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Partial Charge Transfer Contribution on Solvent Isotope Effect and Photosensitized Generation of Singlet Oxygen, $O_2(^1\Delta_g)$, by Substituted Ruthenium (II) bipyridyl Complexes in Aqueous Media.

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Efficiency of singlet oxygen photosensitized by some ruthenium (II) bipyridyl complex ions in aqueous media is reported in this study. Measurements were carried out in H_2O and D_2O. The effect of deuterium isotope on the lifetime of ^{3}MLCT excited states of these complexes is studied in H_2O and D_2O. Deuterium isotope effect was discussed in terms of the vibronic coupling to the solvent in addition to charge transfer to solvent mechanism due to their dependence on the oxidation potential of the sensitizer. Quenching Rate constants, k_q, for quenching of the ^{3}MLCT states of these ruthenium complex ions by molecular oxygen were found to be in the range of (2.08 to 3.84) x 10^9 M^{-1} s^{-1} in H_2O and (1.69 to 3.48) x 10^9 M^{-1} s^{-1} in D_2O. Efficiency of singlet oxygen, $O_2(^1\Delta_g)$, production as a result of the ^{3}MLCT quenching by oxygen, f_Δ^T, is reported in D_2O and found to be in the range 0.25 - 0.56. It has been found that the lifetime of the excited state is longer in D_2O, τ_0^D, than in H_2O, τ_0^H, which was related to partial charge transfer to solvent in addition to vibronic coupling mechanism. Mechanisms by which the excited states of these ruthenium complexes is quenched by molecular oxygen that discusses the competition between charge transfer, non-charge transfer deactivation channels or energy transfer assisted charge transfer deactivation mechanism are reported.

Introduction

Singlet oxygen, $O_2(^1\Delta_g)$ which has relatively long lifetime is a highly reactive species and powerful oxidant in photosensitized oxidations, in photodynamic inactivation of viruses and cells, in photodegradation of dyes and polymers[1-6]. Recently, singlet oxygen has been used in solar water disinfection utilizing ruthenium complexes as photosensitizers[7].

Ruthenium(II) bipyridine and related compounds have been shown to be good photosensitizers of singlet oxygen despite the charge transfer (CT) nature of the lowest excited state of these compounds. The relatively long lifetime of the triplet metal-to-ligand charge transfer states, ^{3}MLCT, of many ruthenium(II) coordination compounds, make these excited states susceptible to quenching by oxygen in normal aerated fluid solutions and subsequently have been shown to be good photosensitizers of singlet oxygen despite the charge transfer (CT) nature of the lowest excited state of these compounds.

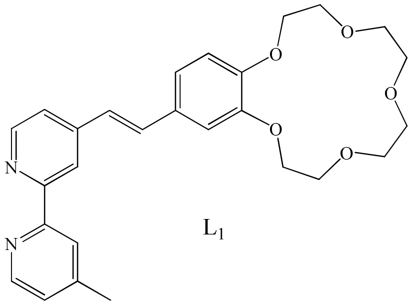
Quantum yields of singlet oxygen production photosensitized by $[Ru(bpy)_3]^{2+}$ have been reported by Garcia-Fresnadillo et al.[8] as 0.73 and 0.22 in CD_3OD and D_2O. They also reported k_q values and showed that the resulting efficiency of singlet oxygen formation, f_Δ^T, was unity for all the five Ru(II) complexes, containing polyazaheterocyclic ligands which they investigated in methanol. However they observed that in D_2O, f_Δ^T values ranged from 0.44 to 1.0 with f_Δ^T equal to 0.48 in the case of $[Ru(bpy)_3]^{2+}$ in agreement with the earlier value of Mulazzani et al.[9] Those complexes with the highest values for k_q tended to show the smallest f_Δ^T values, which these authors suggested[8] was due to charge transfer interactions similar to those reported[10-15] for oxygen quenching of the triplet states of organic compounds, where an inverse correlation between k_q and the resulting efficiency of singlet oxygen formation, f_Δ^T, is firmly established for several classes of compounds.

In a series of papers,[16-22] we investigated the quenching of the ^{3}MLCTstates of ruthenium(II) substituted bipyridyl complexes

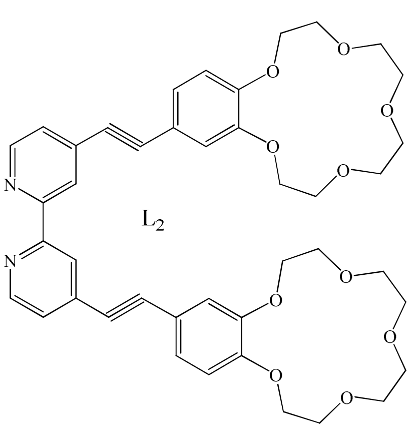
in acetonitrile and in aqueous solution and found that the quenching rate constant k_q values are well below the diffusion controlled rate constant, k_d. We have previously[16] showed for ruthenium complexes of the form $[Ru(diimine)(CN)_4]^{2-}$ that the quenching rate constants are in the range of 3.4-5.7 x 10^9 $M^{-1}s^{-1}$ while the efficiency of singlet oxygen production were in the range 0.3-0.5 in D_2O. We have also observed that solvent deuteration (H_2O to D_2O) was found to have a pronounced effect on the excited state lifetime and quenching rate constant. It has also been observed that the effect of deuteration increases as the number of cyano ligands increases in the complex. The isotope effect in case of $[RuL(CN)_4]^{2-}$ complexes was found to be higher than the homoleptic complexes, $[RuL_3]^{2+}$ which is a consequence of hydrogen bond formation with the cyanide lone pair with stronger vibronic coupling in case of H_2O than D_2O[16].
Photosensitized generation of singlet oxygen by coordination compounds is reported in a minority of singlet oxygen studies, and mostly in non-aqueous media[1,2]. Despite the fact that oxygen quenching of the excited triplet states is believed to be charge transfer assisted energy transfer, studies in the most polar aqueous solutions are very rare. However, in contrast to organic compounds where the range of the excited state energies and/or the oxidation potentials are wide enough for each series of compounds to establish the contribution of the charge transfer assisted energy transfer quenching mechanism; the oxidation potential range for each similar series of coordination compounds is very narrow. Interestingly additional factors are involved in the study of oxygen quenching of the excited states of coordination compounds such as steric factors, charge transfer nature of the excited state and the heavy atom effect of the central atom which are not available for organic series of compounds. In addition the majority of ruthenium complexes are water soluble, which makes it easy to examine the effect of charge transfer mechanism in this highly polar solvent. We have previously[16] investigated the mechanism of oxygen quenching of the excited states of structurally similar series of $[Ru(diimine)(CN)_4]^{2-}$ complexes with oxidation potentials in the range from 0.74 to 0.93 V vs. SCE in water. Since very few reports in literature were interested in the study of charge transfer effect on the quenching by oxygen mechanism in aqueous media, in this work, we extend our investigations on photosensitized generation of singlet oxygen by a series of reuthenium (II) complexes of ligands with variable steric parameters and narrow range of both excited state energy and oxidation potentials in aqueous media in order to investigate the steric effect and charge transfer contribution on the mechanism of their excited state quenching by molecular oxygen. Solvent isotope effect and its dependence on the oxidation potential of the studied complexes is also examined.

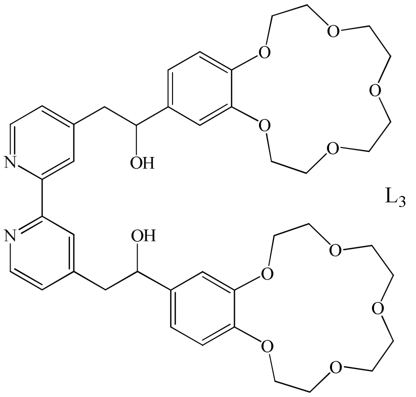
Experimental

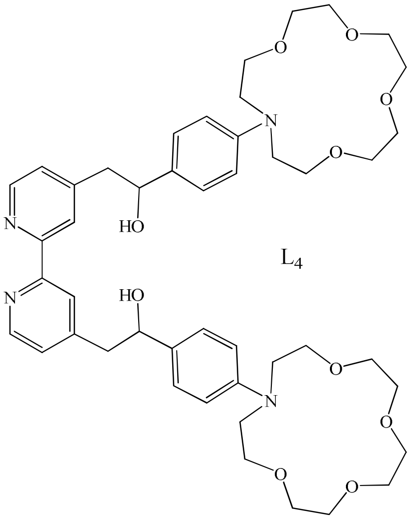
Ruthenium complexes under study were kindly given by Prof Paul Beer (Oxford University). D_2O (Alrdich, 99.9%) was used as supplied. Direct collection of the time resolved luminescence emission from singlet oxygen ($^1\Delta_g$) at 1275 nm was made using pulsed Nd:YAG laser (Brilliant) from Quantel with frequency tripling (4ns FWHM at 355 nm) as an excitation source. The emission was observed in right angle arrangement with Applied Photophysics laser flash photolysis LKS.60 assembly in the emission mode with a monochromator equipped with a diffraction grating from Horiba Jobin Yvon (cat no. 53034110, 600 lines/mm and 1000μm blaze) for emission in the infrared region, adjusted at 1275 nm onto an air cooled Hamamatsu H10330-45 NIR detector. The emission experiments at 1275 nm (20 averages) have been done with air saturated solutions in D_2O at 25°C varying the excitation pulse energy by means of attenuation filters. The absorbances of the sample solutions and the reference $[Ru(bpy)_3]^{2+}$ with singlet oxygen quantum yield of 0.25[16] were optically matched and amounted to about 0.3 at 355 nm. Singlet oxygen luminescence intensity at zero time was measured at different laser intensities and compared with those obtained from optically matched solutions of $[Ru(bpy)_3]^{2+}$ in D_2O as a standard thereby yielding relative Φ_Δ values.
Luminescence decay measurements of the ruthenium complexes measured with the LKS.60 system in the emission mode were signal averaged and fitted using a single exponential function to give the decay constants of samples for nitrogen purged, air saturated, and oxygen saturated solutions. Oxygen concentrations were taken as 0.27 mM and 1.27 mM in air saturated and oxygen saturated H_2O and D_2O.[23] Absorbance of the aqueous solution of ruthenium complexes at the wavelength of excitation did not exceed 0.1 at the wavelength of excitation. Each experiment was repeated three times at least. Steady state emission spectra were recorded with Schimadzu RF-5301 PC spectrofluorophotometer. Absorption measurements were made with Agilent 8453 single beam photodiode array spectrometer.
The structure of the relevant ligands are shown below:

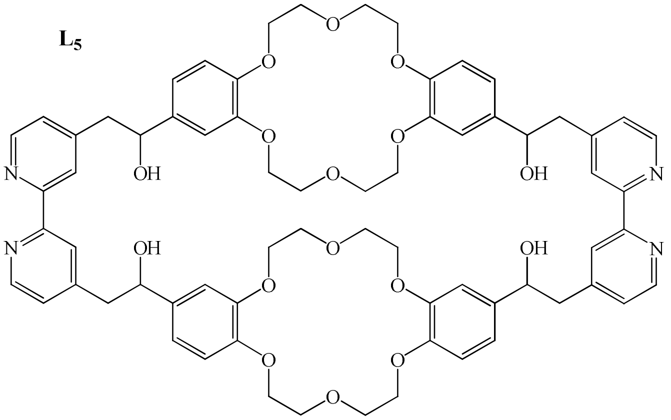


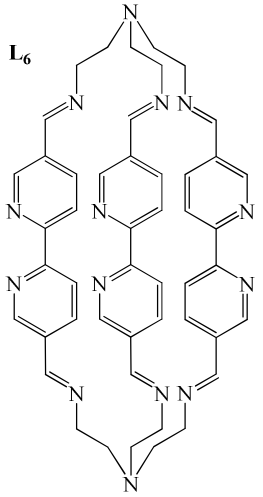
L_1

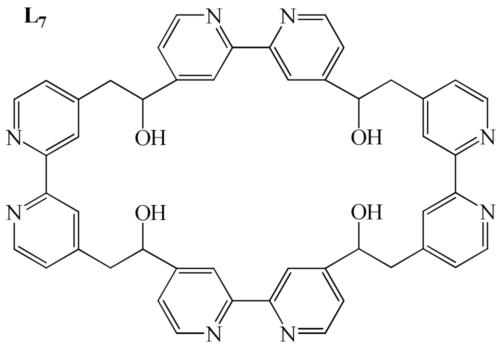

L$_2$


L$_3$


L$_4$


L$_5$


L$_6$


L$_7$

Results and Discussion

The absorption spectra in dilute aqueous solution of the ruthenium(II) complexes under investigation are shown in figure 1. The absorption bands in the range 400-550 nm for all studied ruthenium complexes are due to the spin-allowed d(t_{2g}) → π* transition forming the first excited singlet ^{1}MLCT state. The strong bands in the u.v. region are assigned as the π → π* transitions of the ligands. The absorption maxima of the MLCT band for all metal complexes studied are in the range from 454 nm to 465 nm and are listed in Table 1. It has been established that the metal to ligand charge transfer (MLCT) absorption process produces mainly an excited singlet ^{1}MLCT state which undergoes intersystem crossing populating the lowest ^{3}MLCT state with unit efficiency[8,24-26]. The luminescence spectra of some of the complexes are shown in Figure 2 and their band maxima are given in Table 1 with their emission maxima in the range from 595 nm to 619 nm. It can be seen from Table 1 that the range of absorption and emission energies are very narrow for the current set of complexes so are their oxidation potentials.

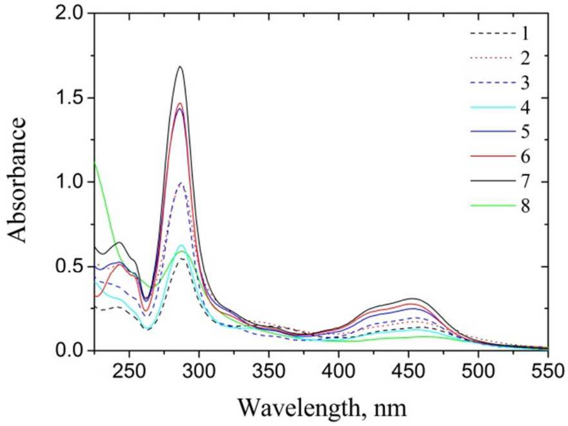


Fig. 1 The absorption spectra of the studied ruthenium (II) complex ions in aqueous solution, numbers are as given in Table 1.

We have previously shown that the energies of the lowest vibrational levels of the ^{3}MLCT states, $E_{0\text{-}0}$, were determined from the plot of the excitation energies $E_{0\text{-}0}$ obtained by spectral fitting for emission at 77 K versus the peak maximum energy E_{em} at room temperature for data collected from different sources from which the linear fit $E_{0\text{-}0} = 209 + 1.08\ E_{\mathrm{em}}\ \mathrm{cm}^{-1}$ results[16]. $E_{0\text{-}0}$ calculated values are listed in Table 1.

The luminescence decay of the excited state of the investigated metal complexes in the presence and absence of oxygen were fitted well by mono-exponential decays. Table 1 shows that the lifetime, τ_0, of the excited ^{3}MLCT state in deoxygenated solution for all complexes are 0.55±0.07 μs in H_2O. Solvent deuteration (H_2O to D_2O) was found to have a pronounced effect on the excited state lifetime (Table 1) being 0.95±0.07 μs in D_2O.

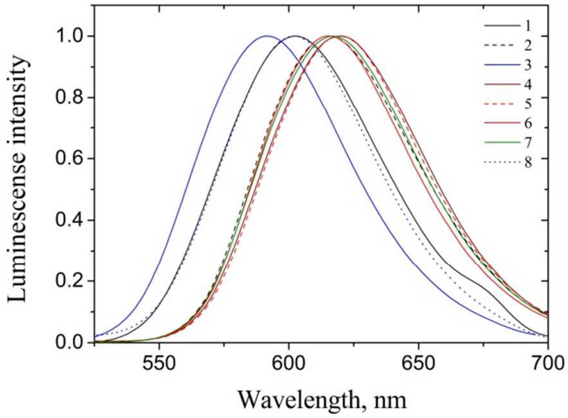


Fig. 2 Normalized Luminescence spectra of the studied ruthenium (II) complex ions in aqueous solution, numbers are as given in Table 1.

The effect of solvent deuteration on the lifetime of ruthenium complexes has been discussed by several groups[16,27-30]. Van Houten and Watts[27] found that the emission lifetime of $[\mathrm{Ru(bpy)_3}]^{2+}$ doubles on changing the solvent from H_2O to D_2O (0.58 to 1.02 μs at 298 K). They explained the solvent O–H vibrational modes' ability to deactivate the lowest ^{3}MLCT states as due to the partial charge-transfer-to-solvent character (CTTS) of the ^{3}MLCT state. They suggested that a significant proportion of the excited state's electron density is distributed over the solvent cage, facilitating transfer of electronic energy to solvent vibrational modes. On the other hand, Sriram and Hoffman[28] have found that the rate constants for the excited states decay in pure H_2O, HDO and D_2O for $[\mathrm{Ru(bpy)_3}]^{2+}$ depend on the fundamental vibrational frequencies of H_2O, HDO and D_2O which led them to conclude that the excited states decay occurs via vibronic coupling to the solvent; however they did not exclude the idea that the excited state has CTTS character in accordance with Van Houten and Watts proposal. Cherry and Henderson[29] have shown for three substituted bipyridyl Ru(II) complexes of different emission energies that the solvent isotope effect is caused exclusively by the change of the non-radiative rate constant which is energy gap dependent. The similarities of the solvent isotope effect for the three complexes suggested that the CTTS is the same for all three complexes. In addition to the qualitative assumption that the deuteration effect of water is ascribed to the contribution from the intramolecular vibration mode of the OH bonds[27-29], Masuda and Kaizu[30] have shown that the isotope effect on the radiationless decay rate, k_{nr}, depends on the existence of a specific interaction between the π electrons of the ligands and the included water molecules in such way similar to the reported interaction between water and benzene that was ascribed to a hydrogen bond between the water proton and the π electron of benzene[32-34]. Therefore, Masuda and Kaizu proposed that electronic-to-vibrational (e-v) energy transfer from Os(II) complex to the included water molecules take place in which case the OH vibration of the included water acts as energy accepting mode. It has also been found that; the isotope effect in case of $[\mathrm{RuL(CN)_4}]^{2-}$ complex ions[16] is higher than the homoleptic complexes, $[\mathrm{RuL_3}]^{2+}$. This has been attributed to the attenuation of the non-radiative decay pathways in D_2O as a consequence of hydrogen bond formation with the cyanide lone pair with stronger vibronic coupling in case of H_2O than D_2O since the fundamental vibrational frequencies of D_2O are about 0.73 that of H_2O[28]. Table 1 shows that the ratio of $\tau_0^{D}/\ \tau_0^{H}$ varies from 1.5 for complexes with E_{ox} of 1.36 V vs SCE and increases as E_{ox} decreases. Even though the variation in the oxidation potential is not that wide; the observed change in the ratio of $\tau_0^{D}/\ \tau_0^{H}$ together with those previously reported by us[16] is clear enough to support the relation between $\tau_0^{D}/\ \tau_0^{H}$ and the oxidation potential which in favour of partial charge transfer to solvent in addition to the vibronic coupling mechanism (figure 3). However, further studies are needed to cover a wider range of the oxidation potential in order to obtain a quantitative treatment of the deuteration effect.

The pseudo-first order rate constant, k_{obs}, of complex luminescence decay is given by

$$k_{\mathrm{obs}} = k_0 + k_{\mathrm{q}}[\mathrm{O_2}] \qquad (1)$$

Table 1 Photophysical properties of the ruthenium complexes in aqueous media, wavelength of maximum absorption, λ_{abs}, wavelength of maximum emission, λ_{em}, energy of the 0-0 transition, $E_{0\text{-}0}$, oxidation potentials, E_{ox}, and lifetimes (τ_0^D and τ_0^H) of the excited ^{3}MLCT states in D_2O and H_2O, respectively.

	Compound	λ_{abs}/nm	λ_{em}/nm	$E_{0\text{-}0}$ /kJ mol^{-1}	$E_{ox}{}^a$ /V vs. SCE	τ_0^D/μs	τ_0^H/μs	τ_0^D/τ_0^H
1	$[Ru(bpy)_2L_1)](PF_6)_2$	463	602	217	1.31	0.94	0.47	2.01
2	$[Ru(bpy)_2L_2)](PF_6)_2$	457	610	214	1.36	1.00	0.60	1.65
3	$[Ru(bpy)_2L_3)](PF_6)_2$	456	595	220	1.36	0.94	0.62	1.51
4	$[Ru(bpy)_2L_4)](PF_6)_2$	457	615	213	1.28	0.95	0.55	1.73
5	$[Ru_2(bpy)_4L_5)](PF_6)_4$	454	620	211	1.26	0.89	0.50	1.76
6	$[Ru_3(bpy)_6L_6)](PF_6)_6$	452	617	212	1.27	0.98	0.58	1.70
7	$[Ru_4(bpy)_8L_7)](PF_6)_8$	454	619	211	1.26	0.95	0.53	1.78
8	$[Ru(L_3)_3](PF_6)_2$	465	600	218	1.41	0.97	0.65	1.50

[a] refs 19-20

where $k_0 = 1/\tau_0$ is the intrinsic first order decay constant of the ^{3}MLCT state in the absence of ground state oxygen. Values of k_q, the rate constants for quenching by oxygen, were obtained as slope of equation (1) of k_{obs} data taken at different oxygen concentrations in H_2O and D_2O (figure 4), are listed in Table 2. Table 2 shows that the quenching by oxygen rate constants in H_2O, k_q^H, are slightly higher than in D_2O, k_q^D. Values of the quenching rate constants in H_2O and D_2O are much lower than that reported for the diffusion rate constant, k_d, of 2.7×10^{10} M^{-1}s^{-1} in H_2O[16] and 2.2 x 10^{10} M^{-1}s^{-1} in D_2O[16]. Values of k_q^H/k_q^D are in the range of 1.02 to 1.23 which are close to the ratio of the rate of diffusion in H_2O and D_2O (k_d^H/k_d^D=1.23)[16].

Luminescence emission signal at 1275 nm were found to compose of a fast component due to the NIR tail of the luminescence of the excited state of the ruthenium complex, while the slow component results from the luminescence of singlet oxygen $O_2{}^*(^1\Delta_g)$. To separate the decay profile of the singlet oxygen signal from that of the fast component, fitting was carried out over the longer times where the contribution

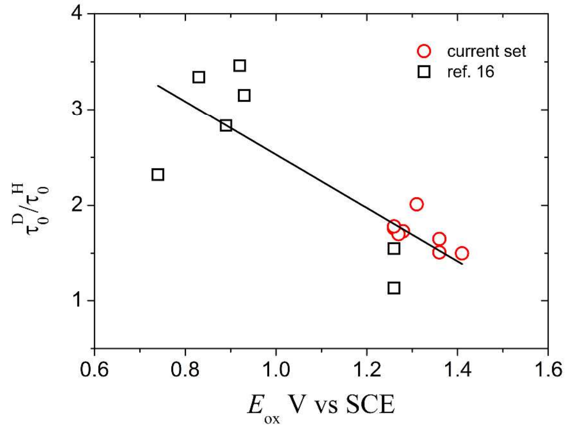


Fig. 3 Dependence of τ_0^D/τ_0^H on the oxidation potential.

Table 2 Singlet oxygen quantum yield, Φ_Δ, the fraction of the ^{3}MLCT states quenched by oxygen, $P_T^{O_2}$, and the efficiency of singlet oxygen production from the ^{3}MLCT states, f_Δ^T, in air equilibrated D_2O. The rate constants for quenching of ^{3}MLCT states of ruthenium(II) complexes by oxygen, k_q, in H_2O and D_2O, and the relative contribution of CT mediated deactivation, p_{CT} calculated using eqn 13 and the driving force of charge transfer interaction, ΔG^{CT}.

	Compound	Φ_Δ	$P_T^{O_2}$ (D_2O)	$P_T^{O_2}$ (H_2O)	f_Δ^{Ta}	k_q^D /10^9 M^{-1}s^{-1} D_2O^b	k_q^H /10^9 M^{-1}s^{-1} H_2O	p_{CT}	ΔG^{CT} /kJ mol^{-1}
1	$[Ru(bpy)_2L_1)](PF_6)_2$	0.03	0.42	0.36	0.25 (0.35)	3.07±0.10 (4.12)	3.49±0.15	0.86	-53.2
2	$[Ru(bpy)_2L_2)](PF_6)_2$	0.14	0.41	0.32	0.34 (0.38)	3.04±0.10 (3.39)	3.09±0.10	0.82	-45.6
3	$[Ru(bpy)_2L_3)](PF_6)_2$	0.23	0.43	0.31	0.53 (0.43)	2.94±0.10 (2.36)	3.47±0.15	0.75	-50.9
4	$[Ru(bpy)_2L_4)](PF_6)_2$	0.07	0.44	0.33	0.16 (0.32)	3.14±0.10 (5.59)	3.49±0.15	0.90	-51.6
5	$[Ru_2(bpy)_4L_5)](PF_6)_4$	0.21	0.41	0.33	0.51 (0.42)	3.48±0.15 (2.80)	3.59±0.15	0.77	-51.8
6	$[Ru_3(bpy)_6L_6)](PF_6)_6$	0.24	0.43	0.37	0.56 (0.43)	3.40±0.15 (2.59)	3.84±0.20	0.75	-51.9
7	$[Ru_4(bpy)_8L_7)](PF_6)_8$	0.21	0.44	0.38	0.48 (0.42)	3.26±0.12 (2.82)	3.66±0.20	0.77	-52.1
8	$[Ru(L_3)_3](PF_6)_2$	0.12	0.31	0.25	0.39 (0.47)	1.69±0.07 (2.09)	2.08±0.10	0.71	-49.1

[a,b] values between parentheses are those calculated using Eqs 14 and 15, respectively (see text).

from the rapid component is minimal. Individual luminescence traces (12 at least) were signal averaged and were fitted using a single exponential function to yield the luminescence intensity I_o at t = 0. The luminescence intensity I_o at zero time was plotted against the laser intensity. The slopes obtained for these straight line plots were compared with those obtained from optically matched standard thereby yielding relative Φ_Δ values. The quantum yield of singlet oxygen sensitization is given by:

$$\Phi_\Delta = \Phi_T P_T^{O_2} f_\Delta^T \qquad (2)$$

where Φ_T is the efficiency of population of the lowest excited ^{3}MLCT state, $P_T^{O_2}$ is the fraction of the ^{3}MLCT states quenched by oxygen, and $f_\Delta{}^T$ is the efficiency of singlet oxygen formation.

$$P_T^{O_2} = \frac{k_q[O_2]}{k_0 + k_q[O_2]}. \qquad (3)$$

The subscript T is used to represent the excited ^{3}MLCT state for simplicity. It can be seen that values of P_T^{O2} is higher in D_2O than in H_2O (Table 2) in most cases due to the mostly significantly smaller values of k_0 in D_2O relative to H_2O (table 1).

Since Φ_T for the ruthenium complexes is assumed to be unity[8,24-26] it follows that:

$$\Phi_\Delta = P_T^{O_2} f_\Delta^T \qquad (4)$$

Values of $\Phi_{\Delta,}$ P_T^{O2} and $f_\Delta{}^T$ are listed in Table 2.

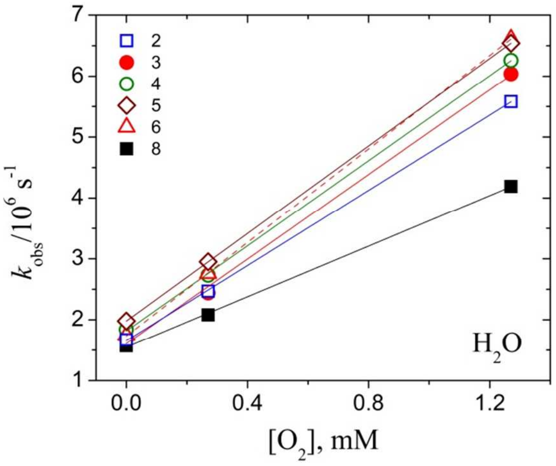


Fig. 4 Dependence of the observed decay rate constants on oxygen concentrations in H_2O, numbers are as given in Table 1.

Table 2 shows that k_q values in H_2O and D_2O are very close to 1/9 k_d. The search for quantitative explanation for the observed inverse relation between k_q and $f_\Delta{}^T$ values[10-15] and their dependence on the driving forces for energy and electron transfer began several decades ago. Our systematic studies[10-15] with series of sensitizers of almost constant E_T but systematic variation of the oxidation potential E_{ox} revealed that increasing CT interactions, i.e. decreasing E_{ox} caused a strong increase of k_q and a decrease of $f_\Delta{}^T$ and that a CT and a non-CT (nCT) pathways compete in the quenching of triplet states by O_2 which both yield $O_2(^1\Delta_g)$ with different efficiency.[10-15,35]

In his very early pivotal work Kautsky proposed that oxygen quenching of electronically excited states could yield the singlet state of molecular oxygen and thereby account for some photosensitized oxidations; an evidence of which came 30 years later from the work of Foote and Wexler and Corey and Taylor[1]. Since then there have been many attempts to elucidate the mechanism of the interactions between electronically excited states and oxygen under a variety of conditions (see for example references 1-6).

The mechanism of quenching by oxygen of the triplet states of organic compounds was first introduced by Gijzeman et. al.[36], who stressed the importance of spin statistical factors. This mechanism modified to include charge transfer complexes of oxygen and the possibility of intersystem crossing between the various quenching channels as proposed initially by Garner and Wilkinson[37] to account for values higher than k_d/9 reported for several systems[13,14,35,37-41]. We have also proposed competition between non-charge transfer assisted energy transfer (i.e. also including the step labelled $^1k_\Delta$ in scheme 1) and charge transfer assisted quenching with and without energy transfer[13,14].

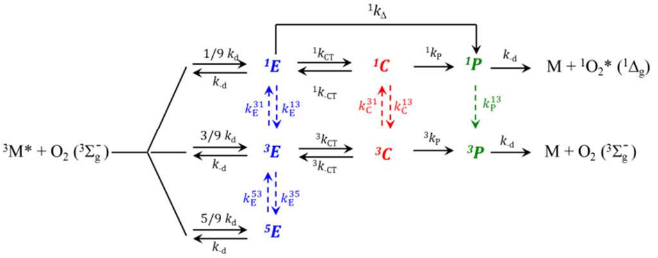
In Scheme 1, $^{1,3}E$ and $^{1,3}C$ are used to represent the encounter complexes $[^{1,3}(^3M^*...O_2,{}^3\Sigma_g{}^-)^*]$ and the charge transfer complexes $[^{1,3}(M^{\delta+}...O_2{}^{\delta-})]$ and ^1P and ^3P represent the precursor/encounter complexes $^1(M...O_2{}^*,{}^1\Delta_g)$ and $^3(M...{}^3O_2,{}^3\Sigma_g{}^-)$ respectively. Scheme 1, have been modified slightly by us[20] to include an extra step as shown with rate constant k_{13}^P to account for possibility that the precursor complex ^1P decays to give ^3P before dissociation to give singlet oxygen occurs. We have previously[20] suggested that complexes containing ligands with extended conjugation and with low oxidation potentials may physically quench singlet oxygen in the precursor complex before dissociation can occur, an evidence of which have been given by us for complexes with low oxidation potentials[16]. According to scheme 1 the first excited triplet state of the sensitizer and oxygen in its ground state, $O_2(^3\Sigma_g{}^-)$, form in the primary step of quenching an excited encounter complexes (intermediates) with multiplicities 1, 3 and 5 with diffusion controlled rate constant, k_d. These excited complexes either dissociate back again with rate constant k_{-d} or react forward via the singlet encounter intermediate ^1E to produce singlet ground state sensitizer, S_0, and $O_2(^1\Delta_g)$ or $O_2(^1\Sigma_g{}^+)$ or via the triplet encounter intermediate, ^3E to produce S_0 and $O_2(^3\Sigma_g{}^-)$.

Rate constants for quenching via the singlet channel resulting in energy transfer to oxygen with formation of singlet oxygen $k_{T\Delta}$ and quenching without energy transfer k_{TO} via the triplet channel as expanded in Scheme 1 are given by:

$$k_{T\Delta} = k_q{}^T f_\Delta{}^T \qquad (5)$$

and

$$k_{TO} = k_q{}^T (1 - f_\Delta{}^T) \qquad (6)$$



Scheme 1.

The free energy change to form ion pairs, ΔG_{CT}, from excited states with energy $E_{0\text{-}0}$ is given by the well-known equation by Rehm and Weller[42]. It has been shown that ΔG_{CT}, the free energy change for complete electron transfer from the sensitizer to O_2, is a useful qualitative measure of the strength of CT interactions in the excited complexes involved.[10-21,35,43-44]

$$\Delta G_{CT} = F(E_{ox} - E_{red}) - E_{0\text{-}0} + C \qquad (7)$$

where F, E_{ox} and E_{red} are the Faraday constant, the oxidation potential of the sensitizer and the reduction potential of molecular oxygen (-0.41V vs. SCE in water),[45] and $E_{0\text{-}0}$ is the excitation energy. Eqn 8 holds for the electrostatic interaction energy, with the elementary charge e (e^2 = 14.43 eV Å) and the relative permittivity of the solvent ε.[46]

$$C = -\frac{e^2}{\varepsilon(r^+ + r^-)} \qquad (8)$$

with r^+ = 6.5 Å for $[\mathrm{Ru(phen)_3}]^{2+}$[47] and r^- = 1.7 Å for oxygen[48] C = -2.1 kJ mol^{-1} results for the solvent water.

Dependence of $k_{T\Delta}$ and k_{TO} on either the driving force for energy transfer $\Delta G_{\Delta E}$ or the driving force for charge transfer ΔG_{CT} was found to be difficult due to the very limited range of either the excited state energy, $E_{0\text{-}0}$, or the oxidation potential of the studied complexes, E_{ox} (see table 1).

Schmidt[36] has also developed a model (Scheme 2) that quantitatively reproduces kinetic data on the sensitization of singlet oxygen for sensitizers of various triplet energies in solvents of strongly different polarities mostly based on our very carefully measured data for the quenching of the excited triplet states of biphenyl and naphthalene derivatives by oxygen together with his data in CCl_4 for the same set of sensitizers. This model differs from our earlier kinetic schemes[13-15] mainly by the fully established ISC equilibrium of the $^{1,3}(T_1..^3\Sigma)$ nCT complexes from which IC to lower-lying nCT complexes $^1(S_0..^1\Sigma)$, $^1(S_0..^1\Delta)$, and $^3(S_0..^3\Sigma)$ is controlled by the proposed polynomial energy gap law (Eqn 12), which was not taken into account in our earlier scheme[13,14] and did not include the formation of $O_2(^3\Sigma_g^-)$ in the nCT deactivation channel. In here Schmidt's model will be used since it enables us to determine the balance between non-charge transfer (nCT) and charge transfer (CT) deactivation for every sensitizer without the knowledge of oxidation potential and solvent polarity.

The overall rate constant k_D of product formation is calculated according to eqn 9 as:

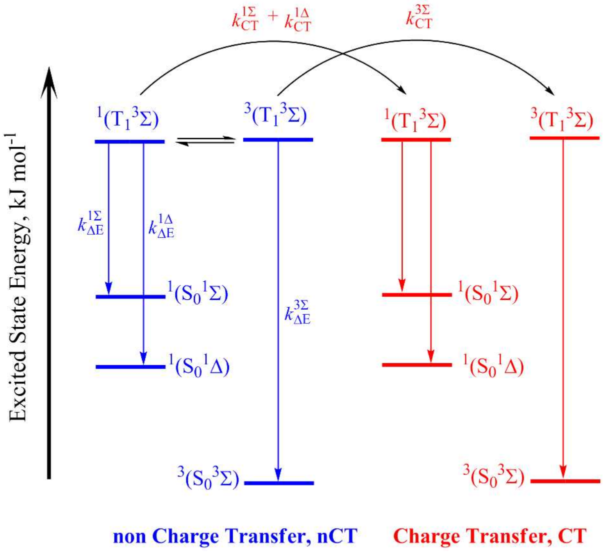
$$k_D = \frac{k_{-d}\, k_q}{k_d - k_q} \qquad (9)$$

According to Scheme 2, the individual rate constants $k_T^{1\Sigma}$, $k_T^{1\Delta}$and $k_T^{3\Sigma}$ of $O_2{*}(^1\Sigma_g^+)$, $O_2(^1\Delta_g)$ and $O_2(^3\Sigma_g^-)$ formation can be obtained using the following equation[49] which are additively composed of the nCT component, $k_{\Delta E}^{P}$, and the CT component, k_{CT}^{P}:

$$k_{T\Delta} = f_\Delta{}^T k_D = k_{CT}^{\Delta} + k_{\Delta E}^{\Delta} \qquad (10)$$

$$k_{TO} = (1\text{-}f_\Delta{}^T)k_D = k_{CT}^{3\Sigma} + k_{\Delta E}^{3\Sigma} \qquad (11)$$

where $f_\Delta{}^T$ is the overall efficiency of $O_2(^1\Delta_g)$ production either directly or indirectly formed via the very fast internal conversion from the short-lived upper excited $O_2(^1\Sigma_g^+)$.



Scheme 2

The balance between charge transfer (CT) and non-charge transfer (nCT) deactivation can easily be described *via* the quantity p_{CT} which is defined as the relative contribution of charge transfer deactivation referred to the overall deactivation of the excited state by O_2. If the sensitizer triplet energy is known, the absolute contribution of the nCT path to deactivation $k_{\Delta E}^{P} = k_{\Delta E}^{\Delta} + k_{\Delta E}^{3\Sigma}$, is calculated by the polynomial of Eqn (12) *via* the corresponding excess energies ΔE which was originally derived for systems with minimal charge transfer contribution (E_{ox} > 1.8 V vs SCE) in CCl_4,[50] however, recent treatment of Schmidt to a wider range of data including ours for biphenyl and naphthalene derivatives in different solvents showed that the equation can be used for deactivation in other solvents.[49]

$$\log(k_{\Delta E}^{P}/\mathrm{m\,/\,s^{-1}}) = 9.05 + 9\times10^{-3}\Delta E - 1.15\times10^{-4}\Delta E^2 + 1.15\times10^{-7}\Delta E^3 + 9.1\times10^{-11}\Delta E^4 \qquad (12)$$

The absolute contribution of the p_{CT} path is simply $\sum k_{\mathrm{CT}}^{\mathrm{P}} = k_{\mathrm{D}} - k_{\Delta\mathrm{E}}^{\mathrm{P}}$. Thus, p_{CT} is obtained by Eqn (13), if the excited state energy, $E_{0\text{-}0}$, and k_{q} are known[49]

$$p_{\mathrm{CT}} = \frac{\sum k_{\mathrm{CT}}^{\mathrm{P}}}{k_{\mathrm{D}}} = \frac{k_{\mathrm{D}} - \sum k_{\mathrm{CT}}^{\mathrm{P}}}{k_{\mathrm{D}}} \qquad (13)$$

Since $k_{\mathrm{D}} = \sum k_{\Delta\mathrm{E}}^{\mathrm{P}}/(1-p_{\mathrm{CT}})$ and $\sum k_{\mathrm{CT}}^{\mathrm{P}} = p_{\mathrm{CT}} \sum k_{\Delta\mathrm{E}}^{\mathrm{P}}/(1-p_{\mathrm{CT}})$ hold true, Eqs 14 and 15, which express the quantities f_{Δ}^{T} and k_{q} in dependence of p_{CT} can be derived (for details see ref 49):

$$f_{\Delta}^{\mathrm{T}} = \frac{k_{\Delta\mathrm{E}}^{\Delta}(1-p_{\mathrm{CT}}) + p_{\mathrm{CT}} \sum k_{\Delta\mathrm{E}}^{\mathrm{P}}/4}{\sum k_{\Delta\mathrm{E}}^{\mathrm{P}}} \qquad (14)$$

$$k_{\mathrm{q}} = \frac{k_{\mathrm{D}} \sum k_{\Delta\mathrm{E}}^{\mathrm{P}}/(1-p_{\mathrm{CT}})}{k_{-\mathrm{d}} + \sum k_{\Delta\mathrm{E}}^{\mathrm{P}}/(1-p_{\mathrm{CT}})} \qquad (15)$$

where $\sum k_{\Delta\mathrm{E}}^{\Delta} = \sum k_{\Delta\mathrm{E}}^{1\Sigma} + \sum k_{\Delta\mathrm{E}}^{1\Delta}$. Eqs 14 and 15 can be used to calculate values of p_{CT} via experimental data of f_{Δ}^{T} and k_{q}. The optimum value of p_{CT} is obtained for each sensitizer by variation of p_{CT} until the sum of the squared differences of calculated and experimental f_{Δ}^{T} and k_{q} data reaches the minimum. Calculated values are shown between brackets in Table 2 next to the experimental values. Errors in the calculated values for f_{Δ}^{T} and k_{q} obtained for the current set of compounds are within the same range as those reported previously by us[16] for a larger set of ruthenium (II) complexes in aqueous media. However we found that the error is getting higher as the experimental values of f_{Δ}^{T} is getting smaller.

The satisfying agreement of calculated and experimental data has only been obtained when taking the rate constant of back dissociation of the encounter complexes as $k_{-\mathrm{d}} = 3\times k_{\mathrm{d}}\times\mathrm{M}$, where M is the unit mole per liter similar to those obtained for $[\mathrm{RL(CN)_4}]^{2-}$ complex ions reported previously by us[16], whereas with non-ionic sensitizers in organic solvents $k_{-\mathrm{d}} = k_{\mathrm{d}}\times\mathrm{M}$ was used[49]. This different behaviour could indicate that dissociation of a charged encounter complex in water is faster than dissociation of an uncharged encounter complex in an organic solvent.

Despite the relatively high value of p_{CT} (Table 2), transient absorption measurements using nanosecond laser flash photolysis equipment gave no evidence for $[\mathrm{RuL_3}]^{3+}$or ion pairs involving the $[\mathrm{RuL_3}]^{3+}$ ion being produced following oxygen quenching of the excited states of these $[\mathrm{RuL_3}]^{2+}$ ions in water under our experimental conditions. In addition, the dependence of the photosensitization outputs, i.e., f_{Δ}^{T} and k_{q} values on the steric factors is not clear for the current set of complexes. However, despite the narrow range of the oxidation potential of the current set of complexes, the dependence of f_{Δ}^{T} on the derived value of p_{CT} is very pronounced as shown in Figure 5. In contrast, the dependence of the quenching rate constant $k_{\mathrm{q}}^{\mathrm{D}}$ on p_{CT} was not clear which is again confirms the importance of intersystem crossing between charge transfer complexes considered in scheme 1 and not included in scheme 2.

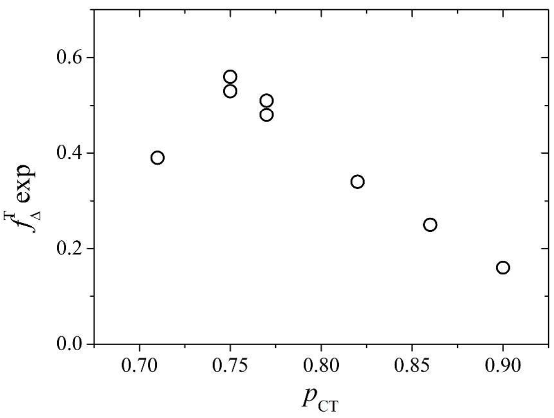


Fig. 5 Dependence of the experimental values of f_{Δ}^{T} on the derived value of p_{CT}.

Ruthenium (II) bipyridyl complexes have shown interesting similarities and interesting differences when compared with organic sensitizers of singlet oxygen. The mechanism of the excited state quenching by molecular oxygen and singlet oxygen thereby produced using ruthenium (II) bipyridyl complexes is much more complicated than the study with organic sensitizers; more variables are participating simultaneously, such as excited state energy, oxidation potential and steric factors vary in the case of ruthenium complexes whereas for each series of the organic sensitizers only the oxidation potentials change significantly. Further work is ongoing with a series of compounds which has a greater variation in $E_{0\text{-}0}$ and in E_{ox} and less steric variation than those reported here in order to further understanding of the quenching mechanism in case of coordination complexes.

Acknowledgements

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