Energy transfer mediated by asymmetric hydrogen-bonded interfaces

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Energy transfer mediated by asymmetric hydrogen-bonded interfaces†

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Abstract

Amidine-appended ferrocene derivatives form a supramolecular assembly with Ru(II)(bpy-COOH)(L)22+ complexes (bpy-COOH is 4-CO2H-4′-CH3-bpy and L = bpy, 2,2′-bipyridine or btfmbpy, 4,4′-bis(trifluoromethyl)-2,2′-bipyridine). Steady-state, time-resolved spectroscopy and kinetic isotope effects establish that the metal-to-ligand charge transfer excited states of the Ru(II) complexes are quenched by proton-coupled energy transfer (PCEnT). These results show that proton motion can be effective in mediating not only electron transfer (ET) but energy transfer (EnT) as well.

Introduction

The influence of proton motion on electron transfer (ET) may be revealed by photoinducing fixed-distance ET across an intervening proton network such as carboxylic acid dimers,5,6 guanine-cytosine base pairs7–9 and related interfaces10,11 and amidinium-carboxylate salt bridges.12–17 The coupling of the proton to the electron occurs by communication between the charge shift resulting from the motion of the proton and electron through the polarization of the surrounding environment.18–20 Even in the absence of formal proton transfer, fluctuations of the proton position within the interface may exert significant influence over ET.17,21,22 To this end, the possibility arises that the proton can also influence events that do not involve single ET. From the perspective of semiclassical models, the influence of the proton appears explicitly in the electronic coupling constant, |V|.

We now explore this possibility by juxtaposing ferrocenyl (Fc) moieties to Ru(II) polypyridyl complexes, [Ru] = Ru(II)(bpy-COOH)(L)22+ where L = btfmbpy (4,4′-bis(trifluoromethyl)-2,2′-bipyridine), RuA, or bpy (2,2′-bipyridine), RuB, via an amidinecarboxylic acid two-point hydrogen bond (−[H+]−) to form a [Ru]−[H+]−[Fc] supramolecular assembly. The excited states of these Ru(II) polypyridyl complexes can be

†Electronic supplementary information (ESI) available: Full experimental details and characterization of ferrocenyl amidinium compounds, and RuB, spectroscopic and electrochemical data, Dexter energy transfer analysis and spectroscopic calculations. See DOI: 10.1039/C1SC00596K

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deactivated by ferrocene via either ET and EnT quenching. The dominant quenching mechanism has generally been difficult to distinguish for previously studied systems in which the quenching process is bimolecular or the ferrocene moiety is tethered to the Ru(II) polypyridyl complex via a conformationally flexible alkane or alkene tether. In these cases, the mechanism and quenching dynamics are obscured by diffusion or conformational changes. The [Ru]–[H+]–[Fc] dyads described here obviate this problem by fixing the [Ru]–[Fc] distance with a strong hydrogen bonding amidinium-carboxylate interface. The distal separation between Ru and Fc can be tuned by varying the covalent linkage between the cyclopentadienyl (Cp) ring of the ferrocene moiety and amidine functionality. Methodologies are presented that permit the amidine to be fused directly to the Cp ring or appended to intervening phenylene or ethynyl spacers. Varying degrees of electronic communication between ferrocene and the pendant amidine are revealed by electrochemistry and UV-visible absorption spectroscopy. Transient spectroscopy and kinetic isotope studies establish proton-coupled energy transfer (PCEnT) as the dominant quenching process within [Ru]–[H+]–[Fc] supramolecular assemblies.

**Experimental**

The supramolecular dyads were prepared according to the pathways listed in Scheme 1. Preparation of the directly linked ferrocene-amidinium conjugate (3) was accomplished in two steps beginning with the lithiation of bromoferrocene (1) followed by reaction with phenyl cyanate (PhOCN). Subsequent reaction with Al(CH₃)(NH₂)Cl under harsh conditions delivers ferrocene-amidinium 3. The phenyl linked ferrocene-amidinium conjugate (5) is delivered from 4-cyanophenylferrocene (4), which is furnished by Suzuki coupling of bromoferrocene (1) with 4-cyanophenylboronic acid. Reaction of 4 with Weinreb’s amide transfer reagent (Al(CH₃)(NH₂)Cl) ultimately generates amidinium derivative 5. Preparation of the alkynyl linked ferrocenyl amidinium (9) is slightly more involved. Bromoferrocene (1) is converted to a trimethylsilyl protected alkynyl-ferrocene synthon (6) via Sonogashira coupling with trimethylsilylacetylene in the presence of a Cu(I) and Pd(II) catalyst. Deprotection under basic conditions delivers the terminal alkyne (7) and subsequent deprotonation and reaction with PhOCN generates the nitrile capped alkynyl-ferrocene derivative (8). Reaction of 8 with Al(CH₃)(NH₂)Cl yields 9 in excellent yield. Detailed syntheses and characterization of all compounds are given in the Supporting Information.†

Time-resolved absorption (TA) and time-resolved emission (TE) measurements were performed by using the third harmonic (355 nm) of the 1064 nm fundamental of a pulsed Nd:YAG laser (Spectra-Physics Quanta-Ray PRO-Series) to pump an optical parametric oscillator (OPO) at a repetition rate of 10 Hz with pulse energies of ~340 mJ/pulse and pulse width of ~7 ns. This laser has been integrated into an experimental set-up for time-resolved emission and absorption studies as described elsewhere. Variable temperature luminescence lifetime measurements were performed on a Hamamatsu C4334 Streak Scope streak camera. Variable-temperature emission spectra were recorded on an automated Photon Technology International (PTI) QM 4 fluorimeter equipped with a 150 W Xe arc lamp and a Hamamatsu R928 photomultiplier tube.

Absorption spectroscopy titrations with 4-dimethylaminopyridine (DMAP), time resolved emission experiments and temperature-dependent emission experiments were performed on samples contained in a high-vacuum cell comprised of a 1 cm pathlength clear fused-quartz

†Electronic supplementary information (ESI) available: Full experimental details and characterization of ferrocenyl amidinium compounds, and RuB spectroscopic and electrochemical data, Dexter energy transfer analysis and spectroscopic calculations. See DOI: 10.1039/c1sc00596k
cuvette (Starna cells) connected to a 10 cm³ solvent reservoir via a graded seal. High-vacuum Teflon valves were used to seal the cell from the environment and the cuvette from the solvent reservoir. The sample manipulations employed for these experiments are described in detail in the Supporting Information.†

Electrochemical measurements were performed with a Bio-analytical Systems (BAS) Model CV – 50 W potentiostat/galvanostat. Differential pulse voltammetry (DPV) was performed using a glassy carbon working electrode, a Ag/AgCl reference electrode and a platinum wire auxiliary electrode. DPV experiments were preformed in CH₂Cl₂ with 0.1 M tetrabutylammonium perchlorate (NBu₄ClO₄) as the supporting electrolyte and in tetrahydrofuran (THF) with 0.1 M tetrabutylammonium hexafluorophosphate (NBu₄PF₆). Concentrations of ~1 mM were prepared for DPV experiments on 3, 5, 9, Ru₂, and Ru₃. A scan rate of 100 mV s⁻¹ and a sensitivity of 10 μA V⁻¹ were used for data acquisition. Prior to each experiment, the solution was sparged with argon to eliminate dissolved O₂. All potentials are reported versus the Ag/AgCl reference electrode.

Results

The syntheses of the ferrocenyl amidinium complexes 3, 5 and 9 proceed by the pathways of Scheme 1. A highly efficient and modular route to these ferrocene amidinium complexes is afforded by using bromoferrocene (1)32 as a starting material for all three derivatives. The introduction of the amidinium unit on the Cp rings of ferrocene follows a strategy that is similar to that used for the preparation of porphyrin amidinium derivatives,33–36 namely, the conversion of ferrocene-nitrile derivatives (2, 4 and 8) to the corresponding amidiniums using Weinreb’s amide transfer reagent.30 Complete details of compound synthesis and characterization are provided in the Supporting Information.†

Electronic coupling between the [Fc] redox site and the protonic interface is evident from the effect of protonation state on the electronic absorption spectra of each of the ferrocenyl amidiniums. As we have observed for amidinium porphyrins,36,37 the absorption spectra of 3, 5 and 9 each display a hypsochromic shift upon amidinium deprotonation (Fig. S1†). The extent of that shift is a measure of the electronic communication of the amidine with the metal complex to which it is appended. Complex 9 exhibits the largest hypsochromic shift. The cylindrical electronic symmetry of the ethynyl spacer ensures that the amidinium remains strongly electronically coupled regardless of the rotation angle assumed by the amidinium.37 The pKₐ of the amidinium is determined by Benesi–Hildebrand analysis of the shifting absorption spectrum as a function of deprotonation.38 Fig. S2† plots the spectral shifts of the absorption band of 3 and 9 upon their titration with DMAP. The ratio of the y-intercept to the slope of linear fit of a plot of 1/ΔλMLCT vs. 1/[DMAP] furnishes the deprotonation constant, Kₐ': values of Kₐ'(3) = 6.44 x 10² M and Kₐ'(9) = 1.65 x 10² M are obtained. Determination of the ferrocene-amidinium pKₐ value is accomplished using the relation,

\[ \text{p}K_a \text{ (am}^{±}) = \text{p}K_a \text{(DMAP)} - \log(K_a') \] (1)

The pKₐ of DMAP in CH₃CN is 12.33,39 yielding pKₐ values of pKₐ(3) = 9.52 ± 0.10 and pKₐ(9) = 10.11 ± 0.10. The small spectral shifts displayed by 5 upon titration with base together with spectral congestion precluded an accurate determination of the pKₐ of this derivative. Notwithstanding, we expect the pKₐ of 3 and 5 to be similar based on the congruence of their spectral shifts (ΔEshift = 193 cm⁻¹ and 217 cm⁻¹). Considering the pKₐ values of carboxylic acids (pKₐ benzoic acid ~20 and the pKₐ of acetic acid ~20–22) in
CH$_3$CN, the $-[H^+]-$ interface should be non-ionized (i.e. amide–carboxylic acid), as has been established previously.

The redox thermodynamics for Ru$^A$, Ru$^B$, 3, 5, and 9 in CH$_2$Cl$_2$ and THF were characterized by DPV. The DPV traces for each compound are shown in Fig. S3.† The reduction and oxidation potentials of the compounds in CH$_2$Cl$_2$ are: $E_p$(3) = 0.84 V; $E_p$(5) = 0.66 V; $E_p$(9) = 0.51 V; $E_p$(Ru$^A$) = −0.74 V; $E_p$(Ru$^B$) = −1.33 V. The perturbation of the redox potential upon salt bridge formation was assessed by measuring the DPVs of Ru$^A$ and Ru$^B$ upon the incremental addition of phenylamidine (Ph-am), which efficiently binds to the carboxylic acid of the Ru complex, but is redox inactive (Fig. S4†). Only a 24 and 30 mV increase is observed in $E_p$ for Ru$^A$ (up to 30 eq of Ph-am) and Ru$^B$ (up to 50 eq), respectively. Thus the redox properties of the Ru complexes are expected to be perturbed insignificantly upon formation of the amidine–carboxylic acid interface within the [Ru]$-[H^+]-[Fc]$ dyads.

Time-resolved emission experiments were undertaken on each of the six possible D–A combinations. Emission quenching is observed for all dyads studied; quenched ($\tau_0$) and unquenched ($\tau_q$) time constants for each system are compiled in Table 1. The lifetime of Ru$^A$ or Ru$^B$ excited states ($\tau_0$) in the absence of a ferrocenyl amidinium conforms to a monoexponential decay. The unquenched lifetimes of Ru$^A$ and Ru$^B$ are 0.84 µs and 1.25 µs, respectively. By contrast, for solutions of Ru$^A$ or Ru$^B$ in the presence of either 3, 5 or 9, a biexponential decay is observed, which corresponds to the excited state deactivation of unassociated Ru$^A$ and Ru$^B$ and their decay within the associated complexes Ru$^A$:Fc or Ru$^B$:Fc. The quenching rate constant is determined from the relation $k_q = \tau^{-1} - \tau_0^{-1}$. The quenching data exhibits a kinetic isotope effect (KIE) for [Ru]$-[D^+]-[Fc]$ supra-molecular assemblies. These data are also shown in Table 1 for the six dyads.

Based on the excited state energy of the [Ru] complexes and the redox potentials of the six D–A dyads, a favorable driving force for ET ($0 \text{ eV} > -\Delta G_{ET} > 0.8 \text{ eV}$) is established between Ru$^A$ and Ru$^B$, and 3, 5 and 9 (Table S1†). Transient absorption spectroscopy was undertaken to search for evidence of a charge separated (CS) state, which would be indicative of an ET quenching pathway. However, no spectral signatures attributed to a CS species were observed. The absence of a CS signature does not necessarily exclude ET as the dominant quenching mechanism if the back ET reaction is significantly accelerated with regard to the forward ET reaction. For such a case, the charge transfer intermediate will not accumulate to detectable levels. Other potential quenching mechanisms include EnT via Dexter (DEnT) or Förster resonance energy transfer (FRET). For the latter, as calculated in the Supporting Information,† the overlap integral for FRET is negligible and results in predicted FRET rates that are 10–200 times slower than the rates observed.

With the FRET mechanism discarded, the two possible primary mechanisms are ET and DEnT. Both processes can be analyzed under the semi-classical formalism to describe rates of nonradiative processes:

$$k_q = \frac{4\pi^2}{h} \cdot |V|^2 \cdot \frac{1}{\sqrt{4\pi \lambda k_B T}} \cdot \exp \left( -\frac{(\Delta G_0 + \lambda)^2}{4\lambda k_B T} \right)$$

where $\Delta G_0$ is the free energy change associated with the reaction, $\lambda$ is the solvent reorganization energy of the process, and $|V|$ is the electronic coupling constant between the donor and acceptor. Of particular importance in distinguishing between ET and DEnT is the solvent reorganization term. Since only small charge redistributions occur within the MLCT excited state of the Ru($i$) polypyridyl complexes, very little charge accrues during DEnT and $\lambda$ should be significantly less for EnT than ET. For Ru($i$) polypyridyl complexes, inner

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sphere reorganization $\lambda_i$ is minimal so that most of $\lambda$ is determined by the outer sphere DEnT reorganization energy, i.e., $\lambda \sim \lambda_o$. Typical $\lambda_o$ values are ~1–2 eV for ET processes,\textsuperscript{41} whereas they are ~0.1–0.2 eV for processes.\textsuperscript{42–45}

The reorganization energy may be determined from the temperature dependence of the emission bandwidth, $\Delta \nu_{0,1/2}$. For the Ru($\omega$) polypyridyl complexes, Ru\textsuperscript{A} and Ru\textsuperscript{B}, the emission spectra bandwidth reflects the reorganization energy associated with conversion of the MLCT excited state to the ground state. The temperature-dependence of the square of fitted emission bandwidth is related to the outer sphere reorganization energy, $\lambda_o$, is given by:\textsuperscript{46–48}

\[ \left( \Delta \nu_{0,1/2} \right)^2 = \left( \Delta \nu_{0,1/2}^0 \right)^2 + 16 (k_B T) \lambda_o \]  

(3)

Fig. 1 plots $\left( \Delta \nu_{0,1/2} \right)^2$ versus temperature; the slope of the line of this fit yields $\lambda_o$. Analysis of these data with eqn (3) yields $\lambda_o (\text{RuA}:3) = 0.102$ eV and $\lambda_o (\text{RuB}:3) = 0.050$ eV. These values are very similar to the outer-sphere reorganization energies of the control systems in which there is no energy accepting [Fc] moiety, $\lambda_o (\text{RuA:Ph-am}) = 0.12$ eV and $\lambda_o (\text{RuB:Ph-am}) = 0.11$ eV. The $\lambda_o$ values are significantly less than the $\lambda_o = 0.85$ eV calculated from Marcus theory for the ET reaction of these dyads.\textsuperscript{49} These results taken together with the inability to observe charge transfer products in time-resolved absorption spectra support the assignment of DEnT as the quenching mechanism in Ru\textsuperscript{A}:3 and Ru\textsuperscript{B}:3. A similar DEnT quenching pathway is expected when 5 or 9 serves as the acceptor.

The proton-coupling of energy transfer via the electronic coupling matrix element is directly revealed by the KIEs listed in Table 1. Whereas [Ru\textsuperscript{A}]–[H\textsuperscript{+}]+–[Fc] exhibits a normal KIE, an inverse KIE is observed for [Ru\textsuperscript{B}]–[H\textsuperscript{+}]+–[Fc]. Theoretical treatments of PCET have shown that small fluctuations within the interface can dynamically modulate electronic coupling, and consequently the rate of transfer becomes sensitive to the nature of proton vibrational modes within the bridge.\textsuperscript{21} Proton interfaces that are not as tightly bound require the proton or deuteron positions to fluctuate by larger amounts in order to induce ET. Because the tails of the proton or deuteron wavefunctions dictate the efficacy of proton tunneling. In such cases, the overlap of the more diffuse proton wavefunction is greater than the overlap of the more localized deuteron wavefunction and a normal KIE is expected (Fig. 2). However, in a more tightly coupled interface, the overlap of the deuteron wavefunction at its equilibrium position with the critical displacement may be greater than the overlap between the proton wavefunction at its equilibrium point. Provided that only small fluctuations of the hydrogen bond are required to attain the equilibrium configuration, an inverse KIE is predicted. Inasmuch as the ET and EnT process are related via the electronic coupling matrix element,\textsuperscript{23} parallels may be drawn between the KIEs of proton-coupled ET and EnT events.

The disparate behavior of the two [Ru] complexes likely stems from the differing nature of the MLCT excited states of the two systems. Soler and McCusker have shown\textsuperscript{50} that Ru($\omega$) polypyridyl complexes covalently bound to dinuclear manganese complexes possess electronic coupling constant that are two orders of magnitude greater when the excited state is localized on the bridging bpy ligand as opposed to the ancillary ligand. Along these lines, Raman studies of functionalized Ru($\omega$) bpy complexes reveal that the electron localizes on the bpy ligands bearing the most electron withdrawing functionality. Hence the MLCT excited state of Ru\textsuperscript{B} is centered on the bridging bpy ligand connected to the $-[\text{H}^+]-$ interface, whereas excitation of the MLCT state of Ru\textsuperscript{A} produces an excited state localized on the fluorinated bpy ligands, remote from the $-[\text{H}^+]-$ interface.
Conclusions

The supramolecular assembly of ferrocenyl-amidinium compounds with two Ru(II) polypyridyl complexes allows for the study of hydrogen-bond mediated quenching through well-defined two-point interfaces. Measurement of the pKₐ of the amidinium affixed to the Cp ring of ferrocene establishes that the two-point hydrogen bonded interface is not that of the salt bridge but is formed from the association of amidine with carboxylic acid. The excited state of Ru(II)(bpy-COOH)(L)₂⁺, where L = btfmbpy (4,4′-bis(trifluoro-methyl)-2,2′-bpy) or bpy (2,2′-bipyridine) is efficiently quenched by the juxtaposed ferrocene, which is electronically coupled to the Ru(II) polypyridyl excited state via the amidine-carboxylic acid salt bridge. Transient and temperature-dependent spectroscopic measurements reveal that the small reorganization energy attendant to the quenching process is consistent with energy transfer rather than electron transfer. Moreover, an observed kinetic isotope effect on the quenching process indicates that the proton dependence on EnT arises via the electronic coupling term between the [Ru] EnT donor and the [Fc] EnT acceptor. To this end, the mechanism of PCEnT is similar to that of PCET; i.e., the electronic coupling matrix element modulates the transfer of energy in PCEnT, as it also does for the transfer of an electron in a PCET reaction. These results on an inorganic-based EnT system add to the emerging trend of organic-based EnT systems⁵¹–⁵⁴ that energy transfer can be mediated by proton-transfer interfaces.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Notes and references

The outer-sphere reorganization energy can be calculated using the Marcus dielectric continuum model for the systems in a solvent of given dielectric constant using the relation:

$$\lambda_s = 14.4 \left( \frac{1}{2r_D^2} + \frac{1}{2r_A^2} - \frac{1}{d_{DA}^2} \right) \times \left( \frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_s} \right)$$

where $r_D$ and $r_A$ are the ionic radii of the donor and acceptor, respectively, $d_{DA}$ is the D–A separation, $\varepsilon_{\infty}$ is equal to the refractive index of the solvent squared, and $\varepsilon_s$ is dielectric constant of the solvent. The refractive index and dielectric constant for CH\(_2\)Cl\(_2\) are 1.4212 and 8.93, respectively. The ionic radii of 3 is 3.2 Å; 5 is 7.3 Å; 9 [PubMed: 16986876]
is 5.5 Å; **RuA** is 6 Å; and **RuB** is 6 Å. D–A separation for **RuA** and **RuB** with 3, 5, and 9 is 12.6 Å, 16.8 Å, and 14.8, respectively.

Fig. 1.
Temperature dependence of full-width-at-half-maximum $(\Delta v_{0,1/2})^2$ of emission from $\text{Ru}^\text{A}:\text{Ph-am}$ (□), $\text{Ru}^\text{A}:3$ (●), $\text{Ru}^\text{B}:\text{Ph-am}$ (○), and $\text{Ru}^\text{B}:3$ (●).
Fig. 2.
Proton fluctuations within the amidinium-carboxylic acid interface may dynamically modulate electronic coupling for PCEnT, and consequently the rate of transfer becomes sensitive to the nature of proton vibrational modes within the bridge. Under typical conditions, wavefunction overlap of the deuterated bridge is smaller than that of the proton and a normal KIE is observed and is shown schematically in the left (blue shaded region). However, thermal population of vibrational excited states may be a cause of the reverse isotope effect in this system, where the low frequency mode of interest is a localized 3-atom N–H–O vibration in the hydrogen bond (red shaded region).
Scheme 1.
Synthetic schemes for the preparation of amidinium ferrocene compounds

(a) 1. CH$_3$Li, 2. PhOCN, (b) (diPyr)PdCl$_2$, Na$_2$CO$_3$, 4-cyanophenylboronic acid, THF, H$_2$O. (c) Trimethylsilylacetylene, CuI, PdCl$_2$(PPh$_3$)$_2$, NEt$_3$, DMF. (d) K$_2$CO$_3$, THF, CH$_3$OH. (e) 1. CH$_3$Li, THF; 2. PhOCN.
Table 1

Quenching rate constants of [Ru]-Fc dyads$^a$

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$^a$All data recorded in DCM at 298 K.

$^b$Unquenched lifetime of Ru$^A$ is 0.84 $\mu$s.

$^c$Unquenched lifetime of Ru$^B$ is 1.25 $\mu$s.