

Photophysics of ruthenium(II) complexes with 2-(2'-pyridyl)pyrimidine and 2,2'-bipyridine ligands in fluid solution

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Received 27 March 1996; received in revised form 11 June 1997; accepted 12 June 1997

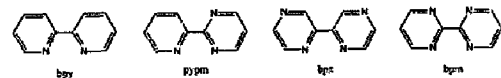
Abstract

The photophysics of three complexes of the form $\text{Ru}(\text{bpy})_{3-p}(\text{pypm})_p^{2+}$ (where $\text{bpy} \equiv 2,2'$ -bipyridine, $\text{pypm} \equiv 2$ -(2'-pyridyl)pyrimidine and $p = 1, 2$ or 3) was examined in H_2O , propylene carbonate, CH_3CN and $4 : 1$ (v/v) $\text{C}_2\text{H}_5\text{OH}-\text{CH}_3\text{OH}$; comparison was made with the well-known photophysical behavior of $\text{Ru}(\text{bpy})_3^{2+}$. The lifetimes of the luminescent metal-to-ligand charge transfer (MLCT) excited states were determined as a function of temperature (between -103 and 90 °C, depending on the solvent), from which were extracted the rate constants for radiative and non-radiative decay and ΔE , the energy gap between the MLCT and metal-centered (MC) excited states. The results indicate that $^*\text{Ru}(\text{bpy})_2(\text{pypm})^{2+}$ decays via a higher lying MLCT state, whereas $^*\text{Ru}(\text{pypm})_3^{2+}$ and $^*\text{Ru}(\text{pypm})_2(\text{bpy})^{2+}$ decay predominantly via the MC state. © 1997 Elsevier Science S.A.

Keywords: Energy gap; Excited states; Photophysics; Ruthenium complexes

1. Introduction

The photophysics of Ru(II) complexes containing 2-(2'-pyridyl)pyrimidine (pypm) and 2,2'-bipyridine (bpy) ligands has been examined in organic solvents [1]. Because of our interest in Ru(II) photosensitizers containing N-heteroatoms on the periphery of the ligands, such as 2,2'-bipyrazine (bpz) and 2,2'-bipyrimidine (bpm), which enable the complexes to undergo protonation in the ground and excited states and in the one-electron-reduced forms [2–13], we recently investigated the acid–base and electrochemical behavior of $\text{Ru}(\text{bpy})_2(\text{pypm})^{2+}$, $\text{Ru}(\text{pypm})_2(\text{bpy})^{2+}$ and $\text{Ru}(\text{pypm})_3^{2+}$ in aqueous solution [14]. In order to use these complexes as photosensitizers in neat and mixed solvents, it is necessary to know the details of the kinetics of decay of the metal-to-ligand charge transfer (MLCT) excited states and their temperature dependence.



In this study, the photophysics of three complexes of the form $\text{Ru}(\text{bpy})_{3-p}(\text{pypm})_p^{2+}$, where $p = 1, 2$ or 3 , was examined in H_2O , propylene carbonate, CH_3CN and $4 : 1$ (v/v) $\text{C}_2\text{H}_5\text{OH}-\text{CH}_3\text{OH}$ as a function of temperature; comparison was made with the well-known photophysical behavior of $\text{Ru}(\text{bpy})_3^{2+}$.

2. Experimental details

2.1. Materials

$\text{Ru}(\text{bpy})_2(\text{pypm})^{2+}$, $\text{Ru}(\text{pypm})_2(\text{bpy})^{2+}$ and $\text{Ru}(\text{pypm})_3^{2+}$, as their PF_6^- salts, were synthesized as described previously [1]; for convenience, these complexes will be referred to as yyp, ppy and ppp respectively. $\text{Ru}(\text{bpy})_3^{2+}$ (yyy) was available in our laboratory supplies. Propylene carbonate (Aldrich) was fractionally distilled three times. CH_3CN (Baker, high performance liquid chromatography (HPLC) grade), CH_3OH (Mallinkrodt, spectrophotometric grade) and $\text{C}_2\text{H}_5\text{OH}$ (Pharmco) were used without further purification. Aqueous solutions were prepared from doubly distilled water that had been passed through a Millipore purification train.

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2.2. Equipment

Absorption spectra were obtained with a Hewlett Packard 8452A diode array spectrophotometer. Emission spectra and quantum yield measurements were performed at ambient temperature (25 °C) on Ar-purged solutions using an SLM phase-shift spectrofluorometer ($\lambda_{ex} = 450$ nm); corrections of the emission spectra for the phototube response were made by the program supplied with the instrument. The values of the quantum yields of emission were obtained relative to that of $Ru(bpy)_3^{2+}$ in the solvent of interest [15]. Emission lifetime measurements were performed using an Nd:YAG pulsed laser ($\lambda_{ex} = 532$ nm; 100 mJ per pulse) and a red filter in front of the monochromator slit; details of the apparatus have been described previously [16]. The output voltage of the photomultiplier (Hamamatsu R928) was controlled to produce a linear response, and the data were averaged for 20 shots.

2.3. Procedures

In the lifetime experiments, all solutions (Ar-purged or air-equilibrated) were contained in 1 cm \times 1 cm or 2 cm \times 1 cm cells; in the latter case, they were excited along the shorter path and interrogated along the longer one. The temperature of the solutions was controlled in the range (5–90) \pm 0.1 °C with a thermostatically maintained circulating water bath; below 5 °C, the temperature was established with an Oxford Instruments controller (\pm 1 °C) connected to a liquid N₂ cryostat. Excited state lifetimes (τ_0) were determined as a function of temperature on Ar-purged solutions (H₂O, CH₃CN, propylene carbonate, 4:1 (v/v) C₂H₅OH-CH₃OH) containing approximately 10 μ M of complex ($\lambda_{exc} = 630$ nm). Values of the first-order rate constant of excited state decay ($k_0 = 1/\tau_0$) were obtained from the average of three duplicate solutions at each temperature; measurements were repeated at least three times on different days with good agreement (\pm 5%).

3. Results

3.1. Temperature dependence of excited state lifetimes

The emission maxima (λ_{max}), quantum yields (Φ_{em}) and τ_0 values in all four solvent systems are given in Table 1; the corrected emission spectra in aqueous solution are shown in Fig. 1. The values of Φ_{em} for all three pyrm complexes in CH₃CN are lower than those previously found in this solvent [1], although the value for ppp is in reasonable agreement with that reported earlier [17]. In general, λ_{max} , Φ_{em} and τ_0

Table 1
Values of λ_{max} , Φ_{em} and τ_0 as a function of the solvent at 25 °C

Complex	λ_{max} (nm) ^a	Φ_{em} ^b	τ_0 (μ s)
H ₂ O			
ppp	630	0.019	0.18
ppy	647	0.0049	0.14
yyp	661	0.0031	0.086
yyy	617	0.042 ^c	0.58
Propylene carbonate			
ppp	618	0.013	0.18
ppy	632	0.038	0.36
yyp	642	0.070	0.36
yyy	617	0.071 ^c	0.96
CH ₃ CN			
ppp	614	0.0065	0.12
ppy	623	0.0097	0.36
yyp	641	0.023	0.39
yyy	618	0.062 ^c	0.90
4:1 C ₂ H ₅ OH-CH ₃ OH			
ppp	616	0.0030	0.15
ppy	630	0.0046	0.31
yyp	641	0.012	0.35
yyy	608	0.042 ^d	0.68

^a From corrected spectra.

^b Error, \pm 10%; $\lambda_{ex} = 450$ nm.

^c Φ_{em} from reference compound in specific solvent [15].

^d Φ_{em} assumed to be the same as in water.

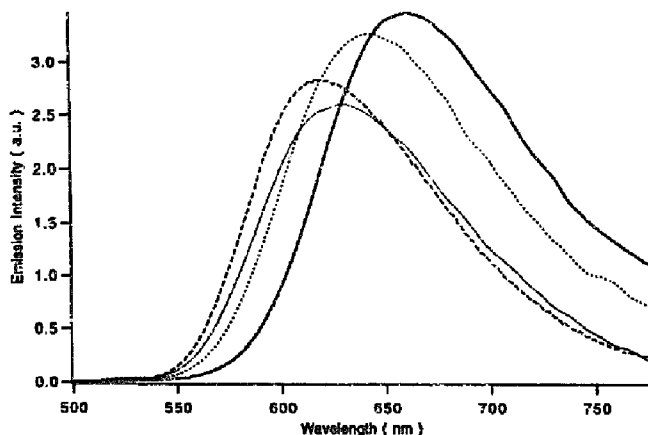


Fig. 1. Corrected emission spectra in aqueous solution at 25 °C: yyy (---), yyp (—), ppy (···), ppp (- · - ·).

increase in the order $ppp < ppy < yyp$; however, in H_2O , τ_0 increases in the opposite order. In all solvents, yyp exhibits the largest values of Φ_{em} and τ_0 , and among the lowest values of λ_{max} . The temperature dependences of τ_0 were determined in the range -103 – $90^\circ C$ as appropriate for the four solvent systems. The results are given in Table 2.

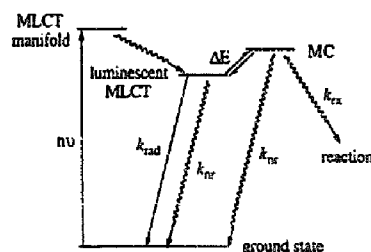
Table 2
Temperature and solvent dependence of τ_0

T ($^\circ C$)	τ_0 (μs)			
	yyy	yyp	ppy	ppp
H_2O				
5	0.704	0.090	0.148	0.214
10	0.667	0.092	0.146	0.228
15	0.649	0.089	0.146	0.198
20	0.633	0.090	0.142	0.196
25	0.578	0.082	0.144	0.176
35	0.505	0.079	0.128	0.136
40	0.474	0.075	0.121	0.120
45	0.420	0.076	0.120	0.108
50	0.372	0.076	0.112	0.089
55	0.322	0.075	0.100	0.072
65	0.246	0.071	0.086	0.054
75	0.174	0.073	0.081	0.037
80	0.140	0.065	0.072	0.029
90	0.106	0.067	0.063	0.024
CH_3CN				
-33	1.85	0.578	0.787	1.12
-18	1.78	0.662	0.757	1.02
-3	1.72	0.671	0.699	0.806
5	1.39	0.440	0.538	0.338
10	1.25	0.438	0.474	0.258
15	1.19	0.448	0.431	0.200
20	1.03	0.429	0.400	0.157
25	0.900	0.394	0.356	0.119
35	0.621	0.376	0.262	0.089
45	0.405	0.306	0.183	0.052
55	0.250	0.288	0.125	0.035
Propylene carbonate				
-33	1.59	0.515	0.694	0.947
-18	1.51	0.515	0.629	0.794
-3	1.45	0.515	0.552	0.666
5	1.37	0.389	0.485	0.370
10	1.28	0.380	0.532	0.298
15	1.19	0.365	0.469	0.270
20	1.08	0.382	0.398	0.219
25	0.962	0.362	0.355	0.178
35	0.725	0.338	0.273	0.108
45	0.560	0.313	0.177	0.050
55	0.333	0.250	0.119	0.034
4 : 1 $C_2H_5OH-CH_3OH$				
-103	1.72	0.398		0.585
-83	1.82	0.397	0.617	0.606
-63	1.85	0.397	0.617	0.602
-43	1.78	0.395	0.568	0.588
-23	1.72	0.395	0.549	0.588
-3	1.67	0.394	0.532	0.555
5	1.27	0.395	0.424	0.332
10	1.12	0.391	0.395	0.265
15	0.980	0.380	0.333	0.230
20	0.813	0.362	0.292	0.192
25	0.685	0.346	0.274	0.151
35	0.444	0.316	0.205	0.096
45	0.284	0.257	0.139	0.062
55	0.181	0.199	0.093	0.040

4. Discussion

4.1 Photophysics

The general model of the photophysics of $Ru(II)$ complexes involves excitation into the MLCT manifold, relaxation to the luminescent MLCT state and deactivation of the latter via radiative and non-radiative decay to the ground state in competition with thermally activated up-conversion to the metal-centered (MC) excited state; this latter state can repopulate the MLCT state, deactivate to the ground state or undergo chemistry to yield photoproducts [1,18–24].



The lifetime data obtained experimentally can be fitted most satisfactorily to Eq. (1)

$$k_0 = 1/\tau_0 = k_1 + k_2 \exp(-\Delta E/kT) \quad (1)$$

where $k_1 = k_{rad} + k_{nr}$ and $k_2 \exp(-\Delta E/kT) = k'$ is the overall rate constant for the population of the MC state. Since $\Phi_{em} = k_1 \tau_0$, all the information can be obtained from a knowledge of Φ_{em} and the measurement of τ_0 as a function of temperature, assuming that k_{rad} is independent of temperature. Since k_1 is independent of temperature above 120 K for $Ru(II)$ polypyridyl complexes, including yyy , this is a reasonable assumption [15,23,25–28].

For complexes in which the MC states play a significant role in dictating the temperature dependence of the luminescence lifetimes, typical values of the parameters in Eq. (1) are $k_1 \sim 10^6 s^{-1}$, $k_2 \sim 10^{12}–10^{14} s^{-1}$ and $\Delta E \sim 2500–4500 cm^{-1}$ [23]; ΔE is interpreted as the activation barrier for $MLCT \rightarrow MC$ conversion and k' is the rate constant of barrier crossing. For some mixed chelate complexes of $Ru(II)$ [1,19,20,23,27–31], Eq. (1) adequately describes the temperature-dependent lifetimes, but the kinetic parameters are strikingly different from the values typically found for $MLCT \rightarrow MC$ conversion; the absence of photosubstitution suggests that MC states are not responsible for the temperature dependence. It has been proposed for these cases that the temperature dependence arises from an additional decay channel involving the population and depopulation of an additional ("fourth") MLCT state [19,20,23,30,31]; typical values are $k_1 \sim 10^6 s^{-1}$, $k_2 \sim 10^6–10^8 s^{-1}$ and $\Delta E \sim 300–800 cm^{-1}$ [23].

Fig. 2 shows a plot of $\log k_0$ vs. $1/T$ for the $pypm$ complexes and yyy in H_2O ; similar plots were obtained for the

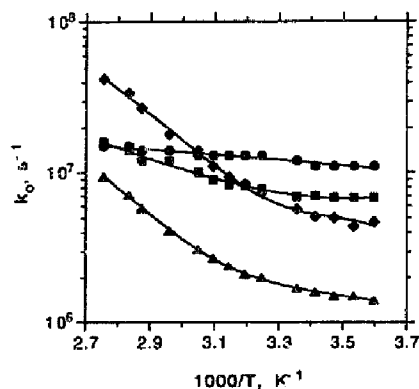


Fig. 2. Plot of $\log k_0$ vs. $1/T$ for ypp (\bullet), ppy (\blacksquare), ppp (\blacklozenge) and yyy (\blacktriangle) in H_2O .

other three solvent systems. A fit of the data to Eq. (1) permits the evaluation of k_1 , k_2 , k_{rad} and k_{nr} ; the values of k_2 are much less reliable than those of ΔE due to the difficulties inherent in the fitting of linked pre-exponential and exponential terms to a restricted number of points over a limited temperature range, which is unavoidable for these solvent systems. These limitations restrict the absolute numerical significance of the values of k_2 and ΔE , but the relative values, and hence the trends, remain significant.

Literature values were reproduced for ppp in 4:1 $C_2H_5OH-CH_3OH$ [1]. In addition, our determination of k_0 for $Ru(bpm)_3^{2+}$ as a function of temperature in 4:1 $C_2H_5OH-CH_3OH$ yielded values of k_1 , k_2 and ΔE that were similar to those obtained for ppp, as may be expected because of the similarity of the ligand structures.

For ppy in 4:1 $C_2H_5OH-CH_3OH$, significantly different values of k_2 and ΔE were obtained than reported in the literature [1]. The error does not lie in the nature of the fitting programs used since the literature parameters are obtained if the literature data are used. Furthermore, the error is not a result of a discrepancy in the values of k_0 , which are similar to those in the literature over the same temperature range. Rather, the range was extended to higher temperatures in this study, which yielded different values of k_2 and ΔE ; in experiments of this type, it is necessary to make the temperature range as large as possible, consistent with the nature of the solvent systems used.

For ypp, the weak temperature dependence of k_0 does not permit k_2 or ΔE to be calculated with confidence from Eq. (1). Instead, an alternative approach was taken for this complex, whereby k_2 and ΔE were estimated from the Arrhenius equation in the manner of Kawanishi et al. [17]; the values are of the order of $10^7 s^{-1}$ and $500 cm^{-1}$ respectively, with a good fit in H_2O , but a less satisfactory fit in propylene carbonate and CH_3CN . In 4:1 $C_2H_5OH-CH_3OH$, a non-linear Arrhenius plot was found, making the values of k_2 and ΔE for ypp in this solvent unobtainable.

A similar behavior of the photophysical parameters has been reported for other heteroleptic bpy systems with the

Table 3
Photophysical parameters of pybm complexes and $Ru(bpy)_3^{2+}$

Complex	k_1 ($10^6 s^{-1}$)	k_2 (s^{-1})	k_{rad} ($10^6 s^{-1}$)	k_{nr} ($10^6 s^{-1}$)	ΔE (cm^{-1})
H_2O					
ppp	3.2	1×10^{11}	1.0	3.1	3200
ppy	6.3	5×10^{11}	0.34	6.3	2700
yyp	10	4×10^7	0.36	10	300
yyy	1.4	3×10^{13}	0.75	1.3	3800
Propylene carbonate					
ppp	1.0	9×10^{14}	0.73	0.93	3900
ppy	1.6	2×10^{14}	1.1	1.5	4000
yyp	1.7	2×10^7	1.9	1.5	440
yyy	0.64	1×10^{14}	0.74	0.57	4000
CH_3CN					
ppp	0.4	2×10^{13}	0.55	0.31	3000
ppy	1.3	1×10^{14}	0.27	1.3	3300
yyp	1.3	5×10^7	0.58	1.2	600
yyy	0.56	3×10^{14}	0.69	0.49	4200
4:1 $C_2H_5OH-CH_3OH$					
ppp	1.6	1×10^{14}	0.20	1.6	3500
ppy	1.7	3×10^{13}	0.15	1.7	3400
yyp	2.5		0.34	2.5	
yyy	0.55	1×10^{14}	0.61	0.49	3850

same substitution patterns [32]. The values for yyp agree with those for other complexes in which the parameters for the mono-bpy complex are approximately the same as those for the complex which does not contain bpy.

The photophysical parameters are given in Table 3. The values for yyy are in excellent agreement with those reported previously [10], and indicate that the luminescent MLCT state undergoes deactivation via the MC state in fluid solution; this point is well established in the literature [23].

The values of k_2 and ΔE suggest that the decay of the luminescent state of yyp is via a higher lying MLCT state; the values of the kinetic parameters for ppp indicate that the dominant decay pathway for this complex is via the MC state. Although the deactivation route for ppy has been described previously in terms of an MLCT mechanism [1], the extended temperature range utilized in this study shows that the decay follows the MC mechanism.

Insight into the possible reason why the MLCT state of yyp decays via thermal activation to an upper MLCT state, whereas ppy and ppp do so via the MC state, comes from the recent work of Sykora and Kincaid [29], who examined the excited state decays of the corresponding bpz and bpy complexes in propylene carbonate. In $Ru(bpz)_3^{2+}$, the MLCT \leftrightarrow MC energy gap is sufficiently small, allowing this pathway to dominate. For $Ru(bpy)_2(bpz)^{2+}$, where two of the bpz ligands are replaced by the relatively strong field bpy ligand, the MC state is sufficiently destabilized so as to render it inaccessible, shifting the decay mechanism to the "fourth" MLCT state. As noted earlier [19], the parameters for $Ru(bpz)_2(bpy)^{2+}$ are intermediate to the other members of the series, which may reflect the participation of both thermally accessible upper states. Other heteroleptic Ru(II) com-

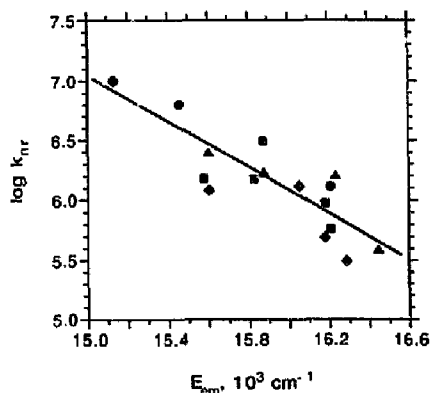


Fig. 3. Plot of $\log k_{nr}$ vs. E_{em} for the complexes in H_2O (●), propylene carbonate (■), CH_3CN (◆) and 4 : 1 $C_2H_5OH-CH_3OH$ (▲).

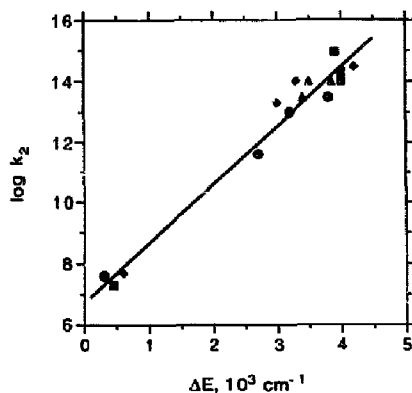


Fig. 4. Barclay-Butler plot ($\log k_2$ vs. ΔE) for the complexes in H_2O (●), propylene carbonate (■), CH_3CN (◆) and 4 : 1 $C_2H_5OH-CH_3OH$ (▲).

plexes with two bpy ligands apparently decay via the "fourth" MLCT state [19,20,23,30,31], whereas yyy decays via the MC state [23].

The effect of the solvent on k_{nr} can be discussed in terms of the energy gap law for radiationless transitions, which predicts an exponential dependence of k_{nr} on the emission energy (E_{em}) [18,19,22–24]. A linear relationship between $\log k_{nr}$ and E_{em} for metal complexes has been verified with a series of related chromophores in a common solvent [22], and for the same chromophore in different solvents [15,24]. A plot of $\log k_{nr}$ vs. E_{em} in the four solvents used here (Fig. 3) shows the expected dependence, albeit over a relatively small range of E_{em} values.

Similarly, solvent effects on k_{rad} are also related to E_{em} by the Einstein coefficient for spontaneous emission, which predicts that k_{rad} should vary as the cube of E_{em} if the dipole matrix element for the transition is constant [33]. Since the range of E_{em} for the complexes in the solvent systems is small, k_{rad} is expected to be relatively insensitive to the variation in the solvent; indeed, the data in Table 3 show that this is so.

Despite the large uncertainties in the values of k_2 , a plot of $\log k_2$ vs. ΔE is linear (Fig. 4); a similar relationship has

been found previously for an extended series of mixed-ligand and tris complexes of bpz, bpm, bpy and pybm in propylene carbonate and 4 : 1 $C_2H_5OH-CH_3OH$ [1]. This linear Barclay-Butler correlation indicates that an increase in the activation energy is accompanied by an increased density of vibrational levels at the point of the crossing of the barrier, thereby opening up a larger number of deactivation channels [34].

Acknowledgements

This research was supported in part by the Division of Chemical Sciences, US Department of Energy, through Grant Nos. DE-FG02-86ER13603 (M.Z.H.) and DE-FG02-94ER14484 (D.P.R.), and in part by the Consiglio Nazionale delle Ricerche of Italy (Progetto Finalizzato Chimica Fine II e Progetto Strategico Tecnologie Chimiche Innovative).

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