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Solvent dependent behavior of energy transfer in a mixed metal ruthenium(II)/rhenium(I) complex

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Abstract

The absorption and emission properties of $(bpy)_2Ru(bb)^{2+}$, $Ru(bpy)_2(bb)Re(CO)_3py^{3+}$ and $(bb)Re(CO)_3py^{1+}$, where bpy is 2,2′-bipyridine, bb is 1,2-bis(4-methyl-2,2′-bipyridyl-4′-yl)ethane and py is pyridine, were studied in various solvents. Absorptions attributed to $d\pi(Ru) \rightarrow \pi^*(1)(bpy)$ were located between 400 and 500 nm, those attributed to $d\pi(Ru) \rightarrow \pi^*(2)(bpy)$ and $d\pi(Re) \rightarrow \pi^*(bb)$ were found between 300 and 400 nm, and those attributed to $\pi \rightarrow \pi^*$ (intraligand) were observed between 200 and 300 nm. The absorption energy maxima of the $d\pi(Ru) \rightarrow \pi^*(1)(bpy)$ transition followed the optical dielectric constant of the solvent defined by the $(1-D_{op})/(2D_{op}+1)$ relationship. In the heterometallic complex, absorption of light in the 300–400 nm region was partitioned between the ruthenium and rhenium centers. Emission in solution at room temperature was observed from the ruthenium center upon excitation at either 436 or 355 nm. While emission was also observed from the rhenium center in $(bb)Re(CO)_3py^{1+}$ when excited at 355 nm, none was observed from the rhenium site of the mixed metal complex. The excitation energy absorbed by the rhenium center in this complex was transferred to the ruthenium center with greater than 80% efficiency. The energy transfer process was rapid as noted by the transient absorption spectrum of the heterometallic complex, which contained only the features related to the bpy^- radical and the Ru(II) bleach. In addition, an inverse $(1-D_{op})/(2D_{op}+1)$ dependence on the emission energy maxima of $(bb)Re(CO)_3py^{1+}$ was observed.

Introduction

The challenge of developing efficient photocatalytic systems for energy conversion requires the trapping of relatively short lived photo-excited states. Complex molecular arrays, where charge separation can be achieved, provide an approach towards solving this problem. Homobimetallic and multimetallic compounds containing like metal complexes linked by a molecular bridge have been extensively investigated [1, 2]. Where differentiation between the metal sites was desired, it was accomplished with different coordination spheres around the respective metals [3, 4]. Alternatively, systems containing two different metal centers (heterometallic or mixed metal) have been examined for this purpose [5, 6].

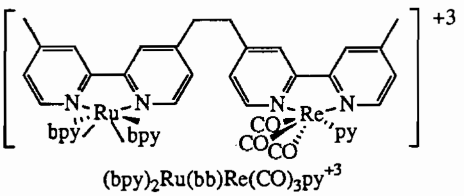

Fig. 1. The molecule $[(bpy)_2Ru(bb)Re(CO)_3py]^{3+}$.

Recently we described the photophysical behavior observed in the heterometallic complex shown in Fig. 1, $Ru(bpy)_2(bb)Re(CO)_3py^{3+}$, where bpy = 2,2′-bipyridine, bb = 1,2-bis(4′-methyl-2,2′-bipyridyl-4-yl)ethane and py = pyridine, as compared to the monometallic model complexes, $Ru(bpy)_2(bb)^{2+}$ and $Re(CO)_3(bb)py^{1+}$ [7]. Excitation of the rhenium chromophore resulted in efficient energy transfer to the ruthenium unit, observed as an enhancement of the ruthenium emission intensity. In the following report, particular attention to the effects of solvent on the intramolecular interaction between the rhenium and ruthenium centers is examined. There was reason to suspect that solvent effects would be present [8]. Solvatochromism of ruthenium polypyridyl complexes has been described in the literature by several authors [9]. The influence of solvent has also been documented for rhenium polypyridyl complexes [10] and for the interaction of two covalently linked chromophores [11].

Here, we focus on the role of solvent in effecting changes in both molecular absorption and emission energies of $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$. The nature of the solvent interaction with this compound was expected

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to be fairly complex, due to the presence of solvent dependencies of each metal center and a solvent dependency arising from the energy transfer process.

Experimental

The preparation and electrochemistry of the complexes $(bpy)_2Ru(bb)^{2+}$, $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ and $(bb)Re(CO)_3py^{1+}$ have been detailed previously [7]. All complexes were isolated as the hexafluorophosphate salts. The solvents used were HPLC grade or higher and used without further purification. The only exception to this was THF, which was distilled from sodium benzophenone immediately prior to use. Absorption data were recorded using a Perkin-Elmer Lambda Array 3840 UV–Vis spectrophotometer. Absorption maxima as a function of solvent were determined with a Cary 14 recording spectrophotometer. Emission quantum yields (ϕ_{em}) were determined from an average of at least three freeze–pump–thaw degassed samples [12] relative to a $Ru(bpy)_3^{2+}/CH_3CN$ standard ($\phi_{stnd}=0.062$ [9e]). The emission quantum yields were calculated from eqn. (1), which incorporates correction for variation in solvent indices of refraction (η) relative to the acetonitrile standard, η_{AcN},

$$\phi_{cm}=\phi_{stnd}(\eta^2/\eta^2_{AcN})(A_{stnd}/A_{cpd})(I_{cpd}/I_{stnd}) \quad (1)$$

absorbance (A) at the excitation wavelength relative to the standard, $Ru(bpy)_3^{2+}$, and the integrated emission intensity (I) relative to the standard, $Ru(bpy)_3^{2+}$. The emission and excitation spectra were obtained from solutions at 23±2 °C using a Spex Fluorolog 212 spectrofluorometer. Excited state lifetimes were obtained with a PRA LN1000 nitrogen laser and a LN 102 dye laser. Samples used to determine emission lifetimes were freeze–pump–thaw degassed and equilibrated at room temperature before measurement.

Transient absorption spectroscopies were performed at the Notre Dame Radiation Laboratory. For measurements in the nanosecond regime, the pump source was a Quanta Ray DCR-1 Nd:YAG laser and the monitoring beam was a pulsed 1000 W Xe lamp. Pump/probe geometries varied from 90 to ~165°. Picosecond experiments were performed on instrumentation modified from the description originally reported [13]. The light source was a mode locked Quantel YB-501 DP Nd:YAG laser which generates the pump energy (4mJ/18 ps at 355 nm) and probe light (~400 to 850 nm) quasi-continuum. The original fiber optic delay lines have now been replaced by a reflector on a computer controlled step rail.

Results

Absorption

The absorption spectra for all three complexes were recorded in various solvents. The molar absorptivities (ϵ) at the excitation wavelengths of $\lambda_{ex}=436$ and 355 nm are listed in Table 1. Both excitation wavelengths are associated with metal-to-ligand charge transfer transitions (MLCT). The $d\pi(Ru)\rightarrow\pi^*(1)(bpy)$ absorption occurs at 436 nm, whereas overlapping $d\pi(Ru)\rightarrow\pi^*(2)(bpy)$ and $d\pi(Re)\rightarrow\pi^*(bpy)$ absorptions take place at 355 nm. Thus, only $(bpy)_2Ru(bb)^{2+}$ and its corresponding component in $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ possess significant absorptions at 436 nm, but at 355 nm light is partitioned between both metal centers nearly in accord with the fractional contribution calculable from each monometallic component*. The data indicate that between 50 and 60% of the incident radiation is absorbed by the ruthenium component of the mixed metal complex at 355 nm. The data in Table 1 also indicate that the ϵ values of $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ at 436 and 355 nm are similar, ranging from $(1 \text{ to } 2)\times10^4$ M^{-1} cm^{-1}. Interestingly, the molar absorptivities at 436 nm are ~20% greater for the mixed metal complex than in the monometallic complex. This is most likely due to a tailing of the rhenium absorption bands out to ~450 nm, which is evident in the UV–Vis and excitation spectra of the $(bb)Re(CO)_3py^{1+}$ complex. Nevertheless, the absorbance at ~436 nm is predominantly ruthenium based.

The maxima (cm^{-1}) of the lowest energy absorption band for the three complexes are listed in Table 2. The bands are well resolved for the absorbance in the

TABLE 1. Absorption coefficients of $(bpy)_2Ru(bb)^{2+}$, $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ and $(bb)Re(CO)_3py^{1+}$ in various solvents[a]

Solvent	$\lambda_{obs}=355$ nm			$\lambda_{obs}=436$ nm[b]	
	Ru(bb)	Ru(bb)Re	(bb)Re	Ru(bb)	Ru(bb)Re
1,4-DXN[c]	'0.97'	'1.1'	0.47	'2.2'	'1.9'
$CHCl_3$[c]	'0.77'	1.39	0.52	'2.2'	1.57
CH_2Cl_2	0.86	1.11	0.43	0.98	1.28
1,2-DCE	0.68	1.25	0.51	1.24	1.43
THF	0.63	1.23	0.57	1.08	1.38
CH_3CN	0.57	1.14	0.49	1.07	1.39
EtOH	0.55	1.15	0.54	1.05	1.37

[a] $\epsilon\times10^{-4}$, units are M^{-1} cm^{-1}, $T=25$ °C, error ±0.01. [b] $(bb)Re(CO)_3py^{1+}$ has no absorbance at 436 nm. [c] Low solubility in 1,4-DXN and $CHCl_3$; 'values' (in single quotes) are approximate.

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*$\alpha_{Ru}=\epsilon_{Ru}(\epsilon_{Ru}+\epsilon_{Re})^{-1}$, where α is the fractional contribution of the ruthenium unit and the ϵ values are for the respective monometallic complexes at 355 nm.

TABLE 2. Absorption energy maxima of $(bpy)_2Ru(bb)^{2+}$, $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ and $(bb)Re(CO)_3py^{1+}$ in various solvents[a]

Solvent	Ru(bb) (cm^{-1})	Ru(bb)Re (cm^{-1})	Re(bb) (cm^{-1})	$(1-D_{op})/(2D_{op}+1)$[b]
EtOH	22.03	22.08	28.61	−0.1811
1,2-DCE	21.94	21.93	28.19	−0.2101
DMSO	21.86	21.83	29.28	−0.2205
CH_2Cl_2	21.95	21.91	29.24	−0.2034
THF	21.96	21.96	28.99	−0.1969
CH_3CN	22.01	22.04	28.21	−0.1746
nBuCN	21.93	21.95	29.21	−0.1895
pyr	21.83	21.86	28.63	−0.2300

[a] Absorption energies are $\times 10^{-3}$, $T=25$ °C, error $= \pm 0.02$. [b] $D_{op}=\eta^2$, η = solvent index of refraction.

450 nm region, but lie on the shoulder of a $\pi \rightarrow \pi^*$ transition for $(bb)Re(CO)_3py^{1+}$. In the latter case, only estimates of the energy maxima are possible. As noted from the data, energy maxima vary as follows: from 21.83×10^3 cm^{-1} in pyridine to 22.03×10^3 cm^{-1} in ethanol for $(bpy)_2Ru(bb)^{2+}$, from 21.83×10^3 cm^{-1} in DMSO to 22.08×10^3 cm^{-1} in ethanol for $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$, and from 28.19×10^3 cm^{-1} in 1,2-dichloromethane to 29.24×10^3 cm^{-1} in dichloromethane for $(bb)Re(CO)_3py^{1+}$.

Emission data

Emission spectra for the complexes were recorded in various solvents. Each were broad, as expected for MLCT based processes. The emission lifetimes and quantum yields of $(bpy)_2Ru(bb)^{2+}$ and $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ obtained at 436 nm are summarized in Table 3. Although equivalent values were found for both complexes in any given solvent, these values varied by approximately a factor of two from solvent to solvent. The smallest emission quantum yields and shortest lifetimes were observed in ethanol; the largest emission quantum yields and longest lifetimes were found in chloronated hydrocarbon solvents. In general, $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ exhibited photophysical properties equivalent to those of the monometallic $(bpy)_2Ru(bb)^{2+}$.

At 355 nm excitation, all three complexes emit and their emission quantum yields and lifetimes are listed in Table 4. Note that only one emission is observed for $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$. Again, as observed with 436 nm excitation, the emission properties were solvent dependent. However, the emission quantum yields and lifetimes of $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ were 10–20% larger than for $(bpy)_2Ru(bb)^{2+}$ in the less polar solvents. Additionally, the emission quantum yields of $(bb)Re(CO)_3py^{1+}$ were about two times greater than those of $(bpy)_2Ru(bb)^{2+}$, but the emission lifetimes were found to be half as large. The values of the emission quantum yield were attenuated in ethanol for all the complexes.

TABLE 3. Emission quantum yields and lifetimes for $(bpy)_2Ru(bb)^{2+}$, $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ and $(bb)Re(CO)_3py^{1+}$ in various solvents ($\lambda_{ex}=436$ nm)[a]

Solvent	(Ru(bb)		Ru(bb)Re	
	ϕ_{em}	τ (ns)	ϕ_{em}	τ (ns)
1,4-DXN[b]	0.041 ±0.001	691	0.054 ±0.001	795
$CHCl_3$[b]	0.047 ±0.003	1093	0.083 ±0.002	1038
CH_2Cl_2	0.080 ±0.001	1048	0.074 ±0.001	1191
1,2-DCE	0.091 ±0.001	923	0.094 ±0.002	1094
THF	0.057 ±0.002	772	0.053 ±0.001	934
EtOH	0.022 ±0.001	767	0.018 ±0.003	708

[a] $T=25$ °C, error in $\tau = 10\%$. [b] $(bpy)_2Ru(bb)^{2+}$ and $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ are very slightly soluble in these solvents.

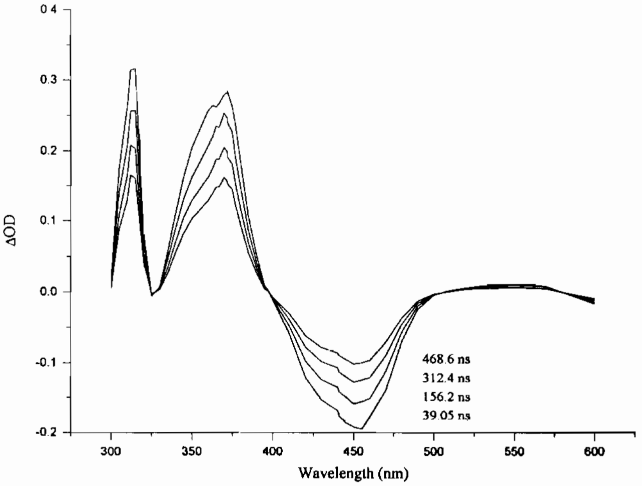

Fig. 2. Transient absorption spectrum of $[(bpy)_2Ru(bb)Re(CO)_3py]^{3+}$ at various delay times after a 355 nm flash, $A=0.5$.

Transient absorption

The transient absorption spectrum of $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ obtained at 355 nm excitation is shown in Fig. 2. The characteristic bipyridine radical absorptions are observed at 315 and 370 nm along with a bleach of the Ru(II) ground state. All three spectral features followed the same kinetics (i.e. recovery of the MLCT Ru(II) bleach coincides with the decay of the bipyridine radical absorptions) with

TABLE 4. Emission quantum yields and lifetimes for $(bpy)_2Ru(bb)^{2+}$, $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ and $(bb)Re(CO)_3py^{1+}$ in various solvents ($\lambda_{ex}=355$ nm)[a]

Solvent	Ru(bb)		Ru(bb)Re			(bb)Re	
	ϕ_{em}	τ (ns)	ϕ_{em}	ϕ_{eff}[c]	τ (ns)	ϕ_{em}	τ (ns)
1,4-DXN[b]	0.046 ± 0.001	670	0.068 ± 0.001	0.11	754	0.081 ± 0.008	362
$CHCl_3$[b]	0.075 ± 0.001	1088	0.086 ± 0.003	0.10	1105	0.137 ± 0.005	748
CH_2Cl_2	0.088 ± 0.002	1015	0.105 ± 0.001	0.14	1148	0.192 ± 0.002	786
1,2-DCE	0.079 ± 0.001	976	0.102 ± 0.001	0.13	989	0.147 ± 0.001	845
THF	0.052 ± 0.002	699	0.060 ± 0.001	0.07	803	0.070 ± 0.006	310
CH_3CN	0.075 ± 0.002	915	0.072 ± 0.002	0.07	942	0.052 ± 0.001	272
EtOH	0.042 ± 0.005	764	0.035 ± 0.001	0.03	617	0.039 ± 0.001	282

[a] $T=25$ °C, error in $\tau=\pm10\%$. [b] $(bpy)_2Ru(bb)^{2+}$ and $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ exhibit low solubility in $CHCl_3$ and 1,4-DXN. [c] $\phi_{eff}=(\phi_{RuRe}^{355}-\alpha_{Re}\phi_{Ru}^{355})/\alpha_{Re}$, Demas and Adamson [20].

$\tau=703$ ns. Similar results were obtained with picosecond excitation.

Discussion

The observed photophysical properties of these materials may be discussed in three broad categories. First is the observed solvent dependencies of the absorption properties. These are apparent in the ruthenium to ligand absorption bands of $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ and $(bpy)_2Ru(bb)^{2+}$. Second is the enhancement of the observed ruthenium centered emission of $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ via energy transfer from the rhenium center to the ruthenium center relative to the emission in $(bpy)_2Ru(bb)^{2+}$. Third are observed spin–orbit coupling effects. These predominate in the photophysics of the rhenium site and therefore manifest themselves in the energy transfer event.

Solvent effects

There are a wide variety of solvent paramcters used to account for properties of compounds and chemical reactivities [14]. Lees and co-workers for example, published a method which allows one to account for solvatochromism in tetracarbonyl complexes of tungsten and molybdenum [11d, e]. The ET-30 factor of Dimroth *et al.* [15] and Kosower's Z factor [16] can be used to account for spectral shifts resulting from optically induced charge separation in organic molecules. In both cases, however, solvent polarities were developed for specific classes of organic molecules. Recently, Kober *et al.* [9d] were able to extend the work of Bayliss [17] and McRae [18] to correlate MLCT absorption energies of $Ru(bpy)_3^{2+}$ in various solvents using the relationship $(1-D_{op})/(2D_{op}+1)$, where D_{op} is the square of the solvent index of refraction, called the effective optical dielectric constant of the solvents.

As shown in Fig. 3, this effective dielectric constant also accounts for the MLCT absorption energy changes in $(bpy)_2Ru(bb)^{2+}$ and $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$. The inset of the Figure shows the apparent lack of a correlation between this constant and the MLCT absorption energies of $(bb)Re(CO)_3py^{1+}$. This failure,

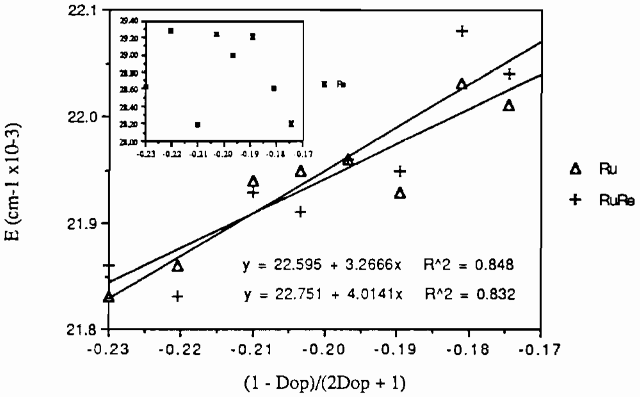

Fig. 3. Correlation between the absorption energy for the low energy MLCT absorption of $[(bpy)_2Ru(bb)]^{2+}$(△) and $[(bpy)_2Ru(bb)Re(CO)_3py]^{3+}$ (+) as a function of the optical dipole, $(1-D_{op})/(2D_{op}+1)$.

however, may be due to the inability to indentify the true MLCT energy maxima. This is a result of significant distortion of the $d\pi \rightarrow \pi^*$ band due to overlap with a $\pi \rightarrow \pi^*$ transition. As shown in Fig. 4, the MLCT absorption maxima reported by Kalyanasundaram [10] for (bpy)Re(CO)$_3$Cl do correlate with the effective dielectric constants of the various solvents. The MLCT absorptions are shifted ~2000 cm^{-1} to the red in (bpy)Re(CO)$_3$Cl compared to (bb)Re(CO)$_3$py^{1+}, thereby reducing the distortion due to spectral overlap with the $\pi \rightarrow \pi^*$ band.

The origin of the solvent dependence is normally attributed to a change in the dipole moment of a complex upon optical excitation, and the consequent disruption of the solvation sphere [14–18]. The solvent surrounding the optically excited complex must respond to accommodate the new equilibrium position by reorienting itself. This reorientation, however, occurs after the absorption event and does not directly influence the absorption energy. This solvent dependence must then involve the pre-equilibrium condition usually referred to as the 'Franck Condon state'. Normally, solvation causes the absorbance to red shift relative to the gas phase, and causes the energy to vary with the effective dielectric constant of the solvent according to the $(1-D_{op})/(2D_{op}+1)$ relationship. The result is a direct relationship between the absorption energy and $(1-D_{op})/(2D_{op}+1)$, i.e. the usual blue shift with decreasing solvent polarity. Thus, the optical dielectric constant is one of numerous solvent factors which shape the ground and excited state manifolds. The extent of its influence would be dependent upon the states involved. For example, the ground state of Ru(bpy)$_3^{2+}$ should be relatively symmetrical with no net dipole moment. Local moments oriented along the metal–nitrogen coordinate axes should be largely shielded from solvent interactions. Consequently, the ground state manifold will be relatively insensitive to solvent. However, the MLCT excited state resultant transient dipole moment would interact strongly with solvent and thus solvent polarity would have significant influence upon the shape of the excited state manifold. Likewise in the case of the ruthenium polypyridyls studied here, the high symmetry of the coordination sphere of the complexes around ruthenium results in a change from a near zero dipole moment to a much larger one upon optical excitation. As noted from the slopes in Fig. 3, the values for the solvent dependence of (bpy)$_2$Ru(bb)$^{2+}$ and (bpy)$_2$Ru(bb)Re(CO)$_3$py^{3+} are comparable to those reported for Ru(bpy)$_3^{2+}$ (3670 cm^{-1}).

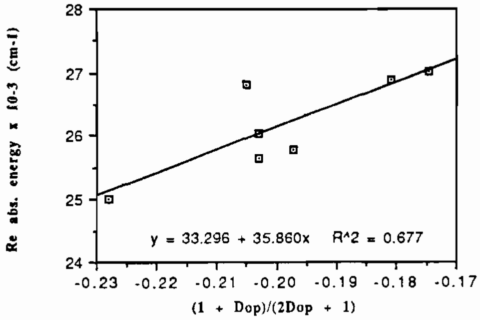

Fig. 4. Correlation between the absorption energy for the low energy MLCT absorption of [(bpy)Re(CO)$_3$Cl] as a function of the optical dipole, $(1-D_{op})/(2D_{op}+1)$.

It is also noteworthy to find a similar solvent dependence for (bpy)Re(CO)$_3$Cl. Unlike Ru(bpy)$_3^{2+}$, rhenium tricarbonyl heterocycles are asymmetric and therefore possess a dipole moment in the ground state. In addition, the carbonyl ligands possess strong local moments which will interact with solvent in a manner not fully accounted for with Bayliss's point dipole treatment of a solvate [19]. Consequently, (bpy)Re(CO)$_3$Cl will have numerous solvent influences upon it both in the ground and excited states. Despite these differences, (bpy)Re(CO)$_3$Cl does follow the same solvent trend as found for (bpy)$_2$Ru(bb)$^{2+}$ and Ru(bpy)$_3^{2+}$. There is every reason to believe (bb)Re(CO)$_3$py^{1+} would also follow the trend as noted above. The most likely reason why this is not observed is due to the distortion in band maxima caused by overlap of the $\pi \rightarrow \pi^*$ transition with the $d\pi \rightarrow \pi^*$ transition.

Similar arguments should hold for the emission energies of these materials but the situation is reversed. No systematic variation in emission energy is observed for the ruthenium complexes, but a correlation inversely proportional to $(1-D_{op})/(2D_{op}+1)$ is found for the monorhenium complex. This is inverse to the relationship observed for the absorption energies of the ruthenium materials. The distinction may be that for the ruthenium complexes, the ground state and excited state interact with solvent in very different ways. Thus, the possibility exists for a more random appearance to the emission energy interaction. In contrast, many of the interactions present in the ground state of the rhenium complex are also present in the excited state of this compound. This similarity between the ground and excited states is perhaps sufficient to simplify the interactions such that a systematic variation with solvent polarity is observed for (bb)Re(CO)$_3$py^{1+}.

Energy transfer

The emission properties can be divided between the observations resulting from 436 and 355 nm excitation, the distinction being the absorption properties of the heterometallic complex at these wavelengths. Upon excitation at either 436 or 355 nm, the emission observed is identifiably that of the ruthenium component, based upon band shape and emission maxima. The excitation spectrum of this emission is a composite of the excitation spectra of the monometallic complexes $(bb)Re(CO)_3py^{1+}$ and $(bpy)_2Ru(bb)^{2+}$. This indicates that energy absorbed by the rhenium component contributes to the ruthenium emission via an energy transfer mechanism [6g]. At 436 nm, only '$(bpy)_2Ru(bb)^{2+}$' has an appreciable absorption of light. Hence emission only occurs from this unit in $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$. The '$(bb)Re(CO)_3py^{1+}$' component can be viewed as a 'spectator'.

Absorption of light at 355 nm by $(bpy)_2Ru(bb)$-$Re(CO)_3py^{3+}$ partitions the light between the rhenium and ruthenium centers. Energy is, however, transferred from the rhenium end of the molecule to the ruthenium chromophore, which then undergoes enhanced emission. This enhanced emission is therefore a summation of the emission intensities due to direct formation of $(bpy^-)(bpy)Ru^{III}(bb)Re(CO)_3py^{3+*}$ itself, plus additional $(bpy^-)(bpy)Ru^{III}(bb)Re(CO)_3py^{3+*}$ resulting from energy transfer from rhenium. Since the ruthenium excited state is achieved by these two pathways, an effective quantum yield (ϕ_{eff}) for emission from $(bpy^-)(bpy)Ru^{III}(bb)Re(CO)_3py^{3+*}$ can be calculated using eqn. (2), previously reported by Demas and Adamson for sensitized emission [20].

$$\phi_{eff} = (\phi_{obs} - \alpha_{Ru}\phi_{Ru})/\alpha_{Re} \qquad (2)$$

The various parameters in eqn. (2) are: ϕ_{eff}, the effective emission quantum yield; ϕ_{obs}, the observed emission quantum yield for the unperturbed emitter (here we use the ϕ_{em} measured for $(bpy)_2Ru(bb)^{2+*}$); α_{Ru}, the fraction of light absorbed by the '$(bpy)_2Ru(bb)^{2+}$' component, α_{Re}, the fraction of light absorbed by the '$(bb)Re(CO)_3py^{1+}$' component of the bimetallic complex, $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$. The values of ϕ_{eff} are listed in Table 4 and range between 0.03 and 0.14.

A necessary consequence of this mechanism is that the concentration of $(bpy^-)(bpy)Ru^{III}(bb)$-$Re(CO)_3py^{3+*}$ is partly dependent upon the efficiency of formation of $(bpy)_2Ru(bb^-)Re^{II}(CO)_3py^{3+*}$, which should be proportional to ϕ_{em} for $(bb)Re(CO)_3py^{1+}$. A plot of ϕ_{eff} versus ϕ_{Re} is shown in Fig. 5. The slope of the line with a zero intercept is 0.84. This plot reveals that the energy transfer process is greater than 80% efficient, which is consistent with experimental observations: no residual emission is observed from the rhenium chromophore in $(bpy)_2Ru(bb^-)$-$Re^{II}(CO)_3py^{3+*}$, transient absorption spectra show no evidence for a rise time in generating the transient species, the bpy^- radicals decay at the same rate as the ruthenium(II) bleach recovery, and the kinetics of transient decay are monoexponential. The conclusion reached is that the energy transfer process is more rapid than emission from rhenium ($k_{ent} > 1/\tau_{Re}$), where k_{ent} is the rate constant for energy transfer and τ_{Re} is the emission lifetime for $(bb^-)Re^{II}(CO)_3py^{3+*}$.

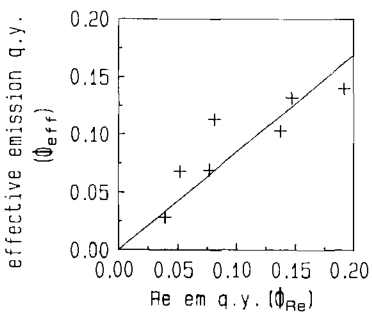

Fig. 5. Relationship between the effective emission quantum efficiency for $[(bpy)_2Ru(bb)Re(CO)_3py]^{3+}$ and the emission quantum efficiency of $[(bb)Re(CO)_3py]^{1+}$.

Spin–orbit coupling

As noted in 'Results', the emission quantum yields were greater for $(bb^-)Re^{II}(CO)_3py^{1+*}$ than for $(bpy)(bpy^-)Ru^{III}(bb)^{2+*}$, yet the emission lifetimes were less by about a factor of two. An explanation using eqns. (3) and (4) can be given, based on the treatment of Caspar and Meyer [9e]. Equation (3) relates the emission quantum yield (ϕ_{em})

$$\phi_{em} = \eta_{isc} k_r \tau_{em} \qquad (3)$$

$$1/\tau_{em} = k_r + k_{nr} \qquad (4)$$

to the intersystem crossing quantum yield, η_{isc}; the radiative rate constant, k_r; and the emission lifetime, τ_{em}. These equations are only valid for $\eta_{isc} = 1$. For $Ru(bpy)_3^{2+}$, η_{isc} has been shown to be near one [21]. For rhenium, others have also assumed it to be near one [22]. Within these constraints, approximation of the radiative (k_r) and non-radiative (k_{nr}) rate constants can be made using eqns. (3) and (4). Results of calculations of both k_r and k_{nr} for $(bpy)_2Ru(bb)^{2+}$ and $(bb)Re(CO)_3py^{1+}$ listed in Table 5 indicate that both constants are two to three times larger for emission decay from $(bb)Re(CO)_3py^{1+}$ than from $(bpy)_2Ru(bb)^{2+}$. The reason for the larger k_r and k_{nr} is most likely due to greater spin–orbit coupling in rhenium [23], analogous to the photophysical difference between $Ru(bpy)_3^{2+*}$ and $Os(bpy)_3^{2+*}$ [24]. The greater emission quantum yield for rhenium is probably due to the greater energy separation between the excited and ground states of rhenium. According to the energy gap law [25], this should retard k_{nr} somewhat and thereby improve the ratio of k_r to $(k_r + k_{nr})$.

Conclusions

The MLCT absorption properties of the ruthenium centers follow typical solvatochromic effects, but the rhenium centers fail to respond in a similar manner

TABLE 5. Radiative (k_r) and non-radiative (k_{nr}) decay rates of $(bpy)_2Ru(bb)^{2+}$, $(bpy)_2Ru(bb)Re(CO)_3py^{3+}$ and $(bb)Re(CO)_3py^{1+}$ in various solvents ($\lambda_{ex}=355$ nm)[a]

Solvent	Ru(bb)		Ru(bb)Re[b]		(bb)Re	
	$k_r\times10^{-4}$ (s^{-1})	$k_{nr}\times10^{-6}$ (s^{-1})	$k_r\times10^{-5}$ (s^{-1})	$k_{nr}\times10^{-6}$ (s^{-1})	$k_r\times10^{-5}$ (s^{-1})	$k_{nr}\times10^{-6}$ (s^{-1})
1,4-DXN	6.87	1.42	1.50	1.18	2.24	2.54
$CHCl_3$	6.89	0.85	0.93	0.81	1.83	1.15
CH_2Cl_2	8.67	8.99	1.22	0.75	2.44	1.03
1,2-DCE	8.09	0.94	1.33	0.88	1.74	1.01
THF	7.44	1.36	0.86	1.16	2.26	3.00
CH_3CN	8.20	1.01	0.72	0.99	1.91	3.49
EtOH	5.50	1.25	0.45	1.58	1.38	3.41

[a] η_{isc} assumed to be unity, $T=25$ °C, error ± 20%. [b] Calculation uses ϕ_{eff} in place of ϕ_{em}.

due to our inability to decipher the true MLCT energy maxima. Generally, absorption energy maxima parallel the solvent parameter $(1-D_{op})/(2D_{op}+1)$, but an inverse dependence was observed for the emission energies of the rhenium complex. To our knowledge, this is the first report of an emission energy dependence and may be only a fortuitous result due to cancellation of a number of effects. In the bimetallic complex, the energy transfer mechanism was found to be at least 80% efficient and rapid, such that no direct solvent effects were observed for this process. However, the efficiency of the energy transfer process may indicate that solvent affects the extent to which energy transfer takes place by moderating the potential energy surface of the rhenium excited state.

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