Direct Observation of Sequential Electron and Proton Transfer in Excited State ET/PT Reactions

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1. Thermodynamic Parameters and spectra of MQ$^+$ and HMQ$^{2+}$:

1.1 Cyclic Voltammetry of N-methyl-4,4'-dibpyridinium

Voltammograms of N-methyl-4,4'-bipyridinium were collected in the presence and absence of a proton source. Protonation of the compound results in a shift in reduction potential of 0.53 V positive. Table S1 has the relevant reduction potentials stated.

\[ E_{1/2} = \frac{E_{p,a} + E_{p,c}}{2} \]

Table S1.

<table>
<thead>
<tr>
<th></th>
<th>( E_{1/2} ) (V) vs. Fc$^{+/0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MQ$^+$</td>
<td>-1.35</td>
</tr>
<tr>
<td>HMQ$^{2+}$</td>
<td>-0.82</td>
</tr>
</tbody>
</table>

Figure S1. Voltammograms of A) N-methyl-4,4'-bipyridinium in acetonitrile and B) N-methyl-4,4'-bipyridium in acetonitrile with 2 mM triflic acid (excess) shown here vs. Ag/AgCl reference.
1.2 Determination of $pK_a$ of HMQ$^{2+}$

The $pK_a$ of $N$-methyl-4,4'-bipyridinium was measured by assessing the proton exchange equilibrium between MQ$^+$ and Cl$_3$CCOOH ($pK_a$(CH$_3$CN)= 10.93). The equilibrium position was assessed using $^1$HNMR chemical shift data. The resonance for the β- proton on the pyridine ring was monitored as a function of acid concentration. The chemical shifts for the limiting cases (MQ$^+$ (1) and HMQ$^{2+}$ (10)) were assessed, using triflic acid (1.2 equivalents) to generate the $^1$HNMR spectrum of HMQ$^{2+}$. The concentrations ranged from 0.0075 M to 1.92 M for Cl$_3$CCOOH, while the concentration of MQ$^+$ initially in each sample was kept at 0.013 M. All spectra were collected in CH$_3$CN-d$_3$.

**Figure S2.** $^1$HNMR spectra of MQ$^+$ in the presence of increasing concentration of Cl$_3$CCOOH. Spectrum 1 is the $^1$HNMR spectrum of MQ$^+$ in the absence of any acid, while spectrum 10 shows the spectrum of HMQ$^{2+}$ generated by adding 1.2 equivalents of triflic acid.

The spectra include labels for the hydroxyl proton chemical shift of Cl$_3$CCOOH, the chloroform proton chemical shift (a low concentration of chloroform is present as a result of purification of Cl$_3$CCOOH), and the chemical shifts from MQ$^+$. The peak labeled with * indicated the chemical shift monitored and used as $\delta_{obs}$ in the expression used to determine the $pK_a$ of HMQ$^{2+}$.
The equilibrium for the proton exchange between MQ$^+$ and Cl$_3$CCOOH is expressed in the following equation:

$$\text{MQ}^+ + \text{Cl}_3\text{CCOOH} \rightleftharpoons \text{HMQ}^{2+} + \text{Cl}_3\text{CCOO}^-$$

where $K_{eq}$ can be expressed as:

$$K_{eq} = \frac{[HMQ^{2+}] * [Cl_3CCOO^-]}{[MQ^+] * [Cl_3CCOOH]}$$

Solving for the [HMQ$^{2+}$] in this equation, the following function can be derived:

$$[HMQ^{2+}] = \frac{K_{eq} * ([Cl_3CCOOH]_0 + [MQ^+]_0) + \sqrt{[Cl_3CCOOH]_0 + [MQ^+]_0)^2 - 4 * (K_{eq} - 1) * K_{eq} * [Cl_3CCOOH]_0 * [MQ^+]_0}}{2 * (K_{eq} - 1)}$$

Knowing that the mole fraction, $x_{HMQ}$, of HMQ$^{2+}$ can be expressed as with the following equations, the final function for fitting the chemical shift data can be resolved. In the equations below, [HMQ$^{2+}$] is the equilibrium concentration of HMQ$^{2+}$, [MQ$^+$]$_0$ is the initial concentration of MQ$^+$, $\delta_{MQ}$ is the chemical shift for the $\beta$-proton of the pyridine ring for MQ$^+$, $\delta_{HMQ}$ is the chemical shift of the $\beta$-proton of the pyridine ring for HMQ$^{2+}$, $\delta_{obs}$ is the observed chemical shift for the mixture of HMQ$^{2+}$ and MQ$^+$, [Cl$_3$CCOOH]$_0$ is the concentration of acid added to each sample.

$$x_{HMQ} = \frac{[HMQ^{2+}]/[MQ^+]_0}{\frac{|\delta_{MQ} - \delta_{obs}|}{\delta_{HMQ} - \delta_{MQ}}}$$

$$[HMQ^{2+}] = [MQ^+]_0 * \frac{|\delta_{MQ} - \delta_{obs}|}{\delta_{HMQ} - \delta_{MQ}}$$

The final equation used to fit the data can be expressed as:

$$\delta_{obs} = \frac{|\delta_{HMQ} - \delta_{MQ}| * (K_{eq} * ([Cl_3CCOOH]_0 + [MQ^+]_0) + [MQ^+]_0 + \sqrt{[Cl_3CCOOH]_0 + [MQ^+]_0)^2 - 4 * (K_{eq} - 1) * K_{eq} * [Cl_3CCOOH]_0 * [MQ^+]_0}}{2 * (K_{eq} - 1) * [MQ^+]_0}$$
From the fit of the data $\delta_{\text{obs}}$ v. $[\text{Cl}_3\text{CCOOH}]_0$ the $pK_a$ of HMQ$^{2+}$ was determined to be 10.3 ± 0.1.
1.3 Determination of $pK_a$ of $\text{HMQ}^{++}$

The $pK_a$ of $\text{HMQ}^{++}$ was determined using a thermodynamic cycle shown below in Scheme S1.

The calculated bond-dissociation free energy (BDFE) was obtained by employing Equation 1. This equation uses Hess’ Law to compute the free energy for hydrogen atom dissociation from the compound in solution. The term $C_G$ refers to the free energy for standard reduction potential of a proton in a specified solvent, here acetonitrile.

$$\text{BDFE}(X-H) = 1.37pK_a + 23.06E^{\circ} + C_G$$

$C_G$ has been measured and reported by Mayer and coworkers in various solvents.\(^2\) For calculation of the $pK_a$ of $\text{HMQ}^+$, the value of 54.9 kcal/mol was used (with reference to Fc\(^{+/0}\)).
1.4 Absorption Spectra of $MQ^+$ and $HMQ^{2+}$

Figure S2 shows the absorbance spectra of the $MQ^+$ and $HMQ^{2+}$.

![Absorption Spectra of MQ+ and HMQ2+](image)

**Figure S4.** Absorbance spectra of $MQ^+$ and $HMQ^{2+}$ in acetonitrile.
2. Thermodynamic Parameters and spectra of [(bpy)Ru(LL)]^{2+}

2.1 Absorption and Emission Spectroscopy of [(bpy)_{2}Ru(LL)](PF_{6})_{2} Complexes

Figure S5. Absorption spectra of [Ru(II)OH]^{2+}, [Ru(II)O]^{+} and [Ru(II)O]^{0} in CH_{3}CN. The deprotonated forms were obtained by adding one and two equivalents of tetra-n-butylammonium hydroxide to a solution of [Ru(II)OH]^{2+}.

Figure S6. Luminescence spectra of [Ru(II)OH]^{2+} (solid line) in CH_{3}CN at 298 K and the complex following addition of 1 eq of TBAH (dashed line).
2.2 Determination of Luminescence Quantum Yield of $[\text{Ru(II)OH}]^{2+}$

The emission quantum yield of $[\text{Ru(II)OH}]^{2+}$ was measured as a relative quantum yield and the emission spectra obtained for the reference and complex are shown in Figure S7.

The quantum yield for emission of $[\text{Ru(II)OH}]^{2+}$ was measured relative to $[\text{Ru(bpy)}_3]^{2+}$. The quantum yield was obtained using the following set of equations:

$$\phi_S = \frac{I_S}{I_R} \times \frac{1 - 10^{-A_R}}{1 - 10^{-A_S}} \times \frac{n_R^2}{n_S^2} \times \phi_R$$

$I_S$: Integrated Emission Area for Sample  
$I_R$: Integrated Emission Area for Reference  
$A_R$: Absorbance at excitation wavelength for reference  
$A_S$: Absorbance at excitation wavelength for sample  
$\phi_R$: Quantum yield of reference  
$n_R$: Refractive index for reference solvent  
$n_S$: Refractive index for sample solvent  
$\phi_S = 0.014$

**Figure S7.** Emission spectra of absorbance matched solutions of $[\text{Ru(bpy)}_3]^{2+}$ and $[\text{Ru(II)OH}]^{2+}$ in acetonitrile.
2.3 Determination of acid dissociation constants for [Ru(II)OH](PF$_6$)$_2$ and [Ru(III)OH](PF$_6$)$_3$

The pK$_a$ of [Ru(II)(OMe)OH]$^{2+}$ was assessed by photometric titration with 4-aminopyridine ($p$K$_a$(CH$_3$CN) = 17.63).$^4$ The pK$_a$ of this complex was used as an estimate for the first pK$_a$ of [Ru(II)OH]$^{2+}$. The Figure S8 shows the attempted titration with 4-aminopyridine and [Ru(II)OH]$^{2+}$. The lack of a clean isosbestic point indicates the presence of greater than 2 absorbing species in solution. It is proposed that pK$_{a,1}$ and pK$_{a,2}$ for [Ru(II)OH]$^{2+}$ are close in value, giving rise to 3 absorbing species in solution. This is not the case with [Ru(II)(OMe)OH]$^{2+}$, where the isosbestic point can be clearly distinguished and the resulting data assessed to determine the equilibrium constant for the proton exchange equilibrium (Figure S9).

Figure S8. Absorption spectra of [Ru(II)OH]$^{2+}$ in the presence of various molar equivalents of 4-aminopyridine.
The following relationships were used to plot the data below, where $A_{obs}$ is the observed absorbance at a wavelength, $A$:

$$A_{obs} = A_{RuO^-} + A_{RuOH}$$

$$A_{obs} = \varepsilon_{RuO^-} \times l \times c_{RuO^-} + \varepsilon_{RuOH} \times l \times c_{RuOH}$$

$$c_T = c_{RuO^-} + c_{RuOH}$$

Substituting out $c_{RuO^-}$ and solving for $c_{RuOH}$ gives the following expression:

$$c_{RuOH} = \frac{A_{obs} - (\varepsilon_{RuO^-} \times c_T)}{\varepsilon_{RuOH} - \varepsilon_{RuO^-}}$$

From here, the equilibrium concentrations of individual species can be determined and the plot of $[B]_{eq}$, where B=base added, vs. $[BH]_{eq}*[RuO^+]_{eq}/[RuOH]_{eq}$ can be made, where the slope is equal to $K_{eq}$, (Figure S13).

Figure S9. Absorption spectra of $[\text{Ru(II)(OMe)OH}]^{2+}$ in the presence of various molar equivalents of 4-aminopyridine.
Using the reported pK_a of the reference base and the log(K_eq), the pK_a of the complex can be determined. Here this value was assessed to be 17.7 ± 0.04.

Using the pK_a calculated for [Ru(II)(OMe)OH]^2+ and the anodic peak potential for the Ru^{III}/II couple of [Ru(III)O^−]^2+ in acetonitrile, along with the Ru^{III}/II potential for the protonated complex, an estimate for the pK_a of the [Ru(III)OH]^3+ can be calculated. Using this approach, the pK_a was found to be 7.74 ± 0.24. The following equations were used to obtain this value:

\[ \Delta G_{PT}(V) = \frac{R \cdot T \cdot 2.303 \cdot pK_a}{23.06} = \frac{1.37 \cdot pK_a}{23.06} \text{ (V)} \]

\[ \Delta G_{PT}^\prime(V) = \Delta G_{PT}(V) + E_{p,a}([\text{Ru(III/II)O}^-]) - E_{1/2}([\text{Ru(III/II)OH}]) \]

\[ pK_a' = \frac{23.06 \cdot \Delta G_{PT}^\prime(V)}{1.37} \]

**Figure S10.** Linear Plot of [B] vs. [BH]^+[RuO]/[RuOH] giving the slope equal to the equilibrium constant for the proton exchange between [Ru(II)(OMe)OH]^2+ and 4-aminopyridine.
Scheme S2. Square scheme depicting the relevant acidity constants and reduction potentials for the complex $[\text{Ru(II)OH}]^{2+}$ (Ru(II)-OH in scheme).

The BDFE was computed using the same equation as shown in section 1.
2.4 Determination of the excited-state pKₐ of [Ru(II)OH]²⁺

The excited-state pKₐ or pKₐ* of [Ru(II)OH]²⁺ was calculated using the emission energy maxima at -41°C in acetonitrile as the E₀₀ energy for the two protonation states of the complex, as [Ru(II)O⁻]⁺ is non-emissive at room temperature. Caspar and Meyer⁵ showed that Franck-Condon fits of emission spectra for a series of Ru(II) diimine complexes at 200 K yielded E₀₀ values that were within 1% of the energies of emission maxima. For this reason, we have simply used emission maxima in place of E₀₀ values for determination of pKₐ*.

The Förster cycle was used to calculate the pKₐ* of the complex and is expressed as the following equation⁶:

\[
pK_a - pK_a^* = \frac{(E_{0-0}([\text{Ru(II)OH}]^{2+}) - E_{0-0}([\text{Ru(II)O}^-]^+))}{2.303RT}
\]

pKₐ* was found to be 15.3 ± 0.1.

Figure S11. Emission spectra of [Ru(II)OH]²⁺ and [Ru(II)O⁻]⁺ in acetonitrile at -41°C
2.5 Summary of Ground and Excited-state Thermodynamic Parameters for [Ru(II)OH]^{2+}

Scheme 3 below summarizes the ground and excited-state oxidation potentials and acid dissociation constants for [Ru(II)OH]^{2+}. The excited-state redox potentials were calculated in the manner described in equations 2-4 of the main text for this publication. The ground-state parameters were taken from the calculated pK_a of [Ru(II)(OMe)OH]^{2+} (shown above) and the oxidation potentials reported by previously by Paul.\(^7\)

**Scheme S3.** Summary of ground and excited-state thermodynamic parameters for [Ru(II)OH]^{2+} with free energies expressed in eV for excited states and V vs. Fc^{+/0} for redox processes.
2.6 Spectroelectrochemistry of [(bpy)$_2$Ru(LL)](PF$_6$)$_2$ Complexes

**Figure S12.** Absorbance spectrum of [Ru(III)OH]$^{3+}$ in acetonitrile generated by spectroelectrochemistry with an applied potential of 1.6 V.

**Figure S13.** Absorbance spectrum of [Ru(III)OMe]$^{5+}$ in acetonitrile generated by spectroelectrochemistry with an applied potential of 1.6 V.
2.7 Quenching of [(bpy)$_2$Ru(LL)]$^{2+}$ by N-methyl-bipyridinium

**Figure S14.** Stern-Volmer quenching of [Ru(II)OH]$^{2+}$ by MQ$^+$. All solutions were prepared with a constant ion concentration of 100 mM, using tetrabutylammonium hexafluorophosphate as an electrolyte.

**Figure S15.** Oxidative quenching of [Ru(II)OMe]$^{2+}$ by MQ$^+$. Each sample was prepared with a constant ionic concentration using TBAPF$_6$ as an electrolyte in acetonitrile solution.
2.8 Nanosecond transient absorption of [Ru(II)OMe](PF_6)_2

Figure S16. nsTA spectrum of [Ru(II)OMe](PF_6)_2 in acetonitrile.

Proton Transfer Rate Dependence on [Ru(II)OH]^{2+} Concentration
Figure S17. Kinetics of ET/PT reaction shown with varying concentrations of [Ru(II)OH]^{2+}. On the left are the kinetic traces at 390 nm for the ET/PT reaction at various concentrations of [Ru(II)OH]^{2+}. The right-hand side shows the extracted rate constants from a global fitting routine (see below) plotted vs. the concentration of [Ru(II)OH]^{2+} present in each sample.
Global Fit Spectra for Laser Flash Photolysis of $[\text{Ru(II)OH}]^{2+}$ and $\text{MQ}^+$

**Figure S18.** Spectra obtained from global fitting of the transient spectral evolution of the $[\text{Ru(II)OH}]^{2+} / \text{MQ}^+$ (0.01 M) system in CH$_3$CN using an A→B→C model. The resulting species have spectra similar to the excited state of $[\text{Ru(II)OH}]^{2+}$ (Blue), the ET* products (Green) and the ET*/PT products (Red).
3. References


