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# Fractional dependence of the free energy of activation on the driving force of charge transfer in the quenching of the excited states of substituted phenanthroline homoleptic ruthenium(II) complexes in aqueous medium†

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The photophysical characteristics of some homoleptic ruthenium(II) phenanthroline derivatives are investigated in aqueous medium. The lifetimes of the excited <sup>3</sup>MLCT state of the studied complexes were found to be very sensitive to the type of the substituents on the phenanthroline ligand and were found to increase from about 0.96 μs in case of the parent [Ru(Phen)<sub>3</sub>]<sup>2+</sup> complex to 2.97 μs in case of [Ru(DPPhen)<sub>3</sub>]<sup>2+</sup>. The transient absorption spectra of the current set of complexes were studied also in aqueous medium. Quenching of the excited <sup>3</sup>MLCT states of the studied complexes by molecular oxygen were studied and quenching rate constants were found to be in the range 1.02–4.83 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>. Values of singlet oxygen quantum yields were found to be in the range 0.01 to 0.25, and the corresponding efficiencies of singlet oxygen thereby produced,  $f_{\Delta}^T$ , were in the range 0.03–0.52. The mechanism by which the excited <sup>3</sup>MLCT state is quenched by oxygen is discussed in light of the spin statistical factor rate constants and the competition between charge transfer and non-charge transfer quenching pathways. The partial charge transfer parameters,  $p_{CT}$ , were obtained and found to be about 0.88 for all complexes except for complexes with  $f_{\Delta}^T$  values lower than 0.25. The correlation of the activation free energies  $\Delta G^{\ddagger}$  of the exciplexes formation with the driving force for charge transfer,  $\Delta G_{CET}$ , gives a charge transfer character of the exciplexes of about 35.0%.

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## 1. Introduction

Singlet oxygen is most frequently produced by photosensitization. Singlet oxygen is essential to both natural and synthetic chemistry. It has a key role in many applications such as wastewater treatment, fine chemicals synthesis, photoactivated insecticides and herbicides, photodynamic therapy for cancer, and photo-sterilization of blood components and in electrochemical cells.<sup>1–7</sup>

Excited state quenching of the aromatic compounds and coordination compounds by molecular oxygen has been studied extensively and reported in many review articles.<sup>8–13</sup> It has been found that the type of the excited state, the excited state energy, the oxidation potential of the sensitizer, and the solvent polarity are the major factors that affect oxygen quenching of the excited

triplet states of aromatic hydrocarbons and efficiency of singlet oxygen thereby produced.<sup>14–35</sup>

It is intriguing to know that there haven't been as many studies on the quenching of the excited states of metal complexes by oxygen as there have been on aromatic compounds.<sup>1–7</sup> The majority of the coordination compound studies focused on ruthenium(II) polypyridyl complexes.<sup>36–50</sup> Singlet oxygen photosensitized by other metal complexes such as chromium(III),<sup>51–56</sup> lanthanide complexes of metal-lotetaphyrin derivatives,<sup>57</sup> and divalent metal complexes of Pt, Mg, Cu, Ni, Ag, Cd, Co, Pd and Zn,<sup>58</sup> palladium and platinum complexes,<sup>59–63</sup> thiolato Au(I) complexes,<sup>64</sup> organoiridium(III)<sup>65</sup> was also reported. Recent studies have shown that osmium(II) terpyridyl derivatives<sup>66</sup> are effective singlet oxygen photosensitizers used for photodynamic therapy. It has also been reported that cyclometallated monocationic complexes of iridium(III) and platinum(II) are effective singlet oxygen photosensitizers.<sup>67,68</sup> Cyclometallated platinum(II) complexes,<sup>69,70</sup> were found to be efficient singlet oxygen photosensitizers. The photophysical properties and efficiency of singlet oxygen production photosensitized by thirty eight Re(I) complexes have been recently collected and singlet oxygen quantum yields were reported with

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the minimum value of 0.20 and highest value approaching unity.<sup>71</sup> Porphyrinic metal-organic frameworks has recently reported as good singlet oxygen photosensitizers and was reported also to be good standard for singlet oxygen quantum yields for solid state materials.<sup>72</sup>

Despite such huge data, the mechanism by which the excited states of coordination compounds are quenched by oxygen is still not fully clear. For example, the clear inverse dependence of the efficiency of singlet oxygen production,  $f_{\Delta}^{\text{r}}$ , and the quenching rate constant,  $k_q$ , on the photosensitizer's oxidation potential is not clearly observed as those reported for aromatic hydrocarbons. In this contribution, we continue our efforts in the study of factors affecting quenching by oxygen of the excited states of metal complexes especially in aqueous medium. The photophysical properties of some homoleptic ruthenium(II) phenanthroline derivatives are studied. Quenching of the excited  $^3\text{MLCT}$  state of the studied complexes by molecular oxygen are investigated in aqueous solution and quantum yield of singlet oxygen thereby produced are also reported. Factors affecting the quenching process are investigated. The obtained efficiency of singlet oxygen production,  $f_{\Delta}^{\text{r}}$ , and quenching rate constant,  $k_q$ , are correlated to the oxidation potential of the photosensitizers. Competition by charge transfer and non-charge transfer quenching mechanism are to be elucidated.

## 2. Experimental

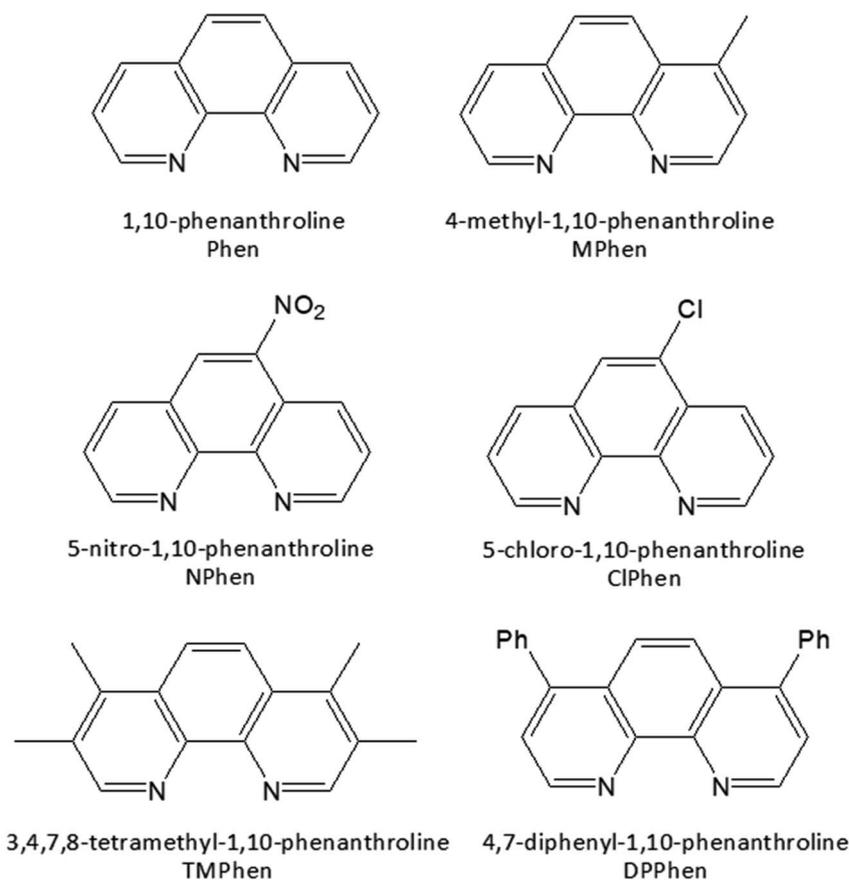
### 2.1. Materials and reagents

$\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ , 1,10-phenanthroline (phen), and its derivatives 5-nitro (NPhen), 5-chloro (ClPhen), 4,7-diphenyl (DPPhen), 4-methyl (MPhen), 3,4,7,8-tetramethyl (TMPhen), dimethylformamide (DMF), lithium chloride (LiCl), and ethanol were purchased from sigma Aldrich.

### 2.2. Instruments and measurements

Shimadzu UV-1900 UV-VIS Spectrophotometer was used for the collection of the steady state absorption spectra and Shimadzu 6000 Spectrofluorophotometer was used for luminescence emission spectra measurements in aqueous medium. LP980 Edinburgh Instruments laser flash photolysis system was used for the collection of the transient absorption spectra, and in the emission mode for the collection of the luminescence decay of the excited states. Singlet oxygen decay at 1270 nm was collected using Hamamatsu H10330-45 NIR detector as previously described.<sup>50</sup> The excitation source is Q-smart (450 mJ) Nd:YAG Quantel Lasers at 355 nm.

Luminescence decay traces in the visible and infrared regions were found to follow a mono-exponential function.



Scheme 1 Structure of the ligands used.



Singlet oxygen quantum yield,  $\Phi_{\Delta}$ , was obtained by comparing the luminescence intensity of singlet oxygen at 1270 nm photosensitized by the current set of complexes with that obtained from the reference  $[\text{Ru}(\text{bpy})_3]^{2+}$  at zero time in air equilibrated  $\text{D}_2\text{O}$  solution. Luminescence decay traces of ruthenium(II) complexes at different oxygen concentrations were collected by purging the  $\text{D}_2\text{O}$  solution for 20 minutes with argon and oxygen and in air equilibrated solutions.<sup>73</sup>

### 2.3. Synthesis of ruthenium complexes

The homoleptic set of ruthenium complexes under investigations were synthesized and characterized as in literature.<sup>74–76</sup> Structure of the ligands are as shown in Scheme 1.

## 3. Results and discussion

Steady state absorption spectra corresponding to the spin allowed  $d(t_{2g}) \rightarrow {}^1\text{MLCT}$  transition for the complexes under investigation in aqueous medium is shown in Fig. 1 and the corresponding luminescence emission spectra of the  ${}^3\text{MLCT}$  transition to the ground state are shown in Fig. 2. The wavelength of maximum absorption,  $\lambda_{\text{abs}}^{\text{max}}$ , and wavelength of maximum emission  $\lambda_{\text{em}}^{\text{max}}$  are listed in Table 1.

Fig. 1 and Table 1 show that values of  $\lambda_{\text{abs}}^{\text{max}}$  are about  $446 \pm 1$  nm except for  $[\text{Ru}(\text{TMPhen})_3]^{2+}$  and  $[\text{Ru}(\text{DPPhen})_3]^{2+}$  which shows an absorption maxima of 439 nm and 464 nm, respectively. On the other hand, the luminescence emission spectra show a clear variation of the wavelength of maximum emission,  $\lambda_{\text{em}}^{\text{max}}$ , with the type of the ligand with a range from 602 nm to 626 nm. The luminescence quantum yields ( $\Phi_{\text{L}}$ ) of the studied series of complexes was calculated relative to  $[\text{Ru}(\text{bpy})_3]^{2+}$  as a standard with  $\Phi_{\text{L}} = 0.094$ .<sup>77</sup> The obtained luminescence quantum yield of the studied complexes were about the same except for  $[\text{Ru}(\text{TMPhen})_3]^{2+}$  with a value of 0.034 and much lower value for  $[\text{Ru}(\text{NPhen})_3]^{2+}$  mainly due to the enhanced non-radiative process as a result of the presence of the nitro group.

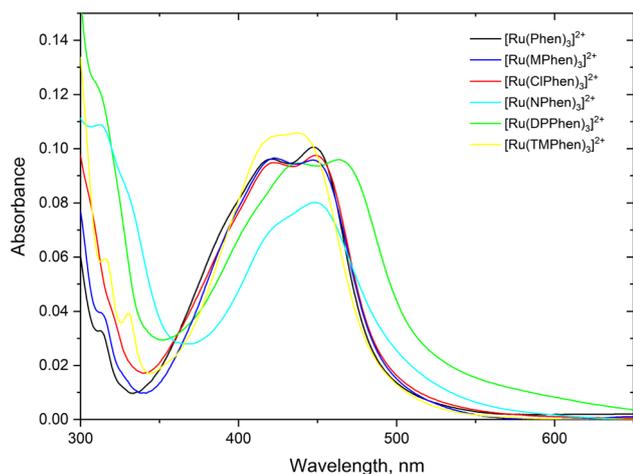


Fig. 1 The absorption spectra of about 5.0  $\mu\text{M}$  the studied complexes, 4.0  $\mu\text{M}$  for  $[\text{Ru}(\text{TMPhen})_3]^{2+}$  and 3.5  $\mu\text{M}$  for  $[\text{Ru}(\text{DPhen})_3]^{2+}$  in water.

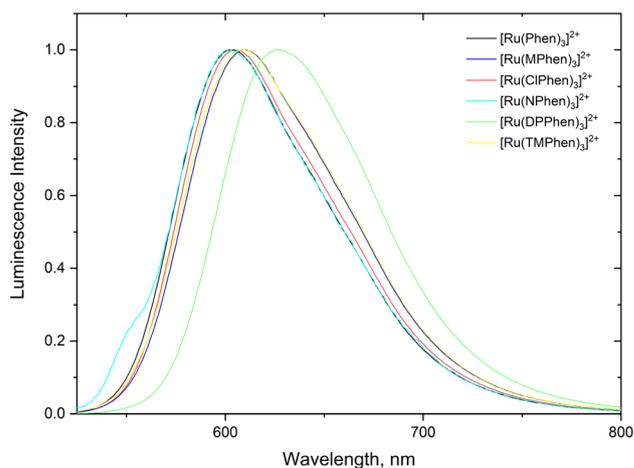


Fig. 2 Normalized luminescence emission spectra the substituted phenanthroline Ru(II) complexes in water.

The transient absorption spectra of the homoleptic Phen, NPhen, ClPhen, MPhen, DMPhen, TMPhen and DPPhen complexes in oxygen free neutral aqueous solution are shown in Fig. 3, from which is clear that the transient absorption covers the range from 300 nm to 800 nm and their decay is consistent with the luminescence lifetime measurements, attributed to deactivation of the lowest  ${}^3\text{MLCT}$  excited state. The transient absorption spectra of the current set of complexes were similar to the previously reported  $[\text{Ru}(\text{phen})_3]^{2+}$  and other derivatives.<sup>78</sup>

The  ${}^3\text{MLCT}$  luminescence lifetime was found to change with the type of the ligand and vary from 0.96  $\mu\text{s}$  in case of  $[\text{Ru}(\text{Phen})_3]^{2+}$  to 2.97  $\mu\text{s}$  in case of  $[\text{Ru}(\text{DPPhen})_3]^{2+}$  in argon purged aqueous solution. Table 1 shows the luminescence lifetime values of all complexes. Luminescence decay of the excited  ${}^3\text{MLCT}$  of the current set of complexes were collected in argon purged, air equilibrated, and oxygen saturated aqueous solution example of which is given in Fig. 4 for  $[\text{Ru}(\text{MPhen})_3]^{2+}$ . Time resolved luminescence emission and excited state absorption decay traces were found to be the same within the experimental conditions. The measured rate constant,  $k_{\text{obs}}$ , was plotted versus oxygen concentrations for all complexes as shown in Fig. 5. The quenching rate constant,  $k_{\text{q}}$ , was obtained from the slope of eqn (1):

$$k_{\text{obs}} = k_0 + k_{\text{q}}[\text{O}_2] \quad (1)$$

where  $k_0$  represents the excited state's decay constant in the absence of oxygen.

The obtained  $k_{\text{q}}$  values from the slope of Fig. 5 were found to be in the range of  $1.02\text{--}4.83 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  which are all  $1/9k_{\text{d}} < k_{\text{q}} < 4/9k_{\text{d}}$  ( $k_{\text{d}} = 2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) in water<sup>37</sup> except for  $[\text{Ru}(\text{NPhen})_3]^{2+}$  where its rate constant is less than  $1/9k_{\text{d}}$  (see Table 1).

It has previously reported that singlet oxygen quantum yield produced as a result of excited  ${}^3\text{MLCT}$  state quenching by oxygen is given by:<sup>79</sup>

$$\Phi_{\Delta} = \Phi_{\text{T}} P_{\text{T}} \text{O}_2^{\text{T}} / \Delta \quad (2)$$



**Table 1** Photophysical properties of Ru(II) phenanthroline derivatives in H<sub>2</sub>O (see text for details) the oxidation potential  $E_{ox}$ , is taken from ref. 89 and corrected for SCE

Complex	$\lambda_{abs}^{max}$ (nm)	$\lambda_{em}^{max}$ (nm)	$\Phi_L$	$E_{ox}/V$		$E_{0-0}/kJ\ mol^{-1}$	$\tau_0/\mu s$	$k_q/10^9\ M^{-1}\ s^{-1}$	$\Phi_\Delta$	$P_T^{O_2}$	$f_\Delta^T$	$p_{CT}$	$\Delta G^\ddagger/kJ$	$\Delta G_{CET}/kJ\ mol^{-1}$
				vs. SCE									$mol^{-1}$	
[Ru(phen) <sub>3</sub> ] <sup>2+</sup>	447	603	0.072	1.28	216.7	0.96	$4.64 \times 10^9$	0.25	0.48	0.52	0.882	13.68	-18.0	
[Ru(NPhen) <sub>3</sub> ] <sup>2+</sup>	449	602	0.002	1.47	217.1	1.28	$1.02 \times 10^9$	0.01	0.29	0.03	0.355	16.18	-0.26	
[Ru(MPhen) <sub>3</sub> ] <sup>2+</sup>	447	610	0.060	1.19	214.3	1.32	$4.77 \times 10^9$	0.23	0.65	0.35	0.883	12.84	-24.2	
[Ru(ClPhen) <sub>3</sub> ] <sup>2+</sup>	449	605	0.062	1.37	216.0	1.22	$3.26 \times 10^9$	0.17	0.52	0.33	0.820	13.91	-8.12	
[Ru(TMPhen) <sub>3</sub> ] <sup>2+</sup>	439	610	0.034	1.05	214.3	2.22	$4.83 \times 10^9$	0.13	0.72	0.18	0.885	12.22	-37.4	
[Ru(DPPhen) <sub>3</sub> ] <sup>2+</sup>	464	626	0.057	1.22	208.8	2.97	$3.40 \times 10^9$	0.03	0.73	0.04	0.810	12.90	-15.9	

where  $\Phi_T$  is the efficiency by which the <sup>3</sup>MLCT state is populated,  $P_T^{O_2}$  is the fraction of the excited <sup>3</sup>MLCT state quenched by oxygen calculated as given by eqn (3), and  $f_\Delta^T$  is the efficiency of singlet oxygen, O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>), production.

$$P_T^{O_2} = \frac{k_q[O_2]}{k_0 + k_q[O_2]} = \frac{\tau_0 - \tau}{\tau_0} \quad (3)$$

It has been proposed that the excited singlet metal-to-ligand charge transfer state (<sup>1</sup>MLCT), which is initially produced by photoexcitation, undergoes an ultrafast intersystem crossing with a near-unity probability to a long-lived triplet state (<sup>3</sup>MLCT) in about 15 fs.<sup>80</sup> Therefore, eqn (2) becomes:

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

The obtained  $\Phi_\Delta$  values in D<sub>2</sub>O, calculated  $P_T^{O_2}$  and  $f_\Delta^T$  values are compiled in Table 1.

The mechanism by which the excited triplet states are quenched by oxygen was first proposed on the basis of spin statistical factors by Gijzeman *et al.*,<sup>81</sup> and modified by Garner and Wilkinson in order to account for oxygen quenching rate constant values higher than  $1/9k_d$  found for multiple systems by including charge transfer complex intermediates and intersystem crossing between them,<sup>82</sup> and later by Wilkinson and Abdel-Shafi who suggested competition between charge transfer assisted quenching with and without energy transfer and non-charge transfer assisted energy transfer,<sup>17,18</sup> and by Schmidt *et al.*<sup>31,83-88</sup> who developed a model that quantifies a parameter  $p_{CT}$  that describes the balance between nCT and CT deactivation pathways and how this balance affect the triplet state quenching rate constant,  $k_q$ , as well as the efficiencies of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) and overall O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) sensitization. For a sensitizer with known triplet energy, it is simple to determine the parameter  $p_{CT}$  from its quenching rate constant.

Fig. 6 shows the dependence of efficiency of singlet oxygen production,  $f_\Delta^T$ , and the quenching rate constant,  $k_q$ , on the oxidation potential of the photosensitizer,  $E_{ox}$ . It is clearly seen that the quenching rate constant decreases as the oxidation potential increases which is consistent with previous findings for aromatic compounds and also for studied coordination compounds. On the other hand, the dependence of  $f_\Delta^T$  on the oxidation potential of the sensitizer is scattered which is inconsistent with previously reported aromatic hydrocarbons data.<sup>17-19</sup> The obtained values of  $k_q$  and  $f_\Delta^T$  can be combined with

previously obtained studies with wider range of oxidation potentials in water for a wider view of the dependence of both parameters on the oxidation potential. Fig. 7a confirms the decrease of the quenching rate constants collected for ruthenium(II) complexes in aqueous solution<sup>37,38,47</sup> with the oxidation potential. On the other hand, the collected efficiencies of singlet oxygen production,  $f_\Delta^T$ , dependence on the oxidation potential for the same sets of complexes (Fig. 7b) show a Boltzmann sigmoidal fit of the form  $y = a_2 + (a_1 - a_2)/(1 + \exp((x - x_0/dx)))$ , with  $a_1$  and  $a_2$  values of  $0.27 \pm 0.05$  and  $1.03 \pm 0.07$ , respectively.

In view of the proposed oxygen quenching of the excited triplet states mechanisms, the initial step of quenching is the formation of the excited encounter complexes of the form <sup>1,3</sup>(<sup>3</sup>M...<sup>3</sup>Σ) with diffusion-controlled rate constant,  $k_d$ , which dissociate back with a rate constant,  $k_{-d}$ , or react forward through a singlet channel, <sup>1</sup>(<sup>3</sup>M...<sup>3</sup>Σ), leading to the formation of the ground state sensitizer and excited molecular oxygen in its first O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>) and/or second excited state O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>), or through the triplet channel, <sup>3</sup>(<sup>3</sup>M...<sup>3</sup>Σ), leading to energy dissipation forming ground state sensitizer and ground state molecular oxygen O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) (Scheme 2).

The overall rate constant  $k_D$  can be evaluated from  $k_q$  using eqn (5) as follows:

$$k_D = k_{-d}k_q/(k_d - k_q) \quad (5)$$

and accordingly, the individual rate constants for the formation of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>),  $k_{1\Sigma}$ , O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>),  $k_{1\Delta}$ , and O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>),  $k_{3\Sigma}$ , can be calculated from eqn (6) and (7) as follows:

$$k_{1\Sigma} = a \times k_D \quad (6)$$

$$k_{1\Delta} = k_D \times (f_\Delta^T - a) \quad (7)$$

$$k_{3\Sigma} = k_D \times (1 - f_\Delta^T) \quad (8)$$

For simple understanding of the differences between Schmidt's treatment and that of Gijzeman *et al.* and its revisions, Scheme 3 is Schmidt's treatment in the framework of an early mechanism by Gijzeman *et al.*<sup>81</sup> As illustrated in Scheme 3, Schmidt *et al.* demonstrate that the production of O<sub>2</sub>(<sup>1</sup>Δ<sub>g</sub>), and O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) proceeds either through a charge transfer channel or a non-charge transfer channel. In Scheme 3,  $k_{\Delta E}^\Delta = k_{\Delta E}^{1\Sigma} + k_{\Delta E}^{1\Delta}$  and  $k_{CT}^\Delta = k_{CT}^{1\Sigma} + k_{CT}^{1\Delta}$ .



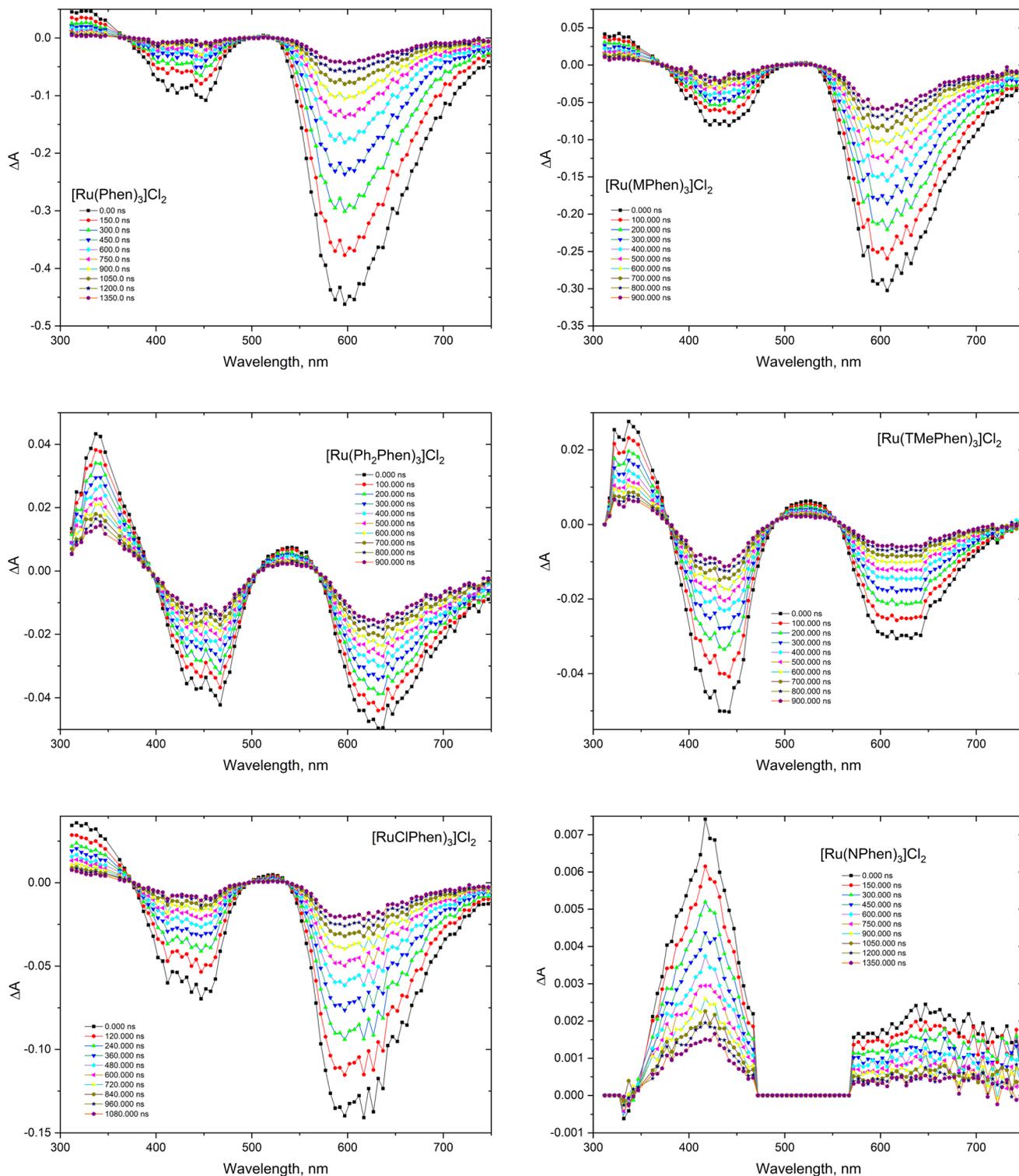


Fig. 3 Transient absorption spectra of the studied complexes in argon purged  $\text{H}_2\text{O}$ .

Schmidt *et al.* model deviates from our earlier kinetic scheme<sup>16–18</sup> primarily by emphasizing the formation of ground molecular oxygen directly from the triplet channel. They have also ignored the equilibrium between the charge transfer exciplexes  $^1(\text{M}^{\delta+} \dots \text{O}_2^{\delta-})$  and  $^3(\text{M}^{\delta+} \dots \text{O}_2^{\delta-})$  a conjecture that we have introduced earlier as well.<sup>41</sup>

The quantity  $p_{\text{CT}}$  is the proportional contribution of charge transfer deactivation to the total deactivation of the excited state by  $\text{O}_2$  defined as:

$$p_{\text{CT}} = \frac{\Sigma k_{\text{CT}}^{\text{P}}}{k_{\text{D}}} = \frac{k_{\text{D}} - \Sigma k_{\Delta\text{E}}^{\text{P}}}{k_{\text{D}}} \quad (9)$$



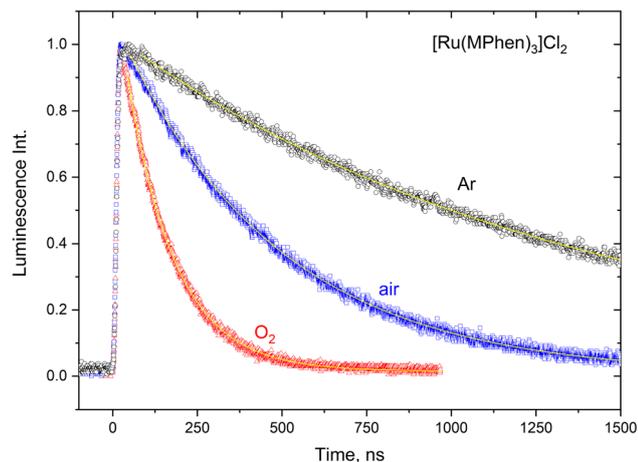


Fig. 4 Luminescence decay traces of the excited  $^3\text{MLCT}$  state of  $[\text{Ru}(\text{MPhen})_3]^{2+}$  at various oxygen concentrations in aqueous solution.

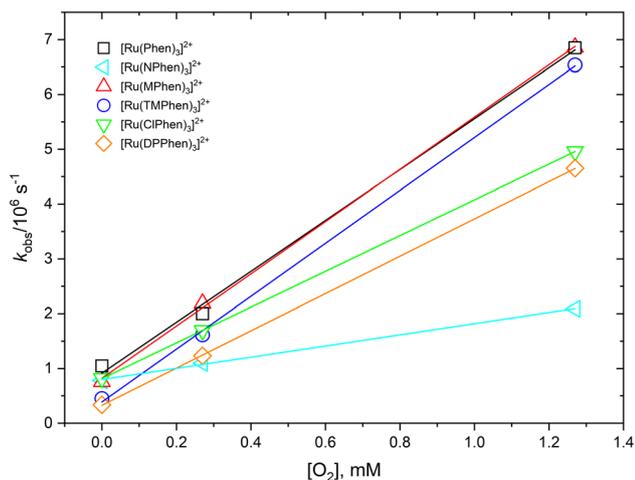


Fig. 5 Dependence of the observed rate constant,  $k_{\text{obs}}$ , versus oxygen concentration for studied complexes in water.

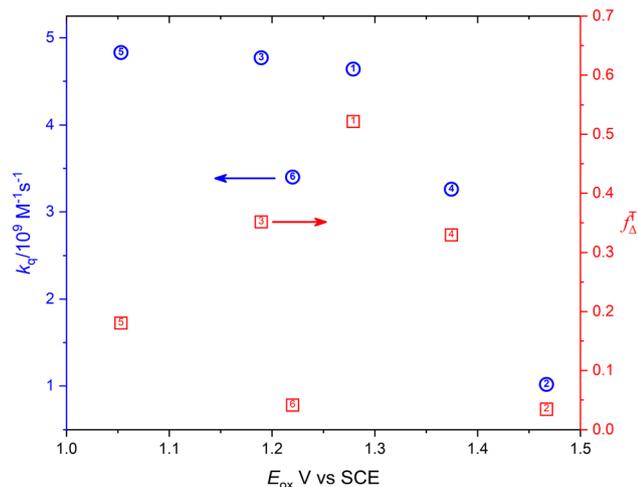


Fig. 6 Dependence of the singlet oxygen production efficiency (red square) and oxygen quenching rate constant (blue circle) on the oxidation potential of the sensitizer.

where  $k_{\text{D}}$  is the overall rate constant of formation of the product,  $k_{\text{D}} = k_{\text{q}}k_{-\text{d}}/k_{\text{d}} - k_{\text{q}}$ ,  $k_{\text{CT}}^{\text{P}} = k_{\text{CT}}^{\Delta} + k_{\text{CT}}^{\Sigma}$ . The  $^{1,3}(\text{T}_1 \dots \Sigma)$  nCT complexes undergo internal conversion (IC) at rates of  $k_{\Delta\text{E}}^{\text{P}} = k_{\Delta\text{E}}^{\Delta} + k_{\Delta\text{E}}^{\Sigma}$  to lower-lying nCT complexes. The energy gap relation  $\log(k_{\Delta\text{E}}^{\text{P}}/m) = f(\Delta E)$  is controlled by the empirical polynomial fit by Schmidt *et al.*<sup>31,83,84,86,90</sup> based on the value of  $\Delta E$ .

$$k_{\text{D}} = \Sigma k_{\Delta\text{E}}^{\text{P}} / (1 - p_{\text{CT}}) \quad (10)$$

Since  $k_{\text{D}} = \Sigma k_{\Delta\text{E}}^{\text{P}} / (1 - p_{\text{CT}})$  and  $k_{\text{CT}}^{\text{P}} = p_{\text{CT}} \Sigma k_{\Delta\text{E}}^{\text{P}} / (1 - p_{\text{CT}})$  hold true, eqn (11) and (12), were used to evaluate the theoretical values of  $f_{\Delta}^{\text{T}}$  and  $k_{\text{q}}$  as follows:<sup>31,83,84,86,90</sup>

$$f_{\Delta}^{\text{T}} = \frac{k_{\Delta\text{E}}^{\Delta}(1 - p_{\text{CT}}) + 0.25 p_{\text{CT}} \Sigma k_{\Delta\text{E}}^{\text{P}}}{\Sigma k_{\Delta\text{E}}^{\text{P}}} \quad (11)$$

$$k_{\text{q}} = \frac{k_{\text{d}} \Sigma k_{\Delta\text{E}}^{\text{P}} / (1 - p_{\text{CT}})}{k_{-\text{d}} + \Sigma k_{\Delta\text{E}}^{\text{P}} / (1 - p_{\text{CT}})} \quad (12)$$

Based on the experimentally determined  $f_{\Delta}^{\text{T}}$  and  $k_{\text{q}}$  the proper values of  $p_{\text{CT}}$  were determined using eqn (11) and (12), by adjusting  $p_{\text{CT}}$  for each sensitizer until the discrepancy between the experimental and calculated values of  $f_{\Delta}^{\text{T}}$  and  $k_{\text{q}}$  is at its smallest, the optimal value of  $p_{\text{CT}}$  is attained. The dependence of  $f_{\Delta}^{\text{T}}$  and  $k_{\text{q}}$  on the estimated values of  $p_{\text{CT}}$  is shown in Fig. 8.

Fig. 7A and B show the dependence of  $f_{\Delta}^{\text{T}}$  and  $k_{\text{q}}$  for the current set of complexes and previously reported results for other series of ruthenium complexes on the reported oxidation potential. Fig. 7A shows that the oxygen quenching rate constant decreases as the oxidation potential of the sensitizer increases. The highest reported value in case of oxygen quenching of the excited  $^3\text{MLCT}$  state of ruthenium complexes in aqueous solution is  $7.01 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ <sup>37</sup> which is smaller than the  $4/9k_{\text{d}}$  based on the diffusion rate constant of  $2.2 \times 10^{10} \text{ s}^{-1}$  in aqueous solution. On the other hand, the reported efficiency of singlet oxygen photosensitized by the same series of ruthenium complexes followed a sigmoidal pattern with approximately minimum value of 0.25, with some exceptions, and highest value of 1.0. The above model is based on the spin statistical factor that led to a minimum value of  $f_{\Delta}^{\text{T}}$  equals 0.25 as expected by eqn (11). It has been found that the inverse correlation between  $f_{\Delta}^{\text{T}}$  and  $k_{\text{q}}$  in case of ruthenium complexes is not always as good as observed for aromatic compounds.<sup>17-19</sup>

It is interesting that the empirical parameter  $p_{\text{CT}}$  can be assessed without knowing the oxidation potential of the sensitizer or the solvent polarity, is extremely intriguing. However, the variations in  $p_{\text{CT}}$  are closely related to modifications in the CT interactions present in excited complexes of sensitizer and  $\text{O}_2$ , which are sensitive to solvent polarity and oxidation potential.

The driving force for charge transfer evaluated by eqn (13) for complete electron transfer from the sensitizer to ground state oxygen,  $\Delta G_{\text{CET}}$ , has been found to be a useful qualitative measure of the strength of CT interactions in the excited complexes involved, despite the fact that in reality there is no full electron transfer observed during these quenching



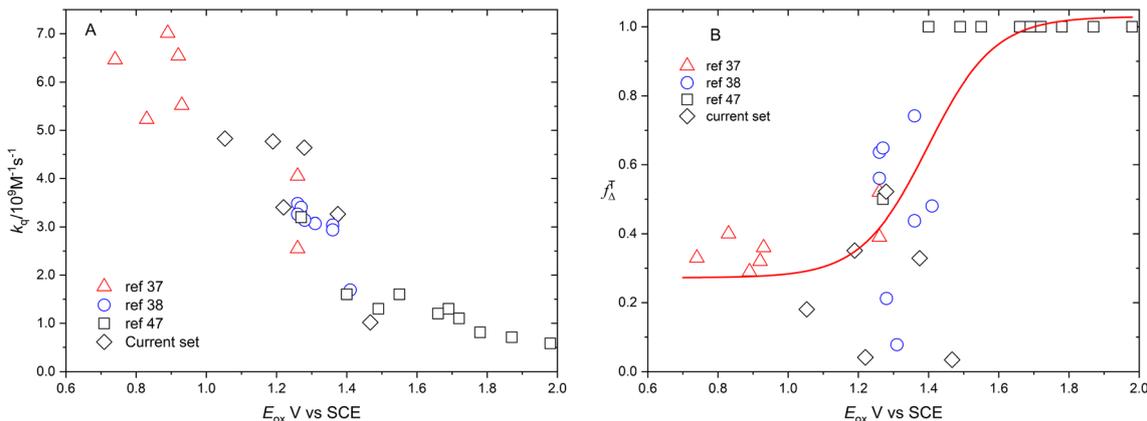
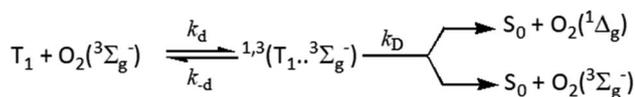


Fig. 7 Dependence of rate constants of quenching by oxygen (A) and efficiency of singlet oxygen production (B) on the oxidation potential of the available ruthenium complexes from literature in aqueous solution together with results of the current work.



Scheme 2

processes. The free energy change,  $\Delta G_{\text{CET}}$ , is calculated by eqn (13)<sup>91</sup> as follows:

$$\Delta G_{\text{CET}} = F(E_{\text{ox}} - E_{\text{red}}) - E_{0-0} + C \quad (13)$$

where  $F$  is Faraday's constant,  $E_{\text{ox}}$  and  $E_{\text{red}}$  are the oxidation potential of the sensitizer and the reduction potential of  $O_2$  (taken as  $-0.41 \text{ V vs. SCE}$  in water<sup>92</sup>), respectively.  $E_{0-0}$  is the excited state energy of the sensitizer (for evaluation see (ref. 37)), and the  $C$  is the electrostatic interaction energy which is taken as  $-2.1 \text{ kJ mol}^{-1}$ .<sup>37</sup>

The experimental free energies of activation,  $\Delta G^\ddagger$ , of the exciplexes  ${}^3(T_1 \cdots O_2)$  and  ${}^1(S_0 \cdots O_2)$  formation can be evaluated by eqn (14) as follows:

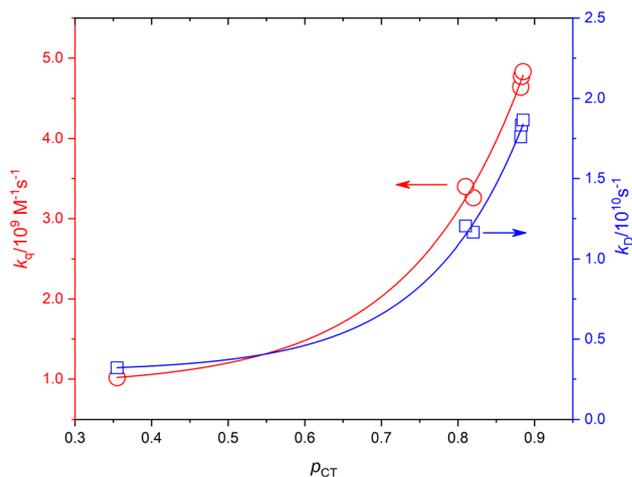
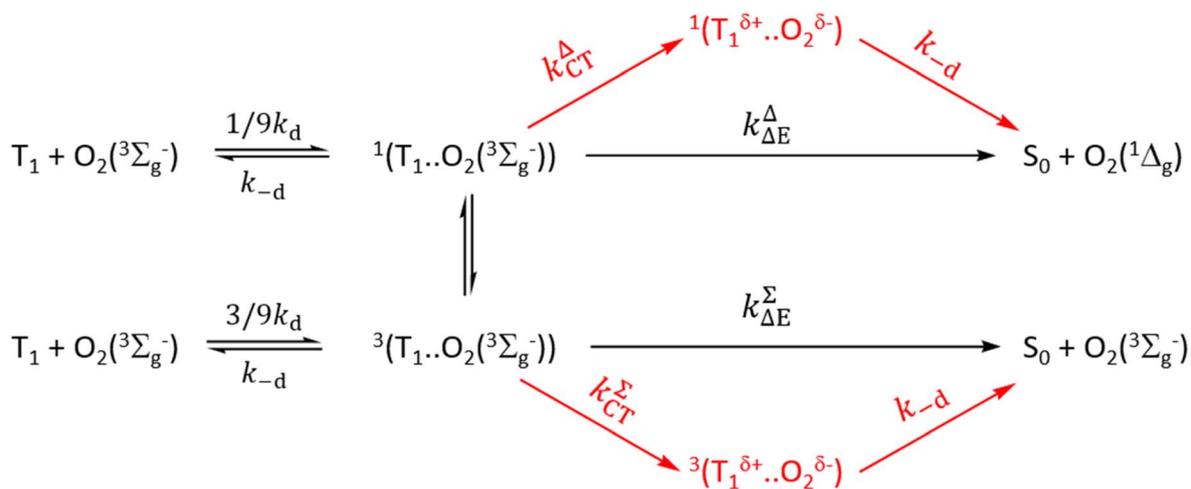


Fig. 8 The dependence of the experimental values of  $k_q$  and calculated values of  $k_D$  on  $\rho_{\text{CT}}$ .



Scheme 3



$$\Delta G^\ddagger = -RT \ln \left( \frac{k_{CT}}{k_B T/h} \right) \quad (14)$$

where  $T$  is the Kelvin temperature,  $k_B$  and  $h$  are the Boltzmann and Planck constants, respectively, and  $k_{CT}$  stands for both  $3 \times k_{CT}^\Sigma$  and  $k_{D,\Delta}$  ( $k_{D,\Delta} = k_{-d} k_q^\Delta / (k_d - k_q^\Delta)$ ).

Eqn (15) describes the dependence of  $\Delta G^\ddagger$  on  $\Delta G_{CET}$  that deviates from the standard Marcus equation by the constant  $f$  as follows:

$$\Delta G^\ddagger = \frac{\lambda}{4} \left( 1 + \frac{f \Delta G_{CET}}{\lambda} \right) \quad (15)$$

The fact that the precise free energy change of exciplex formation  $\Delta G_{CT}$  is unknown but anticipated to be proportional to  $\Delta G_{CET}$  is taken into account by  $f$  such as  $f = \Delta G_{CT} / \Delta G_{CET}$ . The fit of  $\Delta G^\ddagger$  versus  $\Delta G_{CET}$  shown in Fig. 9 accurately depicts the experimental data. The obtained fitting parameters for the corrective factor  $f$  (which is related to the CT character,  $\delta$ , of the exciplexes formed) and the reorganization energy,  $\lambda$ , (which describes the energetic requirements for the reorganization of the complex and its surroundings in the CT step), are 0.125 and 60.0 kJ mol<sup>-1</sup>, respectively. Based on the obtained value of the corrective factor  $f$  which is related to the charge transfer parameter  $\delta$ , by  $\delta = f^{1/2}$ , a charge transfer character of the excited exciplexes  $^3(T_1 \dots ^3\Sigma)$  and  $^1(S_0 \dots ^1\Delta)$  was found to be about 35.3%. The estimated charge transfer character of the excited exciplexes of 35.3% is consistent with the value of 51.5% previously reported by us for a series of ruthenium complexes which is expected to be higher due to their lower oxidation potentials.<sup>37</sup> Slightly higher charge transfer character of the excited exciplexes of 57.5% and 59.2% were reported for a series of biphenyl and naphthalene derivatives in acetonitrile, respectively.<sup>28,34</sup>

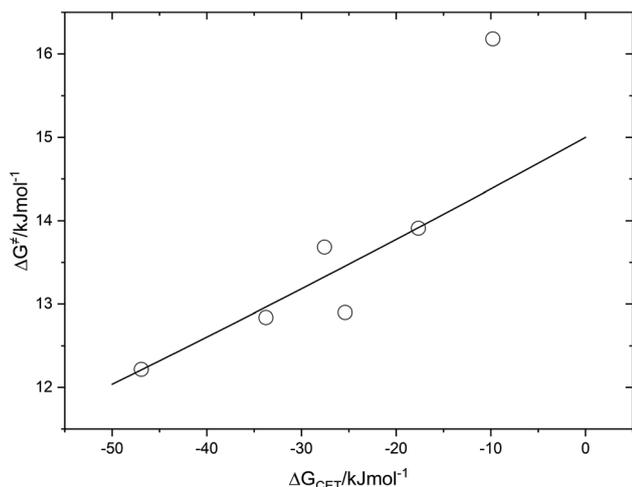


Fig. 9 Correlation of free energy of activation  $\Delta G^\ddagger$  of  $^3(T_1 \dots ^3\Sigma)$  and  $^1(S_0 \dots ^1\Delta)$  exciplex formation on the driving force of charge transfer,  $\Delta G_{CET}$ .

## 4. Conclusion

Photophysical properties of a series of ruthenium(II) phenanthroline derivatives were studied in aqueous medium.  $^3MLCT$  excited state energy,  $E_{0-0}$ , were found to be in the range 215 ± 1 kJ mol<sup>-1</sup> except for [Ru(DPPhen)<sub>3</sub>]<sup>2+</sup> where  $E_{0-0}$  is about 209.0 kJ mol<sup>-1</sup>. The oxidation potential of the current series of sensitizers was in the range from 1.05 V vs. SCE in case of [Ru(TMPhen)<sub>3</sub>]<sup>2+</sup> to 1.47 V vs. SCE in case of [Ru(NPhen)<sub>3</sub>]<sup>2+</sup>. Oxygen quenching rate constants,  $k_q$ , were found to be in the range 1.02 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> for [Ru(NPhen)<sub>3</sub>]<sup>2+</sup> to 4.83 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> for [Ru(TMPhen)<sub>3</sub>]<sup>2+</sup> and were found to decrease as the oxidation potential of the sensitizer increases. On the other hand, the efficiency of singlet oxygen production did not show the familiar correlation with the oxidation potential as has been shown for aromatic compounds. The parameter,  $p_{CT}$ , were estimated for each sensitizer and found to be about 0.84 ± 0.05 except for [Ru(NPhen)<sub>3</sub>]<sup>2+</sup> where  $p_{CT}$  value of 0.355 were used for good evaluation of the calculated  $k_q$  only. It has been found that the experimental values of  $k_q$  and calculated values of  $k_D$  increase as  $p_{CT}$  increases. Data treatment shows a charge transfer character of the excited exciplexes  $^3(T_1 \dots ^3\Sigma)$  and  $^1(S_0 \dots ^1\Delta)$  of about 35.3%. The mechanism of quenching of the excited charge transfer states such as  $^3MLCT$  by molecular oxygen and singlet oxygen thereby produced is much more complicated than with organic sensitizers since more variables are participating simultaneously, such as excited state energy, nature of the excited state, oxidation potential of the sensitizer, spin orbit coupling constant of the central metal in addition to the steric factors imposed by the structural nature of the ligands. Therefore, the exact mechanism of oxygen quenching of the excited states of coordination compounds will not become clear till all these variables are considered and carefully studied.

## Conflicts of interest

There are no conflicts to declare.

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