Supporting Information

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

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Experimental Section

Materials. Amidiniumferrocene chloride (**Fcam1**) was prepared using published methods.[1] Potassium chloride, potassium phosphate monobasic, potassium phosphate dibasic, and potassium permanganate were purchased from Sigma Aldrich and used without further purification. The authors would like to thank John L. Dimeglio and Joel Rosenthal at the University of Delaware for providing **Fcam1**.

Physical measurements. Absorption spectra were obtained using a Perkin Elmer UV/vis/NIR spectrophotometer Lambda 9 (with Lamba 19 Upgrade). Electrochemical experiments were carried out using a CH Instruments Electrochemical workstation model CHI760D.

Electronic absorption spectroscopy. Absorption spectroscopy on samples of **Fcam1** were performed in a 1-cm pathlength clear fused-quartz cuvette (Starna cells). Samples of **Fcam1** were prepared in a 100 mM phosphate buffer. Peaks in the absorption spectra were obtained at 221 nm (ε_{221nm},12,107 $M^{-1}cm^{-1}$), 264 nm (ε_{264nm}, 4,234 $M^{-1}cm^{-1}$), 320 nm (ε_{320nm}, 1,182 $M^{-1}cm^{-1}$), and 443 nm (ε_{264nm}, 365.3 $M^{-1}cm^{-1}$).

pH-dependent electronic absorption spectroscopy. The amidinium acidity constants was determined in water by performing a pH titration in deionized water with 100 mM potassium phosphate. A solution of 0.5 M NaOH in 100 mM potassium phosphate was used to set the pH.

1. E. R.Young, J. Rosenthal, D. G. Nocera, Chem. Sci. 2012, **3**, 455.

The concentration of **Fcam1** in each solution was 160 μM. An absorption spectrum was taken at each pH point in a 1-cm pathlength cuvette. A stock solution of **Fcam1** in 0.5 M NaOH (in 100 mM potassium phosphate) was added to the sample to adjust the pH while maintaining the same **Fcam1** concentration in the sample throughout the course of the experiment.

pH-dependent electrochemistry. Samples for pH-dependent electrochemistry were prepared in a solution of 100 mM potassium phosphate and 100 mM KCl electrolyte in water. The sample concentration employed for electrochemistry ranged from 0.01 to 0.28 mg/mL for **Fcam1**. The pH was adjusted by addition of a 0.5 M NaOH (in 100 mM KCl/100 mM potassium phosphate) solution prior to each scan. Differential pulse voltammetry (DPV) was performed in a 3-electrode system with a glassy carbon working electrode, an Ag/AgCl reference electrode and a platinum wire counter electrode. The glassy carbon working electrode was polished between each electrochemical measurement. A range of 300 to 800 mV was sampled at 20-100 mV/s scan rates and 100-1mA μA sensitivity for DPV measurements.

Bulk electrolysis and spectroelectrochemistry. Bulk electrolysis on a 0.1 mg/mL **Fcam1** sample was performed in a solution of 100 mM potassium phosphate buffer and 100 mM KCl electrolyte in water. The pH of the solution was set to either pH 7 or pH 11. Bulk electrolysis was performed using a 1×4-cm quartz cuvette. Data collection occurred through the 1-cm pathlegth side of the cuvette. A Pt mesh was used as the working electrode, a silver wire was the reference, and a Pt wire was the auxiliary electrode. The sample in the cuvette was sparged with nitrogen before bulk electrolysis was performed. The oxidative potential for bulk electrolysis was set at 850 mV (vs. NHE) for **Fcam1**. An initial spectrum of each sample was recorded. All subsequent spectroelectrochemistry spectra were referenced to the initial spectrum of each sample, which was recorded after the spectrometer was blanked on the initial sample. Difference spectra were collected over thirty minutes. The collected spectra are the difference of the initial spectrum and the spectrum at each time point.

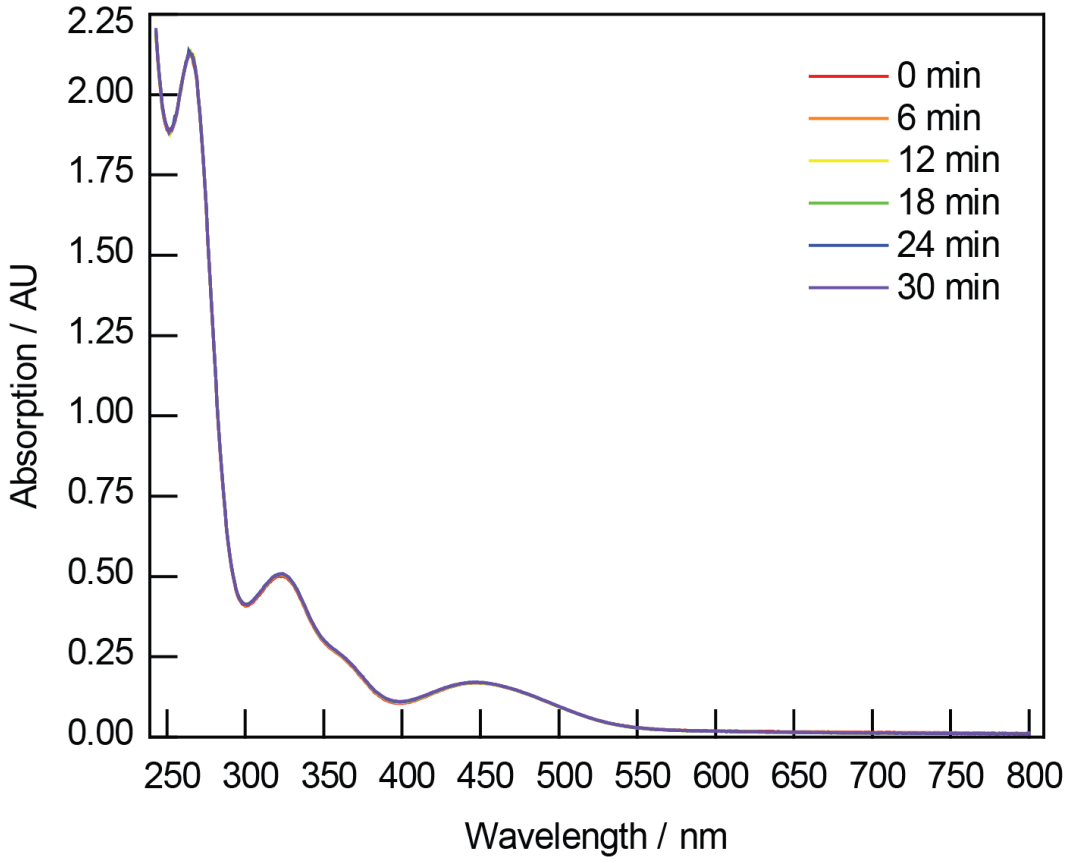

Figure S1: **Fcam1** in 100 mM phosphate buffer and 100 nm KCl electrolyte at pH 7.40. The UV-visible spectrum remains unchanged for over 30 minutes indicating that **Fcam1** is stable under the experimental conditions.

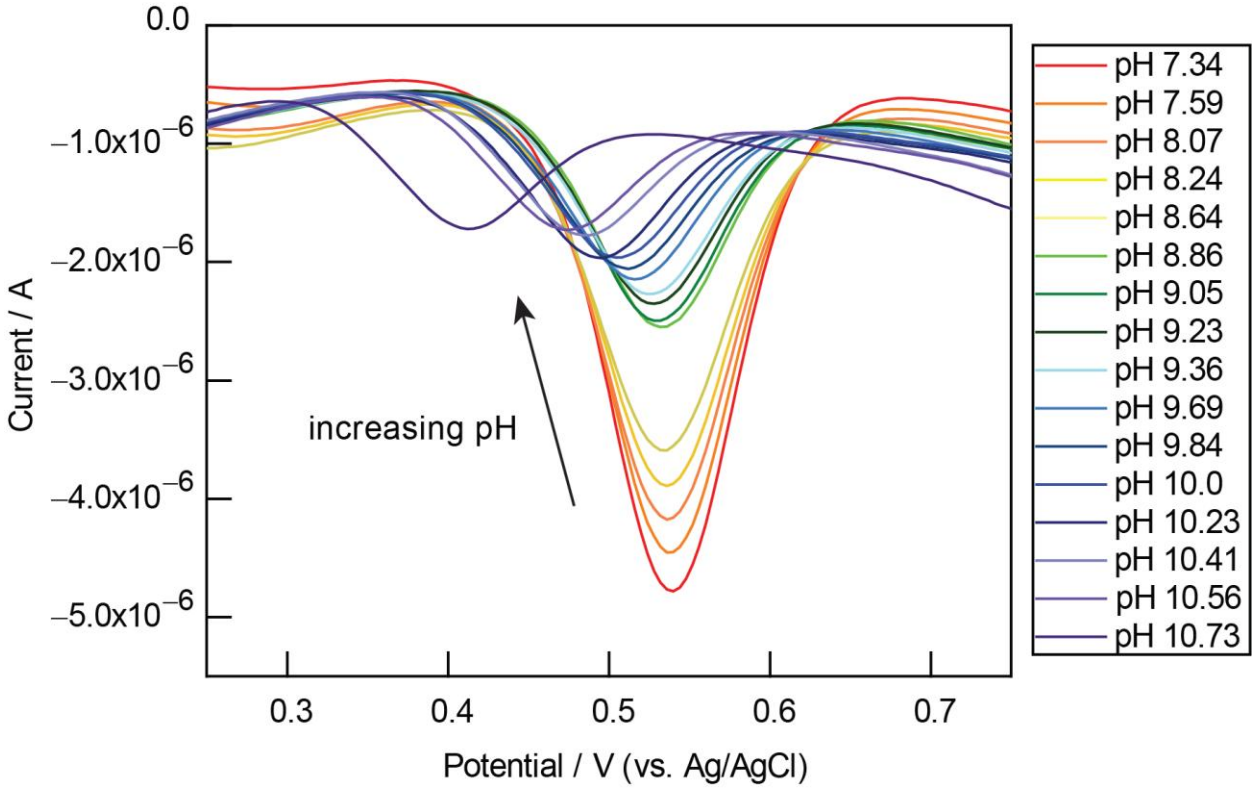

Figure S2: Differential pulse voltammetry scans of **Fcam1** as a function of pH. The current decreases at pH is increases because the concentration of **Fcam1** decreases during the pH titration (as more NaOH is added). This method was employed to conserve the complex and because the peak position and not the current intensity is the data of interest.

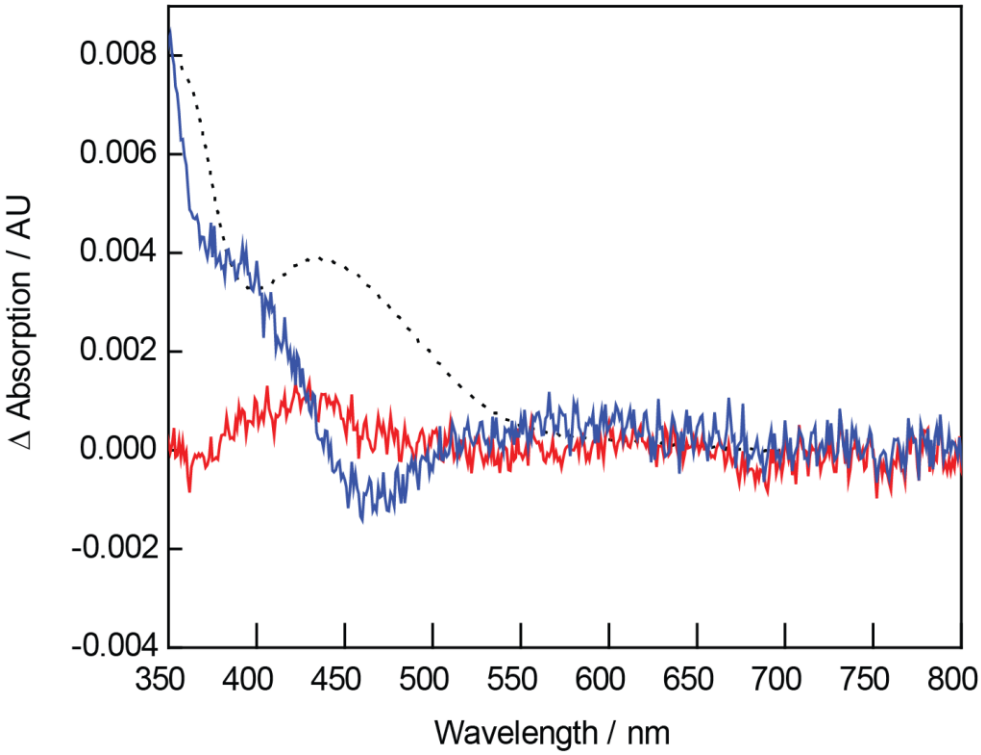

Figure S3: Spectra electrochemistry of **Fcam1** performed at pH 11. The baseline (red) indicates the blanked sample, and the difference spectrum (blue) is obtained upon oxidation of **Fcam1** at 850 V (vs NHE). The peak present at 570 nm is indicative of the **Fcam1**$^{+}$ moiety. The ground-state electronic absorption spectrum of **Fcam1** is shown (dotted line) for reference. The ferrocenium species appears to be less stable at higher pH and thus the observation of the 570 nm is obscured.

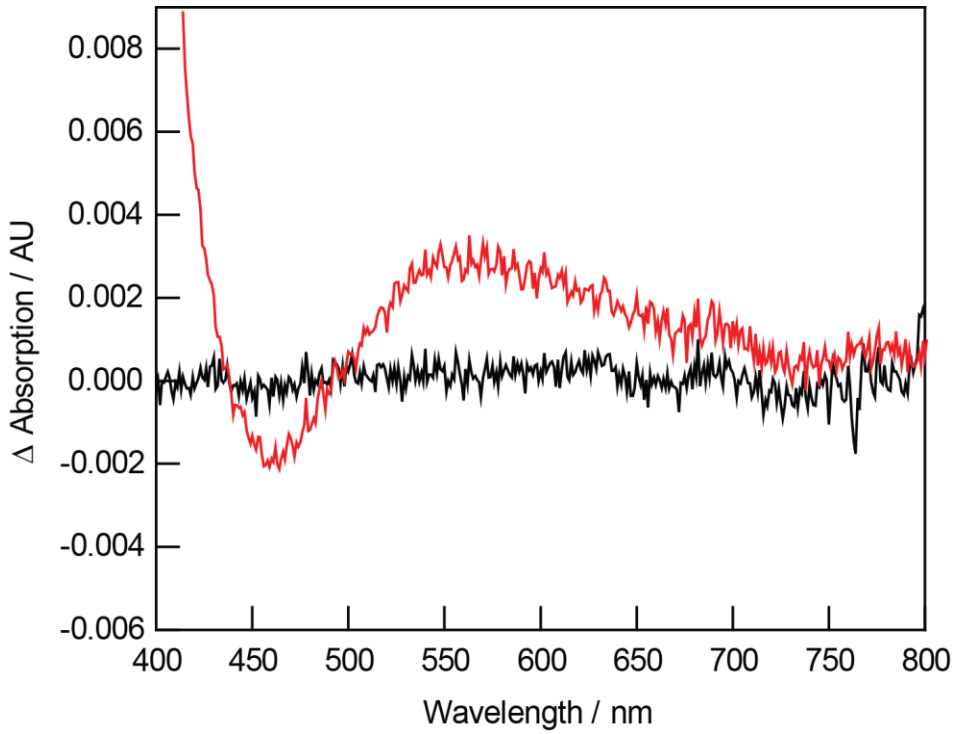

Figure S4: Spectra electrochemistry of **Fcam1** performed in acetonitrile. Depletion of **Fcam1** is observed 460 nm as the species is oxidized (at 1.10 V vs NHE) concomitant with the appearance of a peak at 570 nm corresponding to the formation of **Fcam1**$^{+}$. Acetonitrile appears to stabilize the ferrocenium-amidinium species, which allows for **Fcam1**$^{+}$ to be more clearly observed and enables confirmation of spectral assignment for the feature associated with **Fcam1**$^{+}$ at 570 nm.