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Photoinduced electron transfer reactions of ruthenium(II) complexes containing 2,2′-bipyridine-4,4′-dicarboxylic acid with phenols
Steric and charge effects

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Abstract

Luminescent mixed-ligand ruthenium(II) complexes of type RuL_nX_{3-n} (L = 2,2′-bipyridine, X = 2,2′-bipyridine-4,4′-dicarboxylic acid, n = 0,1,2,3) have been synthesized and their photophysical and electrochemical properties are investigated. The emission lifetime measured for RuL_nX_{3-n} reveals that the lifetime increases as the ligand L is replaced by X. The luminescence quenching of $^*RuL_nX_{3-n}$ with several substituted phenolate ions in aqueous medium is efficient and the change of quenching rate data with the change of structure of ligand of RuL_nX_{3-n} and phenolate ion is explained in terms of exergonicity of the reaction, electron transfer distance and charge effect. The semiclassical theory of electron transfer has been successfully applied to this photoredox system.

Keywords: Ru(II)–polypyridyl complexes; Electron transfer; Steric and charge effects

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1. Introduction

Luminescent d^6 transition metal complexes, in particular Ru(II) complexes, are useful as photosensitizers for energy and electron transfer processes [1–10]. The excited state properties of $Ru(bpy)_3{}^{2+}$ (bpy = 2,2′-bipyridine) are largely affected by the introduction of electron-donating and -withdrawing groups in the 4,4′-position of 2,2′-bipyridine [11–22]. With these changes in the ligand, it is possible to tune the excited state properties like emission lifetime, quantum yield, wavelength of emission maximum and redox potential. In the past one decade, we have done a considerable amount of work on the photophysics and photoinduced electron transfer reactions of Ru(II)–polypyridyl complexes by introducing electron donating alkyl groups in the 4,4′-position of 2,2′-bipyridine and by introducing another nitrogen in the pyridine ring [23–28]. In order to realize the effect of introducing electron withdrawing groups in the 2,2′-bipyridine on the excited state properties of Ru(II) complexes, carboxylic acid, sulphonic acid, phosphonic acid and trifluoromethyl groups have been introduced in the 4,4′-position of 2,2′-bipyridine and the photophysical properties of these complexes have been extensively studied [29–33]. Among the ligands indicated above, the ligand carrying carboxylic acid received special attention, because it can be anchored on a semiconductor to achieve efficient solar energy conversion [34–37].

Many efforts have been made in recent years to design and synthesize molecules to mimic the important light driven process, photosystem II [38–42]. Realizing the importance

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of Ru(II)–polypyridine complexes as model photosensitizers and phenols as electron donors in photosystem II, we have investigated the photoinduced electron transfer reactions of ruthenium(II)–polypyridyl complexes with several phenols in aqueous medium [24–28]. From the recent experimental observations, we have realized that the steric effect on the photoinduced electron transfer reaction is significant only if both the reactants, $^*\mathrm{Ru(NN)_3}^{2+}$ and ArO^-, carry bulky alkyl groups [28]. Apart from the size, the charge on the reactants also affects the rate of the reaction [30,43,44]. As the titled reaction has been studied at pH 12.5 the charge on the metal complex varies from +2 to −4 when we substitute the ligand 2,2′-bipyridine by 2,2′-bipyridine-4,4′-dicarboxlyic acid. Further the introduction of electron-withdrawing groups like $-\mathrm{CO_2H}$ in the ligand makes the Ru(II) complex more powerful electron acceptor, i.e., ΔG^0 more negative and favours the reaction. Considering all these aspects we have prepared Ru(II) complexes using 2,2′-bipyridine-4,4′-dicarboxylic acid as the ligand and used them as photosensitizers to understand the role of steric and charge effects on the photoinduced electron transfer reactions. The observed results on the photophysics of Ru(II) complexes and photoinduced electron transfer reactions of these complexes with phenolate ions are presented in this report. These results are compared with our recent observations on the photoinduced electron transfer reactions of tris(4,4′-dialkyl-2,2′-bipyridine) ruthenium(II) complexes with phenolate ions in aqueous acetonitrile [28].

2. Experimental

2.1. Materials

The ligand, 2,2′-bipyridine and $\mathrm{RuCl_3{\cdot}3H_2O}$ were obtained from Aldrich and the phenols were purchased from Fluka and Aldrich and used as obtained. The ligand 2,2′-bipyridine-4,4′-dicarboxylic acid has been obtained by the oxidation of 4,4′-dimethyl-2,2′-bipyridine by adopting the reported procedure [45]. The four complexes $\mathrm{RuL}_n\mathrm{X}_{3-n}$, where $n = 0, 1, 2, 3$; L = 2,2′-bipyridine(bpy) and X = 2,2′-bipyridine-4,4′-dicarboxylic acid(dcbpy) were prepared by reacting $\mathrm{RuCl_3{\cdot}3H_2O}$ with the corresponding ligands by known procedures[29].

2.2. Absorption and emission spectral measurements

Sample solutions of the metal complexes and the quenchers have been freshly prepared for each measurement. The absorption spectral measurements were carried out using JASCO-7800 double beam spectrophotometer. Emission intensity measurements were carried out using F-4500 spectrofluorometer. All the sample solutions used for emission measurements were dearated for about 30 min by dry nitrogen gas purging by keeping solutions in cold water to ensure that there is no change in volume of the solution.

2.3. Luminescence lifetime measurements

The excited state lifetimes of the four $^*\mathrm{RuL}_n\mathrm{X}_{3-n}$ complexes in aqueous solution at pH 12.5 and 298 K were measured using time-correlated single photon counting (TCSPC) technique, after purging the solutions with dry argon for 30 min and the details are given in the previous reports [25,27].

2.4. Electrochemical measurements

The redox potentials of $\mathrm{RuL}_n\mathrm{X}_{3-n}$ complexes and the oxidation potentials of phenolate ions were determined by cyclic voltammetric technique using EG & G Princeton Applied Research Potentiostat/Galvanostat Model 273A. Samples of 1 mM solutions of the complexes for the electrochemical studies were prepared in aqueous solution (pH 12.5). Potassium chloride was used as the supporting electrolyte. A glassy carbon electrode (working electrode) and a standard calomel reference electrode were used in the electrochemical measurements. Cyclic voltammograms were recorded after purging the solution with dry nitrogen gas for 30 min. The redox potential values of Ru(II) complexes and phenolate ions used in the study are collected in Tables 1 and 3, respectively, and redox potentials are close to the literature values [29,46]. The redox potentials of the excited state couples are calculated from the potentials of the ground state couples and the zero–zero energy, $E_{0\text{–}0}$ (found to be 2.1 eV).

$$E_{(\mathrm{Ru}^{2+*/+})} = E_{(\mathrm{Ru}^{2+/+})} + E_{0-0}$$

2.5. Luminescence quenching measurements

The photochemical reduction of $\mathrm{RuL}_n\mathrm{X}_{3-n}$ complexes with phenolate ions has been studied by the luminescence quenching technique. The sample solutions were purged carefully with dry nitrogen for 30 min. The luminescence measurements were performed at different quencher concentration and the quenching rate constant, k_q, values were determined from the Stern–Volmer plot using the equations given below.

$$I_0/I = 1 + K_\mathrm{sv}[Q]$$

$$K_\mathrm{sv} = k_\mathrm{q}\tau^0$$

Here I_0 and I are the luminescence intensities of Ru(II) complex in the absence and presence of quencher, K_SV, the Stern–Volmer constant k_q, the quenching rate constant and τ^0, the luminescence lifetime of $\mathrm{RuL}_n\mathrm{X}_{3-n}$ in the absence of quencher. A sample Stern–Volmer plot is shown in Fig. 1. Phenolate ions for the quenching studies and electrochemical measurements were prepared by mixing the corresponding phenol with NaOH and the pH of the solution was maintained at 12.5 to confirm that the quencher was present as phenolate ion.

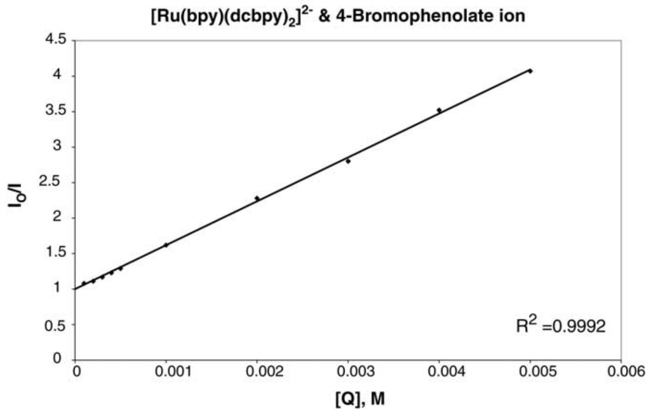


Fig. 1. Stern–Volmer plot for the reductive quenching of $[^{*}Ru(bpy)(dcbpy)_2]^{2-}$ with 4-bromo phenolate ion in aqueous medium at pH 12.5 at 298 K.

3. Results and discussion

The structures of the ligands and the quenchers used in the present study are shown in Fig. 2. The absorption and emission spectral data, the excited state lifetime (τ) and redox potentials of the Ru(II) complexes in aqueous solution at pH 12.5 were measured and the data are collected in Table 1.

3.1. Electronic spectra and luminescence lifetimes

The wavelengths of absorption and emission maxima of RuL_nX_{3-n} complexes in aqueous medium at room temperature and pH 12.5 are presented in Table 1. The strong high-energy absorption in the 285–300 nm region corresponds to the π–π^*(LC) transition and the low energy absorption in the 420–470 nm region is assigned to the dπ–π^*(MLCT) transition [1–10]. The heteroleptic complexes give rise to different absorption maxima corresponding to the ligands coordinated to the metal centre. In the case of $[Ru(bpy)_2(dcbpy)]^0$ and $[Ru(bpy)(dcbpy)_2]^{2-}$ complexes the absorption at 288 nm corresponds to the π–π^* transition of bpy and 300 nm to dcbpy. The MLCT transition involves electronic excitation from the metal orbital [dπ(Ru)] to the ligand centred acceptor π^* orbitals (ligand). The absorption maximum of MLCT transition is red shifted by 15 nm when bpy is replaced by dcbpy. The introduction of –CO_2H group in bpy lowers π^* level of the ligand and thus, shifts the LC and MLCT transition to the red. However, in the emission, though a red shift of 30 nm has been observed when one ligand containing –CO_2H group is introduced in the place of bpy, no substantial change is observed on further substitution. Luminescence lifetimes for the Ru(II) complexes in aqueous medium at pH 12.5 have been measured in the present study and collected in Table 1. Though the τ values of these complexes in aqueous medium are available in the literature the experimental conditions used in this study are different, i.e., pH 12.5. Hence, the measurements have been done at pH 12.5 and the measured τ values vary slightly from the reported values [29].

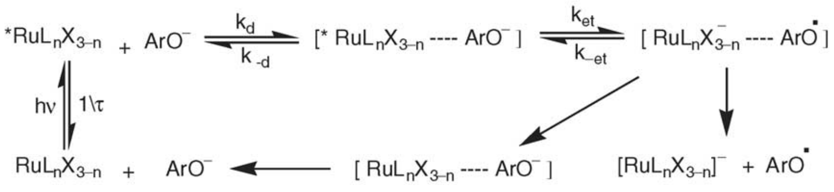
3.2. Redox potentials

The redox potentials collected in Tables 1 and 3 show that the value varies slightly with the change of ligand in RuL_nX_{3-n} but substantially with the structure of phenolate ion. It is to be remembered that the electron-withdrawing carboxyl group present in the ligand is in the form of carboxylate ion and the electron- withdrawing power of –CO_2^- is less compared to –CO_2H, which is clearly understood from the Hammett σ values 0.40 and 0.11, respectively [30]. To have a comprehensive study on the dynamics of the electron transfer reaction of a redox couple there must be a substantial change in the ΔG^0 value. The ΔG^0 values collected in Table 3, show that the change in ΔG^0 value is more than 0.6 eV through the change of the redox couple.

3.3. Luminescence quenching rate constants

The experimental bimolecular quenching rate constants, k_q for the quenching of $^{*}RuL_nX_{3-n}$ with phenolate ion and its substituted analogues in aqueous medium at pH 12.5 are given in Table 2. The Stern–Volmer plots are linear with the intercept unity for all photoredox systems, confirming that the quenching process is predominantly dynamic and contribution from static quenching is negligible. The electron transfer nature of the quenching of $^{*}[Ru(NN)_3]^{2+}$ with phenolate ions has already been established by us from laser flash photolysis study and the spectrum of phenoxyl radical reported in previous publications [25–28]. Thus, the luminescence quenching of $^{*}RuL_nX_{3-n}$ by phenolate ion may be explained by Scheme 1.

After establishing electron transfer nature of the reaction, we have calculated the rate constants of the ET reaction using semiclassical theory of ET [47–50]. The semiclassical



Scheme 1. Mechanism for the luminescence quenching of $^{*}RuL_nX_{3-n}$ with ArO^-.

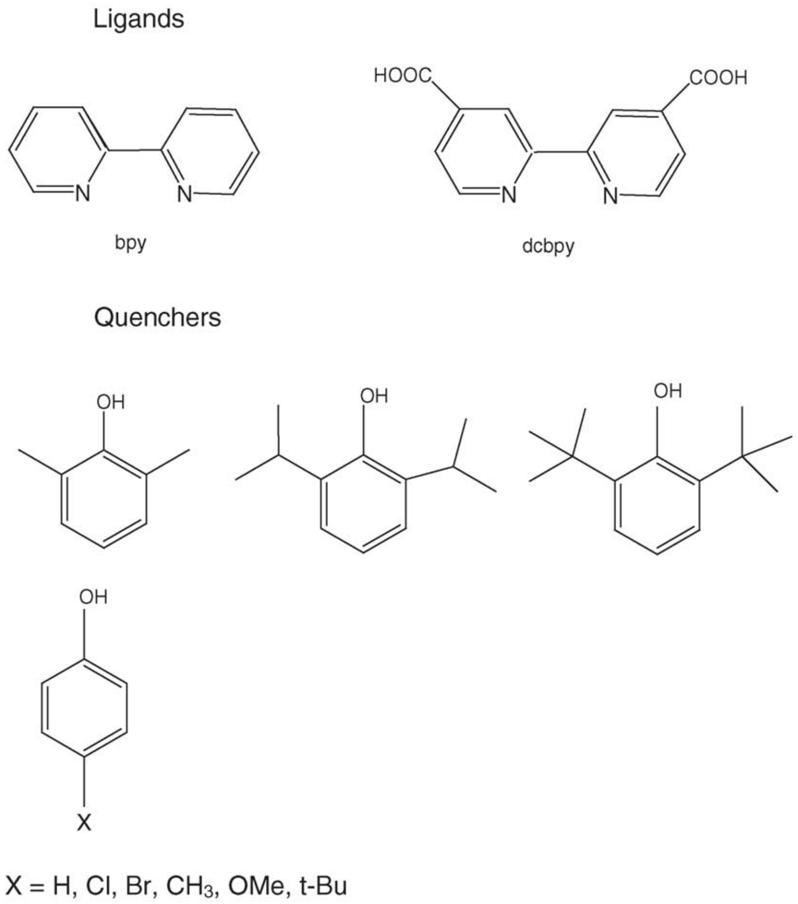


Fig. 2. Structures of the ligands and the quenchers.

Table 1
Absorption and emission spectral data, excited state lifetime and redox potentials of Ru(II) complexes in aqueous medium at pH 12.5 at 298 K

Complex	Absorption maximum, nm (ε_{max}, 10^4 M^{-1} cm^{-1})	Emission maximum (nm[a])	Excited state lifetime τ (ns[a])	Redox potential	
				$E^0{}_{(Ru^{2+/+})}$ V	$E^0{}_{(Ru^{2+*/+})}$ V
$[Ru(bpy)_3]^{2+}$	285 (6.40), 345 (0.68), 423 (1.20), 450 (1.32)	595 (600)	580 (620)	−1.28	0.82
$[Ru(bpy)_2(dcbpy)]^0$	287 (3.52), 300 (3.92), 345(0.76), 438 (1.12), 459 (1.28)	625 (625)	520 (471)	−1.17	0.93
$[Ru(bpy)(dcbpy)_2]^{2-}$	288 (4.0), 300 (4.80), 343 (0.80), 438 (1.10), 465 (1.12)	617 (613)	620 (664)	−1.15	0.95
$[Ru(dcbpy)_3]^{4-}$	300 (2.80), 353 (0.72), 438 (0.80), 467 (0.96)	618 (610)	685 (700)	−1.10	1.00

[a] The value in the parenthesis represent the reported emission maxima and lifetimes of Ru(II) complexes in water at pH > 7, ref. [29].

expression of ET (Eq. (1)) popularized by Closs and Miller [51] has been applied to the reaction of photoinduced ET between the triplet excited state Ru(II) complexes and phenolate ions.

$$k_{et}(r) = 2\pi/h[1/\lambda_0 k_B T]^{1/2}|H_{DA}|^2 \sum_{m=0}^{\infty} e^{-s}s^m/m! \exp \times \left[-\frac{(\lambda_0 + \Delta G^0 + mh\upsilon)^2}{4\lambda_0 k_B T}\right] \quad (1)$$

In Eq. (1) H_{DA} is the electronic coupling matrix element, the reorganisation energy λ is composed of solvational λ_0 and vibrational λ_i contributions with $s = \lambda_i/h\upsilon$, υ is the high-energy vibrational frequency associated with the acceptor and m is the density of product vibrational levels. As all the reactions in the present study fall in the normal region ($-\Delta G^0 < \lambda$) the above equation is simplified to Eq. (2)

$$k_{et}(r) = \frac{2\pi}{h}[1/\lambda_0 k_B T]^{1/2}|H_{DA}|^2 \exp\left[\frac{-(\lambda_0 + \Delta G^0)^2}{4\lambda_0 k_B T}\right] \quad (2)$$

The total driving force, ΔG^0, includes electrostatic corrections for the work required to bring products and reactants together ($\Delta G^0 = \Delta G^{0'} - w_p - w_r$) as described below. When both ET partners are charged, as is the case here,

Table 2
Rate constant, k_q, values for the reductive quenching of *RuL_nX_{3-n} by phenolate ions in aqueous medium at pH 12.5 at 298 K

Quencher	[a]k_q, M^{-1} s^{-1}							
	$[Ru(bpy)_3]^{2+}$		$[Ru(bpy)_2(dcbpy)]^0$		$[Ru(bpy)(dcbpy)_2]^{2-}$		$[Ru(dcbpy)_3]^{4-}$	
	A	B	A	B	A	B	A	B
Phenolate ion	1.7×10^8	1.4×10^7	2.8×10^8	6.2×10^7	1.2×10^9	1.3×10^8		
4-Chloro phenolate ion	1.3×10^8	1.4×10^7	4.2×10^8	1.2×10^8	9.8×10^8	1.6×10^8	6.1×10^8	6.0×10^8
4-Bromo phenolate ion	1.2×10^8	2.0×10^7	5.5×10^8	1.6×10^8	9.9×10^8	2.2×10^8	2.2×10^8	7.8×10^8
4-Methyl phenolate ion		1.9×10^8	1.7×10^9	9.8×10^8	1.7×10^9	1.3×10^9	1.3×10^9	3.2×10^9
4-*tert*-Butyl phenolate ion	1.0×10^9	3.0×10^8	1.4×10^9	1.5×10^8	8.8×10^8	8.9×10^9	8.9×10^8	4.1×10^9
4-Methoxy phenolate ion	3.3×10^9	1.3×10^9	2.2×10^9	3.7×10^8	1.5×10^9	4.2×10^9	1.2×10^9	1.9×10^9
2,6-Dimethyl phenolate ion	3.5×10^9	3.5×10^9	2.1×10^9	1.8×10^8	3.2×10^9	4.9×10^9	2.2×10^9	4.1×10^9
2,6-Diisopropyl phenolate ion	5.1×10^9	6.4×10^9	2.3×10^9	4.6×10^8	2.3×10^9	8.4×10^9	1.3×10^9	1.2×10^9

[a] A represents the experimental and B the calculated k_q values by the semiclassical method.

the intermolecular potential is dominated by the electrostatic forces between reactants. For two spheres, the intermolecular potential $U(r)$ between two reactants can be described within Debye–Huckel formalism as

$$U(r) = \frac{Z_1 Z_2 e^2}{D_s r(1 + \beta r \mu^{1/2})} \tag{3}$$

where Z_1 and Z_2 are the charges on each reactant, e is the charge on the electron, D_s is the static dielectric constant of the solvent and μ is the ionic strength. The value of β is given by

$$\beta = \left[\frac{8\pi N e^2}{1000 D_s k_B T}\right]^{1/2} \tag{4}$$

The solvation reorganization energy, λ_0, can be estimated from the classical dielectric continuum model

$$\lambda_0 = (\Delta e)^2[1/2r_A + 1/2r_B - 1/r][1/D_{op} - 1/D_s] \tag{5}$$

where D_{op} and D_s are the optical and static dielectric constants of the solvent, respectively, and r_A and r_B are the reactants' radii. The values of solvent parameters and radii of the reactants have been collected from the literature [24–28,52]. The value of λ_0 calculated using Eq. (5) is 0.87 eV. The value of λ_i is found to be 0.2 eV and is employed in the calculation of the rate constant for ET reaction. Thus, the value of the reorganization energy (λ) for this redox system is found to be 1.07 eV.

By using Eq. (2) the rate constants for electron transfer, k_{et}, have been calculated and then used to get k_q values from Eq. (6).

$$k_q = \frac{k_{et} k_d}{k_{et} + k_d} \tag{6}$$

where k_d is the diffusion rate constant given by Eq. (7)

$$k_d = \frac{4\pi ND}{1000}\left[\int_r^\infty e^{[-U(r)/k_B T]} r^{-2} dr\right]^{-1} \tag{7}$$

where D is the sum of the diffusion coefficients of the reactants given by the Stokes–Einstien relationship.

The calculated rate constants for ET from phenolates to *RuL_nX_{3-n} by applying semiclassical expression of ET along with experimentally observed values for the above ET reaction are given in Table 2. The k_q data in Table 2 show that the values calculated from semiclassical theory are in fair agreement with experimental values (i.e., the difference between them is in the range 2–10 times). Considering the assumptions involved in the application of Eq. (2) to the titled reaction this agreement can be taken as the success of the Marcus theory to this reaction. The experimental k_q values have been plotted against ΔG^0 (Fig. 3) for all the four Ru(II) complexes. The rate increases with the introduction of dcbpy unit in the metal complex but the rate decreases when we introduce the third dcbpy ligand, i.e., in the case of RuX_3^{4-} complex. These results are interesting because with the introduction of dcbpy unit in the metal complex the reaction

Table 3
$-\Delta G^0$ values (eV) for the quenching of $^*RuL_nX_{3-n}$ with phenolate ions in aqueous medium at pH 12.5 at 298 K

Quencher	$E^0_{oxd,}$ vs. NHE (V)	ΔG^0 (eV)			
		$[Ru(bpy)_3]^{2+}$	$[Ru(bpy)_2(dcbpy)]^0$	$[Ru(bpy)(dcbpy)_2]^2$	$[Ru(dcbpy)_3]^{4-}$
Phenolate ion	0.86	0.04	−0.07	−0.09	−0.14
4-Chloro phenolate ion	0.85	0.03	−0.08	−0.10	−0.15
4-Bromo Phenolate ion	0.84	0.02	−0.09	−0.11	−0.16
4-Methyl phenolate ion	0.71	−0.11	−0.22	−0.24	−0.29
4-*tert*-Butyl phenolate ion	0.70	−0.12	−0.23	−0.25	−0.30
4-Methoxy phenolate ion	0.58	−0.24	−0.35	−0.37	−0.42
2,6-Dimethyl phenolate ion	0.50	−0.32	−0.43	−0.45	−0.50
2,6-Diisopropyl phenolate ion	0.46	−0.36	−0.47	−0.55	−0.54

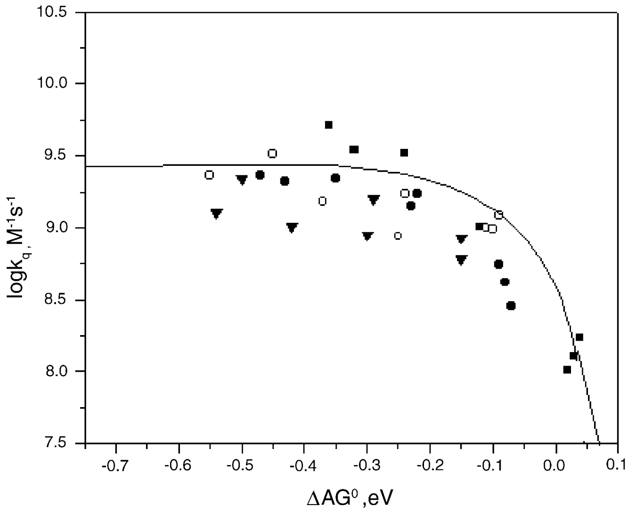


Fig. 3. Plot of $\log k_q$ vs. $-\Delta G^0$, eV of RuL_nX_{3-n} with phenolate ions. (■) $[Ru(bpy)_3]^{2+}$, (●) $[Ru(bpy)_2(dcbpy)]^0$, (○) $[Ru(bpy)(dcbpy)_2]^{2-}$, (▼) $[Ru(dcbpy)_3]^{4-}$.

becomes more exergonic, i.e., ΔG^0 becomes more negative. Though ΔG^0 is favourable the introduction of $-CO_2^-$ in the bpy ligand makes the metal complex more bulky and negatively charged species. Thus, these results deserve detailed analysis (vide infra). Interestingly the rate also decreases, when the size of the phenolate ion increases. Phenolate ions containing alkyl groups in the ortho-position play an important role in the antioxidant activity of phenols [53]. The oxidation potentials of the penolates containing the alkyl groups in the *ortho*- position are very low, i.e., ΔG^0 becomes more negative. Thus, the change in the structure of the ligand of the metal complex and quencher affects the rate of quenching in a complicated way. The important parameters that influence the rate of ET reactions other than exergonicity ($-\Delta G^0$) are the reorganization energy (λ) and the distance (d). The introduction of bulky groups in the reactants affects the rate of ET through the increase in the ET distance. From the data given in Fig. 3, we realize that the k_q values observed for complexes containing dcbpy ligands at a fixed ΔG^0 value are in the following order $RuX_3^{4-} < RuLX_2^{2-} < RuL_2X^0 < RuL_3^{2+}$. The low k_q values for $[Ru(bpy)(dcbpy)_2]^{2-}$ and $[Ru(dcbpy)_3]^{4-}$ complexes, though the reaction is more exergonic, may be attributed to the steric and charge effects which arise due to the introduction of the carboxyl groups in the ligand of the metal complex.

3.4. Steric effects

The quenching rate constant data given in Table 2 show that photoinduced electron transfer reaction of Ru(II) complexes with sterically hindered phenolate ions and of phenolate ions with Ru(II) complexes carrying carboxylic acid groups may be non-adiabatic. According to semiclassical theory of electron transfer (Eq. (2)) the rate of electron transfer is controlled by the electronic coupling matrix element, H_{DA} also. The term H_{DA} is distance dependent and distance dependence of H_{DA} can be explained by Eq. (8),

$$|H_{DA}|^2 = |H_{DA}|_0{}^2 \exp[-\beta(d-d_0)] \quad (8)$$

where $|H_{DA}|_0{}^2$ is the value of the matrix element when the reaction is adiabatic at van der Waals distance (d_0) and β is the attenuation factor and its value is taken as 1.0 Å^{-1}. The value of $|H_{DA}|$ is taken as 200 cm^{-1} when d_0 is equivalent to 3 Å and it decreases with distance by the factor 1 Å^{-1} [47,54].

In order to realize the role of steric effect on this reaction we wanted to utilize 2,6-di-*tert*-butylphenolate ion also as the quencher. But the solubility of this phenolate ion in aqueous medium is poor. Hence, we have changed the medium to 50%(v/v) aqueous acetonitrile and the k_q data obtained for phenolate, 2,6-dimethyl phenolate, 2,6-diisopropyl phenolate and 2,6-di-*tert*-butylphenolate ions have been collected in Table 4. It is interesting to see that though ΔG^0 value is favourable with the introduction of $-CO_2H$ group in the 2,2′-bipyridine ligand of RuL_nX_{3-n} the k_q value decreases when we substitute 2,2′-bipyridine with 2,2′-bipyridine-4,4′-dicarboxylic acid. The minimum and maximum d values in the present study are 10.9 and 14.2 Å, respectively. The value of d is calculated by simply adding the radii of RuL_nX_{3-n} and ArO^- .If these values are substituted in Eq. (8), the value of H_{DA} becomes 0.86 and 0.16 cm^{-1}, respectively. Thus, the decrease in d by 3.3 Å unit leads to decrease in k_{et} by a factor of five. At this stage it is interesting to compare the k_q data observed here with the values obtained by us in the previous study for $Ru(bpy)_3{}^{2+}$, $Ru(dmbpy)_3{}^{2+}$ and $Ru(dtbpy)_3{}^{2+}$ where dmbpy = 4,4′-dimethyl-2,2′-bipyridine and dtbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine. The k_q data obtained for the quenching of $Ru(bpy)_3{}^{2+}$, $Ru(dmbpy)_3{}^{2+}$and $Ru(dtbpy)_3{}^{2+}$ with 2,6-di-*tert*-butylphenolate ion in 80% CH_3CN–20% H_2O are 7.3×10^9, 5.6×10^9 and 2.3×10^8 M^{-1} s^{-1}, respectively. Though $Ru(bpy)_3{}^{2+}$ and $Ru(dtbpy)_3{}^{2+}$ have comparable ΔG^0 values for the reaction with the quencher the k_q value for $Ru(dtbpy)_3{}^{2+}$ is 30 times less than that for $Ru(bpy)_3{}^{2+}$. Here again the similar results are observed when we compare the k_q values of $Ru(bpy)_3{}^{2+}$ and $[Ru(dcbpy)_3]^{4-}$ towards 2,6-di-*tert*-butylphenolate ion. But the important point to be noted here is that the reaction with $*[Ru(dcbpy)_3]^{4-}$ is more exergonic by 0.2 eV compared to that of $*[Ru(bpy)_3{}^{2+}]$. Thus, more steric effect is felt in this study compared to our previous report [28]. But we must note that there is a substantial change in the charge on the sensitizer when we replace bpy with dcbpy but not with dtbpy. Thus, a part of the rate retardation observed with $[Ru(dcbpy)_3]^{4-}$ must be attributed to the charge effect.

3.5. Charge effect

The importance of charge effect on ET reactions has been highlighted in recent publications [30,43,44]. As all the reactions in the present study have been carried out at pH 12.5,

Table 4
Rate constant, k_q, values for the reductive quenching of $^*RuL_nX_{3-n}$ by phenolate ions in 50% aqueous acetonitrile medium at pH 12.5 at 298 K

Quencher	$^a k_q$ ($M^{-1} s^{-1}$)							
	$[Ru(bpy)_3]^{2+}$		$[Ru(bpy)_2(dcbpy)]^0$		$[Ru(bpy)(dcbpy)_2]^{2-}$		$[Ru(dcbpy)_3]^{4-}$	
	A	B	A	B	A	B	A	B
Phenolate ion	1.3×10^9	3.3×10^9	9.4×10^9	8.8×10^9	8.0×10^9	5.3×10^9	8.8×10^9	1.6×10^9
2,6-Dimethyl phenolate ion	5.0×10^{10}	7.1×10^9	3.1×10^9	7.6×10^9	1.1×10^9	8.2×10^9	6.6×10^9	8.0×10^9
2,6-Diisopropyl phenolate ion	4.0×10^9	8.4×10^9	8.4×10^9	8.7×10^9	1.6×10^9	8.9×10^9	5.7×10^9	8.7×10^9
2,6-Di-*tert*-butyl phenolate ion	3.9×10^9	9.3×10^9	9.3×10^9	9.2×10^9	4.5×10^9	9.3×10^9	1.3×10^9	1.6×10^9

[a] A represents the experimental and c refers to the calculate k_q value by the semiclassical method.

all quenchers exist as phenolate ions, i.e., they carry one negative charge. On the other hand, when we change the nature of the ligand in RuL_nX_{3-n}, the charge on the metal complex varies from +2 to −4 and the total charge on each complex is shown in Tables 1–4. From the analysis of steric effect we have seen that the change of ET distance by 3.3 Å reduces the rate of ET by five times. The actual rate retardation with the change of sensitizer is about 30 times and a part of rate retardation is attributed to the steric effect through the increase in ET distance. The other major factor, which is responsible for rate retardation with the change of sensitizer, is the change of charge on the metal ion. It is to be noted that when $^*Ru(bpy)_3{}^{2+}$ is the sensitizer the reactants involved bear opposite charges which may facilitate the formation of precursor complex due to Columbic attraction [30–32]. On the other hand, when $^*[Ru(bpy)(dcbpy)_2]^{2-}$ and $^*[Ru(dcbpy)_3]^{4-}$ are the sensitizers, the reaction with ArO^- involves between two ions of like charges which may disfavour the formation of precursor complex due to the electrostatic repulsion. Thus, in the present study we observe the predominant charge effect on the ET reaction between Ru(II) complexes and ArO^-.

It is worthwhile to recall the results on the photoinduced electron transfer reactions of carboxylated [30], sulphonated [31] and phosphonated [32] bipyridine complexes with metal ions and MV^{2+}. In all the systems the metal ions and MV^{2+} form ion pair with $CO_2{}^-$, $SO_3{}^-$ or $PO_4{}^-$ end facilitating the electron transfer. On the otherhand it is interesting to compare the k_q values observed here for $Ru(bpy)_3{}^{2+}$ and $Ru(dcbpy)_3{}^{4-}$ towards ArO^- with those observed for these complexes towards MV^{2+} [52]. When $MV^{2+}$is the quencher the k_q values observed for $Ru(bpy)_3{}^{2+}$($\Delta G^0 = -0.46$ eV) and $Ru(dcbpy)_3{}^{4-}$ ($\Delta G^0 = -0.08$ eV) are 0.74×10^9 and 10×10^9 $M^{-1} s^{-1}$, respectively. The point to be noted here is that though ΔG^0 is not favourable for the latter reaction it is faster by 15 times than the former. The important difference between these two redox reactions is that one is favoured by electrostatic forces and the other is disfavoured. The favourable exergonicity (~0.4 eV) is largely negated by electrostatic repulsion between $Ru(bpy)_3{}^{2+}$ and MV^{2+}. Thus, electrostatic repulsion plays a significant role in the photoinduced electron transfer reaction of Ru(II) complexes. As far as we know the present study seems to be first report where $CO_2{}^-$ end of the sensitizer faces electrostatic repulsion from the quencher ArO^- leading to enormous rate retardation, i.e., to the tune of the six-fold. It is important to mention that this six-fold retardation is observed even though the reaction of $^*Ru(dcbpy)_3{}^{4-}$ with ArO^- is more exergonic by 0.2 eV. This is an interesting and important observation as phenols are important components in natural system. As phenols undergo electron transfer reactions in photosystem II these electrostatic effects should be taken into account when model systems are designed for photosystem II.

In summary the present study clearly establishes the significant role of steric and charge effects on the photoinduced electron transfer reactions between Ru(II) complexes of different charges with phenolate ions. Combination of this with our previous study confirms the operation of several parameters like steric, charge, hydrophobic and π–π interactions on the ET reactions of biologically important phenolate ions with the excited state Ru(II) complexes.

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