Ferrocenyl-amidinium compound as building block for aqueous proton-coupled electron transfer studies

Afua Nti, Ewuradjoa Gadzanku, and Elizabeth R. Young*

*Department of Chemistry, Amherst College, PO Box 5000, Amherst, MA 01002-5000, United States.
E-mail: cyoung@amherst.edu
Fax: 413-542-2735
Tel: 413-542-5480

Abstract: A water-soluble amidinium-appended ferrocene moiety is characterized in which the amidinium functionality is fused directly to the ferrocene ring (Fcam1). This species is designed to form a building block for aqueous proton-coupled electron transfer in which proton transfer occurs to the bulk and electron transfer occurs to a chemical oxidant. pH-dependent absorption spectroscopy and electrochemistry show that the electrochemical potential is directly linked to the protonation state of the amidinium. A thermodynamic square scheme is constructed for Fcam1. The square scheme serves as motivation and provides direction for incorporating this species into a covalently-bound system for the study of proton-coupled electron transfer.

Keywords: Ferrocene, Ferrocene-derivative, proton-coupled electron transfer (PCET), pH-dependent oxidation potential, square scheme, pH-dependence

Ferrocene derivatives have been incorporated into a large number of electron transfer model systems due to their rich redox properties, reversible oxidation and general photostability and thermal stability [1-9]. Previous efforts have revealed that appended acid groups impart pH-dependent oxidation behavior to the ferrocene redox unit [10]. Accordingly, the use of ferrocenyl moieties appended with hydrogen-bonding functionalities is appealing for mechanistic study of proton-coupled electron transfer (PCET). The synthesis of a ferrocenyl amidinium derivative in which the protonic group is fused directly to the redox center enables PCET studies using ferrocene to be carried out in aqueous conditions.

Early mechanistic studies of proton coupled electron transfer (PCET) have focused primarily on assemblies of donor-acceptor (D–A) pairs juxtaposed by hydrogen-bonded interfaces [11-13] formed by carboxylic acid dimers [14,15], and amidinium-carboxylate salt bridges [16-21]. The inspiration for these PCET studies lies in a host of biological systems that employ guaninucleotide base-pairs [22] and arginined-aspartate salt bridges [23-31]. Mechanistic investigation of PCET through hydrogen bonded interfaces addresses the impact of proton motion on through-bond electron transfer (ET) in a co-linear PCET arrangement, in which ET and proton transfer (PT) occur in the same direction. Assembly of these hydrogen-bonded systems, however, requires the use of aprotic solvents of low dielectric constant in order to facilitate efficient binding. Mechanistic interrogation of aqueous PCET systems requires an alternative architectural strategy to co-linear PCET in hydrogen-bonded systems, as water disrupts formation of amidinium-carboxylate hydrogen bonds and prevents formation of D–A dyads. A strategy that can be employed to study PCET that does not necessitate formation of hydrogen-bonded D–A dyads is the use of a bi-directional PCET motif. Specifically, a bi-directional system of relevance to aqueous studies consists of a covalently bound D–A pair to establish an ET coordinate and a PT coordinate that is established through loss of an amidinium proton to the bulk. The ferrocenyl-amidinium species presented in these studies, Fcam1, (Scheme 1) is a building block for such bi-directional aqueous PCET. This system is akin to the bi-directional PCET systems involving deprotonation of tyrosine to the bulk concomitant with oxidation by a Re polypyridyl photo-oxidant [32,33].

Scheme 1 Cartoon depiction of photo-induced bi-directional PCET, in which deprotonation of the appended amidinium functionality facilitates ET to an electron acceptor photo-oxidant (P.O.).

Prior to incorporation of the ferrocenyl-amidinium component into a PCET assembly, it is necessary to characterize the individual Fcam1 moiety, specifically its electronic absorption and electrochemical oxidation potential and their dependence on pH. Significant electronic communication between the ferrocene sub-unit and the pendant amidinium is revealed by UV-visible absorption spectroscopy through observation of spectral shifts that occur upon protonation or deprotonation of the amidinium functionality. pH-Dependent absorption spectroscopy yields the pK_a of the amidinium functionality in water, while pH-dependent electrochemistry clearly reveals that the oxidation potential of the compound is linked to the protonation state of the amidinium functionality. Formation of the oxidized species, Fcam1^*, is monitored by electronic absorption spectroscopy during bulk electrolysis experiments. A thermodynamic square scheme that provides a complete thermodynamic characterization of Fcam1 is presented and serves as an important guide to incorporation of Fcam1 into covalently-bound photo-induced PCET systems.

1Abbreviations: PCET, proton-coupled electron transfer; ET, electron transfer; PT, proton transfer; D–A, donor-acceptor, NHE, normal hydrogen electrode.
Absorption spectra of ferrocene-amidinium (Fcaml) in aqueous 100 mM phosphate solutions buffered at pH 8 exhibit absorption peaks at 221 nm ($\varepsilon_{221nm}$, 12,100 M$^{-1}$cm$^{-1}$), 265 nm ($\varepsilon_{265nm}$, 4230 M$^{-1}$cm$^{-1}$), 320 nm ($\varepsilon_{320nm}$, 1180 M$^{-1}$cm$^{-1}$), and 443 nm ($\varepsilon_{443nm}$, 365 M$^{-1}$cm$^{-1}$). Under basic conditions (pH 11.41) absorption peaks at 264 nm ($\varepsilon_{264nm}$, 4380 M$^{-1}$cm$^{-1}$), 311 nm ($\varepsilon_{311nm}$, 1860 M$^{-1}$cm$^{-1}$), and 428 nm ($\varepsilon_{428nm}$, 414 M$^{-1}$cm$^{-1}$) are produced (Figure 1). Fcaml is stable for extended periods in water in this pH range (Figure S1 in the Supporting Information).

The spectral data provided in the text indicate the presence of multiple absorption bands for Fcaml under different pH conditions. The absorption maxima and their corresponding molar absorptivities are listed, with the pH range spanning from 7 to 11. The text also mentions the spectral stability of Fcaml in water in this pH range.

**Figure 1**: pH-dependent UV-visible absorption spectra of Fcaml as a function of increasing pH (red spectrum, pH 7; blue spectrum, pH 11). Shifts in the spectral features are clearly seen as increasing pH causes deprotonation of the pendant amidinium functionality.

**Figure 2**: The spectral shift in the UV-visible spectrum at 450 nm is plotted versus pH (circle). The spectral shifts are tracked by the redox potential (square) of Fcaml as a function of pH. Redox potentials obtained by DPV ($E_p$) are plotted versus pH. The pH-dependent studies reveal a pK$_a$ value of 8.8 for Fcaml.

**Scheme 2**: Thermodynamic square scheme for Fcaml that fully characterizes the protonation states and redox potentials of the PCET moiety in aqueous conditions.
imperative for incorporation of conditions. Therefore, to demonstrate pH-dependent PCET, it is of the ET and PT properties of Fcam1, as appropriate chemical oxidants for this process suffer from instability at high pH conditions. Therefore, to demonstrate pH-dependent PCET, it is necessary to incorporate Fcam1 into a covalently bound DUA system, in which ET will be initiated from the excited state of a photo-oxidant. Photo-induced ET in a bound system can then be monitored as a function of pH of the aqueous buffered solution. Current investigation is underway into an appropriate photo-oxidant that possesses the necessary driving force for ET and will undergo electron transfer with Fcam1 and is the subject of ongoing work in this direction.

In summary, a water soluble amidinium-appended ferrocenyl moiety is presented that shows spectral and electrochemical properties that vary with pH. The pH-dependent electronic absorption spectra reveal efficient coupling between the ferrocene moiety and appended amidinium functionality. From pH-dependent spectral shifts of the absorption spectrum, the amidinium acidity constant of $pK_a(Fcam1) = 8.8$ is ascertained. The oxidation potential for Fcam1 moves to lower potential with increasing pH, indicating that oxidation of the ferrocene moiety is facilitated by deprotonation of the acid functionality. Further analysis of the thermodynamic square scheme constructed for Fcam1 yields an acidity constant for the ferrocenium-amidinium of $pK_a(Fcam1^+) = 7.26$.

The foregoing analysis provides the underpinning for construction of a PCET system through detailed characterization of the ET and PT properties of Fcam1. The results provide an imperative for incorporation of Fcam1 into DUA networks of bi-directional character that will undergo photo-induced PCET. A photo-induced event will be necessary in order to reach the higher pH range where Fcam1 demonstrates pH-dependent behavior. With the appropriate choice of photo-oxidant, a DUA system can be constructed in which the donor and acceptor are covalently linked and for which the driving force for ET is modulated by the pH of the surrounding environment. These water-based bi-directional PCET studies are of particular interest for understanding PCET in various solvent environments for applications of energy storage and modeling of biological systems.

Acknowledgments

The authors would like to thank John L. Dimeglio and Joel Rosenthal for providing Fcam1. Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for support of this research (52165-UNI4).

Notes and references

† Electronic Supplementary Information (ESI) is available online at: www.

[34] Experimental details can be found in the Electronic Supporting Information.