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Ground-State Properties and Excited-State Reactivity of 8-Quinolate Complexes of Ruthenium(II)

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In an effort to explore new systems with highly reducing excited states, we prepared a series of Ru(II) complexes of the type $Ru(L)_2quo^+$ (L = bpy (2,2′-bipyridine), phen (1,10-phenanthroline), dmphen (4,7-dimethyl-1,10-phenanthroline), tmphen (3,4,7,8-tetramethyl-1,10-phenanthroline); $quo^- =$ 8-quinolate) and investigated their photophysical and redox properties. The absorption and emission spectra of the $Ru(L)_2quo^+$ are significantly red-shifted relative to those of the parent complexes $Ru(L)_3^{2+}$, with emission maxima in the 757−783 nm range in water. The $Ru(L)_2quo^+$ systems are easily oxidized with $E_{1/2}(Ru^{III/II})$ values ranging from +0.62 to +0.70 V vs NHE, making the emissive Ru → phen MLCT (metal-to-ligand charge transfer) excited states ($E_{00} \sim 1.95$ eV in CH_3CN) of the $Ru(L)_2quo^+$ complexes significantly better reducing agents than the MLCT states of the parent $Ru(L)_3^{2+}$ complexes. Emission lifetimes of 17.0 and 32.2 ns were measured for $Ru(phen)_2quo^+$ in water and acetonitrile, respectively, and 11.4 ns for $Ru(bpy)_2quo^+$ in water. Transient absorption results are consistent with the formation of reduced methyl viologen upon $Ru(phen)_2quo^+$ excitation with visible light in water. The possibility of observing the Marcus inverted region in the forward bimolecular electron transfer reaction from the highly reducing $^*Ru(phen)_2quo^+$ excited state was explored with neutral electron acceptors with reduction potentials ranging from +0.25 to −1.15 V vs NHE.

Introduction

The excited states of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline) have been investigated extensively for a wide range of potential applications including solar energy conversion and for the increased understanding of various aspects of electron transfer processes.[1−27] Much effort has been devoted to shifting the absorption maxima of the complexes to lower energy for better utilization of the solar spectrum, while maintaining a redox-active excited state.[2,3,28−30] In addition, the metal-to-ligand charge transfer (MLCT) excited state of Ru(II) complexes has been utilized in pioneering studies of excited-state properties of metal complexes[31] and in the detailed study of various facets of electron transfer reactions. These include solvent reorganization,[32,33]

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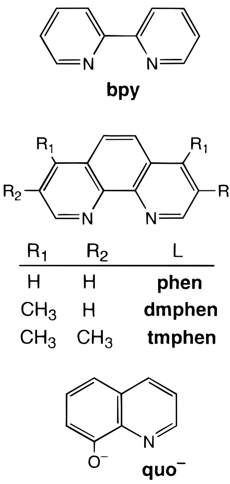
driving force,[34,35] and distance dependence in covalently linked systems,[36−39] electronic coupling within protein frameworks[40] and through hydrogen-bonded interfaces.[41] The long lifetime, high emission quantum yield, and the excited-state redox reactivity of the of these complexes are pivotal properties that permit their use in the applications cited above.



R_1	R_2	L
H	H	**phen**
CH_3	H	**dmphen**
CH_3	CH_3	**tmphen**

Figure 1. Structures of the ligands.

To tune the excited-state and redox properties of Ru(II) polypyridyl complexes substitutions of bpy and phen ligands have been explored; however, these variations lead only to modest electronic changes.[1−3] One such example is the $Ru(L)_3^{2+}$ series (L = phen, 5-methyl-1,10-phenanthroline, 4,7-dimethyl-1,10-phenanthroline, and 4,7-diphenyl-1,10-phenanthroline), where the emission maxima range from 603 to 635 nm, with lifetimes ranging from 1.1 to 3.6 μs, and the oxidation potential varies from 1.1 to 1.26 V vs NHE.[42,43] In contrast, it is known that the introduction of nonchromophoric ligands in $Ru(bpy)_2L_2$ and $Ru(phen)_2L_2$ complexes with L = CN^-, SCN^-, and Cl^- strongly affects the excited-state properties owing to changes in the metal-based orbitals.[1−3] In particular, the introduction of oxygen to the coordination sphere of the metal has been shown to facilitate Ru(II/III) oxidation.[44−46]

In the present work, we designed a series of photoreactive Ru(II) complexes whose absorption spectra are red-shifted relative to those of $Ru(bpy)_3^{2+}$, $Ru(phen)_3^{2+}$, and related systems, with highly reducing MLCT excited states. We explored the excited-state properties and redox behavior of complexes that possess a single oxygen in the coordination sphere of the type $Ru(L)_2quo^+$ (quo^- = 8-quinolate), where the ligands L (structures shown in Figure 1) are bpy, phen, dmphen (4,7-dimethyl-1,10-phenanthroline), and tmphen (3,4,7,8-tetramethyl-1,10-phenanthroline). The highly reducing nature of the $Ru(phen)_2quo^+$ excited state was ascertained by electron-transfer quenching with various electron acceptors with reduction potentials ranging from +0.25 to −1.15 V vs NHE.

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Experimental Section

Materials. $RuCl_3$, phen (1,10-phenanthroline), bpy (2,2′-bipyridine), dmphen (4,7-dimethyl-1,10-phenanthroline), tmphen (3,4,7,8-tetramethyl-1,10-phenanthroline), 8-hydroxyquinoline, and all the substituted quinones and nitrobenzenes were purchased from Aldrich and used without further purification. $Ru(phen)_3^{2+}$ and $Ru(bpy)_3^{2+}$ were purchased from Aldrich, dissolved in acetone, and precipitated with ether followed by filtration to remove excess ligand which was present to up to 30% in the commercial sample. The $Ru(L)_2quo^+$ complexes (L = bpy, phen, dmphen, tmphen) were prepared by the same method from the reaction of purified $Ru(L)_2Cl_2$ with 8-hydroxyquinoline as described in detail below for $Ru(phen)_2quo^+$, in a manner similar to that previously described for $Ru(bpy)_2quo^+$.[47]

$Ru(phen)_2Cl_2$ was synthesized by refluxing 0.1 g of $RuCl_3$ overnight in 30 mL of DMF with 2 equiv of phen ligand in the presence of ∼20-fold excess LiCl. After cooling, the purple $Ru(phen)_2Cl_2$ product was precipitated through the addition of water to the reaction mixture, collected on a filtration frit, and was thoroughly washed with water and ether to remove unreacted $RuCl_3$ and phen ligand. The $Ru(phen)_2Cl_2$ product was further purified through extraction in a separatory funnel with CH_2Cl_2/water to ensure complete removal of the water soluble and highly emissive $Ru(phen)_3^{2+}$. $Ru(phen)_2quo^+$ was prepared by stirring 20 mg of $Ru(phen)_2Cl_2$ with 2 equiv of quoH (8-hydroxyquinoline) in 50 mL of CH_2Cl_2 at room temperature. The initially purple solution turned red after ∼2 h, but the reaction was allowed to continue for 24 h. The solvent was removed, the red product was dissolved in a small amount of acetone and precipitated by the addition of ether, and the solid was collected through filtration. The red complex was separated from any remaining quo^- ligand present using a CM52 (Whatman) cation exchange column eluted with 0.1 M NaCl, after washing the complex loaded on the column with water. After removal of the solvent, the high solubility of $Ru(phen)_2quo^+$ in CH_2Cl_2 was utilized in its separation from NaCl.

The NMR spectra of all the complexes possessed peaks in the aromatic region. The overlap of the resonances for phen and quo protons, in addition to the removal of symmetry of the protons of the ancillary ligands in $Ru(L)_2quo^+$, made it difficult to obtain independent integrated areas. The identity of the $Ru(L)_2quo^+$ complexes was ascertained by mass spectrometry (FAB), where the parent ion peaks of all the complexes and expected fragments were detected. For $Ru(phen)_2quo^+$ strong peaks at m/z = 605 ($Ru(phen)_2quo^+$), 425 ($Ru(phen)quo^+$), and 461 ($Ru(phen)_2^+$) were detected, and for $Ru(bpy)_2quo^+$ the corresponding m/z = 557 ($Ru(bpy)_2quo^+$), 402 ($Ru(bpy)quo^+$), and 413 ($Ru(bpy)_2^+$) were present. Similar results were observed for $Ru(dmphen)_2quo^+$ and $Ru(tmphen)_2quo^+$. $Ru(dmphen)_2quo^+$ exhibited the parent ion peak at m/z = 662 and others at m/z = 454 ($Ru(dmphen)quo^+$) and 516 ($Ru(dmphen)_2^+$), whereas the parent ion peak of $Ru(tmphen)_2quo^+$ was detected at m/z = 718 with additional peaks at m/z = 482 ($Ru(tmphen)quo^+$) and 574 ($Ru(tmphen)_2^+$).

Instrumentation. Absorption measurements were performed in a Hewlett-Packard diode array spectrometer (HP 8453) with HP8453 Win System software installed in an HP Vectra XM 5/120 desktop computer. Emission spectra were collected on a SPEX FluoroMax-2 spectrometer equipped with a 150 W xenon source, a red-sensitive R928P photomultiplier tube, and DataMax-Std software on a Pentium microprocessor. The electrochemical measurements were conducted using a Cypress Systems CS-1190 using a single-compartment three-electrode cell. The working electrode was a 1 mm diameter Pt disk (Cypress) with a Ag/AgCl reference electrode (Cypress) and a Pt wire counter electrode. The electrolyte was 1 M KCl. The $E_{1/2}(Ru^{III/II})$ was estimated using both cyclic voltammetry (ΔE = 100 mV) and differential pulse voltammetry

The transient absorption signal was measured following sample excitation with the 532 nm output from a frequency doubled Spectra-Physics GCR-150-10 Nd:YAG laser (fwhm ∼ 8 ns, ∼5 mJ/pulse). The output from a 150 W Xe arc lamp (USHIO) powered by a PTI PS-220 power supply (in a PTI housing with f/4 focusing lens), pulsed with electronics built in-house, was focused onto the sample at a 90° with respect to the laser beam with an f/4 lens. The lamp light and the laser beam each pass through computer-controlled Uniblitz shutters with Uniblitz (model D122) drivers prior to reaching the sample. The white light transmitted by the sample was collimated and focused with two fused silica plano-convex lenses (f/4, 1 in diameter) onto the entrance slit of a Spex H-20 single monochromator (1200 gr/mm grating blazed at 500 nm), and the signal was detected utilizing a Hamamatsu R928 photomultiplier tube (modified in house to accommodate high light intensity applications) powered by a Stanford Research PS325 power supply. The signal was digitized on a Tektronics 400 MHz oscilloscope (TDS 380) triggered by the signal of a photodiode produced by each laser pulse reaching the sample (∼5% laser light was split by a quartz plate). A PowerMac 7600/132 (Apple) equipped with a National Instruments GPIB interface (NI-488.2) and a National Instruments data acquisition board (PCI-1200) was programmed with Labview 4.1 software to control the data acquisition by the oscilloscope and the PMT voltage. The timing of the triggering of the laser oscillator and Q-switch, the lamp pulser, and various shutters was accomplished using a digital delay generator (SRS DG535), whose action was coupled to the acquisition cycles of the computer through AND-gate circuitry. Attenuated scattered laser light yielded an overall instrument response function with fwhm = 12.5 ns. Emission lifetimes greater than 100 ns were measured on the same instrument with 90° excitation/detection geometry,[48] whereas shorter luminescence decay traces were collected using a model OB900 single photon counting (Edinburgh Analytical Instruments) instrument.

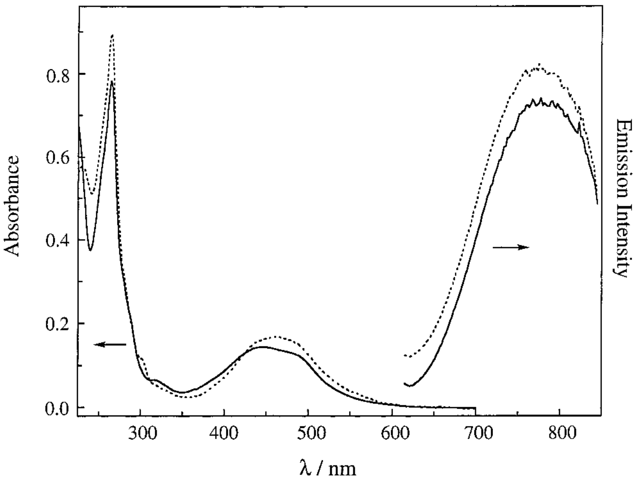

Figure 2. Electronic absorption (left) and emission (right, λ_{exc} = 500 nm) spectra of $Ru(tmphen)_2quo^+$ (—) and $Ru(phen)_2quo^+$ (---) in water.

Results and Discussion

Ground-State Properties. The electronic absorption spectra of $Ru(phen)_2quo^+$ and $Ru(tmphen)_2quo^+$ in water are shown in Figure 2 and are typical of the $Ru(L)_2quo^+$ (L = bpy, phen, dmphen, tmphen) series of complexes. The absorption maxima and extinction coefficients for all the complexes in the $Ru(L)_2quo^+$ series are listed in Table 1. The spectral differences among the quo-containing complexes in the 250−300 nm region are consistent with the variation of the $\pi\pi^*$ transition of the ligand L. In addition, when compared to the parent $Ru(L)_3^{2+}$ systems, the differences are consistent with the presence of quo^- in the ligation sphere. The 8-hydroxyquinoline ligand, quoH, and 8-quinolate, quo^-, possess absorption maxima in water at 241 nm (pH = 7) and 254 nm (pH = 10, adjusted with NaOH), respectively. The contribution of the quo^- ligand to the absorption by the $Ru(L)_2quo^+$ complexes appears as a shoulder of the $\pi\pi^*$ phen, substituted phen, or bpy $\pi\pi^*$ transition, as

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Table 1. Absorption (λ_{abs}) and Emission (λ_{em}) Maxima, Estimated Excited-State Energy (E_{00}), and Ground-State Oxidation Potentials (vs NHE) of the $Ru(L)_2quo^+$ Complexes in Water

L	λ_{abs}/nm ($\epsilon/10^3$ M^{-1} cm^{-1})	λ_{em}/nm[a]	E_{00}/eV	$E_{1/2}(Ru^{III/II})$/V
bpy	245 (66.2), 290 (86.5), 460 (15.8)	767	1.85	+0.69
phen	265 (78.4), 445 (14.4), 490 (12.1)	783	1.82	+0.62
dmphen	271 (69.2), 453 (14.1)	757	1.88	+0.69[b]
tmphen	264 (89.4), 459 (16.8)	776	1.83	+0.70[b,c]

[a] Emission corrected for instrument and detector response. [b] In DMF with 0.1 M tetrabutylammonium hexafluorosphate. [c] Approximate value.

seen in Figure 2 for $Ru(phen)_2quo^+$ and $Ru(tmphen)_2quo^+$. In all the quo-containing Ru(II) complexes, the MLCT absorption is shifted to lower energies (~40 nm) relative to the corresponding $Ru(L)_3^{2+}$ system.[1]

The metal-based Ru(III/II) oxidation potentials for the $Ru(L)_2quo^+$ complexes are listed in Table 1 in 1 M KCl aqueous solution. In general, the $Ru(L)_2quo^+$ systems are easier to oxidize than their corresponding $Ru(L)_3^{2+}$ parent complexes by approximately 0.65 V. A similar shift was observed in $Ru(bpy)_2L^+$ complexes with the bidentate triazene 1-oxide ligands L of the type $RN(O){=}NNH$-*p*-$CH_3C_6H_4$ (R = Et, Ph) that chelate the metal center through coordination by the oxygen and deprotonated NH atoms, where $E_{1/2}(Ru^{III/II})$ values of +0.40 and +0.49 V vs NHE were reported in acetonitrile, respectively.[49] In addition, the reported oxidation potential for $Ru(bpy)_2quo^+$ is +0.72 V vs NHE in CH_3CN and +0.69 V in H_2O,[47] similar to that measured by us in the present work.

The shift in the Ru(II) → L MLCT transition to lower energy in the $Ru(L)_2quo^+$ complexes relative to the $Ru(L)_3^{2+}$ systems along with the ease of oxidation of the former can be explained by a smaller ligand field splitting induced by quo^- compared to bpy, phen, and substituted phen ligands. Nitrogen chelators as part of an aromatic ring result in a larger ligand-field splitting than neutral and anionic oxygen containing ligands, including H_2O and OH^-.[50] Therefore, the ligand field stabilization energy (LFSE) in the $Ru(L)_2quo^+$ is expected to be smaller than that in the $Ru(L)_3^{2+}$ parent complexes owing to the introduction of the oxygen atom in the ligation sphere. In a pseudo-octahedral geometry the lower LFSE in $Ru(L)_2quo^+$ results in higher energy filled metal-centered (MC) t_{2g}-type orbitals and lower energy empty e_g-type orbitals. The energy of the π^* orbital of the phen, substituted phen, and bpy ligands, located below the e_g-type Ru(II) orbitals, is expected to be similar in both $Ru(L)_2quo^+$ and $Ru(L)_3^{2+}$. Therefore, the transition from the ground state, with electron configuration $(t_{2g})^6(\pi^*)^0$, to the MLCT state, $(t_{2g})^5(\pi^*)^1$, is expected to be at lower energy (red shifted) in $Ru(L)_2quo^+$ compared to the homoleptic $Ru(L)_3^{2+}$. The ease in oxidation of the Ru(II) metal center in the $Ru(L)_2quo^+$ systems relative to the $Ru(L)_3^{2+}$ complexes is consistent with a higher energy t_{2g}-type LUMO in the former.

Photophysical Properties. The $Ru(L)_2quo^+$ complexes (L = bpy, phen, dmphen, tmphen) are emissive in various solvents at room temperature, with emission maxima in water listed in Table 1. Typical emission spectra for $Ru(phen)_2quo^+$ and $Ru(tmphen)_2quo^+$ are shown in Figure 2 at room temperature. Inspection of Table 1 reveals a large shift (~150 nm) in emission maxima between the parent tris complexes $Ru(L)_3^{2+}$ (L = bpy, phen, dmphen, tmphen), with λ_{em} in the 603−628 nm range,[1] and the $Ru(L)_2quo^+$ series, with λ_{em} from 757 to 783 nm. The emission lifetimes of $Ru(phen)_2quo^+$ and $Ru(bpy)_2quo^+$ in water are 17.0 and 11.4 ns, respectively, monitored at 770 nm at room temperature. These excited-state lifetimes are significantly shorter than those reported by others and measured by us for $Ru(phen)_3^{2+}$ (1.1 μs) and $Ru(bpy)_3^{2+}$ (670 ns).[1]

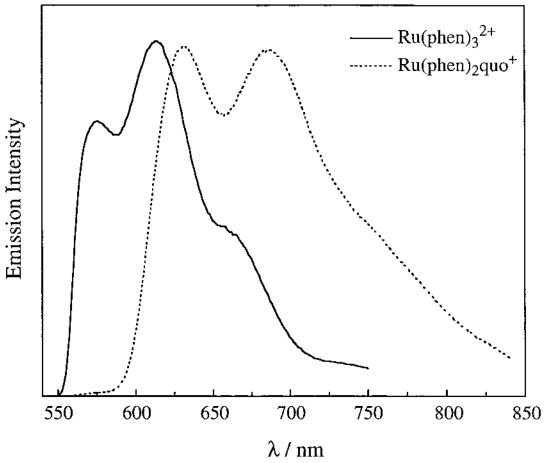

Figure 3. Emission spectra of $Ru(phen)_3^{2+}$ (λ_{exc} = 450 nm) and $Ru(phen)_2quo^+$ (λ_{exc} = 450 nm) at 77 K in ethanol glass.

The low-temperature (77 K) emission spectrum of $Ru(phen)_2quo^+$ collected in an ethanol glass is shown in Figure 3, along with that of $Ru(phen)_3^{2+}$. Both spectra exhibit a vibrational progression with similar relative intensities, consistent with a similar nuclear displacement of the excited-state and ground-state potential energy surfaces. This observation is indicative that in $Ru(phen)_2quo^+$ the emissive state may be Ru(II) → phen MLCT in nature, as is well established for $Ru(phen)_3^{2+}$.[1−3] The transient absorption spectrum of $Ru(phen)_2quo^+$ in water (Figure 4a) is very similar to that measured by us and reported by others for $Ru(phen)_3^{2+}$,[51] where positive absorption in the 300−400 nm region and above 560 nm is observed along with the ground-state bleaching of the MLCT absorption (410−550 nm). This finding provides further evidence that the excited-state populated in $Ru(phen)_2quo^+$ is indeed Ru → phen MLCT.

The bathochromic shift in the emission spectra of the $Ru(L)_2quo^+$ complexes and their short lifetimes compared to $Ru(L)_3^{2+}$ parent complexes are consistent with a lower LFSE in the $Ru(L)_2quo^+$ series relative to the $Ru(L)_3^{2+}$ complexes. The smaller ligand field splitting results in lower energy metal-centered (MC) excited states, with electron configuration $(t_{2g})^5(\pi^*)^0(e_g)^1$, thus placing the MC states closer in energy to the lower energy emissive MLCT excited state. Since it is established that the deactivation of the MLCT excited state of Ru(II) complexes, including $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$, takes place through the thermal population of the MC states,[1−3,14,52,53]

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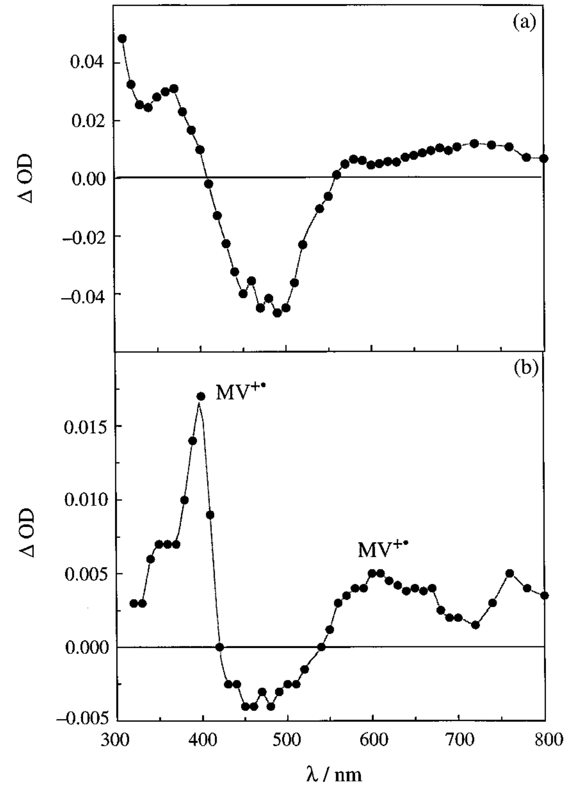

Figure 4. Transient absorption spectra of 0.1 mM Ru(phen)$_2$quo$^+$ in water (a) in the absence and (b) in the presence of 6 mM MV^{2+} (λ_{exc} = 532 nm), collected 20 ns and 1 μs after excitation, respectively.

it is expected that the lower MC states in the Ru(L)$_2$quo$^+$ complexes would lead to the observed shorter excited-state lifetimes.

Excited-State Redox Properties of Ru(phen)$_2$quo$^+$. From the onset of the emission of Ru(phen)$_2$quo$^+$ in acetonitrile the energy of its MLCT state can be estimated to be $E_{00} \sim 1.95$ eV, leading to an excited-state oxidation potential $E_{1/2}$(Ru$^{III/II*}$) ~ -1.33 V vs NHE. The transient absorption spectrum of Ru(phen)$_2$quo$^+$ in the presence of methyl viologen (MV^{2+}) collected ~1 μs after 532 nm excitation in deoxygenated aqueous solution is shown in Figure 4b. The well-known absorption features of reduced methyl viologen, MV$^{\bullet+}$, at 395 and 605 nm are clearly observed in the spectrum, as well as some absorption in the 650−750 nm range that may be assigned to the oxidized complex, Ru(phen)$_2$quo^{2+}.

Table 2. Rate Constants for the Quenching of *Ru(phen)$_2$quo$^+$ by Electron Acceptors with Various Reduction Potentials in CH$_3$CN

acceptor	$E_{1/2}$(A$^{0/-}$)/V^a	$-\Delta G$/V	k_q/M^{-1} s$^{-1\,b}$
3-nitro-*o*-xylene	−1.15	0.18	$<3 \times 10^{8c}$
5-nitro-*m*-xylene	−1.02	0.31	2.2×10^9
1-chloro-4-nitrobenzene	−0.89	0.44	1.1×10^{10}
3-nitrobenzaldehyde	−0.85	0.48	1.8×10^{10}
o-dinitrobenzene	−0.67	0.66	2.5×10^{10}
duroquinone	−0.60	0.73	2.1×10^{10}
p-dinitrobenzene	−0.34	0.99	2.3×10^{10}
p-benzoquinone	−0.27	1.06	3.3×10^{10}
tetrachloro-*p*-benzoquinone	+0.25	1.58	3.3×10^{10}

[a] Vs NHE; values from: *Encyclopedia of Electrochemistry of the Elements, Organic Section, Volume XII*; Bard, A. J., Lund, H., Eds.; Marcel-Dekker: New York; 1978. Mussell, R. D.; Nocera, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 2764. [b] The k_q values were determined from steady-state measurements of the integrated emission spectra. [c] Up to [Q] = 0.1 M.

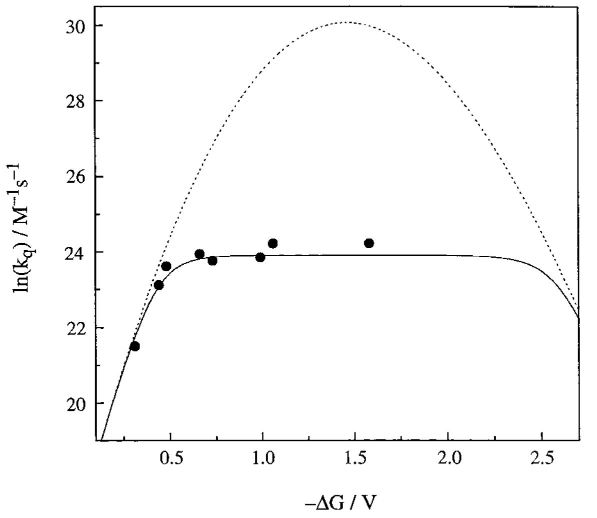

Figure 5. Marcus plot of ln(k_q) vs $-\Delta G$ for the quenching of the *Ru(phen)$_2$quo$^+$ emission by electron acceptors in acetonitrile (Table 2), where the measured (●) and calculated values of k_q (—) and k_{act} (---) are shown. (Equations 1−5 were used with $V_o = 250$ cm^{-1}, $\beta = 1.0$ Å^{-1}, $\lambda_i = 0.2$ eV, and $T = 298$ K; for additional parameters, see text.)

The driving force dependence of the electron-transfer quenching of the *Ru(phen)$_2$quo$^+$ excited state in the presence of neutral electron acceptors in acetonitrile, where the lifetime of the complex is 32.2 ns, was determined from the slope of Stern−Volmer plots. The quenching is dynamic in nature, where the decrease in the lifetime of the complex parallels that of the emission intensity. The oxidative quenching rate constants, k_q, of *Ru(phen)$_2$quo$^+$ by various quinones and nitrobenzene derivatives with reduction potentials ranging from +0.25 to −1.15 V vs NHE are listed in Table 2. Energy transfer quenching of the excited state to the triplet states of the quinones or nitroaromatics can be ruled out, since the energy of the triplet states of the acceptors is above 2.1 eV in all cases.[54] A plot of k_q vs $-\Delta G$ is shown in Figure 5, where the typical bimolecular Marcus behavior is observed. A plateau is reached as the driving force becomes more negative indicative of diffusion-controlled kinetics. The solid line in Figure 5 is the calculated value of k_q as a function of driving force given by eq 1,[55] where k_{diff} and

$$k_q = \frac{k_{act}k_{diff}}{k_{diff} + k_{act}} \qquad (1)$$

k_{act} are the diffusional and activated electron-transfer rate constants. The rate constants k_{diff} and k_{act} can be evaluated to account for electron-transfer processes at distances, r, from closest contact, σ, to ∞ by eqs 2 and 3,[55,56] where N is

$$k_{diff} = \frac{4\pi ND}{1000}\left\{\int_\sigma^\infty \mathrm{d}r\,[\exp(-U(r)/k_BT)r^2]^{-1}\right\}^{-1} \qquad (2)$$

$$k_{act} = \frac{4\pi N}{1000}\int_\sigma^\infty \mathrm{d}r\,\exp(-U(r)/k_BT)k_{et}(r)\,r^2 \qquad (3)$$

Avogadro's number, D is the sum of the diffusion coefficients of the reactants in acetonitrile,[57] k_B is Boltzman's constant, T

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is the temperature, and the interaction energy between the reactants, $U(r)$, is approximately zero when a neutral reactant is involved.[55] The classical fixed-distance electron-transfer rate constant, $k_{et}(r)$, is given by[55,56,58]

$$k_{et}(r) = \frac{2\pi}{h}\left[\frac{1}{\lambda k_B T}\right]^{1/2} V_o^{\,2} \exp[-\beta(r-\sigma)] \exp\left\{\frac{-(\lambda+\Delta G)^2}{4\lambda k_B T}\right\} \tag{4}$$

where λ is the sum of the inner-sphere (λ_i) and outer-sphere (λ_o) reorganization energies, V_o is the electronic coupling between the donor and acceptor at closest contact, β is the electronic coupling damping factor, and ΔG is the driving force.[59] The value of λ_o was estimated from the classical dielectric continuum model[55,56,58]

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

where r_A and r_B are the radii of the reactants and D_{op} and D_s are the optical and static dielectric constants of the solvent, respectively (for acetonitrile $D_{op} = 37.5$ and $D_s = 1.34$). The details of the calculation using eqs 1−5 from donor/acceptor center-to-center distance of 30 Å to closest contact, σ, using average radii of 6.5 and 3.5 Å for the Ru(II) complex and the aromatic acceptors, respectively, was described previously.[35] With these parameters we obtain $k_{diff} = 2.42 \times 10^{10}$ M^{-1} s^{-1}, a value typical for neutral molecules in CH_3CN.[54]

It is apparent from the calculated quenching rate constant as a function of driving force shown in Figure 5 that our measurements are consistent with the predicted Marcus behavior, including the calculated values of k_q at $-\Delta G < 0.2$ V, where an upper limit of $k_q < 3 \times 10^8$ M^{-1} s^{-1} was estimated for the quenching by 3-nitro-*o*-xylene (Table 2, $-\Delta G = 0.18$ V). In addition, the calculation shows that the inverted region for the forward ET reaction between *Ru(phen)$_2$quo$^+$ with the series of substituted benzoquinone and nitrobenzene acceptors in acetonitrile would be observed at $-\Delta G > 2.4$ V. Similar results were obtained using the semiclassical form of eq 4, which accounts for deactivation through vibronic states of the reactant potential energy surface in the inverted region.[35,60] Although the excited state of Ru(phen)$_2$quo$^+$ is highly reducing, the observation of the inverted region for the forward ET is not possible, since with $E_{1/2}$(Ru$^{III/II}$) = +0.62 V and $E_{1/2}$(Ru$^{III/II*}$) = −1.33 V vs NHE the maximum experimental driving force possible is ~1.9 V to avoid ground-state oxidation of Ru(phen)$_2$quo$^+$.

Conclusions

In summary, we prepared a series of Ru(II) complexes of the type Ru(L)$_2$quo$^+$ (L = bpy, phen, dmphen, tmphen) and investigated their photophysical and redox properties. The absorption and emission of the Ru(L)$_2$quo$^+$ are significantly red-shifted relative to the parent complexes Ru(L)$_3^{2+}$, with emission maxima in the 757−783 nm range in water. The Ru(L)$_2$quo$^+$ systems are easily oxidized with $E_{1/2}$(Ru$^{III/II}$) values ranging from +0.62 to +0.70 V vs NHE. The emissive Ru → phen MLCT (metal-to-ligand charge transfer) excited states (E_{00} ~ 1.95 eV) of the Ru(L)$_2$quo$^+$ complexes are significantly better reducing agents than the MLCT states of the parent Ru(L)$_3^{2+}$ complexes by ~0.5 V. Emission lifetimes of 17.0 and 32.2 ns were measured for Ru(phen)$_2$quo$^+$ in water and acetonitrile, respectively, and 11.4 ns for Ru(bpy)$_2$quo$^+$ in water. Transient absorption results are consistent with the formation of reduced methyl viologen upon Ru(phen)$_2$quo$^+$ excitation with visible light in water, and bimolecular Marcus behavior is observed upon electron-transfer quenching of its MLCT excited state by quinones with reduction potentials ranging from +0.25 to −1.15 V vs NHE.

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(57) For reactants A and B, $D = D_A + D_B$, with $D_A = k_BT/6\pi r_A\eta$, where r_A is the radius of reactant A and η is the viscocity of acetonitrile (0.341 g cm^{-1}). From this expression we calculate $D = 2.80 \times 10^{-6}$ cm^2 s^{-1}.

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(59) $\Delta G = \Delta G° + w_r - w_p$, where $\Delta G° = E_{1/2}(A^{0/-}) - E_{1/2}(Ru^{III/II*})$ and w_r and w_p represent the work associated with bringing charged reactants together and separating charged products, respectively, and can be calculated from $U(r) = z_1z_2e^2/D_sr$ (see refs 55, 56, and 58).

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