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pH-Driven Mechanistic Switching from Electron Transfer to Energy Transfer between $[\text{Ru}(\text{bpy})_3]^{2+}$ and Ferrocene Derivatives

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Abstract

The metal-to-ligand charge transfer excited states of $[\text{Ru}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridine) may be deactivated via energy transfer or electron transfer with ferrocene derivatives in aqueous conditions. Stern–Volmer quenching analysis revealed that the rate constant for $[\text{Ru}(\text{bpy})_3]^{2+}$ excited-state quenching depends on solution pH when a ferrocenyl-amidinium derivative (**Fc-am**) containing a proton-responsive functionality tethered to the ferrocene center was present. By contrast, the rate constant with which the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state is quenched by an analogous ferrocene derivative (ferrocenyltrimethylammonium, **Fc-mam**) that lacks a protonic group does not depend on pH. These results show that the presence (or absence) of a readily transferrable proton modulates quenching rate constants in bimolecular events involving $[\text{Ru}(\text{bpy})_3]^{2+}$ and ferrocene. More surprisingly, transient absorption spectroscopy reveals that the *mechanism* by which the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state is quenched by **Fc-am** appears to be modulated by solution proton availability, switching from energy transfer at low pH when **Fc-am** is protonated, to electron transfer at high pH when **Fc-am** is deprotonated. The mechanistic switching that is observed for this system cannot be aptly explained using a simple driving force dependence

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b03933.

Crystallographic data, pH-dependent electronic absorption spectroscopy, electrochemistry, and time-resolved photoluminescence data, as well as Stern–Volmer plots, and details of diffusion rate constant calculation and Stern–Volmer quenching analysis correction (PDF)

Crystal data (CIF)

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argument, suggesting that more subtle factors dictate the pathway by which the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state is deactivated by ferrocene in aqueous solutions.

INTRODUCTION

A substantial body of work has shown that single electron transfer (ET) events in a host of biological, chemical, and physical systems can be influenced by nearby protons.¹ Less well understood, however, is the connection between energy transfer (EnT) and proton motion, particularly with respect to how proton motion can influence the rate of EnT processes.² For both ET and EnT, semiclassical models have been developed to describe the dependences of the proton motion explicitly in the electronic coupling constant, $|V|$.³ However, to the best of our knowledge, the extent to which proton transfer phenomena can cause a switch between ET and EnT mechanisms for a specific donor–acceptor pairing, has not been demonstrated.

Much effort has been focused toward the study of proton-coupled electron transfer (PCET) processes, and the study of photoinduced ET through hydrogen-bonded networks has been integral in developing the field of PCET.^{4,5} For such systems, hydrogen bonds provide a noncovalent pathway that mediates ET and/or proton transfer between disparate sites. In these model systems ET is mediated by hydrogen bonding interactions,^{1,5–10} which include carboxylic acid dimers,^{11,12} guanine-cytosine base pairs^{13–15} and related interfaces,^{16,17} as well as amidinium-carboxylate salt bridges.^{18–23}

Although far less emphasis has been placed on studying the influence of protonation state/proton motion on EnT processes, these two processes may be expected to be kinetically coupled for properly designed systems. The connection between EnT kinetics and proton motion arises from semiclassical ET models. Since the electronic coupling constants for both ET and EnT are related to each other,³ it follows that proton-coupled energy transfer (PCEnT) may be observed when proton motion is possible in certain donor–acceptor systems that undergo EnT. For example, a series of ferrocenyl moieties juxtaposed with two different Ru(II) polypyridyl complexes using a two-point amidinium-carboxylate hydrogen-bonded network have been shown to participate in PCEnT.² In these constructs, EnT was found to proceed from the excited state of the Ru(II) polypyridyl complexes to the ferrocene

(Fc) moieties with rates that were influenced by the intervening protonic interface. A series of kinetic isotope experiments were conducted by replacing the hydrogen atoms in the amidinium–carboxylate interface with deuterium atoms and revealed kinetic isotope effects ranging from 0.84–3.14. These first PCEnT studies were performed in nonpolar, aprotic solvents in order to promote formation of the hydrogen-bonded amidinium-carboxylate assemblies, and to enable EnT through the intervening protonic interface.

In contrast to the $[\text{Ru}(\text{bpy})_3][\text{H}^+]\text{-Fc}$ assemblies that have been previously studied in nonpolar media, one may ask the how these donor–acceptor systems would interact if the model system were altered to probe bimolecular PCEnT in water. Toward this end, the current work explores the MLCT excited-state deactivation of $[\text{Ru}(\text{bpy})_3]^{2+}$ by the two ferrocene derivatives shown in Figure 1 under aqueous conditions. These ferrocene derivatives include ferrocenyl-amidinium (**Fc–am**) and ferrocenyl-trimethylammonium (**Fc–mam**). In studying the ability of both of these ferrocene derivatives to deactivate the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state, we have sought to understand how the possibility of proton motion might impact the mechanism and rate of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited-state quenching.

For the constructs shown in Figure 1, the quenching process between $[\text{Ru}(\text{bpy})_3]^{2+}$ and the ferrocene derivatives is bimolecular, which is unlike that for prior PCEnT studies in which $[\text{Ru}(\text{bpy})_3]^{2+}$ and ferrocene were spanned via amidinium-carboxylate hydrogen bonding interfaces. Installation of hydrogen-bonding residues on both the $[\text{Ru}(\text{bpy})_3]^{2+}$ and ferrocene moieties is not required for the present bimolecular quenching study, which simplifies consideration of proton-motion for the systems of Figure 1.^{2,24} As a result, for the present study, the protonic handle has been installed exclusively on one of the ferrocenyl quenchers (**Fc–am**). Moreover, since the quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state is now bimolecular and is not directly mitigated by the amidinium moiety, if ET or EnT occurs in concert with a proton transfer event, these processes will proceed along orthogonal coordinates, as shown in Figure 1.

The **Fc–am** derivative may exist as the protonated amidinium or the deprotonated amidine, each of which will have different thermodynamic and electrostatic parameters for bimolecular PCET and/or PCEnT with the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state. As we show herein, the quenching mechanism between $[\text{Ru}(\text{bpy})_3]^{2+}$ and **Fc–am** is modulated by the protonation state of the amidinium/amidine functionality, which is ultimately dictated by the pH of the aqueous solutions. That is, for the $[\text{Ru}(\text{bpy})_3]^{2+}/\text{Fc–am}$ pairing, solution pH serves to tune the protonation state of the protonic residue on the ferrocene, providing a handle to switch the excited-state quenching mechanism between PCEnT and PCET. As we demonstrate in the pages that follow, energy transfer occurs at low pH when **Fc–am** is protonated (pH $\approx$ 8.0), while electron transfer dominates under conditions of high pH when **Fc–am** is deprotonated (pH $>$ 8.0). Although thermodynamics might be considered to explain this mechanistic switching, a standard driving force argument, does not adequately explain these observed phenomena. As G_{ET} increases, the rate constant for quenching increases, as would be expected for ET in the normal region. However, carrying out quenching experiments between $[\text{Ru}(\text{bpy})_3]^{2+}/\text{Fc–mam}$ for which the thermodynamics of charge transfer are similar shows quenching via EnT, suggesting that ET driving force is not

the only factor dictating the pathway by which $[\text{Ru}(\text{bpy})_3]^{2+}$ is quenched by ferrocene in aqueous solutions.

RESULTS AND DISCUSSION

Synthesis and Crystal Structures.

The route employed for synthesis of **Fc-am** is shown in Scheme 1. This synthesis began with the conversion of ferrocene to cyanoferrocene, which was accomplished by deprotonation of ferrocene with $t\text{BuLi}$ at 0 °C followed by reaction with phenyl cyanate at -70 °C. The resulting cyanoferrocene product was purified by column chromatography on silica and converted to the amidinium derivative by reaction with chloromethylaluminum amide²⁵ in dry toluene at 90 °C under an atmosphere of N_2 . The **Fc-am** derivative was purified by column chromatography using C2 silica and was characterized by NMR spectroscopy as well as high resolution mass spectrometry. X-ray quality crystals of **Fc-am** were obtained allowing for the molecular structure of this compound to be elucidated as shown in Figure S1 and Table S1 (see the Supporting Information).

Ground-State Characterization of Ferrocenyl-Derivative Quenchers and $[\text{Ru}(\text{bpy})_3]^{2+}$.

Previous work has characterized the electronic and electrochemical properties of **Fc-am** under aqueous conditions.²⁶ In those studies, clear spectral shifts in the electronic absorption spectrum of **Fc-am** were evident upon modulation of the **Fc-am** protonation state, indicating significant electronic coupling between the ferrocene redox site and the protonic handle. The $\text{p}K_a$ of **Fc-am** is 8.8, and the $\text{p}K_a$ of this complex upon oxidation to the corresponding ferrocenium amidinium ($[\text{Fc-am}]^+$) species is 7.26 (both in water). The $\text{Fe}(\text{III}/\text{II})$ potential of **Fc-am** shifts from 522 mV vs Ag/AgCl for the protonated amidinium derivative to 438 mV vs Ag/AgCl for the deprotonated ferrocenyl amidine. Taken together, these results demonstrate clear coupling of electronic and redox properties with protonation state of the amidinium functionality on **Fc-am**. These properties motivate the use of the ferrocene-amidinium compound to explore the pH-dependent bimolecular quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ by **Fc-am**.

A second ferrocenyl-derivative, **Fc-mam**, is employed in these studies as a control compound to ensure that any pH-dependent quenching behavior observed between $[\text{Ru}(\text{bpy})_3]^{2+}$ and **Fc-am** may be attributed to the pH-dependent properties of the **Fc-am** (i.e., protonation state, redox potential, and/or charge of the species) and is not an anomalous feature of the D $\cdots$ A system under interrogation. The key feature in the design of **Fc-mam** is that it retains the ferrocene core with a single functionalization on one of the Cp rings, however in this case, the trimethylammonium functional group, does not possess an acidic/exchangeable proton. Absent the protonic functionality, **Fc-mam** affords an appropriate control system to demonstrate how modulating solution pH influences the ability of ferrocene derivatives to deactivate the excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$. This case was made clear through a series of UV-visible absorption spectroscopy (Figure S4) and voltammetric experiments (Figure S5) in which the solution pH was varied to reveal that the electronic absorption spectra and $\text{Fe}(\text{III}/\text{II})$ potentials (368 mV vs Ag/AgCl) of **Fc-mam** remain constant over the entire pH range employed in these studies (pH = 6–11). These observations

in conjunction with the lack of a protonic residue motivate the use of **Fc-mam** as an appropriate control compound that would be expected to demonstrate pH-independent quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$.

Voltammetric and spectroscopic analyses of $[\text{Ru}(\text{bpy})_3]^{2+}$ were undertaken to yield the excited-state reduction potential, as well as the spectroscopic marker for $[\text{Ru}(\text{bpy})_2(\text{bpy}^{\bullet-})]^+$ under the experimental conditions employed for these studies. DPV scans show the reduction potential of $[\text{Ru}(\text{bpy})_3]^{2+}$ in 100 mM potassium phosphate (pH = 7) to be -0.680 V vs Ag/AgCl (Figure S6). Further, spectroelectrochemical experiments were carried out in MeCN containing 100 mM tetrabutylammonium hexafluorophosphate (TBAPF₆) to yield the spectrum of $[\text{Ru}(\text{bpy})_2(\text{bpy}^{\bullet-})]^+$, which is characterized by a clear peak at 510 nm (Figure S7).²⁷ Accordingly, this peak at 510 nm represents an unambiguous spectroscopic marker indicative of the formation of $[\text{Ru}(\text{bpy})_2(\text{bpy}^{\bullet-})]^+$ which can be used to verify the formation of a charge transfer species upon quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state via ET with the ferrocenyl donors shown in Figure 1.

Bimolecular Proton-Coupled Quenching via Stern–Volmer Analysis.

A series of pH-dependent Stern–Volmer quenching titrations were carried out in buffered aqueous solutions to probe the influence of the **Fc-am** protonation state in quenching the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state. $[\text{Ru}(\text{bpy})_3]^{2+}$ emission is quenched by both **Fc-am** and **Fc-mam** over a range of pH conditions (pH = 6–11). Steady-state fluorescence spectroscopy was used to monitor fluorescence intensity changes as a function of the ferrocene moiety quencher concentration. At each pH that was sampled, either **Fc-am** or **Fc-mam** was titrated into a sample of $[\text{Ru}(\text{bpy})_3]^{2+}$ and the emission spectrum was recorded for each addition. Stern–Volmer quenching analysis correlates the initial fluorescence intensity (I_0) over the intensity of emission (I) after addition of the ferrocenyl quenchers (I_0/I) against the total quencher concentration (either **[Fc-am]** or **[Fc-mam]**). For simple bimolecular quenching mechanisms these analyses yield a linear plot the slope of which is equal to $\tau_0 k_q$. The Stern–Volmer relationship is expressed as

$$\frac{I_0}{I} = 1 + \tau_0 k_q [Q]$$

where τ_0 is the unquenched excited state lifetime of the $[\text{Ru}(\text{bpy})_3]^{2+}$ luminophore at each pH, and k_q is the determined rate constant of quenching.

Figure S8 shows time-resolved photoluminescence decay traces recorded for solutions of $[\text{Ru}(\text{bpy})_3]^{2+}$ in aqueous phosphate buffer at three pH points in the range utilized in these experiments, specifically pH = 6, pH = 8 and pH = 11. The emission lifetime of $[\text{Ru}(\text{bpy})_3]^{2+}$ does not vary as a function of pH ($\tau_0 \sim 409$ ns) indicating that the inherent photophysical properties of this species are not affected by changes to solution pH. The Stern–Volmer analysis was performed for both of the D···A pairings shown in Figure 1: $[\text{Ru}(\text{bpy})_3]^{2+}$ with either **Fc-am** or **Fc-mam** in buffered aqueous solutions of pH = 6–11. A correction was applied to the typical Stern–Volmer analysis (summarized in the Supporting

Information) to account for the fact that the ferrocene moiety absorption spectra overlap slightly with the absorption spectrum of $[\text{Ru}(\text{bpy})_3]^{2+}$.²⁸

Figure S9 shows representative Stern–Volmer plots of the D···A pairs of Figure 1 after correction under low (pH ~ 7.0, which is below the $\text{p}K_a$ of **Fc–am**) and high (pH ~ 11.0, which is above the $\text{p}K_a$ of **Fc–am**) pH conditions. Since the slope of the Stern–Volmer plots informs on the rate constant for quenching, the observed difference in the slopes of the plots in Figure S9 (top) indicates that the rate constant for $[\text{Ru}(\text{bpy})_3]^{2+}$ excited-state deactivation by **Fc–am** is clearly sensitive to solution pH, suggesting that the **Fc–am** may quench the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state via disparate pathways depending on its protonation state. In contrast, when **Fc–mam** serves as the quencher, the slopes of the Stern–Volmer plots remain virtually identical at multiple pH values (Figure S9: bottom tile) *confirming that the rate constant by which Fc–mam quenches the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state is pH-independent.*

Figure 2 shows the average quenching rate constants at each pH point for the two D···A pairings of Figure 1. The distinct pH sensitivity/insensitivity of the **Fc–am** and **Fc–mam** compounds, respectively, as noted in Figure S9 are readily apparent in Figure 2. The quenching rate constant remains constant from pH = 6–11 when **Fc–mam** is used to quench the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state, while a pronounced change in quenching rate constant is observed over the pH range when **Fc–am** is instead utilized. The distinct rise in the value of the rate constant for $[\text{Ru}(\text{bpy})_3]^{2+}$ excited-state quenching by **Fc–am** upon going from pH = 8.0 to pH = 8.5 is coincident with the $\text{p}K_a$ of **Fc–am**, indicating that the protonation state of the ferrocenyl amidinium/amidine group is of critical importance in controlling the kinetics, and possibly the pathway of the quenching process.

Using Transient Absorption Spectroscopy To Identify Mechanistic Details of Quenching.

Transient absorption (TA) spectroscopy was performed to provide insight into the pathway(s) by which the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state is deactivated by **Fc–am** and **Fc–mam**, as a function of pH. The samples were set at either pH = 7.0 or pH = 10.0 and contained 250.0 μM $[\text{Ru}(\text{bpy})_3]^{2+}$, 5.0 mM ferrocenyl moiety, and 100 mM potassium phosphate monobasic. Figure 3 shows TA data for the D···A pairs under the two pH conditions. The spectra show a small tail of the ground state MLCT peak of $[\text{Ru}(\text{bpy})_3]^{2+}$ observed as a bleach to the blue of 500 nm. To the red, a clear growth is seen between 550 and 950 nm indicative of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state. Analysis of the sample containing $[\text{Ru}(\text{bpy})_3]^{2+}$ and the **Fc–am** quencher at pH 10 (Figure 3B) showed an additional, small growth in the TA signal at ~510 nm, consistent with formation of $[\text{Ru}(\text{bpy})_2(\text{bpy}^{\bullet-})]^+$ (vide supra) via ET from the **Fc–am** quencher. The $[\text{Ru}(\text{bpy})_2(\text{bpy}^{\bullet-})]^+$ intermediate grows in after the initial excited state is formed and can be seen in spectra after approximately 300 ns. The growth persists out to the maximum time range (1.5 μs) taken in this experiment. Importantly, the 510 nm peak corresponding to $[\text{Ru}(\text{bpy})_2(\text{bpy}^{\bullet-})]^+$ formation is only observed for the TA experiment shown in Figure 3B, suggesting that quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state by **Fc–am** at pH = 7.0 or by **Fc–mam** at either pH = 7.0 or 10.0 does not involve ET.

To further probe the charge transfer quenching pathway for the $[\text{Ru}(\text{bpy})_3]^{2+}$ + **Fc–am** sample at pH = 10 and the lack of this signal in the other samples, single wavelength kinetics

were collected at 510 nm for $[\text{Ru}(\text{bpy})_3]^{2+}$ at pH = 10, $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH = 7 and $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH = 10. Figure 4 shows the results of these experiments and tracks the temporal evolution of the peak at 510 nm, as seen in the TA spectra of the sample containing $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH = 10 (dashed blue trace). For comparison, the single wavelength traces of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the absence of ferrocenyl quencher at pH = 10 (black trace), and $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH = 7 (red trace) are also reproduced in Figure 4. A monoexponential decay of the single wavelength trace is seen for the $[\text{Ru}(\text{bpy})_3]^{2+}$ in the absence of ferrocenyl quencher at pH = 10 and $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH 7, while a long-lived kinetic trace that extends past the temporal window (1.5 μs) is seen for the sample containing $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH = 10. The extended kinetic trace for the $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH = 10 would be expected if the excited state of the $[\text{Ru}(\text{bpy})_3]^{2+}$ was quenched via electron transfer from **Fc-am** to produce the $[\text{Ru}(\text{bpy})_2(\text{bpy}^{\bullet-})]^+$ (Figure S7). Accordingly, the data in Figure 3 and 4 clearly indicates a different quenching process takes place between deprotonated **Fc-am** and the excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ at pH = 10 as compared to that between protonated **Fc-am** and the excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ at pH = 7. Moreover, we note that no extended-lifetime signal at 510 nm was observed when **Fc-mam** was used as the quencher at either pH = 7 or pH = 10, suggesting that the **Fc-mam** quencher likely does not deactivate the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state via an ET pathway.

Pathway of $[\text{Ru}(\text{bpy})_3]^{2+}$ Excited-State Quenching Modulated by pH.

The data presented above is consistent with pH-induced mechanistic switching between energy and electron transfer for the photoinduced quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state by **Fc-am**. To our knowledge, this marks the first report of mechanistic switching between ET and EnT based on pH changes to an aqueous environment for a specific D $\cdots$ A system. The kinetic data and excited-state spectral evolution derived from TA analysis yield information related to the nature of the quenching process between photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ and the two ferrocenyl-derivatives at either pH = 7 or pH = 10. The principal takeaway from this analysis is the observation that the rate constant for $[\text{Ru}(\text{bpy})_3]^{2+}$ excited-state quenching by the **Fc-am** donor is modulated by the protonation state of the ferrocenyl amidinium/amidine functionality. Moreover, the mechanism by which quenching occurs for the $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ system switches from EnT at lower pHs when the protonic group of **Fc-am** is protonated (amidinium) to ET at higher pHs when the protonic group is deprotonated (amidine). For cases in which the excited-state dynamics between $[\text{Ru}(\text{bpy})_3]^{2+}$ and the **Fc-mam** control compound, which lacks a protonic residue, were probed, the quenching pathway and kinetics were found to be pH-independent.

Ground-State and Excited-State Characteristics of D $\cdots$ A System.

Steady-state absorption spectroscopy and voltammetric measurements were used to characterize $[\text{Ru}(\text{bpy})_3]^{2+}$ and the ferrocenyl derivatives (**Fc-am** and **Fc-mam**) employed in this study.

The ground-state properties of the ferrocenyl quenchers are revealed by steady-state absorption spectroscopy and voltammetry experiments. The redox behavior of **Fc-am** depends intimately on the protonation state of the amidinium/amidine functionality, which may be modulated by the solution pH. DPV experiments show that the **Fc-am** complex

undergoes single e^- oxidation at $E_{\text{Fe(III/II)}} = 522$ mV vs Ag/AgCl when protonated (i.e., at pH < 8.0), and that this potential shifts to $E_{\text{Fe(III/II)}} = 438$ mV vs Ag/AgCl when the amidinium functionality of **Fc-am** is fully deprotonated (i.e., at pH = 10). In contrast, **Fc-mam** shows no variation in its spectral or redox properties ($E_{\text{Fe(III/II)}} = 368$ mV vs Ag/AgCl), as a function of solution pH owing to the lack of a readily abstractable proton for this ferrocenyl derivative.

The excited-state properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ are also of critical importance as the zero-point energy of the $^3\text{MLCT}$ state (E_0), as well as the excited-state reorganization energy, determine the overall driving force for bimolecular ET between photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ and either **Fc-am** or **Fc-mam**. The excited-state properties of $[\text{Ru}(\text{bpy})_3]^{2+}$ have been reported using several different experimental techniques.^{29–31} For example, the value of E_0 can be determined by fitting the $[\text{Ru}(\text{bpy})_3]^{2+}$ emission spectrum as carried out by Caspar and Meyer,^{29,30} or by using thermal lensing or photoacoustic methods as reported by Song and Endicott.³¹ Using the spectral fitting method, the values of E_0 for $[\text{Ru}(\text{bpy})_3]^{2+}$ are shown to vary slightly with solvent, ranging from $E_0 = 2.076$ eV for dichloromethane to $E_0 = 2.002$ eV for *N,N*-dimethylformamide. A modest deviation in the value of E_0 is encountered when the value is determined by the thermal lensing ($E_0 = 2.082$ eV) or photoacoustic ($E_0 = 2.108$ eV) methods in aqueous conditions. For the purposes of this study, which takes place in aqueous solutions, a value of $E_0 = 2.08$ is used to calculate the excited-state reduction potential for $[\text{Ru}(\text{bpy})_3]^{2+}$. The oxidation and excited-state reduction potentials of **Fc-am**, **Fc-mam** and $[\text{Ru}(\text{bpy})_3]^{2+}$, respectively, permit a discussion of the relationship between ET driving force, the kinetics of the bimolecular reaction and the mechanism of quenching (vide infra).

Comparison of Calculated Diffusional Rate Constants and Experimental Bimolecular Quenching Rate Constants.

Owing to the bimolecular quenching process at work for the $\text{D}^{\cdots}\text{A}$ systems shown in Figure 1, collision between the ferrocenyl donor and photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ acceptor moieties are required for excited-state quenching to take place. The ET and proton transfer processes are kinetically limited by the frequency with which the two molecules can come into physical contact with each other. In this sense, the theoretical collision rates of ions in solution form the upper boundary for the quenching rate constant in the $\text{D}^{\cdots}\text{A}$ systems considered in this work.

The rate constant for diffusion of charged particles can be calculated using the Debye–Smoluchowski relation for the frequency of collision of two charged particles, specifically A^{2+} (representing $[\text{Ru}(\text{bpy})_3]^{2+}$) and B^+ (representing protonated **Fc-am**, or **Fc-mam**) through the relation $k_{\text{diff}} = 4\pi N_{\text{A}}(D_{\text{A}^{2+}} + D_{\text{B}^+})\beta$, in which the diffusion constant (k_{diff} is related to Avogadro's number (N_{A}), the diffusion coefficients for the participating molecules (D_{A} and D_{B}), and the effective reaction radius (β). The details of this calculation are described in the Supporting Information. The diffusional rate constants between $[\text{Ru}(\text{bpy})_3]^{2+}$ + **Fc-am** and between $[\text{Ru}(\text{bpy})_3]^{2+}$ + **Fc-mam** were found to be $32.3(3.4) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $30.9(3.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, respectively Table 1).

The bimolecular quenching rate constants for $[\text{Ru}(\text{bpy})_3]^{2+}$ and either **Fc-am** or **Fc-mam** approach the typical diffusion limit of $k_{\text{diff}} = \sim 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{Ru}(\text{bpy})_3]^{2+}$ and a quencher in an unbuffered aqueous or organic solution.^{32,33} However, in these experiments, use of a 100 mM potassium phosphate buffer leads to higher diffusional rate constants (see Supporting Information). Analysis of the experimental results presented above yield EnT rates of $k_{\text{EnT}} = 1.26 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{Ru}(\text{bpy})_3]^{2+}$ and protonated **Fc-am** and $k_{\text{EnT}} = 2.44 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for $[\text{Ru}(\text{bpy})_3]^{2+}$ and **Fc-mam**. As such, the experimental *EnT rates* are more than an order of magnitude smaller than the *diffusional rates* predicted by the Debye–Smoluchowski relation for two charged species of 2+ and 1+ approaching each other under the conditions employed for these studies. Furthermore, variation of approximated input parameters by 10% to the Debye–Smoluchowski calculation do not yield diffusion rates that approach the experimentally determined quenching rates, resulting in an error range of only $\pm 0.34 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The predicted diffusion rates of $[\text{Ru}(\text{bpy})_3]^{2+}$ with the deprotonated amidine form of **Fc-am**, which is a neutral species (i.e., charge of 0), would be expected to fall between the predicted rate constants of diffusion from the Debye–Smoluchowski equation ($\sim 31.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and the diffusion controlled limit of two neutral species ($2.4 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$). However, the experimentally observed ET rate constant of $k_{\text{ET}} = 1.68(20) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ observed for $[\text{Ru}(\text{bpy})_3]^{2+}$ and the deprotonated **Fc-am** is well below the predicted diffusion-controlled limits. By accounting for the interactions of charged particles, the diffusion constant provides a good approximation of the frequency of $[\text{Ru}(\text{bpy})_3]^{2+}$ and **Fc-am** (or **Fc-mam**) collisions. The measured quenching rates are significantly slower than the predicted collision frequencies, suggesting that chemical interaction(s) beyond simple collisional contact must occur for excited-state ET and EnT to take place for the D $\cdots$ A systems of Figure 1.

Thermodynamic and Kinetic Comparison of Quenching Rates.

Single ET involves transfer of an electron between D $\cdots$ A pairs driven by thermodynamic factors including the redox potentials and excited-state energies of the involved species. As such there should be a relationship between the thermodynamic driving force for ET and kinetics of the observed quenching in these D $\cdots$ A pairs. The driving force for photoinduced ET ($-G_{\text{ET}}$) under acidic and basic conditions is related to the energy difference between the excited-state reduction potential of $[\text{Ru}(\text{bpy})_3]^{2+}$, $E_{\text{Ru}(\text{II}^*/\text{I})}$, and the Fe(III/II) potentials of **Fc-am** and **Fc-mam** via the relation $-G_{\text{ET}} = E_{\text{Ru}(\text{II}^*/\text{I})} - E_{\text{Fe}(\text{III}/\text{II})}$. Relevant thermodynamic properties leading to the calculation of $-G_{\text{ET}}$ are presented in Table 2.

The driving force calculations verify that ET from both ferrocenyl derivatives to photoexcited $[\text{Ru}(\text{bpy})_3]^{2+}$ is indeed thermodynamically feasible; however, products of ET are only seen via TA measurements for *one* of the systems probed in this study, namely $[\text{Ru}(\text{bpy})_3]^{2+}$ and **Fc-am** when it exists as the amidine (pH = 10). Figure 5 plots the rate constant of quenching versus the driving force for ET and reveals that as the driving force for ET increases along the series ($[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am (protonated)} < ([\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am deprotonated}) < ([\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-mam})$), the observed quenching rate also increases. Interestingly, the systems that do not show evidence for excited-state $[\text{Ru}(\text{bpy})_3]^{2+}$ quenching via ET, (i.e., protonated **Fc-am** (pH = 7.0) and **Fc-mam** (pH = 6.5–11.0), possess the lowest and highest driving force for ET, respectively. Indeed, based on the

transient absorption measurements described above, it is only the ferrocene derivative that has an intermediate driving force for ET (i.e., deprotonated **Fc-am**) that shows evidence for quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state via a charge transfer mechanism. These results suggest that there are factors at play that determine the pathway by which ferrocene derivatives can deactivate the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state other than simple thermodynamic driving force.

Unexpected Change in Mode of Quenching (ET or EnT).

The mechanistic switching between ET and EnT in the $[\text{Ru}(\text{bpy})_3]^{2+}\cdots\text{Fc}$ systems considered in this work is unexpected and has hitherto not been reported in the literature. The collection of the three D $\cdots$ A pairs studied herein present an interesting suite of systems that reveals continued work is needed to fully understand all the parameters that govern charge transfer phenomena. As demonstrated (vide supra), a simple ET driving force argument does not fully explain the results obtained for the three $[\text{Ru}(\text{bpy})_3]^{2+}\cdots\text{Fc}$ systems probed in these studies. Further, this observation represents a process different than a traditional proton-coupled ET (PCET) event in which the *rate* of ET is modulated by the ability of the system to transfer a proton in concert with the electron. For a prototypical PCET model system, the rate of charge-transfer would be modulated by protonation state, but the mechanism would remain the same. By protonating the amidinium functionality, in addition to slowing down the rate of the reaction (as would be expected for a PCET mechanism), the pathway for the quenching process shifts to energy transfer. The absence of a charge transfer signal for the TA experiments conducted for $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-mam}$ and $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH 7 strongly indicated that ET does not serve to quench the excited state in these D $\cdots$ A systems. Because the systems studied herein involve bimolecular quenching, one would expect ET products formed between each of the D $\cdots$ A systems to rapidly cage escape, and have lifetimes long enough for detection by TA, since in all cases the products of charge transfer would be positively charged. The fact, therefore, that TA signatures corresponding to ET products for $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-mam}$ and $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH 7 are not observed, strongly indicates the quenching occurs via an EnT pathway.

The realization that ET is only seen for $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH 10 may be due to electrostatic factors. For both D $\cdots$ A systems in which the ferrocene moiety has a net positive charge (protonated **Fc-am** and **Fc-mam**), EnT dominates as the quenching mechanism. The deprotonated **Fc-am** is neutral in charge prior to the charge transfer and bears a 1+ charge as the result of the ET event. While the electrostatic contribution may not be the only reason for the mechanistic switch, it is a discernible trend in the systems that can be identified from this study. More broadly, these results suggest that there is still work to be done in considering the factors that govern ET in molecular systems.

CONCLUSIONS

In this work, we have explored the manner by which the metal-to-ligand charge transfer excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$ is quenched by ferrocene derivatives under aqueous conditions. Stern–Volmer quenching experiments reveal that the rate of quenching is sensitive to

solution pH, depending on the identity of the ferrocene quencher used in a given experiment. In particular, when a ferrocene amidinium derivative (**Fc-am**), which contains a proton-responsive functionality appended to the ferrocene center is used as the quencher, the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state is deactivated more quickly at higher pH (i.e., when the ferrocene exists as the deprotonated amidine, as opposed to the protonated amidinium). By contrast, when a ferrocene derivative (ferrocenyl-trimethylammonium, **Fc-mam**), which does not contain an acid/base sensitive function group is used to quench the excited state of $[\text{Ru}(\text{bpy})_3]^{2+}$, the quenching rate constant was found to be pH-independent.

The principal results of this study provide further evidence that the presence of a readily transferrable protons can modulate the rates observed for bimolecular excited-state quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$. This finding is coupled with the unexpected observation that the mechanism by which $[\text{Ru}(\text{bpy})_3]^{2+}$ is deactivated appears to proceed via distinct pathways depending on the ferrocene quencher used and its protonation state. Transient absorption spectroscopy only shows evidence for charge transfer products being formed upon quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited by deprotonated **Fc-am** (i.e., at $\text{pH} > 7$), which is consistent with an ET quenching mechanism. Similar experiments performed for $[\text{Ru}(\text{bpy})_3]^{2+}$ and protonated **Fc-am** (i.e., at $\text{pH} < 7$) or for $[\text{Ru}(\text{bpy})_3]^{2+}$ and **Fc-mam** at any pH do not show evidence for charge transfer products suggesting that EnT is the dominant quenching pathway for these D $\cdots$ A systems.

The results highlighted above are, to the best of our knowledge, the first demonstration of a pH-induced mechanistic switch between EnT and ET for a bimolecular D $\cdots$ A construct, and complement important work on inorganic and organic-based systems indicating EnT, as well as ET, may be coupled to proton transfer.^{34–37} The mechanistic switching (between ET and EnT that is observed for $[\text{Ru}(\text{bpy})_3]^{2+}\cdots\text{Fc-am}$ at high versus low solution pH cannot be aptly explained by driving force dependence analyses, suggesting that subtle factors ultimately dictate the pathway(s) by which the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state may be deactivated by ferrocene derivatives in aqueous solutions. Moreover, comparison of the calculated diffusion rate constants and the experimental quenching rate constants determined herein, reveal that the pH-dependence observed in this study is intimately tied to the interaction between $[\text{Ru}(\text{bpy})_3]^{2+}$ and the ferrocenyl moieties, as it is not diffusion-limited. Further, comparison of the photoinduced ET thermodynamics (G_{ET}) and the observed kinetics reveal a trend consistent with the normal region of Marcus theory; as the driving force for ET increases, so too does the rate constant for the quenching process. However, the mechanistic switching between EnT and ET does not correlate purely to the driving force dependence. As such, it is possible that electrostatic factors may help to drive the mechanistic switch between EnT and ET for the $[\text{Ru}(\text{bpy})_3]^{2+}\cdots$ ferrocene systems probed in this work. Future work from our laboratories will be aimed at unravelling the factors that dictate the pathway(s) by which charge and energy transfer take place for model D $\cdots$ A systems and taking advantage of such gains to direct energy conversion schemes that demonstrate high degrees of plasticity.³⁸

EXPERIMENTAL PROCEDURES

General Methods.

Reactions were performed in oven-dried round-bottomed flasks unless otherwise noted. Reactions that required an inert atmosphere were conducted under a positive pressure of N₂ using flasks fitted with Suba-Seal rubber septa. Air and moisture sensitive reagents were transferred using standard syringe or cannula techniques. Column chromatography was performed with 40–63 μ m silica gel with the eluent reported. Analytical thin-layer chromatography (TLC) was performed on precoated glass plates and visualized by UV or by staining with KMnO₄. Tris(2,2-bipyridyl)-dichlororuthenium(II) hexahydrate, (Ferrocenylmethyl)-trimethylammonium iodide, and potassium phosphate monobasic were purchased from Sigma-Aldrich and used without further purification. Other reagents and solvents were purchased from Sigma-Aldrich, Acros, Fisher, Strem, or Cambridge Isotopes Laboratories. Solvents for synthesis were of reagent grade or better and were dried by passage through activated alumina and then stored over 4 Å molecular sieves prior to use.³⁹ Phenyl cyanate was prepared using published methods.⁴⁰ Nanopure water (EASYPure UF compact bioresearch water system, 18 MOhm resistance) was used to prepare all solutions for UV–visible spectroscopy, electrochemical measurements, and transient absorption spectroscopy.

Physical Measurements.

¹H NMR and ¹³C NMR spectra were recorded at 25 °C on a Bruker AV400 (400 MHz) or an AV600 (600 MHz) spectrometer. Proton spectra are referenced to the residual proton resonance of the deuterated solvent and carbon spectra are referenced to the carbon resonances of the solvent. All chemical shifts are reported using the standard δ notation in parts-per-million; positive chemical shifts are to higher frequency from the given reference. LR-ESI MS data was obtained using a LCQ Advantage from ThermoFinnigan. High-resolution mass spectrometry analyses were performed within the Mass Spectrometry Laboratory within the Department of Chemistry and Biochemistry at University of Delaware. Absorption spectra were recorded with a PerkinElmer UV–vis–NIR Lambda 9 (with Lambda 19 upgrade) spectrometer. Electrochemistry was performed with a CH Instruments Electrochemical workstation model CHI760D. Transient absorption spectroscopy was performed using a Coherent Libra amplified laser system with a Light Conversion TOPAS-C optical parametric amplifier as an excitation source. An Ultrafastsystems Helio/EOS transient absorption spectrometer experimental setup was used for transient absorption measurements. Time-resolved photoluminescence life-times were collected using a time-correlated single photon counting (TCSPC) system at the MIT Nanostructured Materials Metrology Laboratory within the MIT Center for Materials Science and Engineering on equipment provided by the Eni-MIT Solar Frontiers Center.

X-ray Crystallography.

X-ray structural analyses for **Fc-am**, **Fc-mam** and [**Fc-mam**]⁺ were accomplished as follows. Crystals were mounted onto plastic mesh using viscous oil and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II Duo CCD diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) for **Fc-**

mam, and **Fc-am**; and with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) focused with Goebel mirrors for **[Fc-mam]⁺**. Unit cell parameters were obtained from 60 data frames, $0.3^\circ \omega$, from three different sections of the Ewald sphere. The systematic absences in the diffraction data are consistent with *Pbcm* and *Pca2₁* (*Pbc2₁*) for **Fc-mam**; with *Pna2₁* and *Pnma* (*Pnam*) for **[Fc-mam]⁺**; and, uniquely, with *P2₁2₁2₁* for **Fc-am**. Solution in the centrosymmetric space group option, *Pbcm*, for **Fc-mam** yielded chemically reasonable and computationally stable results of refinement but only the noncentrosymmetric space group option, *Pna2₁* yielded chemically reasonable and computationally stable results of refinement for **[Fc-mam]⁺**. The absolute structure parameter refined to nil for **Fc-am** and **[Fc-mam]⁺** indicating that the true hand of each data set has been determined.⁴¹ The data sets were treated with absorption corrections based on redundant multiscan data. The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F^2 . The ion pair is located at a mirror plane with cyclopentadienyl rings treated as idealized, rigid, pentagons in **Fc-mam**. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Atomic scattering factors are contained in the SHELXTL program library.⁴²

The CIF files for **Fc-mam**, **[Fc-mam]⁺** and **Fc-am** have been deposited with the Cambridge Crystallographic Database Centre under depositary number CCDC 1531329, 1823000 and 1531328, respectively. Labeled thermal ellipsoid plots for **Fc-am**, **Fc-mam** and **[Fc-mam]⁺** are reproduced in Figures S1–S3 and crystallographic parameters for each structure are shown in Table S1.

Synthetic Protocols.

C2 Functionalized Silica.—Silica gel (100 g) was suspended in chloroform (200 mL) in a four-neck round-bottomed flask equipped with an overhead mechanical stirrer. The silica slurry was chilled in an ice bath, while nitrogen was gently flowing through the headspace. Ethyltrichlorosilane (4.12 mL, 31 mmol) was added dropwise to the slurry, after which time, the suspension was left stirring overnight at room temperature. The yellow suspension was filtered through sintered glass, and the collected solid was washed with chloroform and methanol until the solid was white. The C2 silica was transferred to a round-bottomed flask and was dried by heating under vacuum.

Cyanoferrocene (Fc-CN).—This compound was synthesized by amending previously published procedures.^{2,43,44} Ferrocene (3.00 g, 16 mmol) was placed in a 250 mL Schlenk flask, which was evacuated and backfilled with N₂ three times. Dry THF (100 mL) was added to the flask, which was subsequently backfilled with nitrogen. The resulting red solution was cooled in an ice bath while ^tBuLi (1.6 M, 8.4 mL, 14 mmol) was added in dropwise fashion. This solution was further cooled in a dry ice/acetone bath and phenyl cyanate (2.88 mL, 27 mmol) was added in dropwise fashion. The red solution was stirred in the dry ice/acetone bath for 1 h and then allowed to slowly warm to room temperature over the course of several hours. Once at room temperature, the reaction was quenched with 6 M NaOH. The crude product was extracted into diethyl ether and this organic extract was washed sequentially with brine and water. The organic layer was then dried over Na₂SO₄ and concentrated in vacuo. Chromatography of the crude product on silica using hexanes

and dichloromethane (3:1) as the eluent yielded the title compound as a red microcrystalline powder (0.591 g, 20% yield). ^1H NMR (400 MHz, CDCl_3 , 25 °C), δ /ppm: 4.66 (t, J = 1.6 Hz, 2H), 4.39 (t, J = 1.6 Hz, 2H), 4.34 (s, 5H). ^{13}C NMR (101 MHz, DMSO, 25 °C), δ /ppm: 120.34, 71.85, 70.83, 70.71. HR-LIFDI-MS $[\text{M}]^+$, m/z calc for $\text{C}_{11}\text{H}_9\text{FeN}$, 211.0084; found, 211.0093.

Amidiniumferrocene Chloride (Fc-am).—Cyanoferrocene (200 mg, 0.943 mmol) was added to a 100 mL Schlenk flask, which was evacuated and backfilled with N_2 three times. Dry toluene (25 mL) was added to the flask, which was then backfilled with nitrogen. The resulting orange solution was heated to 90 °C and chloromethylaluminum amide⁴⁵ (14.5 mL, 0.77 M in toluene) was added via syringe. The orange solution was stirred at 90 °C for 53 h and after cooling to room temperature, was poured onto a slurry of silica and chloroform. The resulting mixture was stirred under air for 10 min and filtered through a sintered glass. The filtercake was rinsed with 25% methanol in acetonitrile until the eluent was colorless. The resulting orange filtrate was concentrated in vacuo. Purification was accomplished by column chromatography on C2 silica using 3% MeOH in CH_2Cl_2 as the eluent, which delivered 185 mg of the title compound as a red microcrystalline powder (Yield = 75%). ^1H NMR (400 MHz, DMSO, 25 °C) 8.75 (d, J = 56 Hz, 4H), 5.20 (s, 2H), 4.67 (s, 2H), 5.29 (s, 5H). ^{13}C NMR (101 MHz, DMSO, 25 °C), δ /ppm: 168.31, 72.58, 70.58, 68.78, 68.53. HR-LIFDI-MS $[\text{2M}-\text{Cl}-2\text{H}]^{2+}$ m/z Calc for $\text{C}_{22}\text{H}_{24}\text{Fe}_2\text{N}_4$: 229.0428; found, 229.0430.

(Ferrocenylmethyl)trimethylammonium Hexafluorophosphate (Fc-mam).—(Ferrocenylmethyl)trimethylammonium iodide (0.245 g, 0.636 mmol), thallium hexafluorophosphate (0.222g, 0.636 mmol), and acetonitrile (70 mL) were added to a round-bottom flask and magnetically stirred for 1 h. The precipitate that formed (assumed to be ThI) was removed via filtration through Celite. The solvent was removed from the solution under reduced pressure and the resulting yellow solid was collected and dried overnight to yield 255 mg of the title compound as a yellow solid (Yield = 93%). ^1H NMR (400 MHz, CD_3CN , 25 °C) δ 4.44 (t, J = 1.8 Hz, 2H), 4.39 (t, J = 1.8 Hz, 2H), 4.28 (s, 2H), 4.24 (s, 4H), 2.88 (s, 9H). ^{13}C NMR (101 MHz, CD_3CN , 25 °C) δ 73.31, 73.00, 71.40, 70.08, 67.76, 52.81. HR-LIFDI-MS $[\text{M}]^+$, m/z calc for $\text{C}_{14}\text{H}_{20}\text{FeN}$, 258.0945; found, 258.0938. Samples of **Fc-mam** could be oxidized with benzoquinone in the presence of $\text{HBF}_4\cdot\text{OEt}_2$ to generate the corresponding ferrocenium compound ($[\text{Fc-mam}]^+$). X-ray quality crystals of $[\text{Fc-mam}]^+$ were grown via slow evaporation of concentrated MeCN solutions.

Spectroscopy and Electrochemistry.

UV-Visible Absorption Spectroscopy.—The spectral properties of **Fc-am** have been shown to depend upon the pH of aqueous solutions and have been reported elsewhere.²⁶ In this report, pH-dependent absorption spectroscopy was performed on **Fc-mam** to ensure that its spectral properties did not vary with changing acidity or basicity of the aqueous solution. UV-visible absorption spectra were recorded at room temperature in a 1 cm path length clear-fused quartz cuvette (7Q, Starna cells). A 4 mL sample of 1.16 μM **Fc-mam** was prepared in 100 mM potassium phosphate at pH 5.5 (stock 1) using nanopure water. Two milliliters of stock 1 was used to prepare a 2 mL solution of 1.16 μM **Fc-mam** in 1.0 M

NaOH and 100 mM potassium phosphate (stock 2). Following the recording of an initial spectrum of stock 1, the stock 2 solution was added in 10–25 μL aliquots to adjust the pH of stock 1 while ensuring that the concentration of **Fc–mam** in the sample remained constant throughout the course of the experiment. An absorption spectrum of stock 1 was taken after each addition of stock 2 and the pH at each point was recorded. A pH range of pH 5.5 to pH 11 was sampled in these titrations.

Electrochemistry.—Differential pulse voltammetry (DPV) on **Fc–mam** was performed using a standard three-electrode configuration with a platinum working electrode (2 mm diameter), a Ag/AgCl reference electrode (BASi MF-2079, 3 M KCl) and a platinum mesh counter electrode. DPV scans were run from 200 to 600 mV (vs Ag/AgCl) and were sampled at 20–100 mV/s scan rates and sensitivities of 100 $\mu\text{A/V}$ to 1 mA/V. pH-Dependent electrochemistry of **Fc–mam** was performed using solutions of 100 mM potassium phosphate as the supporting electrolyte in nanopure water. Sample concentrations employed for electrochemistry were approximately 2 mg/mL **Fc–mam**. An initial sample of **Fc–mam** at pH $\sim$ 5 was prepared and a DPV measurement was recorded. The pH of the sample was adjusted by addition of a 1.0 M NaOH in 100 mM potassium phosphate solution. The pH was measured and a DPV scan recorded. The concentration of **Fc–mam** was allowed to vary slightly throughout this pH titration because for the purposes of these measurements only the peak position, reporting the Fe(III/II) potential of **Fc–mam**, is of interest and not the overall current or charge passed. Potentials are reported relative to the Ag/AgCl reference electrode (BASi MF-2052 RE-5B) where Ag/AgCl in 3 M KCl is 0.210 vs NHE.⁴⁶ DPV experiments conducted for $[\text{Ru}(\text{bpy})_3]^{2+}$ were performed using a standard three-electrode configuration with a glassy carbon working electrode (2 mm diameter), a Ag/AgCl reference electrode (BASi MF-2079) and a platinum wire counter electrode. DPV scans were run from –100 to –900 mV (vs Ag/AgCl) and were sampled at 20–100 mV/s scan rates and sensitivities of 100 $\mu\text{A/V}$ to 1 mA/V. $[\text{Ru}(\text{bpy})_3]^{2+}$ solutions contained 100 mM potassium phosphate as the supporting electrolyte in nanopure water. Spectroelectrochemistry was performed on $[\text{Ru}(\text{bpy})_3]^{2+}$ to determine the spectroscopic marker for the $[\text{Ru}(\text{bpy})_3]^{2+}$ radical anion. Spectroelectrochemistry was conducted under inert conditions in a glovebox. A small amount of $[\text{Ru}(\text{bpy})_3]^+$ was dissolved in 5 mL of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile. A platinum mesh working electrode, platinum counter electrode, and silver wire quasi-reference electrode were used to construct an electrochemical cell in a 2 mm glass cuvette. Potentials from –0.80 to –1.30 V vs the Ag quasi reference were run across the sample in –100 mV increments for 5 min each.

Diffusional coefficients for $[\text{Ru}(\text{bpy})_3]^{2+}$, **Fc–am** and **Fc–mam** were experimentally determined via variable scan rate (ν = 20, 40, 60, 80, 100 mV/s) cyclic voltammetry experiments coupled with Randles–Sevcik analysis.⁴⁷ These experiments were conducted for 5.0 mM solutions of each of the above three complexes in nanopore water (pH = 7.0) containing 100 mM potassium phosphate as the supporting electrolyte. CV experiments employed a glassy carbon disk working electrode (A = 0.07 cm²) coupled with a large piece of platinum mesh as the auxiliary. Potentials were measured with respect to a Ag/AgCl (3 M KCl) reference electrode.

Ambient Temperature Steady-State Fluorescence Spectroscopy and Stern–Volmer Quenching Experiments.—Spectra were recorded using an ISS ChronosBH fluorimeter with steady-state upgrade. Samples were excited at $\lambda = 458$ nm and emission was monitored from 500 to 800 nm with a step size of 2 nm and an integration time of 1 s.

A 10 μM stock solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ was prepared in 100 mM potassium phosphate. The desired pH of each stock solution was set using a solution of 10 μM $[\text{Ru}(\text{bpy})_3]^{2+}$, 1.0 M sodium hydroxide and 100 mM potassium phosphate immediately prior to each titration. A second stock solution was prepared by dissolving an aliquot containing 1×10^{-6} moles of the ferrocenyl moiety (**Fc–am** and **Fc–mam**) in 2.0 mL of the $[\text{Ru}(\text{bpy})_3]^{2+}$ stock solution at the desired pH. To carry out the Stern–Volmer quenching experiments, two milliliters of the $[\text{Ru}(\text{bpy})_3]^{2+}$ stock solution at the desired pH was added to a 1 cm squared clear fused-quartz cuvette (7Q, Starna cells) and an initial emission spectrum was recorded. To the cuvette, the second stock solution (containing the ferrocenyl moiety and $[\text{Ru}(\text{bpy})_3]^{2+}$) was added in 20 μL increments and the fluorescence spectrum was recorded after each addition. Since both stock solutions were 10.0 μM $[\text{Ru}(\text{bpy})_3]^{2+}$, this procedure ensured that the concentration of $[\text{Ru}(\text{bpy})_3]^{2+}$ remained constant throughout the entire experiment thus simplifying the Stern–Volmer analysis. The intensity at the fluorescence peak of $[\text{Ru}(\text{bpy})_3]^{2+}$ decreased with each addition of the second stock solution (containing the ferrocenyl moiety and $[\text{Ru}(\text{bpy})_3]^{2+}$) indicating efficient quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. Titrations were performed until a total of 264 μM **Fc–am** or 290 μM **Fc–mam** were added. The data was analyzed using the Stern–Volmer equation.

Time-Resolved Photoluminescence (TCSPC).—Time-correlated single photon counting (TCSPC) was used to collect the photoluminescence time decay traces. The samples were excited using ~ 30 ps pulses with a repetition rate of 250 kHz at a wavelength of 400 nm. The collimated beam from the laser is directed into the back of an inverted optical microscope and reflected into the objective lens by a long-pass dichroic mirror with a cutoff wavelength of $\lambda = 415$ nm. A 20 $\times$ objective lens focuses the laser beam onto the sample through a glass cover slide. The fluorescence from the sample is collected by the same objective and the resulting collimated beam passes through the dichroic mirror and then through a long-pass filter with a cutoff at $\lambda = 416$ nm to remove any residual scattered or reflected excitation light. The fluorescence beam is then focused by an achromatic lens to a single photon detecting avalanche photodiode (APD). The output of the APD is connected to a timing module with a resolution of 4 ps that detects the arrival time of each photon. This produces a histogram of photon arrival times which corresponds to the time-dependent rate of photon emission from the sample.

The emission lifetime of $[\text{Ru}(\text{bpy})_3]^{2+}$ was recorded at three pH conditions spanning the pH range of interest to ensure the excited state lifetime does not change with pH by utilizing samples of 10 μM $[\text{Ru}(\text{bpy})_3]^{2+}$ at pH 6, 8, and 11 in 100 mM potassium phosphate. The data were fit to a single exponential function that revealed lifetime of 409 ns for $[\text{Ru}(\text{bpy})_3]^{2+}$ that was independent of pH.

Transient Absorption Spectroscopy.—A 250 μM stock solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ in 100 mM potassium phosphate monobasic was prepared and a pH of either 7 or 10 was set

using a basic stock solution of $[\text{Ru}(\text{bpy})_3]^{2+}$ (at 250 μM $[\text{Ru}(\text{bpy})_3]^{2+}$, 1.0 M sodium hydroxide and 100 mM potassium phosphate monobasic). Sample preparation involved adding 1 mL of the $[\text{Ru}(\text{bpy})_3]^{2+}$ solution at the desired pH to 5×10^{-6} moles of the desired ferrocene sample. This solution was added to a 2 mm high-vac cuvette and sparged with nitrogen for 45 min. The cuvette was then sealed using a Kontes value to ensure that the solutions remained under nitrogen throughout the experiment. The samples were excited with a power of about 1 mW at 305 nm and observed over a 2- μs time scale. Excitation pulses were delivered from an optical parametric amplifier (TOPAS-C, Coherent) that was pumped by 96% of a Coherent Libra Ti:sapphire laser system. The pulses were approximately 100 fs in duration. A continuum laser (NKT) was used to generate a probe with a spectral range of about 450–850 nm. A UV-vis spectrum was taken, using the PerkinElmer UV-vis-NIR Lambda 9 spectrometer over the 200–700 nm wavelength range with a 240 nm/min step rate, prior to running TA spectroscopy and directly after in order to monitor degradation. Monitoring the degradation revealed that a five-minute TA experiment did not cause sample degradation and still produced data with reasonable signal-to-noise.

Supplementary Material

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Figure 1. Potential bimolecular, bidirectional quenching pathways between $[\text{Ru}(\text{bpy})_3]^{2+}$ by either (a) a ferrocenyl-amidinium complex (**Fc-am**) or (b) a ferrocenyl-trimethylammonium complex (**Fc-mam**).

Figure 2.

Variation in the quenching rates of the $[\text{Ru}(\text{bpy})_3]^{2+}$ excited state by either **Fc-am** or **Fc-mam** as a function of pH, as obtained by Stern–Volmer quenching analysis. All experiments were carried out for 10 μM solutions of $[\text{Ru}(\text{bpy})_3]^{2+}$ in 100 mM potassium phosphate at the indicated pH, and a range of 0–264 μM **Fc-am** or 0–290 μM **Fc-mam**. Error bars represent one standard deviation from the mean.

Figure 3.

Representative TA spectra of (A) [Ru(bpy)₃]²⁺ + **Fc-am** at pH = 7.0, (B) [Ru(bpy)₃]²⁺ + **Fc-am** at pH = 10.0, (C) [Ru(bpy)₃]²⁺ + **Fc-mam** at pH = 7.0, and (D) [Ru(bpy)₃]²⁺ + **Fc-mam** at pH = 7.0. Each sample contained 250 μM [Ru(bpy)₃]²⁺ and 5.0 mM of the ferrocenyl quencher in 100 mM potassium phosphate buffered Millipore water. The pH of each sample was adjusted using 1.0 M NaOH in 100 mM potassium phosphate solution. All experiments were carried out using an excitation wavelength of 305 nm at approximately 1 mW.

Figure 4.

Single-wavelength kinetic traces recorded at 510 nm for $[\text{Ru}(\text{bpy})_3]^{2+}$ at pH = 7.0 (black, solid line), $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH = 7.0 (red, solid line), and $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ at pH = 10.0 (blue, dotted line). Each sample contains an aqueous solution of 250 μM $[\text{Ru}(\text{bpy})_3]^{2+}$, 5.0 mM of the appropriate ferrocenyl derivative, and 100 mM potassium phosphate monobasic. All experiments were carried out using an excitation wavelength of 305 nm at approximately 1 mW.

Figure 5.

Kinetic and thermodynamic trends for the quenching reactions of $[Ru(bpy)_3]^{2+}$ with the three ferrocene derivatives studied in this work. The graph depicts the rate constant at which the $[Ru(bpy)_3]^{2+}$ excited state is quenched (k_q) versus the driving force for photoinduced electron transfer (ΔG_{ET}) and reveals that as the ET driving force increases, so does the rate constant at which the excited state of $[Ru(bpy)_3]^{2+}$ is deactivated.

Scheme 1.
Synthesis of Fc-am from Ferrocene

Table 1.

Comparison of Theoretical and Observed Quenching Rates between $[\text{Ru}(\text{bpy})_3]^{2+}$ and Either Fc-am or Fc-mam^a

fluorophore	quencher	$k_q \times 10^9 \text{ (M}^{-1} \text{ s}^{-1})^b$	$k_{\text{diff}} \times 10^9 \text{ (M}^{-1} \text{ s}^{-1})^c$
$[\text{Ru}(\text{bpy})_3]^{2+}$	Fc-am	1.26(18)	32.3(3.4)
$[\text{Ru}(\text{bpy})_3]^{2+}$	Fc-mam	2.44(36)	30.9(3.3)

^aThe k_q value for the $[\text{Ru}(\text{bpy})_3]^{2+} + \text{Fc-am}$ quenching reaction represents an average of the experimental results obtained for $\text{pH} < 8.5$ so as to facilitate accurate comparison with the value of k_{diff} for the same reaction in which the **Fc-am** moiety is taken to have a 1+ charge.

^bError represents the standard deviation of the population of experimental values.

^cAverage error determined by varying the approximated input parameters in the Debye-Smoluchowski equation by 10%.

Table 2.

Electrochemical and Thermodynamic Driving Force for D...A Systems^a

	Fc-am		Fc-mam	
	pH 5.5	pH 11	pH 5.5	pH 11
$E_{\text{Fe(III/II)}}^b$ (V)	0.522 (0.732)	0.438 (0.648)	0.368 (0.578)	0.368 (0.578)
G_{ET}^c (eV)	-0.878	-0.962	-1.032	-1.032

^aThe reduction potential of the $[\text{Ru}(\text{bpy})_3]^{2+}$ is -0.680 V vs Ag/AgCl (-0.470 vs NHE) and the excited-state reduction potential is 1.61 V. All electrochemical measurements were carried out in solutions of 100 mM potassium phosphate supporting electrolyte in nanopure water.

^b vs Ag/AgCl (vs NHE), where Ag/AgCl in 3 M KCl is 0.210 vs NHE.⁴⁶

^c $G_{\text{ET}} = E_{\text{Ru(II*/I)}} - E_{\text{Fe(III/II)}}$ and $E_{\text{Ru(II*/I)}} = G_{\text{es}} + E_{\text{Ru(II/I)}}$ vs NHE, where $G_{\text{es}}([\text{Ru}(\text{bpy})_3]^{2+}) = 2.08$ eV