Photoinduced Electron Transfer within a Donor–Acceptor Pair Juxtaposed by a Salt Bridge

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The coupling of proton motion to charge separation is a fundamental mechanism in bioenergetic conversions. Energy-storing processes of small molecule activation and the translocation of protons across membranes in the proteins and enzymes of photosynthesis[1–4] and respiration[5–7] are predicated on proton-coupled electron transfer (PCET). One approach to investigating the mechanism of PCET is to photoinduce electron transfer within a donor/acceptor pair that is juxtaposed by proton transfer interfaces such as those formed from carboxylic acid dimers[8] or guanine–cytosine base pairs.[9] For the symmetric $-(COOH)_2-$ interface, proton displacement on one side of the dicarboxylic acid interface is compensated by displacement of a proton from the other side. In this case, proton motion within the interface influences only the electronic coupling within the donor/acceptor pair and electron transfer is facile.[8,10] However, this may not be the case for asymmetric interfaces where proton motion is accompanied by changes in charge and polarity within the interface. In view of these possible energetic barriers, we wondered whether electron transfer would be coupled to protons in asymmetric interfaces such as salt bridges, which show significant charge redistribution upon proton motion within the interface. One attractive salt bridge for PCET studies is the amidinium–carboxylate interface, which models arginine–aspartane salt bridges found to be important in many structures including RNA stem loops,[11] zinc finger/DNA complexes,[12,13] and the active site of dihydrofolate reductase.[14] But unlike the guanidinium–carboxylate interaction of Arg-Asp, amidinium shows only one specific binding mode for carboxylate thereby simplifying PCET studies. We now report the kinetics for **1** in which an electron is transferred from the photoexcited Ru(bpy)$_3^{2+}$ (bpy = bipyridine) donor to a 3,5-dinitrobenzene acceptor through an intervening amidinium–carboxylate interface. This model system was chosen to exploit the well-known electron transfer chemistry of electronically excited Ru(bpy)$_3^{2+}$ with nitroaromatics.[15] **1** is compared to **2** where a symmetric $-(COOH)_2-$ interface has been introduced within the donor/acceptor pair.

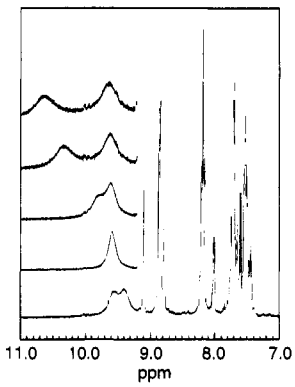
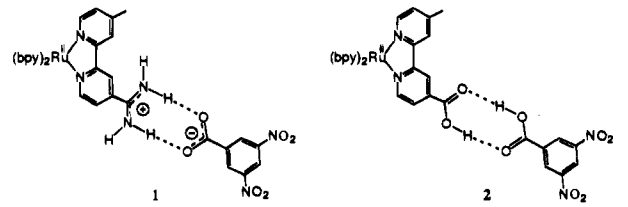


Figure 1. ^{1}H NMR spectrum of (bpy)$_2$Ru^{II}(bpy-amidinium)$^{3+}$. Selected spectra are shown upon addition of the tetramethylammonium salt of 3,5-dinitrobenzoate carboxylate at the concentrations 0, 0.44, 0.89, 2.2, and 3.1 mM in DMSO-d_6 (bottom to top). The ^{1}H resonances of the bipyridines appear between 7.3 and 9.2 ppm; two broad singlets flanking 9.5 ppm signify the ^{1}H resonances of the amidinium protons. For the spectrum at 0.44 M carboxylate added, the two resonances are coincident.



The amidinium–carboxylate salt bridge is formed directly upon mixing the appropriate carboxylic acid with free base amidine. We have adapted Garigipati's strategy[16] for the preparation of amidines from nitriles in high yield.[17] Two favorable secondary electrostatic interactions[18] within the amidinium–carboxylate interface are manifested in high association constants even when the solvent is polar. Figure 1 shows the ^{1}H NMR spectrum of (bpy)$_2$Ru^{II}(bpy-amidinium)$^{3+}$ in DMSO-d_6 at 19.5 °C. The ascending traces highlight the changes in the chemical shifts of the amidinium protons, which appear as broad singlets at ~9.5 ppm, upon titration with the tetramethylammonium salt of the 3,5-dinitrobenzoate. A concentration-dependent downfield shift of >2.0 ppm is observed for the protons involved in hydrogen bonding to the carboxylate whereas the chemical shift of the adjacent protons, which are not bound to the carboxylate, varies marginally from 9.55 to 9.65 ppm over all concentrations. A least squares fit of a plot of the chemical shift of the hydrogen-bonded amidinium protons vs the carboxylate concentration at 19.5 °C yields $K_{assoc} = 1136 \pm 93$ M^{-1}.[19] Unfortunately, the solubility of **1** in CH_2Cl_2, the solvent in which electron transfer kinetics were determined, is too low to permit K_{assoc} to be reliably ascertained by NMR titration experiments. Nonetheless we observe the association

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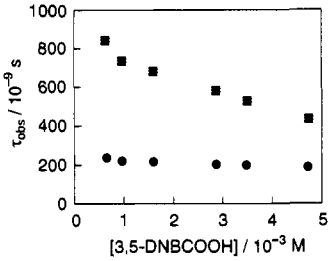

Figure 2. Plot of the concentration-dependent (■) and concentration-independent (●) decay lifetimes for the quenching of $(bpy)_2Ru^{II}$(bpy-amidine)$^{2+}$ (0.2 mM) by 3,5-DNBCOOH.

constant for **1** to increase with decreasing solvent polarity (K_{assoc} = 2432 M^{-1} in CH_3CN at 19.5 °C). On this basis, the DMSO and CH_3CN association constants represent a lower limit for the formation of **1** in our electron transfer experiments. For the case of **2**, K_{assoc}, measured by techniques previously described by us for the symmetric $-(COOH)_2-$ interface,[8] is 702 M^{-1} in CH_2Cl_2, which is comparable to our previous measurements of a dicarboxylic acid interface bridging a dinitrobenzene acceptor and a porphyrin donor (K_{assoc} = 552 M^{-1}).

The luminescence of $(bpy)_2Ru^{II}$(bpy-amidine)$^{2+}$ in CH_2Cl_2 is quenched upon the addition of 3,5-dinitrobenzoic acid (3,5-DNBCOOH). This result is consistent with an electron transfer quenching mechanism, which is well-established for the reaction between electronically excited (Ru^{II})tris(polypyridyl) complexes and nitroaromatic acceptors.[15] In the absence of 3,5-DNBCOOH, the decay of the $(bpy)_2Ru^{II}$(bpy-amidinium)$^{3+}$ excited state is monoexponential with a lifetime of 1300 ns, which decreases upon complexation to aliphatic carboxylates or benzoate (τ_0 = 850 ns). However, when 3,5-DNBCOOH is present, a biexponential decay of the luminescence is observed whereupon one lifetime component is dependent on the concentration of acceptor and the other is not over a 3,5-DNBCOOH concentration range of 0.1−5 mM ([$(bpy)_2Ru^{II}$(bpy-amidine)$^{2+}$] = 0.1 mM) (see Figure 2). The origin of the concentration-dependent decay is easily understood. The Stern−Volmer plot of the concentration-dependent lifetime is linear over the entire quencher concentration range and the intercept is unity. The bimolecular rate constant of 2.4 × 10^9 M^{-1} s^{-1} is in accordance with that measured by Meyer et al. for $Ru(bpy)_3^{2+}$ and 3,5-dinitrobenzoic acid (k_{ET} = 1.6 × 10^9 M^{-1} s^{-1}).[15] More significantly, the bimolecular kinetics of **1** is similar to that for the reaction of $(bpy)_2Ru^{II}$(bpy-amidinium)$^{3+}$ with the ester 3,5-DNBCOOEt (k_{ET} = 1.9 × 10^9 M^{-1} s^{-1}), which is unable to associate with the amidine (association of the amidinium with the nitro functionality is not likely,[20] which we also confirmed by NMR). The concentration-independent lifetime decay component is attributable to electron transfer for the associated pair shown **1**. An intramolecular rate constant of 4.3(9) × 10^6 s^{-1} is determined from the concentration-independent lifetime decay component.

The reaction of $(bpy)_2Ru^{II}$(bpy-COOH)$^{2+}$ with 3,5-DNBCOOH in CH_2Cl_2 exhibits similar characteristics to the reaction of the quencher with $(bpy)_2Ru^{II}$(bpy-amidine)$^{2+}$. Lifetime decays are biexponential, also exhibiting concentration-independent and -dependent components. The bimolecular rate constant derived for the latter is 1.4 × 10^9 $M^{-1}s^{-1}$, which is comparable to the reaction rate constant of $(bpy)_2Ru^{II}$(bpy-COOH)$^{2+}$ with the ester 3,5-DNBCOOEt (k_{ET} = 1.1 × 10^9 M^{-1} s^{-1}). Despite a 0.07 V smaller driving force (ΔG(**1**) = −0.21 V, ΔG(**2**) = −0.14 V),[21] the intramolecular rate constant of 8.0(4) × 10^6 s^{-1} for **2** is nearly a factor of 2 greater than that observed for **1**.

Does the attenuated PCET process in **1** suggest that the salt bridge is affecting the rate of the ET? To more directly address this issue, we exchanged the ^1H atoms of the amidine and carboxylic acid by ^2H and measured the electron transfer kinetics of the associated pair. The intramolecular rate constant for deuterated **1** was 3.2 × 10^6 s^{-1}, yielding k_H/k_D = 1.34(3). This isotope effect is similar to the k_H/k_D = 1.5 for **2**, and it is consistent with our previous electron transfer measurement of a porphyrin donor−$(COOH)_2$−acceptor complex (k_H/k_D = 1.6 and 1.7). As recently discussed, a deuterium isotope effect in these hydrogen-bonded systems arises from the modulation of the electronic coupling matrix element by the proton's position within the interface,[10,22] thereby providing a mechanism for the asymmetric salt bridge to engender a PCET reaction.

The effect of proton motion on the electron transfer rate may be manifested in ways other than the electronic coupling. Unlike the $-(COOH)_2-$ interface, significant charge rearrangement occurs upon proton motion in the salt bridge, and this charge redistribution will couple to solvent (i.e., to give rise to additional Franck−Condon factors arising from proton motion).[10b] Moreover, the electron is transferred through the permanent electrostatic field of the salt bridge thereby modifying the energetics of the overall reaction. These issues may be addressed by comparing the rates of electron transfer for a donor−(amidinium-carboxylate)−acceptor complex to those for its congener where the interface is switched (i.e., donor−(carboxylate−amidinium)−acceptor). For the systems here, such a comparative study is obscured by the possibility of transferring an electron from the ancillary bipyridine ligand in addition to the transfer of an electron from the derivatized bipyridine ligand because the two metal-to-ligand charge transfer states are close in energy.[23,24] We are therefore currently assessing the issue of PCET rates for switched interface systems with complexes featuring a single bipyridine ligand, and with complexes in which the energy of the metal-to-ligand charge transfer state for the ancillary ligands are energetically far removed from the derivatized amidinium or carboxylate bipyridine ligand.

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Supporting Information Available: Fit of the chemical shift data in Figure 1 to obtain K_{assoc}, representative lifetime decays of the quenching reactions between $(bpy)_2Ru^{II}$(bpy-amidine)$^{2+}$ and 3,5-DNBCOOH, $(bpy)_2Ru^{II}$(bpy-COOH)$^{2+}$ and 3,5-DNBCOOH, $(bpy)_2Ru^{II}$(bpy-amidine)$^{2+}$ and 3,5-DNBCOOEt, $(bpy)_2Ru^{II}$(bpy-COOH)$^{2+}$ and 3,5-DNBCOOEt, and $(bpy)_2Ru^{II}$(bpy-COOD)$^{2+}$ and 3,5-DNBCOOD in CH_2Cl_2, and Stern−Volmer plots of concentration-dependent decays for $(bpy)_2Ru^{II}$(bpy-amidine)$^{2+}$ and 3,5-DNBCOOH, $(bpy)_2Ru^{II}$(bpy-COOH)$^{2+}$ and 3,5-DNBCOOH in CH_2Cl_2, $(bpy)_2Ru^{II}$(bpy-amidine)$^{2+}$ and 3,5-DNBCOOEt in CH_2Cl_2, and $(bpy)_2Ru^{II}$(bpy-COOH)$^{2+}$ and 3,5-DNBCOOEt in CH_2Cl_2 (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet. See any current masthead page for ordering information and Internet access instructions.

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