the pyrene-centered $^1(\pi–\pi^*)$ transitions, a new absorption band is observed near 400 nm for both complexes. Absorption spectral data for the Re(I) complex strongly suggest the presence of a pyrene(π) to bpy(π^*) intraligand charge transfer (ILCT) transition. Emission spectra at room temperature and at 77 K are almost identical for the Ru(II) and Re(I) complexes containing the bpb ligand. The ^{3}MLCT emission of related bipyridyl compounds lacking the pyrene is observed at higher energy than for the pyrene-containing complexes, $\{[(bpy)_2Ru]_2bpb\}^{4+}$ and $[(CO_3ReCl(bpb)]$. The Ru(II) complex emits at room temperature with a remarkably long lifetime (130 μs in degassed DMSO). This emission is also strongly sensitive to oxygen and is almost entirely quenched in an aerated solution. In addition, excited-state absorption spectra exhibit features not consistent with ^{3}MLCT or $^3(\pi–\pi^*)$ states of the parent chromophores. The combined characteristics suggest the emission arises from either $^3(\pi–\pi^*)$ or ^{3}ILCT states or a state with mixed parentage.

Introduction

There are a large number of transition metal complexes that have metal-to-ligand charge transfer (MLCT) excited states involving diimine ligands.[1] Within this group, the photophysical behavior of complexes of Re(I), Ru(II), and Os(II), have been investigated in considerable detail.[1,2] This is in part due to the fact that diimine complexes of these metals serve as effective sensitizers for photochemical reactions involving net electron transfer.[3] Since nonradiative relaxation in these complexes is dominated by a combination of energy gap effects and a thermally activated population of ligand-localized excited states that decay rapidly to the ground state, recent efforts of several groups have been focused on making complexes with longer excited-state lifetimes.[4−11]

One approach is to prepare diimine complexes having ligand localized excited states that are lower in energy than the ^{3}MLCT state of the complex. These complexes generally

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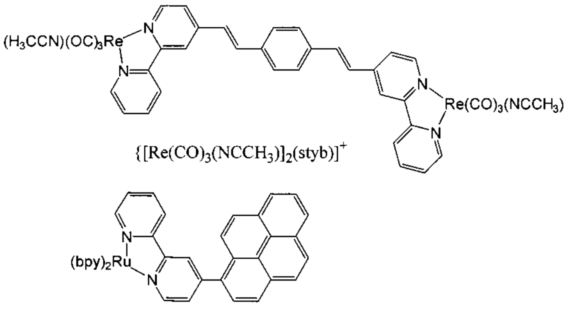

Figure 1. Complex structures from refs 6 and 9.

exhibit no luminescence in solution at room temperature but occasionally have structured luminescence in solid matrixes and frozen solution arising from the ligand localized excited state. In the mid-1970s Wrighton and co-workers attributed the low-temperature emission of [Re(I)(bpy)(pyC(O)Ph)Cl] to phosphorescence from the coordinated benzoylpyridine n$-\pi^*$ excited state.[4] More recently, Re(I) complexes having low-temperature ligand-localized luminescence from diimine $\pi-\pi^*$ excited states were observed by Demas and DeGraff.[5] Room-temperature solution phosphorescence from a ligand localized $\pi-\pi^*$ state was observed by our group in 1991 for the bimetallic Re(I) complex $[Re(CO)_3(NCCH_3)(styb)]^+$ (Figure 1).[6] In all of these cases, except for a few of the complexes reported by Demas and DeGraff, a relatively large energy gap (>1000 cm^{-1}) exists between the ^{3}MLCT state and the ligand localized excited state.

In the early 1990s Rodgers' group reported a Ru(II) diimine complex covalently linked to pyrene by an alkyl bridge.[7] In addition, Sasse and co-workers observed similar behavior in a related complex with a shorter alkyl tether.[8] The energy gap between the ^{3}MLCT of the Ru(II) complex and the $^3(\pi-\pi^*)$ state of the tethered pyrene in these complexes is small, almost certainly under 500 cm^{-1}. The complexes have relatively long-lived (>5 μs) emission from the MLCT state, resulting from reversible intramolecular energy transfer between the ^{3}MLCT state and the $^3(\pi-\pi^*)$ state of pyrene. Photoexcitation of the MLCT transition of the complex is followed by rapid relaxation to an equilibrium mixture of the two states. Significantly, the transient absorption spectra reveal features that can be assigned to the ^{3}MLCT state of the Ru(II) complex and the $^3(\pi-\pi^*)$ state of pyrene. More recently, we reported similar behavior for a complex having pyrene covalently attached to 2,2′-bipyridine through a single C$-$C bond ($[Ru(bpy)_2(bpy\text{-}pyr)]^{2+}$, Figure 1).[9] The complex has a remarkably long excited-state lifetime of 50 μs in deaerated CH_3CN at room temperature. In this case, it was concluded the pyrene localized triplet is not in equilibrium with the ^{3}MLCT state and the long excited-state lifetime is due to slow back energy transfer from the $\pi-\pi^*$ state to the ^{3}MLCT state. This work was followed by reports of Castellano and co-workers showing that further synthetic elaboration of pyrene$-$diimine systems yields complexes with excited-state lifetimes in excess of 100 μs.[10]

Very recently, McMillin's group examined the photophysical behavior of a Pt(II) terpyridyl$-$pyrene complex and presented convincing evidence that luminescence arises, at least in part, from a pyrene to terpyridyl intraligand charge transfer (ILCT) state.[11] Observation of the transition in the visible occurs because of the relatively low one-electron oxidation potential of the pyrene. In addition, Albano et al. attributed unique absorption and emission features of protonated and Zn^{2+} complexes of a terpyridyl$-$anthracene derivative to anthracene to terpyridyl ILCT transitions.[12] There are several interesting characteristics of such complexes. First, the terpyridyl pyrene ligand only exhibits visible ILCT absorption and emission when the terpyridyl is protonated or coordinated to various metals; this occurs because the one-electron reduction potential of the terpyridine is decreased significantly (approximately 400 mV) upon coordination, thus lowering the energy of the ILCT transition. In addition, the complex reported by McMillin and co-workers has a ^{3}ILCT state with a lifetime long enough (possibly due to spin$-$orbit coupling effects of the Pt) to make it a viable sensitizer for photoredox reactions. The excited state redox potentials of ILCT states will depend on the energy of the excited state and the one-electron potentials of the appropriate ligand components (in the McMillin case, this is the pyrene oxidation and the first reduction of the coordinated terpyridine). Last, it is in principle possible to make complexes having both MLCT and ILCT transitions in the visible, with one of the triplet CT states as the active state for photoredox reactions. As such, this represents a new approach to preparing chromophores that absorb throughout the visible and have a long-lived charge transfer excited state for use in photoredox reactions. In principle, the energies of the MLCT and ILCT states can be independently controlled.

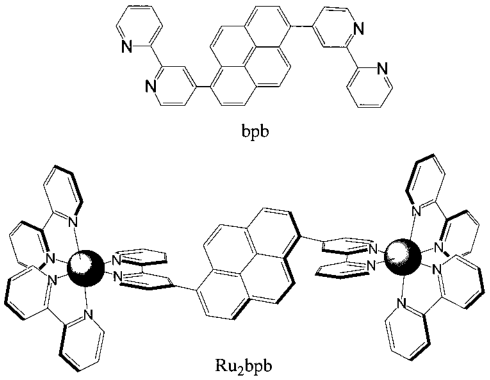

Figure 2. Ligand bpb and geometric representation of the meso diastereoisomer of the complex Ru_2bpb.

In an effort to explore the possible role of ILCT states in the photophysics of Ru(II) and Re(I) complexes, we have examined the behavior of two complexes of the pyrene-containing ligand bpb (Figure 2): $\{[(bpy)_2Ru]_2(bpb)\}(PF_6)_4$ (Figure 2) and $[(CO)_3ClRe(bpb)]$. The combined results of luminescence, excited-state absorption, and solvent-dependent behavior suggest that the emission arises from either a ^{3}ILCT state or a ^{3}ILCT state with a significant amount of ^{3}IL (pyrene $^3(\pi-\pi^*)$) character.

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Experimental Section

Synthesis. The synthesis of the bpb ligand has been described elsewhere.[13] **$[[Ru(bpy)_2]_2(bpb)]^{4+}$ (Ru_2bpb)** was prepared from a mixture of bpb (52 mg, 0.1 mmol) and an excess of $Ru(bpy)_2Cl_2$[14] (145 mg, 0.3 mmol) in chloroform:ethanol 7:3 by refluxing under argon for several hours. The complex was extracted from the dried reaction mixture with pure ethanol; the unreacted ligand remained undissolved. The complex was then further purified by several reprecipitations in ether and finally by flash chromatography on silica (eluent, H_2O:KNO_3 (1 M):MeCN 4:1:5 + 1−5% trimethylamine). The nitrate salt was then converted into a PF_6 salt by adding an excess of KPF_6 to an aqueous solution of the complex and by subsequently filtering the precipitated complex. The red solid was washed several times with water, dissolved in ethanol, and dried on a watch glass (analyses: C, 45.1; H, 2.84; N, 8.01; $Ru_2C_{76}H_{54}N_{12}P_4F_{24}\cdot C_2H_6O\cdot 0.65KPF_6$: C, 45.0; H, 2.90; N, 8.07). A fraction of this complex was then converted into its chloride salt by using an anion exchange column (Sephadex A25).

$[Re(CO)_3Cl(bpb)]$ (Rebpb) was prepared by refluxing bpb (52 mg, 0.1 mmol) and an excess of $Re(CO)_5Cl$ (0.3 mmol) in toluene under argon for several hours. The Re(I) complex readily precipitates from the solution and is subsequently filtered, washed with toluene, dissolved in MeCN, and reprecipitated several times from ether. The complex was then dissolved in CH_2Cl_2 (a fraction of the solid does not dissolve), and the solution remaining after filtration is evaporated on a watch glass to yield Rebpb. The complex was characterized by cyclic voltammetry, UV−vis spectroscopy, and MALDI-TOF mass spectrometry (using α-cyano-4-hydroxycinnamic acid as a matrix). The MALDI spectrum showed a prominent peak at 782.6, corresponding to M − Cl (calculated 780.8). Further evidence that Rebpb is a monometallic complex is provided by the appearance in acetonitrile of a new absorption band at 365 nm with the addition of Zn(acetate), arising from the chelation of the free bipyridine by Zn^{2+}.

$[Re(CO)_3Cl(mpb)]$ (Rempb). The same procedure as that used for Rebpb was used to synthesize the monometallic complex Rempb (mpb = 4-(4-methylphenyl)-2,2′-bipyridine). The complex was characterized by UV−vis spectroscopy and MALDI-TOF mass spectrometry, exhibiting a prominent peak at 518.6, which corresponds to M − Cl (calculated 516.5).

Electrochemistry. Cyclic voltammograms and differential pulse polarograms were recorded using an EG&G Versastat according to procedures described earlier.[9] The complexes were dissolved in freshly distilled and nitrogen-purged acetonitrile with 0.1 M triethylammonium perchlorate as supporting electrolyte. SCE was used as reference electrode and ferrocene was added when necessary as an internal reference.

Spectroscopic Methods. UV−vis absorption spectra were obtained using a Varian Cary 100 scanning spectrometer. Steady-state luminescence spectra were obtained using a SPEX fluorolog equipped with a 450 W Xe arc lamp. Emission was detected using either a liquid nitrogen cooled CCD (setup 1) or a Hamamatsu R928 PMT in a thermoelectrically cooled housing (setup 2). Reported spectra are not corrected for detector response. Phosphorescence spectra and lifetimes at 77 K were obtained on a Varian Eclipse spectrometer (setup 3). The excitation source is a pulsed Xe arc lamp, and detection is achieved using a Hamamatsu R928 PMT. The gating was adapted according to the phosphorescence lifetime, and the acquisition was started after a delay of 0.1 ms. To compare all the spectra obtained at 77 K, the phosphorescence spectrum of protonated bpb (see Results, Figure 6c, setup 3) has been corrected, using the ratio of the spectra of Ru_2bpb obtained with the two different setups (1 and 3).

Luminescence lifetimes were acquired using laser excitation (N_2 pumped coumarin 460 at 460 nm, or Quantel Brilliant Nd:YAG at 532 nm), by filtering the emitted light through a Heath-McPherson Model EU-700 monochromator and detecting the emitted light with a Hamamatsu R928 PMT. Decays typically represented the average of 50−500 pulses and were collected on a Lecroy 9370 digital oscilloscope. The same system served to measure transient absorption spectra, using as an excitation source the 355 nm output of a Coherent Infinity 40-100 Nd:YAG laser or the output of a Quantel Brilliant Nd:YAG at 532 nm. A 150 W Xe arc lamp (Osram) was used as the light source for the analytical beam.

Radiative Rate Constants. In the case of a monoexponential emission decay, the radiative constant can simply be estimated by $\eta_{isc}k_r = \Phi_{em}/\tau_{em}$. For Ru_2bpb, two components contribute to the emission, and several cases can be distinguished (see Results). (i) At 665 nm, the emission intensity of Ru_2bpb is 18% relative to that of the reference $[Ru(bpy)_3]^{2+}$ and has an amplitude-weighted average lifetime of 26 μs. If both emission components have the same radiative constant, the product of the intersystem crossing efficiency and radiative decay rate constant, $\eta_{isc}k_r$, can be estimated from

$$(\eta_{isc}k_r)_{sample} = (\eta_{iisc}k_r)_{ref}\left(\frac{I_{665}^{sample}}{I_{665}^{ref}}\right)\left(\frac{F_{abs}^{ref}}{F_{abs}^{sample}}\right)\left(\frac{\tau_{ref}}{\tau_{sample}}\right) = 6 \times 10^2\ s^{-1}$$

At 665 nm, 98% of the emission intensity is due to the component with the long lifetime of 100 μs. If the two components have a different radiative constant and we assume that the short component has the same radiative constant as $[Ru(bpy)_3]^{2+}$, 99% of the excited states contribute to the long component, and

$$\eta_{isc}k_{r(long)} = 10^5(0.18 \times 0.98)_{em}(0.99)_{abs}(86 \times 10^{-8})/(100 \times 10^{-6})_{\tau long} = 2 \times 10^2\ s^{-1}$$

Results

Syntheses. The bimetallic complex $[[Ru(bpy)_2]_2(bpb)]^{4+}$ (Ru_2bpb, Figure 2) was prepared by reacting an excess of $[Ru(bpy)_2Cl_2]$ with bpb and was purified by column chromatography on silica. The bimetallic complex, Ru_2bpb, exists as a mixture of diastereomers, since each metal center is chiral. Keene and co-workers have recently succeeded in separating the diastereomeric forms of a variety of bimetallic Ru(II) diimine complexes, and unique redox and spectroscopic behavior is only observed in rare cases.[15] This work reports the redox and photophysical behavior of the mixed diastereomers of Ru_2bpb. $[Re(CO)_3Cl(bpb)]$ (Rebpb) and $[Re(CO)_3Cl(mpb)]$ (Rempb) were prepared by reacting an excess of $[Re(CO)_5Cl]$ with the modified bipyridine and were purified by repeated reprecipitation and washing to remove unreacted ligand.

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Table 1. Absorption and Emission Properties of Mono- and Bimetallic Complexes in Various Solvents[a]

	Ru_2bpb			Rebpb		Rubpy	Rempb
solvent	λ_{max}^{abs}, nm (*log* ϵ)	λ_{max}^{em}, nm	ϕ_{em}	λ_{max}^{abs}, nm	λ_{max}^{em}, nm	λ_{max}^{em}, nm	λ_{max}^{em}, nm
H_2O	380 (*4.45*), 394 (*4.44*), 459 (*4.50*)	669	0.0083				
MeCN	381 (*4.43*), 397 (*4.43*), 459 (*4.50*)	670	0.0086	402	674	620	593
EtOH	381 (*4.43*), 402 (*4.44*), 458 (*4.50*)	677	0.0035				
DMSO	385 (*4.42*), 403 (*4.43*), 462 (*4.50*)	679	0.013	407	680		
THF	384 (*4.44*), 403 (*4.74*), 460 (*4.50*)	678					
CH_2Cl_2	385 (*4.50*), 405 (*4.39*), 461 (*4.50*)	682	0.0065	407		605	584
toluene		686					

[a] $Ru_2bpb = \{[(bpy)_2Ru]_2(bpb)\}^{4+}$; Rebpb = $[(CO)_3ClRe(bpb)]$; Rubpy = $[Ru(bpy)_3]^{2+}$; Rempb = $[(CO)_3ClRe(mpb)]$.

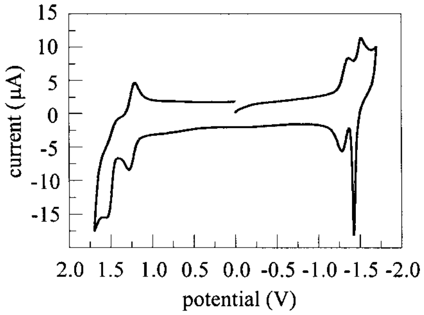

Figure 3. Cyclic voltammogram of Ru_2bpb in nitrogen-purged acetonitrile. The supporting electrolyte is tetraethylammonium perchlorate (0.1 M) and the potentials are reported versus SCE, which was used as a reference electrode.

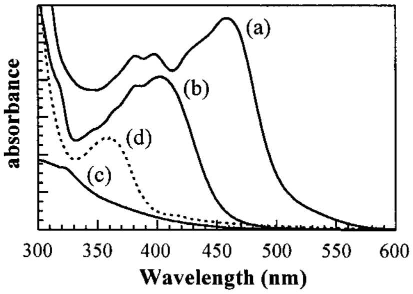

Figure 4. Electronic absorption spectra of (a) Ru_2bpb, (b) Rebpb, (c) Rempb, and (d) bpb in acetonitrile. Spectra have been scaled in order to simplify their comparison. (Extinction coefficients are reported in Table 1).

Electrochemistry. The redox behavior of Ru_2bpb was examined by cyclic voltammetry (Figure 3) and differential pulse polarography in acetonitrile. A reversible Ru(III)/(II) wave is observed at +1.17 V vs SCE ($\Delta E_p = 78$ mV) and oxidation of the pyrene is observed as an irreversible wave with a peak of +1.40 V. This Ru(III/II) potential is thus slightly less positive than that of $[Ru(bpy)_3]^{2+}$ ($E_{ox} = +1.25$ V).[16] The oxidative voltammetry differs from that of the closely related complex $[(bpy)_2Ru(bpy\text{-}pyr)]^{2+}$, which has only a single bipyridine linked to pyrene;[9] this complex exhibits a single quasireversible oxidation with an anodic peak potential of +1.5 V vs SCE. Another feature of the oxidative portion of the cyclic voltammogram of Ru_2bpb is that only a single, presumably two-electron, Ru(III/II) wave is observed. In addition, differential pulse polarograms of the Ru(III/II) wave are not broadened. This suggests minimal electronic interaction of the two Ru centers of the complex. This behavior is consistent with that observed for other bimetallic Ru(II) diimine complexes having aromatic hydrocarbon bridges between the two metal centers.[17]

The first reversible reduction of Ru_2bpb occurs at −1.38 V, more negative than the first reduction of $[Ru(bpy)_3]^{2+}$ (−1.3 V). The reduction of the bpb coordinated to Ru(II) might be expected to be at a slightly more positive potential, based on the potentials observed for other 4-aryl-substituted bipyridine complexes.[1] The voltammetric results for Ru_2bpb make determination of localization of the electron on a particular bipyridine unclear. The cathodic peak of the second reduction is observed at −1.55 V. The reoxidation wave, shown in Figure 3, appears as a sharp anodic peak. This behavior is characteristic of adsorption of reduced complexes followed by anodic desorption from the electrode surface (Pt or glassy carbon).[18]

The redox potentials of Rebpb have been estimated by cyclic voltammetry and differential pulse polarography; limitations in solubility prevent a definitive determination of the reversibility of the redox processes. The first oxidation of the complex is observed at a potential of +0.96 V and, by comparison with other Re(I) complexes, is assigned as a Re(II/I) wave. The pyrene oxidation is observed at +1.4 V, similar to the pyrene oxidation in Ru_2bpb. The reduction of the coordinated bpb ligand occurs at −1.32 V.

Electronic Absorption Spectroscopy. Absorption spectra of Ru_2bpb were measured in a variety of solvents, and absorption maxima are reported in Table 1. By analogy with the parent compound $[Ru(bpy)_3]^{2+}$, the lowest energy absorption band of the complex can be attributed to a metal-to-ligand charge transfer (MLCT) transition ($\lambda_{max} = 459$ nm in MeCN, Figure 4a). The energy of the transition is similar to that of the related monometallic complex $[(bpy)_2Ru(bpy\text{-}pyr)]^{2+}$,[9] but it is slightly lower than that of $[Ru(bpy)_3]^{2+}$; the results are in qualitative agreement with correlations of redox data and absorption maxima for charge-transfer transitions.[19,20] The extinction coefficient of the MLCT

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[19] On the basis of the correlation of ΔE_p, the difference between the $E°$ values for the Ru(III/II) and bpy(0/−1) couples, with the energy of the MLCT absorption maximum. This correlation has been made for several series of Ru(II) diimine complexes.[20]

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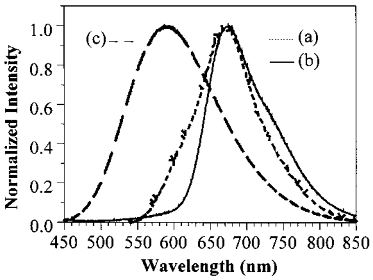

Figure 5. Normalized emission spectra of Ru_2bpb (a, dashed line), Rebpb (b), Rempb (c, full lines) in degassed acetonitrile at room temperature. The excitation wavelength is 459 nm for the Ru(II) complex (8 μM) and 402 nm for the Re(I) complexes (20 μM).

transition in Ru_2bpb ($\epsilon_{459} = 3.2 \times 10^4$ M^{-1} s^{-1}) is consistent with that of other bimetallic Ru−diimine complexes. The magnitude is essentially equal to twice that of $[Ru(bpy)_3]^{2+}$, indicating the two Ru diimine centers covalently linked through the pyrene are very weakly coupled to the pyrene substituent (MLCT dipole does not extend onto the pyrene). Two distinct absorption bands are observed at lower wavelengths (λ_{max} = 382 and 397 nm in MeCN). The two transitions have a lower energy than the $\pi-\pi^*$ transition of the free bpb ligand (broad absorption at 361 nm in MeCN, Figure 4d). A large bathochromic shift of the absorption of bpb is also observed upon protonation or chelation by Zn(II), with the Zn(II) complex having a maximum of 380 nm. The superposition of different transitions in Ru_2bpb prevents a more thorough examination of the solvent effect.

The absorption spectra of the Re(I) complexes Rebpb and its parent compound Rempb are very different. The mpb complex has only a long wavelength tail from a higher energy absorption in the 350−450 nm wavelength region (Figure 4c). For closely related Re(I) diimine complexes, the lowest energy absorption occurs in this wavelength range and has been assigned as a MLCT transition.[5] In contrast, Rebpb has two distinct absorption maxima at 382 and 402 nm in MeCN (Figure 4b). The unique longer wavelength transition of the Re(I) complex of bpb at 402 nm is not MLCT and is similar to the unique band observed at 400 nm in the spectrum of Ru_2bpb. It was also found that the long wavelength absorption transition of Rebpb exhibits some degree of solvatochromism; a 5 nm red shift is observed when the solvent is changed from acetonitrile to the less polar solvent dichloromethane.

Luminescence Spectroscopy. Emission spectra and quantum yields were recorded at room temperature in various solvents, and the observed maxima are displayed in Table 1. The λ_{max} of Ru_2bpb emission in CH_3CN is red-shifted as compared to that of the parent compound $[Ru(bpy)_3]^{2+}$ and the closely related complex $[(bpy)_2Ru(bpy\text{-}pyr)]^{2+}$ (λ_{max} = 670, 620, and 640 nm, respectively). The emission quantum yield exhibits a complex concentration dependence due to a self-quenching process; yields were therefore determined at complex concentrations of 3−8 μM.[21] In degassed MeCN (Figure 5), the emission of Ru_2bpb is 10 times less intense than that of $[Ru(bpy)_3]^{2+}$,[22] with a quantum yield in degassed MeCN of 0.0086. The emission is nearly completely quenched (>97%) in aerated solutions; thus, quenching is much more efficient than oxygen quenching of $[Ru(bpy)_3]^{2+}$. The emission of Ru_2bpb also exhibits a subtle shoulder at shorter wavelength. In aerated solutions, the emission is extremely weak and the emission maximum is somewhat blue-shifted (655 nm). This suggests that two different states contribute to the emission, and the states are very likely not in equilibrium, since they are quenched by oxygen with vastly different efficiencies.[23] It is also possible that the weak emission component at shorter wavelength arises from an impurity; we have not been able to exclude impurity emission, although the weak component persists even following a variety of micropreparative TLC separations immediately prior to spectroscopic analysis.[24]

A blue shift of the emission maximum of deaerated solutions of Ru_2bpb occurs upon increasing the solvent polarity (e.g., λ_{max} = 670 nm in MeCN and 682 nm in CH_2Cl_2). This effect is opposite to that observed for $[Ru(bpy)_3]^{2+}$ (λ_{max} = 620 nm in MeCN and 605 nm in CH_2Cl_2), where the emission has clearly been assigned as arising from a ^{3}MLCT state. While assignment of the emission transition based on solvent shifts is complicated by effects due to mixing of transitions and a variety of other factors,[25] the fact that the qualitative trend differs from that of the parent chromophore ($[Ru(bpy)_3]^{2+}$) indicates that the emission transition is very likely *not* MLCT in origin. It should also be noted that no definite trend is observed for the emission quantum yields as a function of the polarity of the solvent.

Emission spectra of Rebpb in various environments are very similar to those of Ru_2bpb. As shown in Figure 5, the emission spectra of Rebpb and Ru_2bpb have nearly identical emission maxima in MeCN, but the emission yield for the Re(I) complex is much lower than that of Ru_2bpb. The emission spectrum of Rebpb in aerated solution also differs from that in degassed solution. An extremely weak, higher energy emission component is observed at shorter wavelength; however, the emission is so weak that a definitive determination of the maximum is not possible. When the solvent is changed from acetonitrile to DMSO, a red shift of the emission occurs, as is the case for Ru_2bpb. A comparison with the less polar solvents dichloromethane and THF is prohibited by the limited solubility of the complex.

The emission of Rebpb differs markedly from the parent complex, Rempb, which has a weak emission with a

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(21) In MeCN, the absorption at 458 and 397 nm increases linearly with concentration up to 10 μM.

(22) Kawanishi, Y.; Kitamura, N.; Kim T.; Tazuke, S. *Riken. Q.* **1984**, *78*, 212−219.

(23) The state emitting at higher energy is quenched by oxygen with a much smaller efficiency, due to its shorter lifetime (see below). If the state had been in equilibrium with the longer lived, lower energy state, the higher energy emission would have been quenched with an efficiency paralleling that of the long-lived state.

(24) In an attempt to separate possible impurities in Ru_2bpb and the Re complexes, samples were subjected to micropreparative TLC immediately prior to spectroscopic examination. Following TLC plate development using a variety of eluents, the band containing the complex was scraped from the plate and washed from the support (silica or alumina) into the cuvette with an appropriate solvent.

(25) For a review of solvent effects on charge-transfer transitions, see ref 2.

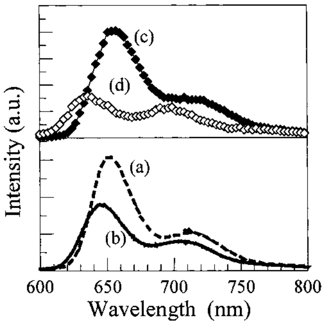

Figure 6. Emission spectra of Ru_2bpb (a, ---, λ_{exc} = 459 nm) and Rebpb (b, —, λ_{exc} = 402 nm) in EtOH:MeOH (4:1) glass at 77 K. Phosphorescence of $Hbpb^+$ (c, ◆, λ_{exc} = 450 nm) in EtOH:MeOH (4:1) plus 10% of ethyl iodide and bpb (d, □, λ_{exc} = 360 nm) in butyronitrile (+10% EtI).

maximum 80 nm to the blue of the Rebpb emission maximum. In addition, the solvent effect on the emission maximum is the opposite that of Rebpb. Since it is known that the emissive excited state of Rempb is a ^{3}MLCT state, the emission of Rebpb is very likely *not* of MLCT origin given the observed behavior.

In EtOH/MeOH (4:1) glasses at 77 K, all the complexes exhibit structured luminescence. Spectra of Ru_2bpb, Rebpb, and the ligand are shown in Figure 6. All four exhibit structured emission with a maximum at approximately 650 nm and a shoulder at 710 nm. The emission spectrum of Ru_2bpb is similar in band shape, but significantly red-shifted as compared to $[Ru(bpy)_3]^{2+}$ *and* $[(bpy)_2Ru(bpy\text{-}pyr)]^{2+}$.[9] The emission lifetime of Ru_2bpb in the EtOH/MeOH frozen glass is 510 μs. The spectrum of the protonated ligand, bpb, obtained in matrixes containing ethyl iodide (which favors intersystem crossing to the triplet state), has a maximum at 653 nm with a shoulder around 710 nm and a lifetime of 410 μs (Figure 6). However, the nonprotonated ligand, bpb, when excited at 360 nm, exhibits phosphorescence with a maximum of 638 nm. The Re complex of bpb has a maximum at slightly higher energy than Ru_2bpb and a lifetime of nearly 2 ms. The parent analogues of the two bpb complexes, Rempb and $[Ru(bpy)_3]^{2+}$, both emit from ^{3}MLCT states with maxima that differ from one another and from the bpb complexes, providing further evidence that the lowest lying excited states of the bpb complexes are not ^{3}MLCT states.

Room-Temperature Time-Resolved Absorption and Emission Spectroscopy. Room-temperature luminescence decays of the bpb complexes can all be fit as double exponentials. The emission decay of Ru_2bpb with two exponential components in the microsecond time scale is shown in Figure 7. In MeCN, analyses of the longer decay gives a lifetime of 100 μs, which is much longer than that of the parent compound $[Ru(bpy)_3]^{2+}$ (τ = 0.8 μs).[1] This lifetime is solvent dependent and reaches 130 μs in DMSO. The short component has a lifetime of 1.8 μs in MeCN, and its contribution to the emission decreases with increasing emission wavelength (23% at 600 nm vs 5% at 660 nm), consistent with the shorter lived emission being associated with the weaker emission of Ru_2bpb. The self-quenching process mentioned above affects the long lifetime, whereas the shorter component does not change significantly. The wavelength dependence of the relative amplitude of each decay and the difference of the emission spectra under aerated and deoxygenated conditions indicate the existence of two different emitting excited states. The faster decaying excited state, probably the ^{3}MLCT state, emits at shorter wavelength and is rapidly deactivated, either to the ground state or to the longer lived emissive excited state. It is also possible that the short lifetime emission component arises from an impurity; however, samples obtained from different micropreparative TLC purification routines give very similar relative intensities and lifetimes for the two emission components. The double exponential behavior observed for Ru_2bpb parallels that observed for $[(bpy)_2Ru(bpy\text{-}pyr)]^{2+}$.[9]

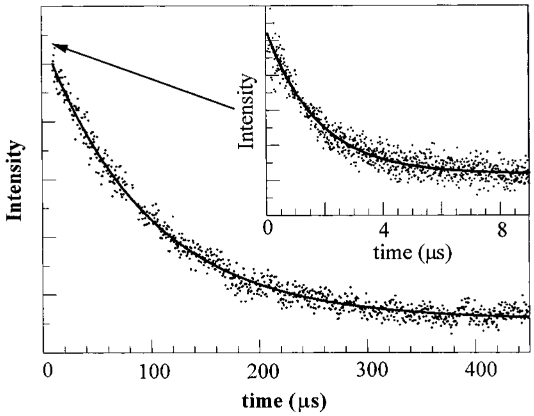

Figure 7. Emission decay at 660 nm after pulsed excitation (λ_{exc} = 532 nm) of Ru_2bpb (5 μM) in acetonitrile at room temperature. The solid line shows the exponential fitting of the data (τ_{long} = 100 μs). The inset shows a measurement taken at a shorter time scale (τ_{short} = 1.8 μs).

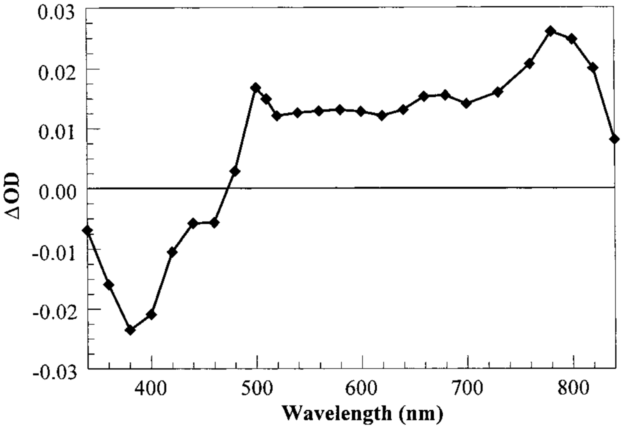

Figure 8. Transient absorption spectrum of Ru_2bpb (10 μM) in acetonitrile at room temperature 5 μs after pulsed excitation (λ_{exc} = 355 nm). The spectrum is build by measurement of the decays each 10 or 20 nm. The same spectra are obtained by exciting at 532 nm, and with a complex concentration of 50 μM. Decays are single exponential at each wavelength.

In an effort to further explore the nature of the emissive excited state, nanosecond transient absorption spectra were obtained for the complexes studied. The spectrum of Ru_2bpb exhibits a bleaching of the ground state between 350 and 470 nm, with a minimum at 380 nm (Figure 8). At longer wavelengths, a broad positive transient extends to the near-IR detection limit of the system used, with apparent maxima at 490 and 780 nm. At each wavelength, the transient decay is monoexponential with a time constant identical within experimental error to that of the long decay observed in the emission. The transient absorption spectrum of Rebpb also has characteristics similar of those of the Ru complex, with a bleaching that occurs farther to the blue. The lifetime of the Re complex in acetonitrile is shorter than the Ru(II) complex (11 μs) but still much longer than the lifetime of the parent complex (Rempb). These transient spectra differ significantly from both the transient absorption spectra of related complexes having ^{3}MLCT excited states and the absorption spectrum of the pyrene triplet. The triplet excited states of pyrene and substituted pyrene derivatives have a strong absorption between 450 and 500 nm and no significant absorption in the red and near-infrared.[26] In addition, transient spectra of Ru(II) bipyridyl complexes covalently linked to pyrene with an alkyl tether have maxima characteristic of the pyrene triplet state (maximum between 400 and 500 nm) and exhibit *no* absorption to the red of 600 nm.[8] Thus, the transient spectra observed for Ru_2bpb and Rebpb suggest that the long-lived excited states of these complexes are *not* pyrene triplet (^{3}IL) or ^{3}MLCT in nature.

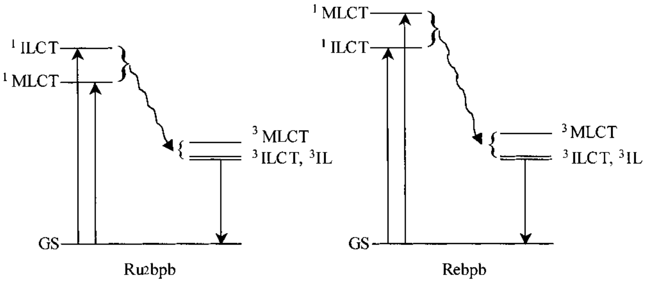

Figure 9. Schematic state diagram for the complexes Ru_2bpb and Rebpb. The absorption and emission are shown as solid lines. Waved arrows represent intersystem crossing and nonradiative decays.

Discussion

The vast difference in the transient absorption features observed for the Ru(II) and Re(I) complexes of bpb relative to other covalently linked metal diimine/pyrene complexes[7,8] clearly indicate that the lowest energy excited state is not a MLCT state. The combined spectroscopic data are most consistent with the emitting excited-state being either a triplet state localized on the pyrene (^{3}IL) or a pyrene (π) to bipyridine (π*) charge transfer state (^{3}ILCT) similar to that observed by McMillin and co-workers for [ClPt(tpy-pyr)]$^+$.[11] The discussion below relates each piece of spectroscopic evidence to this conclusion.

The electrochemical data indicate that the one-electron oxidation potential of pyrene in bpb is close to that of the Ru(III/II) and Re(II/I) potentials. The redox data of Ru_2bpb indicate that the potential for one-electron oxidation of the Ru(II) is *less than* 150 mV more negative than the pyrene oxidation. On the reductive side, it is known that protonated and metalated bipyridine ligands are much more easily reduced than free bipyridines.[27] These combined redox data indicate that it is possible for protonated bpb to have a relatively low-energy pyrene (π) to bipyridine (π*) ILCT transition and that it is reasonable that the pyrene (π) to bpy (π*) ILCT and the Ru(II) (dπ) to bpy (π*) MLCT absorption transitions may be relatively close in energy. In addition, Re(I) complexes such as Rempb have Re(II/I) and bpy (0/−1) potentials nearly the same as those of Rebpb, yet the MLCT absorption of Rempb is at significantly higher energy than the lowest energy absorption band observed for Rebpb. The implication is that the absorption of Rebpb at 402 nm arises from a pyrene (π) to bpy (π*) ILCT transition.

The luminescence spectra of Ru_2bpb and Rebpb in solution at room temperature and in low-temperature glasses are very similar. This would not be expected if emission arose from a ^{3}MLCT state, since related Ru(II) and Re(I) complexes have significantly different emission energies, especially in low-temperature glasses. The solvent dependence of the emission of Ru_2bpb also serves as evidence that the emission of the two complexes examined here is not of MLCT origin. The emission of Ru_2bpb exhibits a decrease in λ_{max} with decreasing solvent polarity, a trend opposite that observed for $[Ru(bpy)_3]^{2+}$.[28] The protonated bpb ligand also exhibits phosphorescence at nearly the same energy as the Ru and Re complexes; in an independent study, the lowest energy absorption transition of protonated bpb was proposed to be a pyrene (π) to bpy(H$^+$) (π*) CT transition.[13] The similarity of the emission spectra suggests that the emitting state of the three substances is related and may be of ILCT origin.[29] However, the weak 77 K phosphorescence observed for the *unprotonated* bpb ligand has maxima and vibronic structure very similar to the protonated bpb, suggesting that the two states cannot be distinguished by 77 K luminescence spectroscopy. The high degree of oxygen quenching observed for both Ru_2bpb and Rebpb is characteristic of aromatic hydrocarbon triplet states and might serve to suggest that intramolecular energy transfer to a pyrene localized triplet is important in these complexes, like other covalently linked metal diimine−pyrene complexes.[6−10] However, it is worth noting that the pyrene to bipyridine ILCT state also proposed here is similar to widely studied twisted intramolecular charge transfer (TICT) states of purely organic chromophores; in fact, triplet TICT states are known to be readily quenched by oxygen in organic solvents.[30]

Further evidence for the emitting excited state being of ILCT origin in these complexes is derived from the broad and complex transient absorption spectra that are not consistent with either MLCT or IL excited states. In other systems exhibiting reversible energy transfer between pyrene triplet and a MLCT excited state, transient absorption spectra resemble some clear combination of the spectra of the pyrene triplet and the MLCT excited state of the complex.[7,8]

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[26] Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904−15.

[27] (a) Krejcik, M.; Vlcek, A. A *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *313*, 243−57. (b) Braterman, P. S.; Song, J. I. *J. Org. Chem.* **1991**, *56*, 4678−82.

[28] Kober, E. M.; Sullivan, B. P.; Meyer, T. J. *Inorg. Chem.* **1984**, *23*, 2098−104.

[29] The protonated ligand differs from the chelated ligand in that the rotation about the bond linking the two pyridines is inhibited in the chelated ligand; the protonated ligand can adopt a variety of conformers where electronic interaction of the two pyridines is much less than that of the metal-chelated bipyridine.

[30] Hashimoto, M.; Hamaguchi, H. *J. Phys. Chem.* **1995**, *99*, 7875−7.

Given these considerations, a state diagram for the complexes studied is as shown in Figure 9. The spin-allowed absorption involves overlapping MLCT and ILCT transitions as the lower energy transitions. The Re(I) complex has an ILCT that is distinctly lower in energy than the MLCT transition. The initially formed singlet charge transfer state intersystem crosses rapidly into the triplet manifold. The lowest energy, long-lived, emissive triplet state appears to be either the ^{3}IL (pyrene $\pi-\pi^*$) or ^{3}ILCT state for Ru_2bpb and Rebpb. The ^{3}MLCT state is at slightly higher energy in each complex and could be at the origin of the weak shorter lived emission.

It should be mentioned that the transient spectra of both Ru_2bpb and Rebpb are similar to those of $[(bpy)_2Ru(bpy\text{-}pyr)]^{2+}$ previously reported by our group. The long-lived excited state of $[(bpy)_2Ru(bpy\text{-}pyr)]^{2+}$ was assigned to coexisting ^{3}MLCT and $^3(\pi-\pi^*)_{pyr}$ states;[9] however, data obtained for this complex are also consistent with a single ^{3}ILCT state. In fact, the transient absorption data obtained for $[(bpy)_2Ru(bpy\text{-}pyr)]^{2+}$ are more easily explained in terms of the ^{3}ILCT state model.

Conclusion

The similarity between the emission properties and the transient absorption spectra of Ru_2bpb and Rebpb strongly suggests that the long-lived excited state is very likely a ^{3}ILCT state or a ^{3}ILCT state with significant pyrene triplet character. The presence of heavy atoms substantially increases the spin−orbit coupling and allows observation of luminescence from the triplet ILCT state in Ru_2bpb, Rebpb, and protonated bpb (in the presence of ethyl iodide). In each case, the attribution of the triplet state to a MLCT transition can be excluded, and transient absorption data argue against the emission arising exclusively from a pyrene $^3(\pi-\pi^*)$ state. The presence of ILCT states, in addition to MLCT states, provides an additional approach for tuning excited-state energies in metal diimine complexes.

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