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Ground and excited state characterization of self-assembled Ru^{II}-*tris*-bipyridine-iron porphyrin complexes

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Abstract

The ability to couple the well known excited state redox properties of Ru^{II}(bpy)$_3$ (bpy = 2,2′-bipyridyl) with the catalytic attributes of metalloporphyrins is of specific importance in designing efficient energy conversion systems. In this study, we report the quenching of the Ru^{II}(bpy)$_3$ metal-to-ligand charge transfer excited state (^{3}MLCT) by Fe^{III}-*meso*-tetra(4-Sulfanatophenyl)porphyrin (Fe^{III}4SP) in aqueous solution. Our results indicate that Fe^{III}4SP forms a 1 : 1 complex with Ru^{II}(bpy)$_3$ under low ionic strength conditions (5 mM HEPES, pH 7) with a binding constant of $(1.5\pm0.01)\times10^4$ M^{-1}. Complexation leads to extensive quenching of the ^{3}MLCT state of the Ru^{II}(bpy)$_3$ with $k_q \approx 5\times10^9$ M^{-1} s^{-1}. In contrast, at higher ionic strengths ($\mu = 500$ mM) or when the anionic Ru^{II}(dcbpy)$_3$ (dcbpy = 4,4′-dicarboxy 2,2′-bipyridine) is used the ruthenium excited state quenching is purely diffusional and no evidence for complexation is observed. Time resolved fluorescence data reveals a life time of Ru^{II}(bpy)$_3$ within the complex on the order of 10 ps in air saturated solutions. These results demonstrate extremely facile electron transfer within self-assembled complexes of Ru^{II}(bpy)$_3$ and Fe^{III}4SP. © 1997 Elsevier Science S.A.

Keywords: Porphyrin; Ruthenium tris-bipyridine; Electron transfer

1. Introduction

Ruthenium(II) complexes containing a variety ligands have long been exploited as photo-active redox reagents due to the long lifetime and high redox potential of their excited-states [1–5]. In fact studies involving Ru^{II}(L)$_3$ (L = 2,2′-bipyridine, 1,10-phenanthroline, etc.) have made some of the most significant contributions to the understanding of fundamental mechanisms of electron transfer reactions in chemistry and biology. A majority of these studies have involved the examination of diffusionally controlled or fixed distance redox reactions between the excited Ru^{II}(L)$_3$ metal-to-ligand charge transfer state (MLCT) and both inorganic and organic quenchers [1–6]. Photo-induced electron transfer between non-covalent self-assembled donor–acceptor complexes is now gaining wide interest since a number of physiologically important electron transfer reactions proceed via non-covalent pathways [7–12].

Self-assembled complexes between ionic metalloporphyrins and Ru^{II}(L)$_3$ complexes represent an attractive system with which to investigate fundamental aspects of electron transfer associated with non-covalent complexes as well as to develop novel porphyrin-based photocatalysts. The versatility of these complexes arises from the ability to systematically alter the structure and electronic environment of both the electron donor (excited-state Ru^{II}(L)$_3$) and electron acceptor (iron porphyrin) either by changing the nature of the Ru^{II}–Fe coordination or through modification of the porphyrin ring substituents. Within the framework of Marcus theory this allows for a detailed analysis of reaction driving force, donor–acceptor orientation, inner and outer sphere reorganization, and electronic coupling on the rate of electron transfer within the self-assembled complex [13].

With this in mind we have examined the ground- and excited-state optical properties of solutions containing Ru^{II}(L)$_3$ (L = 2,2′-bipyridine (bpy) or 2,2′-dicarboxybipyridine (dcbpy)) and the water soluble anionic Fe^{III}-tetrakis(4-sulphonatophenyl) porphyrin (Fe^{III}4SP) under varying ionic strength conditions. Under low ionic strength conditions complexation between the Fe^{III}4SP and and Ru^{II}(bpy)$_3$ is observed with a 1 : 1 stoichiometry. In addition, complexation results in extensive quenching of the Ru^{II}(bpy)$_3$ MLCT excited state with $k_q \approx 5\times10^9$ M^{-1} s^{-1}. Time resolved fluorescence data indicates very fast excited state deactivation (10 ps) of the MLCT of complexed Ru^{II}(bpy)$_3$. Examination of the thermodynamics suggests photo-induced electron transfer from Ru^{II}(bpy)$_3$ to Fe^{III}4SP as the most likely source of deactivation.

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2. Materials and methods

$Ru^{II}(bpy)_3$ was prepared from $Ru^{III}Cl_3$ (Aldrich) and 2,2′-bipyridyl (Aldrich) according to previous methods [14]. $Fe^{III}4SP$ (Porphyrin Products) and HEPES (Sigma) were used without further purification. $Ru^{II}(bpy)_3$ and $Fe^{III}4SP$ stock solutions were prepared by dissolving solid material in 5 mM HEPES, pH 7.0 to give a final concentration of 16 mM ($Ru^{II}(bpy)_3$) and 3.5 mM ($Fe^{III}4SP$). Concentrations of stock solutions were determined using $\epsilon_{453\,nm} = 14.0$ $mM^{-1}\,cm^{-1}$ for $Ru^{II}(bpy)_3$ and $\epsilon_{398\,nm} = 155$ $mM^{-1}\,cm^{-1}$ for $Fe^{III}4SP$ [14,15].

Samples for absorption difference measurements were prepared by diluting appropriate aliquats of each stock solution to 10 μM in 5 mM HEPES, pH 7.0. 1 ml of each dilution was then placed in each side of a quartz tandem mixing cell (total pathlength is 1 cm) that is subsequently sealed with a Teflon cover and the absorption spectrum recorded. The tandem cell was then inverted to allow mixing of the two components. After a 20 min incubation period to allow for equilibration, the absorption spectrum of the mixed solutions was recorded. The optical difference spectrum was obtained by subtracting the spectrum obtained prior to mixing from that obtained after mixing.

Emission titrations were carried out by diluting an aliquat of the $Ru^{II}(bpy)_3$ to 20 μM in 5 mM HEPES, pH 7.0 in an 0.5 cm quartz optical cell that was then sealed with a septum. The solution was then deoxygenated by purging the sample with a stream of Ar for 20 min. An aloquat of the porphyrin stock solution was placed into a separate vial that was subsequently sealed with a septum and deoxygenated with an Ar stream for 20 min. The titrations were performed using a gas tight Hamilton syringe.

Optical absorption measurements were performed using a Milton-Roy Spectronic 3000 diode array spectrophotometer. Emission intensity and lifetime measurements were carried out by exciting the sample with a 532 nm pulse (7 ns, 150 mJ) from the second harmonic of a Q-switched Nd:YAG laser (Surelite II, Continium). The transient emission was imaged onto the entrance slit of a SPEX 1680B double monochrometer centered at 600 nm. The signal was detected using a Hamamtsu R928 photomultiplier tube and amplified using a 500 MHz pre-amplifier of our own design. The signal was recorded using an RTD-710A 200 MHz transient digitizer (Tecktronix). The digitzed signal was transfered and manipulated on an IBM 486DX-based personal computer. Transient emission profiles were fit to a single exponential function using Enzfitter™ software. Emission values (I) used for the Stern–Volmer plots were obtained by extrapolating the exponential decay functions to time $t = 0$. Transient were the average of 10 laser pulses.

Time resolved fluorescence measurements were performed using an ISSK2 multifrequency and phase modulation spectrofluorimeter (Champaign, IL) equipped with an Ar ion laser (SpectraPhysics Model 2045) as the excitation source. Data were collected with the 514 nm emission line (see Ref. [16] for a description of phase and modulation time resolved fluorescence methods). The concentration of $Ru^{II}(bpy)_3$ was 10 μM while the concentration of $Fe^{III}4SP$ was varied between 2 and 18 μM. Emission lifetimes were extracted using software provided by ISS.

3. Results and discussion

The ground-state absorption spectrum of a solution containing an equimolar mixture of $Ru^{II}(bpy)_3$ (bpy = 2,2′-bipyridine) and $Fe^{III}4SP$ in 5 mM HEPES buffer, pH 6.0 is displayed in Fig. 1, Panel A. This spectrum exhibits absorption maxima at 273 nm (bpy π–π^* transition), 399 nm (Soret maximum for $Fe^{III}4SP$), 455 nm ($Ru^{II}(bpy)_3$ metal-to-ligand charge transfer absorption band, MLCT), and 530 nm (α-band for $Fe^{III}4SP$). The position of the Soret absorption band of the $Fe^{III}4SP$ is indicative of the monomeric form

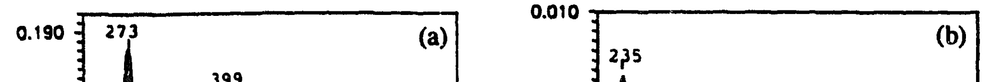

Fig. 1. Panel A: Optical absorption spectrum of (a) a solution containing equimolar concentrations of $Ru^{II}(bpy)_3$ and $Fe^{III}4SP$ (5 μM) in 5 mM HEPES pH 6.0 and (b) a spectrum composed of a mathematical sum of the absorption spectra obtained for individual solutions of 5 μM $Ru^{II}(bpy)_3$ and 5 μM $Fe^{III}4SP$ in 5 μM HEPES pH 6.0. Panel B: Optical difference spectra ($Ru^{II}(bpy)_3$–$Fe^{III}4SP$ solution spectrum minus $Ru^{II}(bpy)_3$–$Fe^{III}4SP$ mathematically composed spectrum) obtained for solutions containing (a) 5 mM HEPES pH 6.0 and (b) 5 mM HEPES pH 6.0 + 250 mM NaCl. Spectra were recorded in a 1-cm quartz optical cuvette.

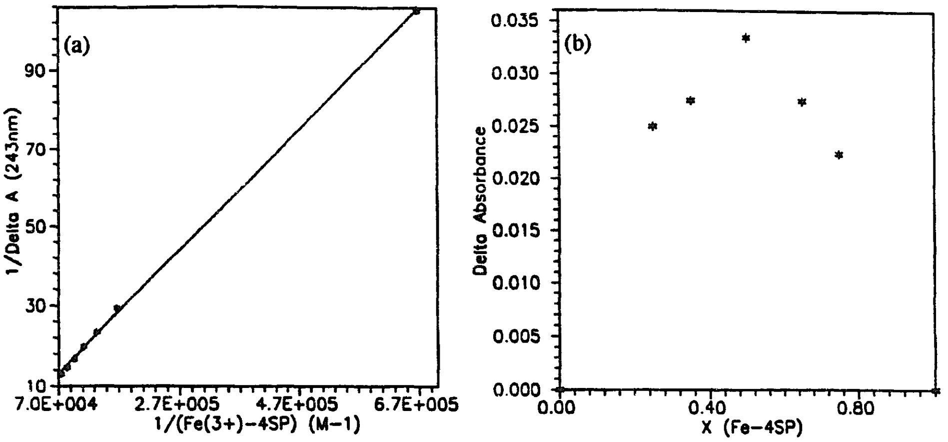

Fig. 2. Panel A: Double recipricol plot of the change in absorbance at 398 nm versus concentration of Ru^{II}(bpy)$_3$. Initial Fe^{3+}4SP concentration is 5 μM. Solution conditions are the same as described in Fig. 1. Panel B: Molar fraction plot of the change in absorbance at 398 nm versus concentration of Ru^{II}(bpy)$_3$.

of the porphyrin [15]. Comparison of this absorption spectrum to a spectrum composed of a mathematical sum of the absorption spectrum of Fe^{III}4SP and Ru^{II}(bpy)$_3$ ('uncomplexed' spectrum) reveals systematic shifts in absorption bands of both the Fe^{III}4SP and Ru^{II}(bpy)$_3$ in the mixture. This is most evident in the absorption difference spectrum displayed in Fig. 1, Panel B. The absorption blue-shift observed in the 200 to 350 nm as well as the red-shift observed between 430 and 480 nm are attributed to perturbations in the Ru^{II}(bpy)$_3$ complex while red-shifts observed between 520 and 580 nm and the absorption decrease observed at 390 nm can be assigned as perturbations to the porphyrin electronic environment. In contrast, a solution containing equimolar concentrations of Ru^{II}(bpy)$_3$ and Fe^{III}4SP in 5 mM HEPES containing 250 mM NaCl or equimolar concentrations of Ru^{II}(dcbpy)$_3$ (dcbpy = 4,4′-dicarboxybipyridine) and Fe^{III}4SP in 5 mM HEPES show no spectral changes relative to 'uncomplexed' Fe^{III}4SP/Ru^{II}(L)$_3$ spectrum. This indicates that the Ru^{II}(bpy)$_3$ and Fe^{III}4SP form electrostatic complexes under low ionic strength conditions. Examination of the absorption change as a function concentration (Fig. 2, Panel A) and the corresponding plot of absorption change versus mole fraction (Fig. 2, Panel B) yield an association constant of $(1.5 \pm 0.012) \times 10^4$ M^{-1} and a 1:1 stoichiometry.

The excited-state properties of a solution containing equimolar Ru^{II}(L)$_3$ and Fe^{III}4SP (L = bpy or dcbpy) in 5 mM HEPES are summarized in Fig. 3. The Stern–Volmer plot of the quenching of Ru^{II}(bpy)$_3$ excited-state by Fe^{III}4SP in 5 mM HEPES displays pronounced upward curvature indicative of complex formation. The data can be fit to a modified Stern–Volmer equation given by:

$$I_0/I = (1 + K_A[Q])(1 + K_{SV}[Q])$$

where K_A is the association constant, K_{SV} ($= k_q\tau_0$) is the Stern–Volmer constant, and $[Q]$ is the concentration of quencher [7–12,17]. Non-linear least squares fits of the quenching of Ru(bpy)$_3$ by Fe^{III}4SP in 5 mM HEPES give values for $K_A = (1.37 \pm 0.5) \times 10^4$ M^{-1} and a quenching constant of (k_q) of $(2.49 \pm 0.8) \times 10^{10}$ M^{-1} s^{-1}. In contrast a plot of τ_0/τ vs. concentration of Fe^{III}4SP in 5 mM HEPES is linear and gives a quenching constant of $(5.25 \pm 0.6) \times 10^9$ M^{-1} s^{-1} which is consistent with the calculated diffusional rate constant of 7×10^9 M^{-1} s^{-1}.[1] The corresponding Stern–Volmer plot for the quenching of the Ru^{II}(dcbpy)$_3$ excited-state by Fe^{III}4SP is linear indicating that the quenching process is purely diffusional with a quenching constant of $(3.27 \pm 0.60) \times 10^9$ M^{-1} s^{-1}. In addition, the quenching constant for Ru^{II}(dcbpy)$_3$ correlates well with the calculated diffusional rate, corrected for solution ionic strength, of 1.3×10^9 M^{-1} s^{-1}.

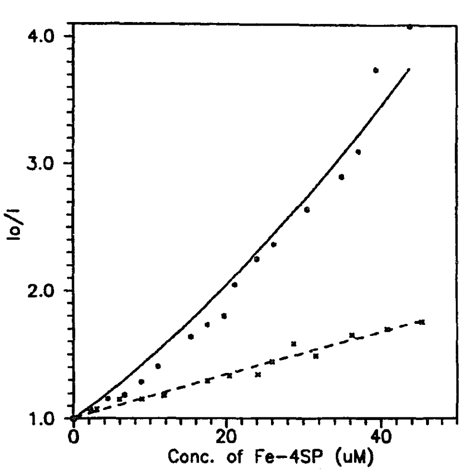

Fig. 3. Stern–Volmer plot for the quenching of (a) Ru^{II}(bpy)$_3$ and (b) Ru^{II}(dcbpy)$_3$ emission by Fe^{III}4SP at 25 °C in 5 mM HEPES pH 6.0. The data are the average of 50 laser pulses.

The corresponding time resolved fluorescence data (Fig. 4) could be fit to two discrete components in the presence of Fe^{III}4SP with life times of 10 ps and 378 ns in air saturated solutions. In the absence of Fe^{III}4SP, only a single component at 378 ns is observed. In addition, the contribution of the 10 ps component increased as the concentration of

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[1] Diffusional quenching rates for the Ru^{II}(L)$_3$ and Fe^{III}4SP were calculated using the equation $k_q^{diff} = (8NkT/3000\eta)b(e^{-b}-1)^{-1}$ where $b = z_D z_A e_0^2/(r\epsilon kT)$, η is the solvent viscocity, k is Boltzmans contant, z is the charge on the donor/acceptor, r is the distance between the donor and acceptor, ϵ is the solvent dielectric constant, N is Avogadro's constant.

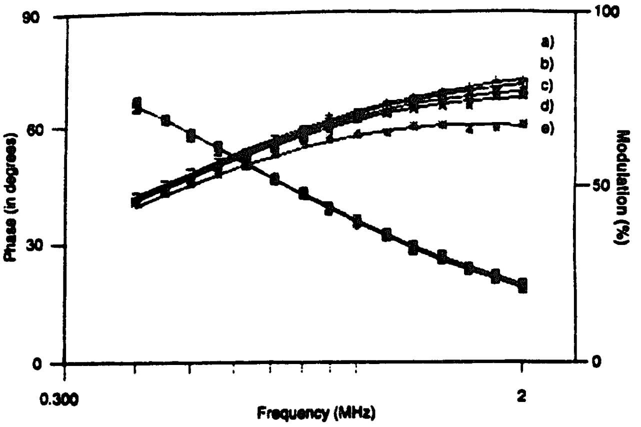

Fig. 4. Multifrequency phase and modulation data in the absence (trace a) and presence (traces b–e) of $Fe^{3+}4SP$. Concentrations of $Fe^{3+}4SP$ are as follows: (b) 2.4, (c) 7, (d) 12, and (e) 18 μM. Solution conditions are the those described in Fig. 1. Solid lines represent best fits for a single exponential decay (trace a) with $\tau = 378$ ns and double exponential (traces b–e) with $\tau_1 = 378$ ns and $\tau_2 = 0.01$ ns.

$Fe^{III}4SP$ was increased indicating that this component arises from the formation of the $Ru^{II}(bpy)_3$:$Fe^{III}4SP$ complex.

In the absence of added quenchers, the $Ru^{II}(bpy)_3$ ^3MLCT state exhibits a lifetime of ca. 600 ns (ca. 380 ns in air saturated solution). This long lived excited state has been previously shown to be reactive toward a wide variety of electron donor/acceptor compounds as well as energy acceptors [1–6]. In the present case, the ^3MLCT state of $Ru^{II}(bpy)_3$ quenched by $Fe^{III}4SP$ with the extent of quenching being highly dependent upon solution ionic strength. Both the steady state absorption and fluorescence quenching data indicate the formation of 1 : 1 $Ru^{II}(bpy)_3$:$Fe^{III}4SP$ complex under low ionic strength resulting in rapid quenching of the ^3MLCT state while higher ionic strengths favor purely diffusional quenching.

There are two possible mechanisms of quenching. Due to the overlap of the visible absorption bands of $Fe^{III}4SP$ with the emission band of $Ru^{II}(bpy)_3$ and $Ru^{II}(dcbpy)_3$, an energy transfer mechanism can contribute to the observed emission quenching. For an energy transfer process proceeding through a Forsters mechanism ([18–20]) the rate of energy transfer can be calculated as follows:

$$k = [(8.8\times10^{-25})K^2\Phi J]/(n^4\tau_0 R^6)$$

where J is an overlap integral (calculated graphically by the methods previously reported [19]), K^2 is the relative orientation of the transition dipoles of the donor and acceptor (approximated to 2/3), n is the refractive index of the medium (1.33) and Φ is the fluorescence quantum yield of $Ru^{II}(bpy)_3$ (0.07) [20–22]. The value for R was estimated to be 5.9 A from an energy minimized geometry of the complex obtained using HyperChem molecular modeling software with an MM+ force field. For $Ru^{II}(dcbpy)_3$, the overlap integral was calculated using absorption and normalized fluorescence spectra and found to be 2.63×10^{-18} mol^{-1} cm^6 while that of $Ru^{II}(bpy)_3$ was calculated to be 3.01×10^{-17} mol^{-1} cm^6. With these parameters, the calculated rate of energy transfer is found to be ca. 3×10^6 s^{-1}. Since the diffusional quenching constant is found to be 3.27×10^9 M^{-1} s^{-1} very little contribution from the energy transfer can be attributed to the diffusional quenching of the ^3MLCT of both $Ru^{II}(bpy)_3$ and $Ru^{II}(dcbpy)_3$.

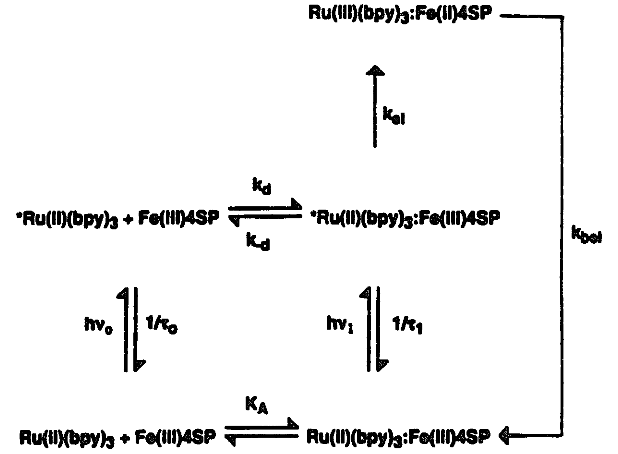

Fig. 5. Reaction scheme for photo-induced electron transfer associated with the $Ru^{II}(bpy)_3$:$Fe^{3+}4SP$ complex. K_a = ground state association constant, k_d, k_{-d} = rate constants for association/dissociation in the excited state, respectively, k_{el}, k_{bel} = forward and back electron transfer rate constants, respectively.

Previous studies have shown that for closely coupled systems, the R^6 dependence of Forsters transfer may not hold [23]. Such deficiencies in the Forsters transfer have been attributed to a Dexters mechanism (valid at shorter distances). For the system involving $Ru^{II}(bpy)_3$ and $Fe^{III}4SP$, since the changes in absorption can be construed as evidence for a strong electronic coupling, we realize that both Dexter and Forsters energy transfer processes may contribute to the singlet quenching. However, since the Forsters overlap integral for the system is very small (3.01×10^{-17} mol^{-1} cm^6) and the limiting rate for the inter-complex quenching obtained from the singlet lifetime measurements is very fast ($>10^{11}$ s^{-1}), the efficiency of the energy transfer from either the Forsters or Dexter mechanisms is expected to be extremely low.

Alternatively, examination of the reduction potentials of excited-state $Ru^{II}(bpy)_3$ and $Fe^{III}4SP$ ($E^0 = -0.80$ V versus SCE for $Ru^{III} \rightarrow Ru^{II*}$ and $E^0 = -0.23$ V versus SCE for $Fe^{III}4SP \rightarrow Fe^{II}4SP$) reveals favorable thermodynamics for quenching due to electron transfer from the ^3MLCT of $Ru^{II}(bpy)_3$ to $Fe^{III}4SP$ [24]. The free energy for this reaction is −14.5 kcal mol^{-1} while that of the thermally activated back electron transfer is −34.4 kcal mol^{-1}. [2] Since the rate of energy transfer is calculated to be much smaller than the observed quenching rate we conclude that ^3MLCT quenching of both the $Ru^{II}(bpy)_3$ and $Ru^{II}(dcbpy)_3$ by $Fe^{III}4SP$ proceeds primarily via electron transfer.

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[2] Calculated using $\Delta G = 23.06[E_D - E_A] - E(D^*)$ with E_D and E_A being the reduction potentials for $Ru^{III} \rightarrow Ru^{II*}$ and $Fe^{III}4SP \rightarrow Fe^{II}4SP$, respectively and $E(D^*)$ is the energy of the MLCT state of $Ru^{II}(bpy)_3$ and is equal to 48.9 kcal/mol (see Ref. [2]). The E^0 value for the Fe^{III}-4SP was obtained from Ref. [19].

The quenching scheme for the $Fe^{III}4SP–Ru^{II}(bpy)_3$ system is given in Fig. 5. In this scheme the ground state species undergo complex formation with an equilibrium constant K_A. Excitation of this complex results in rapid electron transfer from the $Ru^{II}(bpy)_3$ excited ^{3}MLCT state to the ground state of the $Fe^{III}4SP$ complex with rate constant k_{el} followed by rapid charge recombination with rate constant k_{bel}. The excited state complex can also decay radiatively with a rate constant k_{rd}. In the absence of any quenching processes it would seem reasonable that the lifetime of the emissive ^{3}MLCT of $Ru^{II}(bpy)_3$ would be of the same order of magnitude in both the free and bound complexes. The decrease in lifetime of the ^{3}MLCT in the complex demonstrates competition between natural emission and electron transfer. Thus, the rate of electron transfer (k_{el}) must be of the same order of magnitude (or larger) than that of the emission lifetime ($1/\tau_1$). Thus, k_{el} is expected to be $\geq 1 \times 10^{11}$ s^{-1} ($1/\tau_1$). In addition, we do not observe charge separated products on a nanosecond time scale (as judged by nanosecond transient absorption spectroscopy) indicating rapid charge recombination.

In summary, we demonstrate for the first time formation of a high affinity self-assembled 1 : 1 $Ru^{II}(bpy)_3/Fe^{III}4SP$ complexes under low ionic strength conditions. The complex undergoes reversible electron transfer subsequent to photoexcitation of the $Ru^{II}(bpy)_3$ as evident by the emission quenching of the $Ru^{II}(bpy)_3$ MLCT excited state. The estimated rate constant for the forward electron transfer rate is on the order of the emission decay rate of the complex ($\geq 1 \times 10^{11}$ s^{-1}). Overall, this study provides a framework with which to investigate fundamental aspects of electron transfer within non-covalent assemblies as well as providing a bases for future development of novel photocatalysts.

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References

[1] V. Balzani, L. Moggi, M.F. Manfrin, F. Bolleta, G.S. Laurence, Coord. Chem. Rev. 15 (1975) 321.

[2] G.J. Kavarnos, N.J. Turro, Chem. Rev. 86 (1986) 401.

[3] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Belser, A. Von Zelewsky, Coord. Chem. Rev. 84 (1988) 85.

[4] D.M. Roundhill, in: J.P. Fackler, Jr. (Ed.) Photochemistry and Photophysics of Metal Complexes (Plenum Press, New York, 1994).

[5] O. Horvath, K.L. Stevenson, in: Charge Transfer Photochemistry of Coordination Compounds (VCH, New York, 1993).

[6] J.-P. Collin, A. Harriman, V. Heitz, F. Odobel, J.-P. Sauvage, J. Am. Chem. Soc. 116 (1994) 5679.

[7] F. Bolleta, M. Maestri, L. Moggi, V. Balzini, J. Phys. Chem. 78 (1974) 1374.

[8] W. Rybak, A. Halm, T. Netzel, N. Sutin, J. Phys. Chem. 85 (1981) 2856.

[9] R. Frank, H. Rau, J. Phys. Chem. 87 (1983) 5181.

[10] R. Ballardini, M.T. Gandolfi, V. Balzini, Chem. Phys. Lett. 119 (1985) 459.

[11] H.S. White, W.G. Becker, A.J. Bard, J. Phys. Chem. 88 (1985) 1840.

[12] J.L. Sessler, B. Wang, A. Harriman, J. Am. Chem. Soc. 115 (1993) 10418.

[13] R.A. Marcus, N. Sutin, Biochem. Biophys. Acta (1985) 265.

[14] A. El-Awady, P.C. Wilkins, R.G. Wilkins, Inorg. Chem. 24 (1985) 2053.

[15] E.B. Fleischer, J.M. Palmer, T.S. Srivastava, A., Chatterjee, J. Am. Chem. Soc. 93 (1971) 3162.

[16] R.W. Larsen, R. Jasuja, R.K. Hetzler, P.T. Muraoka, V.G. Andrada, D.M. Jameson, Biophys. J. 70 (1996) 443.

[17] W.R. Laws, P.B. Contino, Meth. Enzym. 210 (1992) 448.

[18] L. Stryer, Annu. Rev. Biochem. 47 (1978) 819.

[19] I.D. Campbell, R.A. Dwek, in: P. Elias (Ed.), Biological Spectroscopy (Benjamin/Cummings, Menlo Park, CA, 1984) pp. 113-119.

[20] T. Forsters, Discuss. Faraday 27 (1959) 7.

[21] K. Kalyanasundaram, in: Photochemistry of Polypyridine and Porphyrin Complexes (Academic Press, London, 1992).

[22] V.M. Kenkre, R.S. Knox, Phys. Rev. Lett. 33 (1974) 803.

[23] J.M. Jean, C.K. Chan, G.R. Fleming, Israel J. Chem. 28 (1988) 169.

[24] M.H. Barley, K.J. Takeuchi, T.E. Meyer, J. Am. Chem. Soc. 108 (1986) 5876.