Proton-Coupled Electron Transfer at Anthraquinone Modified Indium Tin Oxide Electrodes

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ABSTRACT: The molecular modification of electrode surfaces enables synthesis of materials with atomic-level specificity. In order to fully realize the benefits of molecularly modified materials, immobilized molecules must maintain their solution-phase reactivity upon attachment to surfaces. We report the noncovalent immobilization of a pyrene-appended anthraquinone derivative onto indium tin oxide electrodes. X-ray photoelectron spectroscopy and cyclic voltammetry confirm the attachment of anthraquinone on the electrode surface. Cyclic voltammetry is reported between pH 5 and 9. The reduction potential of immobilized anthraquinone shifts cathodically with increasing pH by 60 mV/pH unit, consistent with proton-coupled electron transfer. The electron transfer rate constant also increases with increasing pH. Analogous electrochemical experiments performed using a water-soluble anthraquinone derivative freely diffusing in aqueous solution exhibit the same pH dependence in reduction potential. Thus, anthraquinone maintains its proton-coupled electron-transfer behavior upon noncovalent immobilization onto indium tin oxide electrodes.

KEYWORDS: modified ITO electrodes, proton-coupled electron transfer, non-covalent attachment, anthraquinone

Molecular modification of conducting and semiconducting electrodes has been utilized to produce functional materials for a wide variety of applications such as catalysis, sensing, electronics, and optics. Tailoring electrode surfaces with molecular species enables atomic-level control of surface properties, including selective reactivity with incoming substrates. The attachment of molecular electrocatalysts onto electrode surfaces is also of significant interest for the enhancement of heterogeneous redox catalysis. Integrating molecular electrocatalysts with electrodes can exploit the high selectivity of the former to fabricate heterogeneous catalysts more suitable for use in conventional electrolytic or fuel cells. Additionally, immobilization of catalysts for electrolytic fuel forming reactions onto light absorbing materials could be used directly in monolithic photoelectrochemical cells, enabling direct sunlight driven electrolysis.

Catalytic reactions of interest include the production and utilization of chemical fuels and atom-efficient organic synthesis. Nearly all of these targeted redox reactions require both proton and electron transfer. In order to achieve optimal efficiency, electrocatalysts often utilize proton-coupled electron-transfer (PCET) steps to avoid high-energy catalytic pathways. Traditional methods of immobilizing molecular species onto electrode surfaces can significantly affect their reactivity due to changes in solvation and electron density of the molecule after adsorption and lateral interactions between attached molecules.

We recently developed a modular and robust molecular attachment strategy that integrates covalent and noncovalent attachment methods to immobilize molecules onto surfaces. Pyrene is covalently attached to an electrode surface which enables noncovalent physisorption of a pyrene-appended molecule of interest via π−π interactions. Our attachment route circumvents many of the synthetic challenges that result from directly immobilizing sensitive molecular complexes to surfaces through traditional covalent functionalization. We demonstrated the viability of our hybrid attachment technique by attaching ferrocene to gold surfaces and establishing facile electron transfer between the electrode and immobilized ferrocene. Subsequent work applied this methodology to the attachment of ferrocene to indium tin oxide (ITO) electrodes, highlighting the versatility of this approach across different electrode surfaces. Furthermore, our attachment method demonstrates enhanced electron-transfer kinetics compared to an analogous covalent attachment method. Extension of our attachment system to redox catalysts that utilize PCET requires the retention of solution-phase behavior for molecular species immobilized onto the surface.

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Anthraquinones are an ideal molecular species to compare proton-coupled electron-transfer properties before and after immobilization. Quinones and their derivatives are biologically prevalent organic compounds with redox chemistry that plays a vital role in energy storage and transduction. The biological importance of quinones has prompted numerous studies analyzing their electrochemical properties both in solution and immobilized on surfaces. Quinones undergo a two-electron reduction to give the quinone dianion, the dihydroquinone, or the hydrogen-bonded quinone dianion depending on the nature of the solvent. In buffered solution with a pH lower than the pKₐ of the phenolic protons, the two-electron reduction is coupled with two protonation steps to form the dihydroquinone.

In the present work, we immobilize a pyrene-appended anthraquinone (Pyr(AQ)₂) onto pyrene-bound ITO electrodes as depicted in Scheme 1 and analyze the pH-dependent electrochemical behavior of the system. We also report the pH-dependent electrochemistry of a water-soluble anthraquinone derivative, sodium anthraquinone-2-sulfonate (AQS), in order to compare the proton-coupled electron transfer of anthraquinone immobilized on ITO surfaces and diffusing in solution. Our results indicate that the thermodynamic and kinetic electrochemical behavior of Pyr(AQ)₂ immobilized on ITO surfaces is analogous to the electrochemical behavior exhibited by AQS in aqueous solution. The retention of the pH-dependent electrochemical behavior of anthraquinone after attachment to the electrode surface illustrates the feasibility of extending our methodology to proton-coupled redox catalysis.

## EXPERIMENTAL SECTION

### General Procedures

All reactions and manipulations were performed under an atmosphere of N₂ unless otherwise specified. Solvents were degassed by sparging with argon. Nonaqueous solvents were dried by passing through columns of neutral alumina or molecular sieves under an inert atmosphere. ITO on borosilicate glass with a thickness of 0.5 mm and a sheet resistance of 5–15 Ω/sq was purchased from Delta Technologies. 1-Vinylpyrene and 1-[bis(2-anthraquinonyl)aminomethyl]pyrene were prepared using previously published procedures. All other materials and reagents were purchased from commercial suppliers and used without purification (Aldrich and Fisher). All buffers were prepared with water purified by a Barnstead NANOpure ultrapure water system. The pH of buffered solutions was measured using a Thermo Scientific Orion Star A216 pH meter.

### Physical Methods

X-ray photoelectron spectra were acquired with a Kratos Analytical AXIS Supra spectrometer utilizing monochromatic Al Kα radiation (1486.7 eV, 250 W) under ultrahigh-vacuum (UHV) conditions (∼10⁻⁹ Torr). Survey spectra were collected with a pass energy of 160 eV, and high-resolution scans were performed with a pass energy of 20 eV. The binding energies were referred to the C 1s signal at 285 eV. Spectral data were analyzed using computer-aided surface analysis for X-ray photoelectron spectroscopy (CasaXPS). Shirley or linear backgrounds and Gaussian–Lorentzian line shapes were used to model peaks.

### Electrochemical Experiments

Three-electrode cyclic voltammetry experiments were performed with a Pine Wavedriver 10 potentiostat and Aftermath software (Version 1.4.7881). Modified ITO electrodes were cycled between 0 and −0.75 V vs SCE (saturated calomel electrode) prior to analysis to ensure retention of immobilized species throughout electrochemical experiments. Aqueous experiments were performed in 100 mM buffered solutions (pH 5 and 6, citrate buffer; pH 7 and 8, 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES buffer); pH 9, borate buffer) with 100 mM KCl as the supporting electrolyte, and nonaqueous experiments were performed in 100 mM NButPF₆ in anhydrous dimethylformamide (DMF). Solution-phase experiments were performed using a 1 mm diameter glassy carbon disk working electrode. A glassy carbon rod was used as the counter electrode in all electrochemical experiments. Aqueous potentials are referenced to SCE, and nonaqueous potentials are referenced to Fe(C₅H₅)₂⁺⁻/0. Chromamperometry was performed on a 1 mM Fe(C₅H₅)₂ solution in CH₂CN with 100 mM NButPF₆ as electrolyte in order to determine the electroactive surface area of the glassy carbon disk working electrode. After a 15 s induction period at −0.51 V vs Fe(C₅H₅)₂⁺⁻/0, the potential was stepped to 0.49 V vs Fe(C₅H₅)₂⁺⁻/0 and the current decay was recorded. The electroactive surface area was then calculated using the Cottrell equation, the literature value for the diffusion constant of Fe(C₅H₅)₂ in CH₂CN (2.4 × 10⁻⁵ cm²/s), and the slope of the plot of the current vs (time)⁻¹/₂ for 0.01 s ≤ time ≤ 0.2 s. All reported peak current densities are corrected for capacitive currents using the Regression baseline mode in Aftermath software.

### Substrate Modification

ITO electrodes were cleaned by immersing samples in a series of solvents at 50 °C for 10 min each. The order of solvents was as follows: trichloroethylene, acetone, and methanol. The electrodes were rinsed with H₂O and dried under a stream of air after each solvent. Electrodes were functionalized immediately after cleaning. Clean ITO samples were placed in vial, ITO side facing up, and immersed in a 1 mM solution of 1-vinylpyrene in anhydrous toluene. The solution was heated to 65 °C for 24 h. The samples were removed from the vial and rinsed with anhydrous toluene and CH₂Cl₂ to yield pyrene-modified ITO (ITO-Pyr). ITO/Pyr samples were placed in a 2.5 mM solution of 1-[bis(2-anthraquinonyl)aminomethyl]pyrene in anhydrous CH₂Cl₂ for 12 h. The samples were removed from the solution, rinsed with anhydrous CH₂CN to remove loosely bound species, and dried to give noncovalently modified ITO/Pyr[Pyr(AQ)₂].

## RESULTS AND DISCUSSION

### Modification of ITO Electrodes

1-Vinylpyrene and 1-[bis(2-anthraquinonyl)aminomethyl]pyrene were prepared using reported procedures. Indium tin oxide was covalently modified with 1-vinylpyrene following proce-
dures previously published by our laboratory with the following modifications: clean ITO samples were immersed in toluene solutions of 1-vinylpyrene at 65 °C for 24 h to yield pyrene-modified ITO (ITO|Pyr). Subsequent attachment of Pyr(AQ)₂ was achieved by immersing ITO|Pyr in CH₂Cl₂ solutions of Pyr(AQ)₂ for 12 h, yielding noncovalently modified ITO|PyrPyr(AQ)₂. Pyr(AQ)₂ coverage, calculated by integrating the cathodic peak of the cyclic voltammograms (CVs) of ITO|PyrPyr(AQ)₂, ranged from 40 to 80 pmol/cm². These coverage values are an order of magnitude greater compared to the values reported in our previous work on the immobilization of 1-pyrenylferrocene on ITO|Pyr. The increase in coverage may be due to hydrogen-bonding interactions between the Pyr(AQ)₂ and the terminal hydroxyl groups on the ITO surface and the potential for additional π–π interactions between anthraquinone and the surface-bound pyrene.

Characterization of Modified ITO Electrodes. X-ray photoelectron spectroscopy (XPS) was used to characterize modified ITO electrodes. The survey spectra of bare ITO, ITO|Pyr, and ITO|PyrPyr(AQ)₂ are shown in Supporting Information Figures S1–S3. Each spectrum exhibits peaks expected from indium, tin, oxygen, and carbon. Upon attachment of 1-vinylpyrene to the ITO surface, the C 1s peak in the XPS spectrum increases in intensity while the peaks attributed to indium, tin, and oxygen decrease in intensity, consistent with the formation of a carbonaceous thin film on the electrode surface. Noncovalent attachment of Pyr(AQ)₂ onto ITO|Pyr results in the appearance of an N 1s peak in the XPS spectrum. The high-resolution XPS spectrum of the N 1s region of ITO|PyrPyr(AQ)₂ is displayed in Figure 1. The peak at 400 eV, attributed to the tertiary amine of Pyr(AQ)₂, is consistent with literature reports of alkyl amines deposited on carbon electrodes. The high-resolution XPS spectra of the N 1s region of ITO and ITO|Pyr, displayed in Figures S4 and S5, do not exhibit any peaks. These results confirm the presence of Pyr(AQ)₂ on the modified electrode surface.

Electrochemical Behavior of Modified ITO. The cyclic voltammogram (CV) of ITO|PyrPyr(AQ)₂ in pH 7 HEPES buffer is displayed in Figure 2 (green trace). The CV exhibits a redox couple with anÆ1/2 of −0.52 V vs SCE attributed to the two-electron reduction of anthraquinone. TheÆ1/2 of the two-electron reduction agrees well with reported literature values of the reduction of immobilized anthraquinone on gold and carbon nanotubes at pH 7.

Due to the insolubility of Pyr(AQ)₂ in water, the variable scan rate CVs and the corresponding peak current vs scan rate plot of Pyr(AQ)₂ was measured in dimethylformamide (DMF) (Figure S6). In DMF solution, the anthraquinone moieties of Pyr(AQ)₂ undergo two quasi-reversible one-electron reductions at −1.33 and −2.00 V vs Fe(C₅H₅)₂⁺/0 and a third irreversible reduction at −2.56 V vs Fe(C₅H₅)₂⁺/0. The two one-electron events align with previous reports wherein quinones and their derivatives undergo two one-electron reductions in aprotic solvents and a single two-electron reduction in protic solvents.

In addition to the CV of ITO|PyrPyr(AQ)₂, Figure 2 displays the CVs of bare ITO, ITO|Pyr, and a bare ITO electrode soaked in a solution of Pyr(AQ)₂ (denoted as ITO|Pyr(AQ)₂) in pH 7 HEPES buffer. The CVs of bare ITO (black trace) and ITO|Pyr (gray trace) do not display notable features, ensuring the couple exhibited in the CV of ITO|PyrPyr(AQ)₂ is attributed to Pyr(AQ)₂. The CV of ITO|Pyr(AQ)₂ (black dashed trace), which has no pyrene monolayer, also exhibits a redox couple at the same potential observed with ITO|PyrPyr(AQ)₂ (green trace). We hypothesize that Pyr(AQ)₂ hydrogen bonds to the terminal hydroxyl groups on the ITO surface, enabling adsorption without the presence of the pyrene monolayer.

Integration of the cathodic peak of the CV of ITO|PyrPyr(AQ)₂ yields an electrochemically active coverage of 20 pmol/cm². Thus, the pyrene monolayer allows for two to four times the Pyr(AQ)₂ coverage compared to physisorption without a pyrene monolayer. Finally, the variable scan rate cyclic voltammetry of ITO|PyrPyr(AQ)₂ at pH 7 and the corresponding peak current density vs scan rate plot is shown in Figure 3. Peak currents vary linearly with scan rate, confirming that Pyr(AQ)₂ is bound to the surface.

In order to probe the dependence of ITO|PyrPyrPyr(AQ)₂ reduction on pH, CVs were recorded in buffered solutions between pH 5 and 9. The variable scan rate CVs and corresponding peak current density vs scan rate plots of ITO|PyrPyrPyr(AQ)₂ at pH 5, 6, 8, and 9 are displayed in Figures S7–

Figure 1. High-resolution XPS spectrum of the N 1s region of ITO|PyrPyr(AQ)₂.

Figure 2. Cyclic voltammogram of ITO|PyrPyrPyr(AQ)₂ and control experiments performed at 50 mV/s in 100 mM pH 7 HEPES buffer with 100 mM KCl as a supporting electrolyte.
The CVs at each pH display the two-electron redox couple corresponding to the reduction of anthraquinone to dihydroquinone. At all pH values, peak current varies linearly with scan rate, ensuring the attachment of Pyr(AQ)2 on the ITO surface across all pH conditions. The $E_{1/2}$ at each pH is listed in Table 1, and the plot of $E_{1/2}$ vs pH is shown in Figure 4. As the pH increases, the $E_{1/2}$ decreases linearly by 60 mV per pH unit. The linear dependence is consistent with a two-electron/two-proton process, confirming the formation of the dihydroanthraquinone upon reduction within the tested pH range.$^{44,56}$ Although we would expect a more shallow slope above pH 9 due to deprotonation of the phenolic protons, we were unable to perform electrochemical experiments under these conditions due to the instability of ITO at high pH.$^{57}$

Cyclic voltammetry of sodium 2-anthraquinonesulfonate, a water-soluble anthraquinone derivative, was performed to compare the electrochemical behavior of anthraquinone on the ITO surface and diaphragm using in solution. The variable scan rate cyclic voltammetry of AQS at pH 5−9 is displayed in Figures S11−S15. As seen in the CVs of ITO|Pyr|Pyr(AQ)2, AQS exhibits a two-electron reduction at all pH conditions studied, corresponding to reduction to the dihydroanthraquinone species. The peak currents of AQS vary linearly with the square root of the scan rate, indicative of a diffusion-limited electrochemical process. The $E_{1/2}$ value for the reduction of AQS at each pH is listed in Table 1. The reduction potential of AQS in solution is about 50 mV more positive than that of ITO|Pyr|Pyr(AQ)2. This shift in reduction potential is expected based on the strong electron-withdrawing character of the sulfonate group on AQS, enabling reduction at milder potentials. As seen in the reduction of ITO|Pyr|Pyr(AQ)2, the $E_{1/2}$ of AQS decreases linearly with pH by 50 mV/pH unit (Figure 4), indicating a coupled two-electron/two-proton process. These results highlight the retention of proton-coupled electron transfer in anthraquinone upon noncovalent attachment to ITO surfaces.

**Electron-Transfer Kinetics of Modified ITO.** In the variable scan rate cyclic voltammograms of ITO|Pyr|Pyr(AQ)2 in Figures 3 and S7−S10, the difference between the cathodic and anodic peak potentials increases with increasing scan rate. Under ideal reversible conditions, the peak-to-peak separation of immobilized redox-active species is expected to be 0 mV.$^{56}$ The increase in peak-to-peak separation with faster scan rate suggests slow electron transfer between ITO and Pyr(AQ)2.

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**Table 1. Redox Potentials and Rate of Electron Transfer ($k_{app}$) of ITO|Pyr|Pyr(AQ)2 and Anthraquinone Sulfonate (AQS) under Varying pH Conditions**

<table>
<thead>
<tr>
<th>pH (buffer)</th>
<th>$E_{1/2}$ (V vs SCE)</th>
<th>$k_{app}$ (cm/s)</th>
<th>$E_{1/2}$ (V vs SCE)</th>
<th>$k_{app}$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 (citrate)</td>
<td>−0.39</td>
<td>0.01 ± 0.01</td>
<td>−0.34</td>
<td>0.003 ± 0.001</td>
</tr>
<tr>
<td>6 (citrate)</td>
<td>−0.45</td>
<td>0.02 ± 0.01</td>
<td>−0.40</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>7 (HEPES)</td>
<td>−0.52</td>
<td>0.2 ± 0.1</td>
<td>−0.46</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>8 (HEPES)</td>
<td>−0.57</td>
<td>0.4 ± 0.1</td>
<td>−0.51</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>9 (borate)</td>
<td>−0.63</td>
<td>0.4 ± 0.1</td>
<td>−0.55</td>
<td>0.8 ± 0.3</td>
</tr>
</tbody>
</table>
Electron-transfer kinetics can be analyzed using the following Laviron equations:\textsuperscript{58}

\[ E_{p,a} = E^{°a} - \frac{2.3RT}{nF} \log \left( \frac{anFk_{app}}{RTk_{app}} \right) \]  

\[ E_{p,c} = E^{°c} - \frac{2.3RT}{(1 - \alpha)nF} \log \left( \frac{(1 - \alpha)nFk_{app}}{RTk_{app}} \right) \]  

where \( E_{p,a} \) is the potential of the anodic peak, \( E_{p,c} \) is the potential of the cathodic peak, \( E^{°a} \) is the formal potential calculated by averaging the anodic and cathodic potentials at slow scan rates, \( v_a \) and \( v_c \) are the critical scan rates, \( \alpha \) is the electron-transfer coefficient, \( k_{app} \) is the apparent rate constant, \( R \) is the ideal gas constant, \( F \) is the Faraday constant, and \( n \) is the number of electrons transferred. Electron-transfer parameters \( (v_a, v_c, \alpha, \text{and } k_{app}) \) are determined by plotting \( E_p - E^{°} \) against the log of the scan rate to generate a trumpet plot. \( v_a \) and \( v_c \) are determined by extrapolating the linear portions of the plot where \( (E_p - E^{°}) > 100 \text{ mV/n} \) to 0 and \( \alpha \) is obtained from the slopes of the linear fits. \( k_{app} \) is calculated using \( v_a, v_c, \alpha \) and reported as the average of \( k_{app,a} \) and \( k_{app,c} \) across three individually prepared samples. A detailed sample calculation can be found in the Supporting Information.

The trumpet plot for ITO/Pyr/Pyr(AQ)\textsubscript{2} at pH 7 is shown in Figure 5. Using eqs 1 and 2, \( k_{app} \) for ITO/Pyr/Pyr(AQ)\textsubscript{2} at pH 7 was calculated to be 0.2 ± 0.1 s\textsuperscript{-1}. This rate is significantly slower than the electron transfer rate constant reported in our previous work on the immobilization of 1-pyrenylferrocene on ITO/Pyr (100 s\textsuperscript{-1}). \textsuperscript{48} It is possible that the distance between the redox-active anthraquinone moieties of Pyr(AQ)\textsubscript{2} and ITO is greater than the distance between ferrocene and ITO in our previous studies, which would result in slower electron transfer.\textsuperscript{59} However, \( k_{app} \) for ITO/Pyr/Pyr(AQ)\textsubscript{2} is consistent with literature reports of anthraquinone attached to gold electrodes at pH 7.\textsuperscript{34,47} The slow electron transfer relative to 1-pyrenylferrocene on ITO/Pyr may therefore be due to intrinsically slow electron transfer between an electrode and anthraquinone. The trumpet plots for ITO/Pyr/Pyr(AQ)\textsubscript{2} at pH 5, 6, 8, and 9 are displayed in Figure S16, and \( k_{app} \) at each pH is listed in Table 1. It should be noted that while the Pyr(AQ)\textsubscript{2} coverage varies between 40 and 80 pmol/cm\textsuperscript{2}, we do not see coverage dependence on \( k_{app} \). Within the pH range explored in this study, electron transfer between ITO and immobilized Pyr(AQ)\textsubscript{2} increases in rate as pH increases. Similar increases were observed in monolayers of 1,4-hydroxynaphthaquinone on gold.\textsuperscript{60} However, we hesitate to draw firm conclusions from the \( k_{app} \) dependence on pH because the buffer composition changes across the pH range. The identity of the buffer can impact proton-transfer processes, leading to changes in mechanism or variable proton-transfer rates.\textsuperscript{58} These variations may contribute to the inconsistent \( k_{app} \) vs pH relationships for immobilized quinone species in the literature.\textsuperscript{39,44,46} The limited pH range of citrate, HEPES, and borate buffers precluded exploring the rate of electron transfer using a single buffer across the entire pH range studied. CVs of ITO in phosphate buffer, which has a larger pH range, displayed inconsistent electrochemical features at cathodic potentials, likely due to a binding event between the buffer and ITO (Figure S19). The inconsistency of this feature prevented a thorough analysis of the Pyr(AQ)\textsubscript{2} redox couple. More detailed analyses of the electron-transfer rate on pH for immobilized anthraquinone species can be found in the literature.\textsuperscript{39,44,46–48}

Similar to the CVs of ITO/Pyr/Pyr(AQ)\textsubscript{2}, the CVs of AQ\textsubscript{S} exhibit greater peak separation with increasing scan rate. Electron transfer rate constants for AQ\textsubscript{S}, determined by applying the Kochi method to the experimentally determined peak separation (see Supporting Information),\textsuperscript{47} are listed in Table 1. The electron transfer rate constant for AQ\textsubscript{S} increases with increasing pH, similar to the \( k_{app} \) dependence on pH exhibited for ITO/Pyr/Pyr(AQ)\textsubscript{2}. Again, we note the increase in \( k_{app} \) may not reflect the change in proton activity across the pH range but, instead, may be due to the variation in buffer composition.

**CONCLUSIONS**

Pyrene-appended Pyr(AQ)\textsubscript{2} was successfully immobilized onto pyrene-bound indium tin oxide (ITO) electrodes using a versatile hybrid noncovalent attachment method. X-ray photoelectron spectroscopy and cyclic voltammetry confirmed the attachment of Pyr(AQ)\textsubscript{2} on the surface. Facile electron transfer between the ITO electrode and immobilized Pyr(AQ)\textsubscript{2} is observed across a range of pH conditions. In the pH range studied, the two-electron reduction of anthraquinone is coupled with two proton transfers to form dihydroanthraquinone. The electrochemical behavior of immobilized Pyr(AQ)\textsubscript{2} aligns with the pH-dependent cyclic voltammetry of AQ\textsubscript{S} dissolved in buffered solution. These results highlight the thermodynamic similarities between proton-coupled electron transfer of anthraquinone in solution and on the ITO surface. Kinetic analysis of the electron transfer for both ITO/Pyr/Pyr(AQ)\textsubscript{2} and AQ\textsubscript{S} in solution exhibits an increase in electron transfer rate constant with increasing pH, suggesting faster electron transfer at higher pH. The retention of molecular character and proton-coupled electron-transfer processes using this attachment method is a critical component of its applicability for heterogenizing redox catalysts onto electrodes.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsaem.8b01568.
X-ray photoelectron spectra, variable scan rate cyclic voltammograms, and analysis of electron transfer kinetics.

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Notes

The authors declare no competing financial interest.

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