Research Article

Proton coupled electron transfer reaction of phenols with excited state ruthenium(II) – polypyridyl complexes

K. Swarnalatha[a], E. Rajkumar[b], S. Rajagopal[b]*, R. Ramaraj[b], I. Sadhiya Banu[c] and P. Ramamurthy[c]

The reaction of phenols with the excited state, $^*[Ru(bpy)_3]^{2+}$ ($E_0 = 0.76$ V) and $^*[Ru(H_2dcbpy)_3]^{2+}$, (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) ($E_0 = 1.55$ V *vs.* SCE) complexes in CH_3CN has been studied by luminescence quenching technique and the quenching is dynamic. The formation of phenoxyl radical as a transient is confirmed by its characteristic absorption at 400 nm. The k_q value is highly sensitive to the change of pH of the medium and ΔG^0 of the reaction. Based on the treatment of k_q data in terms of energetics of the reaction and pH of the medium, proton coupled electron transfer (PCET) mechanism has been proposed for the reaction. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: photooxidation of phenols; proton coupled electron transfer; Ru(II)-polypyridyl complexes

INTRODUCTION

The conversion of phenol to phenoxyl radical is of interest to chemists because of its involvement in biologically important processes.[1–10] As oxidants, the ruthenium(II) – polypyridyl complexes, in the excited state, have favorable redox potentials and are chemically stable.[8–10] Miedlar and Das[11] presented a detailed report on the reductive quenching of $^*[Ru(bpy)_3]^{2+}$ by several substituted phenolate ions. In the past decade, we have examined the efficiency of the photoexcited state of ruthenium(II) complexes containing electron-donating and -withdrawing groups in the 4,4'-position of 2,2'-bipyridine $[Ru(NN)_3]^{2+}$, to have electron transfer (ET) reactions with phenolate ions.[12–16] These $[Ru(NN)_3]^{2+}$ complexes in the excited state have not been used for the oxidation of neutral phenols because the reaction is endergonic.[11,17–19] However, the intramolecular ET from phenol to Ru(III) generated from the oxidative quenching of excited state $[Ru(NN)_3]^{2+}$ with external electron acceptors has been reported recently from the laboratory of Hammarstrom.[20–22] Studies on systems with tyrosine appended to Ru(II) and Re(I) complexes showed pH-dependent rate constant for the proton coupled electron transfer (PCET) oxidation of tyrosine.[23] The nature of this pH dependence has recently been of great interest and consensus that these reactions are subject to general base catalysis. Recently Yuasa and Fukuzumi[24] reported interesting mechanistic borderline between one-step hydrogen transfer and sequential transfers of electron and proton in reactions of NADH analog with triplet excited states of tetrazines and $[Ru(bpy)_3]^{2+}$. The one-step hydrogen atom transfer pathway is completely changed to the rate-limiting ET followed by fast proton transfer (PT) when the phenyl group in tetrazine is replaced by pyridine. Ruthenium(II) complex of 4,4'-dicarboxy-2,2'-bipyridine (H_2dcbpy), $^*[Ru(H_2dcbpy)_3]^{2+}$ has higher excited state reduction potential (1.55 V) compared to the parent complex $^*[Ru(bpy)_3]^{2+}$ (0.76 V).[8–10,15,16,25–30] In our recent report, we have shown that $^*[Ru(dcbpy)_3]^{4-}$ (reduction potential = 1.0 V) (at high pH H_2dcbpy

is in the form of 2,2'-bipyridine 4,4'-dicarboxylate ion (dcbpy)) is a better oxidant than $^*[Ru(bpy)_3]^{2+}$ in aqueous alkaline medium (pH 12.5) and the reaction is more exergonic by 0.2 eV.[15,16] As far as H_2dcbpy ligand is concerned, the interesting aspect is that it exists as an anion, CO_2^- (dcbpy), in an alkaline medium but it is in neutral $—CO_2H(H_2dcbpy)$ form in neutral and acidic medium. This aspect is significant here because $—CO_2H$ (Hammet σ value = 0.40) is a better electron-withdrawing group than $—CO_2^-$ ($\sigma = 0.11$) which makes $^*[Ru(H_2dcbpy)_3]^{2+}$ (E_0 1.55 V) a better oxidant than $^*[Ru(dcbpy)_3]^{4-}$ (E_0 1.00 V).[25–27] Because of its favorable reduction potential, we thought it would be interesting to study the luminescence quenching of $^*[Ru(H_2dcbpy)_3]^{2+}$ by neutral phenols in CH_3CN. The photochemical conversion of $PhOH \rightarrow PhO^\bullet$ may take place in a single step (H atom transfer) or sequence of steps (ET followed by PT or vice versa). The mechanism of the photochemical conversion of $PhOH \rightarrow PhO^\bullet$ is a topic of recent interest because of its relevance to the oxidation of tyrosine in photosystem II. As far as the photochemical oxidation of $PhO^- \rightarrow PhO^\bullet$ is concerned, ET is the rate controlling step which has been well established by us and others.[12–16,22–37] On the other hand, the conversion of $PhOH \rightarrow PhO^\bullet$ involves H atom transfer i.e., ET accompanied by PT. In recent years, many group of

---

* Correspondence to: S. Rajagopal, School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India.
  E-mail: seenirajan@yahoo.com

a K. Swarnalatha
  Department of Chemistry, Manomanium Sundaranar University, Tirunelveli, India

b E. Rajkumar, S. Rajagopal, R. Ramaraj
  School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India

c I. S. Banu, P. Ramamurthy
  Department of Inorganic Chemistry, University of Madras, Chennai 600 025, India

workers[22–48] have made sincere attempts to understand whether these ET and PT processes take place in Concerted transfer of electron and proton (CEP) or in stepwise fashion (PCET).

In CH_3CN, ArOH exists predominantly as the $ArOH/CH_3CN$ hydrogen-bond complex, with only minor amounts of the 'free' ArOH being present. Thus, the efficiency of the reaction $ArOH \rightarrow ArO^{\bullet}$ is determined by the strength of the interaction between ArOH and CH_3CN. If the conversion takes place by single step, hydrogen atom abstraction, the rate of reaction is usually related to the bond dissociation energy of phenol. If the phenol is in the form of hydrogen-bonded complex with solvent, the conversion of $ArOH \rightarrow ArO^{\bullet}$ is unlikely to proceed through H-atom transfer reaction. Alternatively the reaction may take place by rate controlling ET followed by fast PT.

A concerted transfer of electron and proton (CEP) facilitates a low energy pathway for the ET process by avoiding the charged intermediates, $PhO^{\bullet}H^+$ and PhO^-, of the stepwise mechanism. The CEP mechanism need not be the fastest one, because the transition state configuration may be more constrained that would increase the activation free energy. This means that the reactant nuclei have to distort into a position where the reactant and product free energy surfaces for CEP are isoenergetic. These geometrical changes involved in the formation of transition state correspond to high reorganization energy (λ). The concerted mechanism is favored energetically and stepwise mechanism has low λ value. These arguments point out that though CEP is a low energy pathway it involves large λ value. Though these views have been considered in detail in recent years on the intramolecular ET from tyrosine to Ru(III), no attempt has been made so far on the bimolecular photoinduced ET reactions of Ru(II) complexes with phenols.[20–22,30–36] To address this problem we have studied the reaction of several phenols with excited state $[Ru(H_2dcbpy)_3]^{2+}$ and $[Ru(bpy)_3]^{2+}$ in CH_3CN by luminescence quenching technique. As the rate of ET from 4-methoxy phenol to $*[Ru(H_2dcbpy)_3]^{2+}$ is facile in a wide pH range and the reaction can be studied by luminescence quenching technique, we are able to address the mechanism of the reaction, concerted electron and proton transfer or stepwise here. To confirm that the quenching process proceeds through the formation of phenoxyl radical we have recorded the spectrum of the transients by laser flash photolysis technique. This study indicates the formation of phenoxyl radical as a transient during the course of the reaction.

EXPERIMENTAL SECTION

Materials

Chloride salts of $[Ru(NN)_3]^{2+}$ (NN = 2,2'-bipyridine, 4,4'-dicarboxyl-2,2'-bipyridine) complexes were prepared by reacting $RuCl_3.3H_2O$ (Aldrich) with the corresponding ligands according to the procedures previously described.[26,49,50] Then the complexes were treated with ammonium hexafluorophosphate to get the PF_6^- salts $[Ru(NN)_3](PF_6)_2$.[49,50] Phenol and its derivatives were purchased from Fluka and Aldrich; phenol was further purified by distillation. HPLC grade solvents were used in all experiments. Buffer solutions were prepared by known literature procedure.[51]

Equipment

The absorption and emission spectral studies were made with SPECORD S100 diode-array spectrophotometer and JASCO FP

6300 spectrofluorometer, respectively. Excited state lifetime and transient absorption measurements were made with laser flash photolysis technique using an Applied Photophysics SP-Quanta Ray GCR-2(10) Nd:YAG laser as the excitation source.[52] The time dependence of the luminescence decay is observed using a Czerny–Turner monochromator with a stepper motor control and a Hamamatsu R-928 photomultiplier tube. The production of the excited state on exposure to 355 nm was measured by monitoring (pulsed Xenon lamp of 250 W) the absorbance change. The change in the absorbance of the sample in laser irradiation was used to calculate the rate constant as well as the time-resolved absorption transient spectrum. The change in the absorbance on flash photolysis was calculated using the expression

$$\Delta A = \log\left(\frac{I}{I_0 - \Delta I}\right) \quad (1)$$

$$\Delta I = (I - I_t) \quad (2)$$

where ΔA is the change in the absorbance at time t, I_0 is the voltage after flash, I is the pretrigger voltage and I_t is the voltage at particular time. A plot of $\ln (\Delta A_t - \Delta A_\infty)$ *versus* time gives a straight line. The slope of the straight line gave the rate constant for the decay. The reciprocal of these values gave the lifetime of the triplet. The time-resolved transient absorption spectrum was recorded by plotting the change in absorbance at a particular time *versus* wavelength.

The redox potentials of $[Ru(NN)_3]^{2+}$ complexes in an acetonitrile medium were determined by cyclic voltammetric technique using EG & G Princeton Applied Research Potentiostat/Galvanostat Model 273A. A glassy carbon (working electrode) and a standard (Ag/Ag+) electrode (reference electrode) were used for the electrochemical measurements and tetrabutylammonium perchlorate (0.1 M) was the supporting electrolyte.

Quenching studies

Freshly prepared solutions were used for the spectral measurements. The solutions used for the excited state lifetime and emission measurements were deaerated by dry argon and N_2 gas respectively for 20 min. The change of emission intensity of $*[Ru(NN)_3]^{2+}$ with change of [Q] measured at 298 K is shown in Fig. 1. The quenching rate constant, k_q, for the reaction was
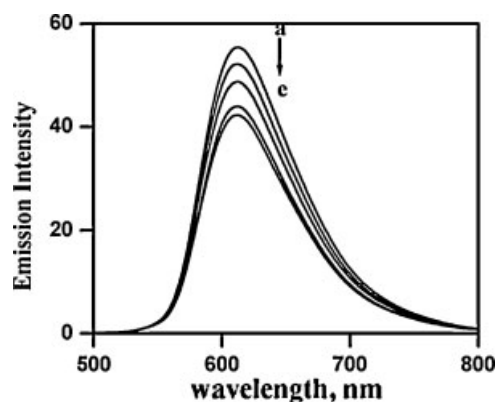

Figure 1. The change of emission intensity of (i) $*[Ru(H_2dcbpy)_3]^{2+}$ with different concentrations of 2,6-dimethyl phenol in acetonitrile of (a) 0, (b) 0.001, (c) 0.002, (d) 0.003, (e) 0.004 M
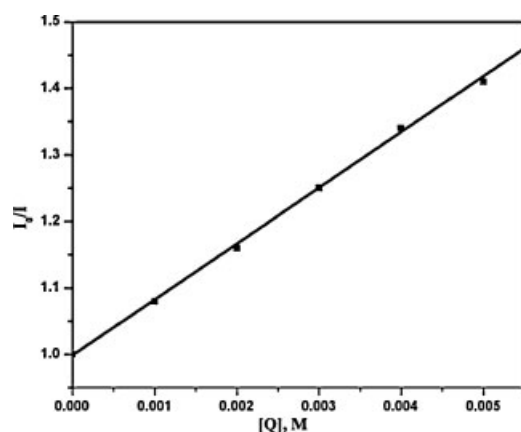
Figure 2. Stern–Volmer plot for the reductive quenching of $^*[Ru(H_2dcbpy)_3]^{2+}$ with 2,6-di-*tert*-butyl phenol

determined by the luminescence-quenching technique from the Stern–Volmer equation using emission intensity data[53]

$$\frac{I_o}{I} = 1 + k_q \tau_o [Q] \qquad (3)$$

where I_o and I are the emission intensities in the absence and presence of the quencher respectively and τ_o is the emission lifetime of Ru(II) complexes in the absence of the quencher. A sample Stern–Volmer plot for the luminescence quenching of $^*[Ru(NN)_3]^{2+}$ with phenol is shown in Fig. 2.

RESULTS AND DISCUSSION

The structures of the ligands of $[Ru(NN)_3]^{2+}$ complexes used in the present study are shown in Chart 1. The absorption and
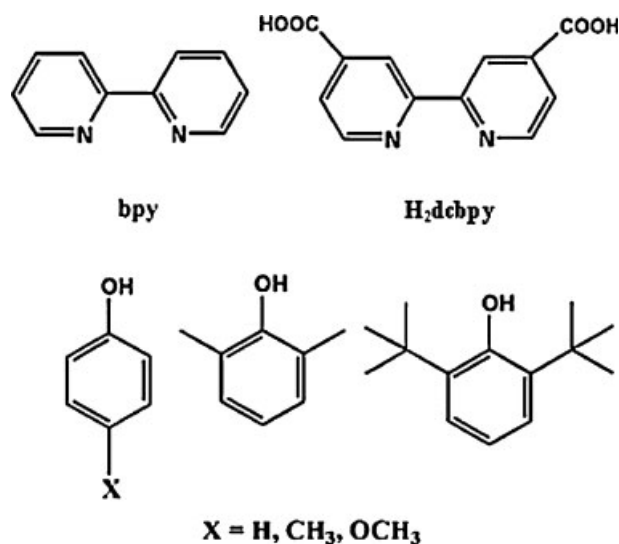

Chart 1. Structure of the ligands and the quenchers

emission spectral data and the excited state lifetimes and the redox potentials of $[Ru(NN)_3]^{2+}$ complexes used in the present study are collected in Table 1. These values are close to the already reported values.[8–10,25–30] The bimolecular quenching rate constant, k_q, values for the reductive quenching of two Ru(II) complexes $^*[Ru(bpy)_3]^{2+}$ and $^*[Ru(H_2dcbpy)_3]^{2+}$ with various phenols measured from the Stern–Volmer plots along with the values for the quenching on $^*[Ru(dcbpy)_3]^{4-}$ with phenolate ions are given in Table 2. The free energy change (ΔG^0) values calculated from the reduction potentials of $[Ru(NN)_3]^{2+}$ and oxidation potentials of phenols/phenolate ions are collected in Table 3. The reductive quenching of $^*[Ru(bpy)_3]^{2+}$ and $^*[Ru(H_2dcbpy)_3]^{2+}$ with *p*-methoxy-phenol has been studied

Table 1. Absorption and emission spectral data, excited state lifetime (in ns), and redox properties of $[Ru(NN)_3]^{2+}$ complexes in acetonitrile medium at 298 K

Photophysical data	$[Ru(bpy)_3]^{2+}$	$[Ru(H_2dcbpy)_3]^{2+}$
Absorption maximum, λ_{abs}, max nm (ε_{max}, $M^{-1} cm^{-1}$)	452(14 500)	467(11 600)
Emission maximum	612	636
Life time (ns)	850	1080
E_{em} (eV)	2.12	2.1
$E^0{}_{Ru}{}^{2+*/+}$ (V) *vs.* SCE	0.76	1.55

Table 2. Rate constant, k_q, values for the reductive quenching of $^*[Ru(NN)_3]^{2+}$ with phenols in acetonitrile at 298 K

Quencher	$[Ru(bpy)_3]^{2+}$	$[Ru(H_2dcbpy)_3]^{2+}$	$^a[Ru(dcbpy)_3]^{4-}$
Phenol	—	—	5.2×10^8
4-Methyl phenol	4.2×10^6	9.2×10^6	1.3×10^9
4-Methoxy phenol	3.8×10^7	7.6×10^8	1.2×10^9
2,6-Dimethyl phenol	7.3×10^6	2.0×10^7	2.2×10^9
2,6-Di-*tert*-butyl phenol	1.0×10^7	1.3×10^6	—

^{a} As the reaction has been carried out at pH = 12.5 all phenols present in the form of phenolate ions.

Table 3. ΔG^0 (eV) values for the reductive quenching of $^*[Ru(NN)_3]^{2+}$ with phenols in acetonitrile at 298 K

Quencher	E^0_{oxd} (V) *vs*. SCE	$[Ru(bpy)_3]^{2+}$	$[Ru(H_2dcbpy)_3]^{2+}$
Phenol	1.69 (0.86)	0.93	0.14
4-Methyl phenol	1.67 (0.71)	0.91	0.12
4-Methoxy phenol	1.30 (0.58)	0.54	−0.25
2,6-Dimethyl phenol	1.81 (0.50)	1.05	0.26
2,6-Di-*tert*-butyl phenol	1.86	1.10	0.31

Values in the parenthesis are the oxidation potentials of phenols *versus* NHE in aqueous medium.[68]

at different acid concentrations using trichloroacetic acid and the k_q values are given in Table 4.

Luminescence quenching rate constants

The Stern–Volmer plots from the emission intensity data (Fig.2) are linear for all photoredox systems, indicating that dynamic quenching is the predominant process and the contribution from static quenching is negligible. In order to check the ground-state complex formation, phenol is added in increments to the $[Ru(NN)_3]^{2+}$ complexes and the spectra recorded at different (phenol) are shown in Fig. 3. There is no significant change in the absorption spectra of $[Ru(NN)_3]^{2+}$ in the presence of phenol under the present experimental conditions which helps us to conclude that the contribution from the static quenching is negligible here (Fig. 3). At this juncture it is relevant to mention the observations of Hoffman *et al.*[6,17,19] on the interaction between $[Ru(bpy)_3]^{2+}$ and the solutes that possess aromatic regions (phenol) by ^1H NMR technique. Phenol with its hydrophobic and hydrophilic regions engages in both π-stacking with the Ru(II) complex and H-bonding with water forming a pseudo-micellar structure.[17–19,54] The importance of H_2O in the observed phenomena was supported by the observation of a lack of any ground-or excited-state effects when CH_3CN was used as the solvent.
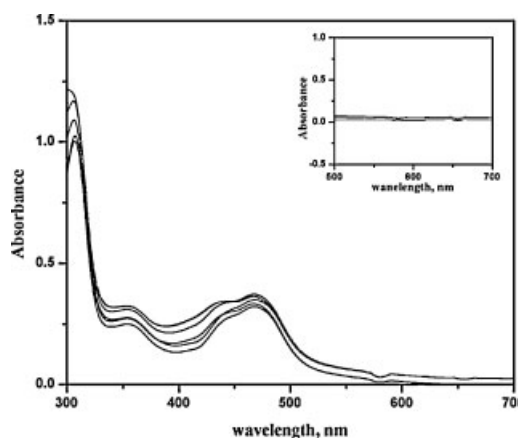
Miedlar and Das[11] have reported that the quenching rate constant for the photoreduction of $[Ru(bpy)_3]^{2+}$ with 4-methoxy phenol is $1.8 \times 10^7 M^{-1} s^{-1}$ in aqueous solution at pH 7. On the other hand, it is found from the present study that for the same reaction in acetonitrile, the k_q value is $3.8 \times 10^7 M^{-1} s^{-1}$. When we use $^*[Ru(H_2dcbpy)_3]^{2+}$ as the photosensitizer, the quenching rate constant becomes $7.6 \times 10^8 M^{-1} s^{-1}$ i.e., when the ligand bipyridine is replaced by 4,4′-dicarboxyl-2,2′-bipyridine, the k_q value increases by more than one order (20 times). If ΔG^0 is the

only important parameter and the reaction proceeds through the rate controlling ET process then the difference should be still higher because ΔG^0 values differ by ~ 0.8 eV. These results seem to point out that other factors also play a role and the reaction is unlikely to proceed through simple ET mechanism. In order to understand the role of other factors like the steric effect on the rate of the reaction, quenching reaction has been studied using phenols with bulky substituents such as methyl and *tert*-butyl groups on the 2- and 6-positions. Interestingly, the quenching rate constant value is varied slightly when we introduce methyl in the 2,6-positions compared to 4-methyl phenol (Table 2). On the other hand, substantial decrease in k_q value is observed when *tert*-butyl group is introduced in the 2, 6-positions of phenol. In our recent reports, we have unequivocally established that steric effect is predominant only if both reactants, $^*[Ru(NN)_3]^{2+}$ and phenolate ions, carry bulky groups.[7] We have shown previously that we could observe noticeable steric effect (30 times) when $[Ru(dtbpy)_3]^{2+}$ (dtbpy = 2,6-di-*tert*-butyl-2,2′-bipyridine) and 2,6-di-*tert*-butyl phenolate ion were used as the photosensitizer and quencher, respectively.[15,16]

In the present study also we are able to observe predominant steric effect for the reaction between $^*[Ru(H_2dcbpy)_3]^{2+}$ and 2,6-di-*tert*-butylphenol as the reactants. This steric effect can be ascribed to the increase of ET distance when the reaction occurs between two reactants carrying bulky groups. It is important to mention that though *tert*-butyl group is bulky it is an electron donating group and has negative Hammett σ values. The

Table 4. The k_q, $M^{-1} s^{-1}$ values for the reductive quenching of $^*[Ru(NN)_3]^{2+}$ with 4-methoxy phenol as a quencher at different pH in aqueous medium

pH	$[Ru(bpy)_3]^{2+}$	$[Ru(H_2dcbpy)_3]^{2+}$
4	No quenching	4.1×10^8
6	No quenching	5.5×10^8
8	2.2×10^7	4.0×10^8
10	1.2×10^9	2.0×10^8
12.5	3.3×10^9	1.2×10^9

Figure 3. Absorption spectra of $[Ru(H_2dcbpy)_3]^{2+}$ in the presence of 2,6-di-*tert*-butyl phenol in acetonitrile medium at the concentrations of (a) 0, (b) 0.001, (c) 0.002, (d) 0.003, and (e) 0.004 M. (Inset:Subtracted spectra of Ru(II) complex and Phenol from the reaction mixture)

predominant steric effect observed here seems to point out PCET rather than simple ET from phenol to the sensitizer in the rate controlling step.

Effect of pH on the rate of luminescence quenching reaction

In recent years, much importance is given to understand the correct mechanism for the conversion of $Tyr_z \rightarrow Tyr_z^*$ in photosystem II.[20–22,55–57] To get an idea on this problem, model systems have been designed involving $[Ru(NN)_3]^{2+}$ as photosensitizers. The excited state $[Ru(NN)_3]^{2+}$ complex is oxidized by external electron acceptors, MV^{2+} or Co^{3+} to generate $[Ru(NN)_3]^{3+}$. This tripositive ion abstracts H atom from tyrosine to generate tyrozyl radical. Based on the pH dependence of this process, the authors concluded that if the reaction is pH dependent it proceeds through PCET mechanism. If the reaction is pH independent the reaction proceeds through H-atom transfer mechanism. Thus to get a clue on the mechanism of the reaction the quenching of $*[Ru(bpy)_3]^{2+}$ and $*[Ru(H_2dcbpy)_3]^{2+}$ has been studied at different pH and the k_q values are given in Table 4. Interestingly, the quenching of $[Ru(bpy)_3]^{2+}$ with 4-methoxy phenol is highly sensitive to pH and thus the reaction is likely to proceed through PCET mechanism particularly at $pH < pK_a$ of phenol. At $pH > pK_a$, the reaction proceeds through ET mechanism.

The k_q data collected in Table 4 show that the k_q value for $[Ru(H_2dcbpy)_3]^{2+}$ is little sensitive to the change of pH when $pH < pK_a$; the k_q value is high at $pH > pK_a$ compared to the values at low pH. As far as $[Ru(H_2dcbpy)_3]^{2+}$ ion is concerned at low pH H_2dcbpy is in the form of undissociated acid but it gets dissociated when $pH > 7$. In between pH 2 and 7 the extent of dissociation may vary depending on the pH of the medium. As already pointed out in the introduction, the reduction potential of $[Ru(H_2dcbpy)_3]^{2+}$ is high (1.55 V) if H_2dcbpy is in the undissociated form. When it is in the form of dianion at high pH the reduction potential of $[Ru(dcbpy)_3]^{4-}$ is low (1.0 V) (*vide infra*). However, the k_q data collected on the quenching of $*[Ru(bpy)_3]^{2+}$ with 4-methoxy phenol help us to conclude that the reaction proceeds through PCET mechanism when phenol is in neutral form.

Driving force dependence of the quenching rate constants

The rate of ET from a donor molecule to an acceptor in a solvent is controlled by free energy change of the reaction (ΔG^0), the reorganization energy (λ), and the electronic coupling between the reactant and product states (Eqn (4)).[58–60]

$$k_{et} = \frac{2\pi H_{rp}^2}{\hbar (4\pi\lambda k_B T)^{1/2}} \exp\frac{-(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \quad (4)$$

The free energy change (ΔG^0) of ET reaction can be calculated by the following expression:

$$\Delta G^0 = E_{(ArOH/ArO\cdot)} - E_{Ru}^{*2+/+} + w_p - w_r \quad (5)$$

and λ_o, the solvational reorganization energy is given by

$$\lambda_o = (\Delta e)^2 / 4\pi\varepsilon_0 [1/2r_A + 1/2r_B - 1/r][1/D_{op} - 1/D_s] \quad (6)$$

In Eqn (5) and (6), $E_{(ArOH/ArO\cdot)}$ and $E_{Ru}^{*2+/+}$ are the oxidation potential of phenol and excited state reduction potential of $[Ru(NN)_3]^{2+}$, w_p and w_r are the work terms accounting for the work required to bring the products and reactants together, D_{op}

and D_s are the optical and static dielectric constants of the solvent, respectively, and r_A and r_B are the radii of the reactants.[15,16,61] The value of λ_o calculated from Eqn (6) was found to be 0.83 eV at this pH. The ΔG^0 values calculated using Eqn (6) are given in Table 3.

It is important to point out that the oxidation potential of ArOH is pH dependent and the variation of $E_{(ArOH/ArO}\bullet)$ with pH is given by the following equation for $pH < pK_a$.

$$E_{ArOH} = [E_{ArOH}^0 - (RT \ln 10 \times pH)/F] \quad (7)$$

Recently Hammarström and co-workers[31–39] have demonstrated that the driving force ($-\Delta G^0$) for the reaction of phenol with Ru(III) (both inter- and intramolecular processes) increases with pH as represented by Eqn (8) for the intramolecular process in the Ru–Tyr complex.

$$\Delta G^0 = FE_{ox} - 0.059 \times (pH + 2) \, V \quad (8)$$

The data collected in Table 4 show that the luminescence quenching of $[Ru(bpy)_3]^{2+}$ with 4-methoxyphenol is pH dependent and it varies from 2.2×10^7 at $pH = 8$ to 3.3×10^9 at $pH = 12.5$. On the other hand at acidic pH (pH 4 and 6) no quenching is possible. At low pH, the reaction is endergonic and thus the quenching process is slow.

As far as *p*-methoxyphenol is concerned $E = 1.30$ V when it is in the unionized form and the value is 0.58 V when it is in the form of phenolate ion. The pK_a value of 4-methoxy phenol is 10.2. Thus from the pH dependence of k_q values we realize that at $pH < pK_a$, the k_q value is largely pH dependent and at pH values more than pK_a, k_q value is little sensitive to the change of pH of the medium. When we look at the k_q values obtained for the quenching of $*[Ru(bpy)_3]^{2+}$ with 4-methoxy phenol at different pH there is no quenching at $pH < 8$. At pH 8, the k_q value is 2.2×10^7 and at $pH = 10$, the value becomes $1.2 \times 10^9 \, M^{-1} \, s^{-1}$ and at $pH > 10$ the change in k_q value is small. These data clearly point out that the quenching process is highly sensitive to pH and the change of oxidation potential of phenol with pH should be considered to account for the effect. Using a pH-dependent driving force (Eqn (8)) in the Marcus equation (Eqn (4)), it is possible to derive an expression for the pH dependence of the ET rate constant. When the phenol is in the unionized form, the electron and proton transfer occur simultaneously in one reaction step, with one common transition state. For PCET, the reaction coordinate region must be where the free energy surfaces for the reactant and product state cross (the transtition state). Since the O—H bond is broken in the reactions, the product free energy surface is repulsive in the O—H coordinate, and the transition state involves an elongated O—H bond and leads to large λ at $pH < 10$. With an increase in pH, the entropy of mixing due to protonation increases, whereas the free energy of the product state decreases (Fig. 4). These arguments indicate that $\Delta G^\#$ for the proton coupled ET reaction decreases with pH thus accounting for the increase in k_q values with pH for the quenching of $[Ru(bpy)_3]^{2+}$ with 4-methoxy phenol. The marked increase (> 100 fold) in the rate constant going from the protonated form of phenol to the unprotonated form is mainly due to the decrease in λ. At low pH $\lambda = 2.0$ eV compared to 0.9 eV at high pH. The large λ value at low pH is probably an effect of large inner-sphere reorganization, possibly characteristic for the proton coupled ET bond-breaking reaction.

On the other hand, if we look at the k_q values obtained for the quenching of $[Ru(H_2dcbpy)_3]^{2+}$ with 4-methoxy phenol as a
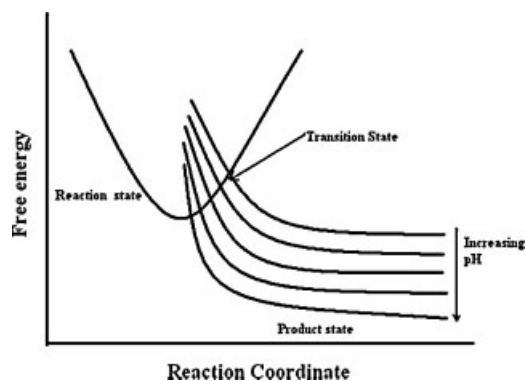
Figure 4. Schematic picture of the potential surface for the reactant and product states. The product state is repulsive in the OH-coordinate. All other contributions to the reaction coordinate are perpendicular to the plane of the figure. The free energy of the product state at equilibrium decreases with pH due to an increased entropy of mixing of the released proton. The decrease in energy is reflected in the transition state position, which gives a pH-dependent reaction rate

function of pH though the k_q value is high at pH > pK_a, there is no clear trend when pH < pK_a. It is important to remember that apart from ArOH, the nature of the ligand in [Ru(H$_2$dcbpy)$_3$]$^{2+}$ depends on the pH of the medium i.e. in the form of —CO$_2$H at low pH and —CO$_2^-$ at high pH. The reduction potential of [Ru(H$_2$dcbpy)$_3$]$^{2+}$ varies substantially with the change of pH of the medium. If the ligand is in the form of —CO$_2$H, the $E^0_{Ru^{2++}/Ru}$ is 1.55 V and if it is in the —CO$_2^-$ form the reduction potential is 1.0 V. Thus, the increase of pH facilitates the oxidation of phenol but retards the reduction potential of *[Ru(NN)$_3$]$^{2+}$ when NN is 4,4'-dicarboxyl-2,2'-bipyridine. This opposing trend observed with the electron donor and acceptor with the change of pH is responsible for the absence of clear trend in the k_q values observed with [Ru(H$_2$dcbpy)$_3$]$^{2+}$.

In order to understand the driving force dependence of the photooxidation of phenols using [Ru(bpy)$_3$]$^{2+}$ and [Ru(H$_2$dcbpy)$_3$]$^{2+}$ as the photosensitizers, the values of log k_{et} are plotted against the ΔG^0 values (Fig. 5). The values of k_{et} were
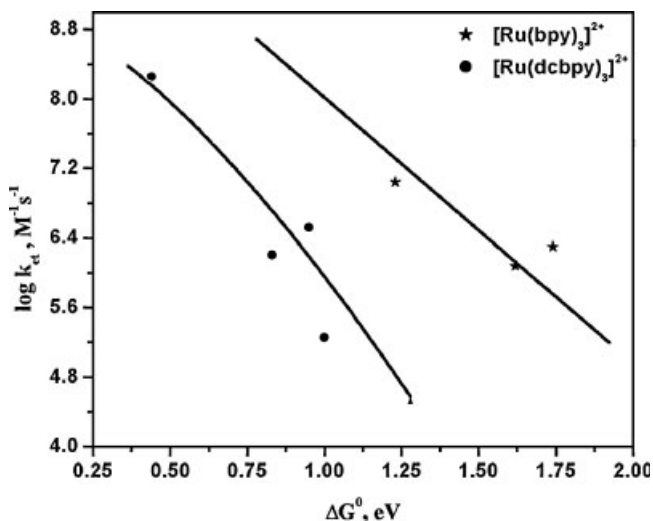

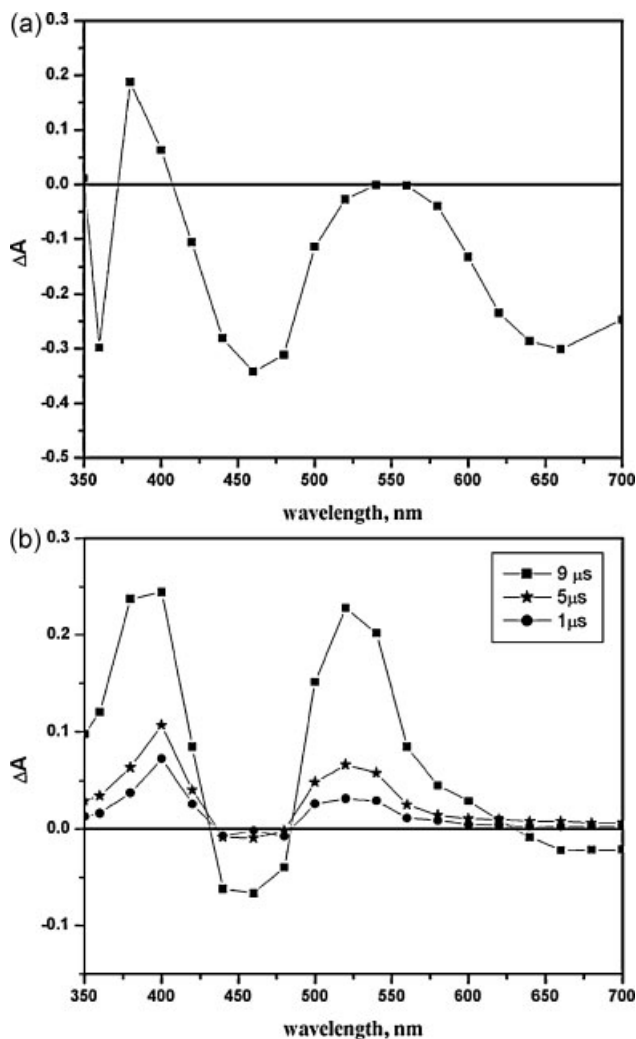**Figure 6.** (a) Transient absorption spectrum of [Ru(H$_2$dcbpy)$_3$]$^{2+}$ in acetonitrile obtained after 1 μs of 355 nm laser flash photolysis. (b) Transient absorption spectrum of [Ru(H$_2$dcbpy)$_3$]$^{2+}$ in the presence of 0.05 M *p*-methoxy phenol in acetonitrile obtained after 1, 5, and 9 μs of 355 nm laser flash photolysis

Figure 5. Plot of log k_{23} versus ΔG^0 (eV) for the reductive quenching of *[Ru(NN)$_3$]$^{2+}$ with phenols

determined from the experimentally observed k_q values using the relation shown below.

$$k_q = \frac{k_d}{1 + (k_d k_{et} K_{eq})}$$

where k_d is the diffusion-controlled rate constant, K_{eq} is the equilibrium constant for the formation of the encounter complex, and k_{et} is the forward ET rate constant. Recently Mayer and co-workers[62] have established that despite its simplifications, the adiabatic Marcus equation is still the logical starting point for the proton coupled ET reactions of phenols. It is important to point out that the inner-sphere reorganization for phenol is unusual because it involves not only small shifts in equilibrium bond distances, as in the standard Marcus model, but also movement of a proton across an OH—oxidant bond. The proton can be thought of as transferring ~0.7 Å between two minima on an adiabatic potential energy surface. This would not seem to fit easily into the standard Marcus model, where a single parabolic surface, defined by the reorganization energy λ, describes all of the solvent and inner-sphere reorganizations. When Mayer[62]
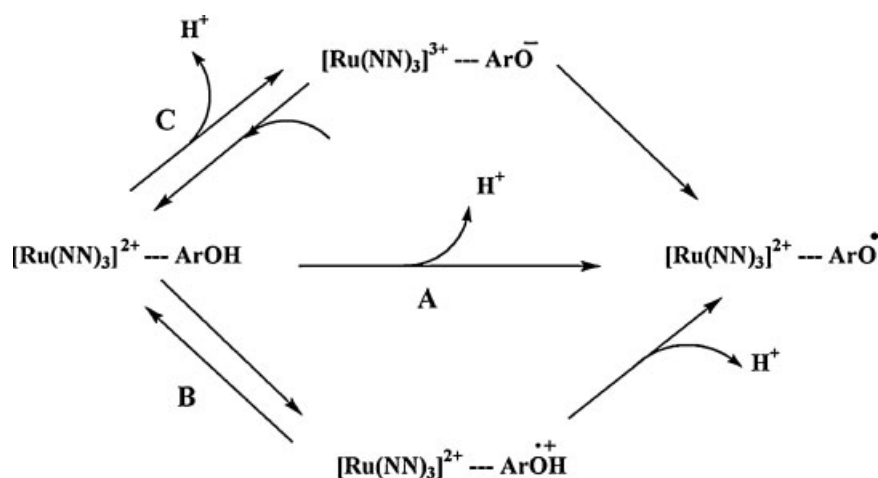
Scheme 1. Mechanism for the luminescence quenching of $^*[Ru(NN)_3]^{2+}$ with ArOH. (A) Proton coupled electron transfer (PCET), (B) Stepwise electron proton transfer (ETPT), (C) proton transfer followed by electron transfer (PTET)

applied Marcus theory for the PCET reaction of phenols with iron(III)-polypyridine complexes he observed log k_{et} *versus* ΔG^0 plot similar to Fig.5 shown here. Thus, the reaction of $[Ru(NN)_3]^{2+}$ with neutral phenols is likely to proceed through proton coupled ET mechanism not by ET. Thus the plot of log k_{et} *versus* ΔG^0 also supports the operation of PCET at low pH. In sum, the dependence of quenching rate constants on the driving force, effect of pH, and transient spectrum are consistent with the PCET mechanism. These conclusions are consistent with the findings of Hammarstrom and co-workers[31–33] for their system.

Absorption spectrum of transient formed from the reaction of $^*[Ru(H_2dcbpy)_3]^{2+}$ with 4-methoxy phenol

The ground-state absorption spectrum of $[Ru(H_2dcbpy)_3]^{2+}$ is shown in Fig. 1. The strong absorption in the 300 nm corresponds to the $\pi-\pi^*$ (LC) transition and the low energy absorption at 467 nm is assigned to the $d_{\pi-\pi}^*$ (MLCT) transition. We have recorded the excited-state absorption for $^*[Ru(H_2dcbpy)_3]^{2+}$ in an acetonitrile medium. In Figs 6(a) and (b), ΔA is proportional to $\varepsilon^*-\varepsilon^g$ where ε^* and ε^g are the extinction coefficients of Ru(II) complex in the excited and ground states, respectively, at the particular wavelength. Figures 6(a) and (b) are the absorption spectra of $^*[Ru(H_2dcbpy)_3]^{2+}$ recorded in the absence and presence of 0.05 M 4-methoxy phenol. The band decay at 467 and 600 nm corresponds to the $[Ru(H_2dcbpy)_3]^{2+}$ absorption. The band formation at 380 nm corresponds to the ligand with anionic character on the basis of its similarity (in location) with the spectrum of 2,2′-bipyridine radical anion.[8–10] The peak formation at 400 nm in the presence of 4-methoxy phenol is attributed to the 4-methoxy phenoxyl radical and another band at 520 nm to the formation of $[Ru(H_2dcbpy)_3]^{+}$ species.[61–65] As shown in Scheme 1, due to PCET from phenol to $^*[Ru(H_2dcbpy)_3]^{2+}$, phenoxyl radical and $[Ru(H_2dcbpy)_3]^{+}$ are formed as the transients. The lifetime of the 4-methoxy phenoxyl radicals formed at the wavelength 400 nm has been calculated to be 1.5 μs.[66,67]

CONCLUSION

The photoinduced reaction of $[Ru(NN)_3]^{2+}$ with neutral phenols in CH$_3$CN proceeds through PCET mechanism. However, when the reaction is carried out at pH $>$ pK_a the reaction occurs via simple ET mechanism. Though the reaction of $^*[Ru(H_2dcbpy)_3]^{2+}$ with 4-methoxy phenol is facile in a wide pH range, these data are not of much value to decide on the nature of the mechanism because of the nature of the H$_2$dcbpy at different pH. On the other hand, the reaction of $^*[Ru(bpy)_3]^{2+}$ with 4-methoxyphenol at different pH clearly shows that reaction at low pH proceeds through PCET mechanism. The reaction of $^*[Ru(H_2dcbpy)_3]^{2+}$ with 2,6-disubstituted phenols entails large steric effect in the wide pH range. These results on model reactions help us to propose the formation of phenoxyl radical from phenol in photosystem II may occur by PCET mechanism at pH $<$ pK_a and by ET at pH $>$ pK_a.

REFERENCES

[1] M. H. V. Huynh, T. J. Meyer, *Chem. Rev.* **2007**, *107*, 5004–5064.
[2] C. J. P. Monteiro, M. M. Pereira, M. E. Azenha, D. Burrows, C. Serpa, L. G. Arnaut, M. J. Tapia, M. Sarakha, P. W.-W-. Chung, S. Navaratnam, *Photochem. Photobiol. Sci.* **2005**, *4*, 617–624.
[3] Z. Rappoport, (Ed.). *The Chemistry of Phenols*, John Wiley & Sons, Ltd., New York, **2003**.
[4] A. Altamirano, A. Senz, H. E. Gsponer, *J. Colloid. Interface Sci.* **2004**, *270*, 364–370.
[5] G. Lente, J. H. Espenson, *Chem. Commun.* **2003**, *10*, 1162–1163.
[6] C. Li, M. Z. Hoffman, *J. Phys. Chem. A* **2000**, *104*, 5998–6002.
[7] C. Wentz, *Hazardous Waste Management*, Mc Graw-Hill, New York, **1989**, pp. 1–10.
[8] K. Kalyanasundaram, *Coord. Chem. Rev.* **1982**, *46*, 159–244.
[9] A. Juris, V. Balzani, F. Barigelletti, S. Campagna, P. Besler, A. von Zelewsky, *Coord. Chem. Rev.* **1988**, *84*, 85–277.
[10] Z. J. Fuller, W. D. Bare, K. A. Kneas, W.-Y. Xu, J. N. Demas, B. A. DeGraff, *Anal. Chem.* **2003**, *75*, 2670–2677.
[11] K. Miedlar, P. K. Das, *J. Am. Chem. Soc.* **1982**, *104*, 7462–7469.
[12] S. Rajagopal, G. Allen Gnanaraj, A. Mathew, C. Srinivasan, *J. Photochem. Photobiol. A Chem.* **1992**, *69*, 83–89.
[13] P. Thanasekaran, T. Rajendran, S. Rajagopal, C. Srinivasan, R. Ramaraj, P. Ramamurthy, B. Venkatachalapathy, *J. Phys. Chem. A* **1997**, *101*, 8195–8199.
[14] P. Thanasekaran, S. Rajagopal, C. Srinivasan, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3339–3344.
[15] T. Rajendran, P. Thanasekaran, S. Rajagopal, G. Allen Gnanaraj, C. Srinivasan, P. Ramamurthy, B. Venkatachalapathy, B. Manimaran, L. Lu, *Phys. Chem. Chem. Phys.* **2001**, *3*, 2063–2069.
[16] K. Swarnalatha, E. Rajkumar, S. Rajagopal, R. Ramaraj, Y.-L. Lu, K.-L. Lu, P. Ramamurthy, *J. Photochem. Photobiol. A Chem.* **2005**, *171*, 83–90.

[17] C. Li, H. Sun, M. Z. Hoffman, *J. Photochem. Photobiol. A Chem.* **1997**, *108*, 129–133.

[18] C. A. Pizzocaro, M. Bolte, *New J. Chem.* **1994**, *18*, 737–743.

[19] H. Sun, M. Z. Hoffman, Q. G. Mulazzani, *Res. Chem. Intermed.* **1994**, *20*, 735–754.

[20] A. Magnuson, H. Berglund, P. Korall, L. Hammarström, B. Åkermark, S. Styring, L. Sun, *J. Am. Chem. Soc.* **1997**, *119*, 10720–10725.

[21] L. Sun, L. Hammarström, B. Åkermark, S. Styring, *Chem. Soc. Rev.* **2001**, *30*, 36–49.

[22] M. Sjödin, S. Styring, B. Åkermark, L. Sun, L. Hammarström, *J. Am. Chem. Soc.* **2000**, *122*, 3932–3936.

[23] S. Y. Reece, D. G. Nocera, *J. Am. Chem. Soc.* **2005**, *127*, 9448–9458.

[24] J. Yuasa, S. Fukuzumi, *J. Am. Chem. Soc.* **2006**, *128*, 14281–14292.

[25] J. Lobedank, E. Bellmann, J. Bendig, *J. Photochem. Photobiol. A Chem.* **1997**, *108*, 89–93.

[26] Md. K. Nazeeruddin, K. Kalyanasundaram, *Inorg. Chem.* **1989**, *28*, 451.

[27] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, **1992**.

[28] E. Eskelinen, S. Luukkanen, M. Haukka, M. Ahlgren, T. A. Pakkanen, *J. Chem. Soc., Dalton Trans.* **2000**, *16*, 2745–2752.

[29] T. Shimidzu, T. Iyoda, K. Izaki, *J. Phys. Chem.* **1985**, *89*, 642–645.

[30] P. G. Potvin, P. V. Luyen, J. Brackow, *J. Am. Chem. Soc.* **2003**, *125*, 4894–4906.

[31] M. Sjodin, S. Styring, B. Akermark, L. Sun, L. Hammarstrom, *J. Am. Chem. Soc.* **2000**, *122*, 3932–3936.

[32] M. Sjodin, S. Styring, H. Wolpher, Y. Xu, L. Sun, L. Hammarstorm, *J. Am. Chem. Soc.* **2005**, *127*, 3855–3863.

[33] M. Sjodin, R. Ghanem, T. Polivka, J. Pan, S. Styring, L. Sun, V. Sundstrom, L. Hammarstrom, *Phys. Chem. Chem. Phys.* **2004**, *6*, 4851–4858.

[34] B. A. Diner, J. A. Bautista, P. J. Nixon, C. Berthomieu, R. Hienerwadel, R. D. Britt, W. F. J. Vermaas, D. A. Chisholm, *Phys. Chem. Chem. Phys.* **2004**, *6*, 4844–4850.

[35] F. Mamedov, R. T. Sayre, S. Styring, *Biochemistry* **1998**, *37*, 14245–14256.

[36] O. Johansson, H. Wolpher, M. Borgstorm, L. Hammarstrom, J. Bergqiust, L. Sun, B. Akermark, *Chem. Commun.* **2004**, *2*, 194–195.

[37] C. Carra, N. Iordanova, S. H. Schiffer, *J. Am. Chem. Soc.* **2003**, *125*, 10429–10436.

[38] M. Sjödin, T. Irebo, J. E. Utas, J. Lind, G. Merényi, B. Åkermark, L. Hammarström, *J. Am. Chem. Soc.* **2006**, *128*, 13076–13083.

[39] T. Irebo, S. Y. Reece, M. Sjödin, D. G. Nocera, L. Hammarström, *J. Am. Chem. Soc.* **2007**, *129*, 15462–15464.

[40] C. J. Fecenko, H. Thorp, T. J. Meyer, *J. Am. Chem. Soc.* **2007**, *129*, 15098–15099.

[41] C. Costentin, M. Robert, J.-M. Savéant, *J. Am. Chem. Soc.* **2007**, *129*, 5870–5879.

[42] T. J. Meyer, M. H. V. Huynh, H. H. Thorp, *Angew. Chem. Int. Ed.* **2007**, *46*, 5284–5304.

[43] C. J. Fecenko, T. J. Meyer, H. H. Thorp, *J. Am. Chem. Soc.* **2006**, *128*, 11020–11021.

[44] E. Hatcher, A. Soudackov, H. S. Schiffer, *J. Phys. Chem. B* **2005**, *109*, 18565–18574.

[45] N. Song, D. M. Stanbury, *Inorg. Chem.* **2008**, *47*, 11458–11460.

[46] J. J. Concepcion, M. K. Brennaman, J. R. Deyton, N. V. Lebedeva, M. D. E. Forbes, J. M. Papanikolas, T. J. Meyer, *J. Am. Chem. Soc.* **2007**, *129*, 6968–6969.

[47] O. Tischenko, D. G. Tryblar, A. Ceulemans, M. T. Nguyen, *J. Am. Chem. Soc.* **2008**, *130*, 7000–7010.

[48] P.- X. Xie, Y.- J. Hou, B.- W. Zhang, Y. Cao, F. Wu, W.- J. Tian, J.- C. Shen, *J. Chem. Soc., Dalton Trans.* **1999**, *23*, 4217–4221.

[49] G. Sprintschnick, H. W. Sprintschnick, P. P. Kirsch, D. G. Whitten, *J. Am. Chem. Soc.* **1977**, *99*, 4947–4954.

[50] M.- J. Kim, R. Konduri, H. Ye, F. M. MacDonnell, F. Puntoriero, S. Serroni, S. Campagna, T. Holder, G. Kinsel, K. Rajeshwar, *Inorg. Chem.* **2002**, *41*, 2471–2476.

[51] J. A. Dean, *Lange's Handbook of Chemistry*, 13th edn, McGraw-Hill, New York, **1992**, pp. 8.103–8.112.

[52] P. Ramamurthy, *Chem. Educ.* **1993**, *9*, 56.

[53] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, 3rd edn, Springer Press: New York **2006**.

[54] C. Li, M. Z. Hoffman, C. Pizzocaro, G. Malhot, M. Bolte, *Inorg. Chem.* **1998**, *37*, 3078–3082.

[55] G. Renger, *Biochim. Biophys. Acta* **2004**, *1655*, 195–204.

[56] C. Tommos, G. T. Babcock, *Biochim. Biophys. Acta* **2000**, *1458*, 199–219.

[57] C. W. Hoganson, G. T. Babcock, *Science* **1997**, *277*, 1953–1956.

[58] R. A. Marcus, N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265–322.

[59] R. A. Marcus, *Angew. Chem.* **1993**, *105*, 1161–1172.

[60] R. A. Marcus, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1111–1121.

[61] A. Yoshimura, Md. Jamal Uddin, N. Amasaki, T. Ohno, *J. Phys. Chem. A* **2001**, *105*, 10846–10853.

[62] I. J. Rhile, T. F. Markle, H. Nagao, A. G. DiPasquale, O. P. Lam, M. A. Lockwood, K. Rotter, J. M. Mayer, *J. Am. Chem. Soc.* **2006**, *128*, 6075–6088.

[63] M. R. Ganapathi, R. Hermann, S. Naumov, O. Brede, *Phys. Chem. Chem. Phys.* **2000**, *2*, 4947–4955.

[64] O. Brede, H. Orthner, V. Zubarev, R. Hermann, *J. Phys. Chem.* **1996**, *100*, 7097–7105.

[65] J. P. Mittal, *J. Photochem. Photobiol. A Chem.* **1999**, *124*, 119–125.

[66] M. Lucarini, V. Mugnaini, G. F. Pedulli, M. Guerra, *J. Am. Chem. Soc.* **2003**, *125*, 8318–8329.

[67] D. Shukla, N. P. Schepp, N. Mathivanan, L. N. Jhonston, *Can. J. Chem.* **1997**, *75*, 1820–1829.

[68] J. Lind, X. Shen, T. E. Eriksen, G. Merényi, *J. Am. Chem. Soc.* **1990**, *112*, 479–482.

21