

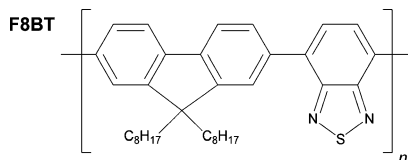
Single-Molecule Spectroelectrochemistry (SMS-EC)

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We describe an approach to the determination of the thermodynamics and kinetics of electron transfer (eT) to single immobilized molecules based on single-molecule spectroelectrochemistry (SMS-EC). Such eT reactions are of interest in solar cells, flat-panel displays, and chemical sensors.^{1–5} The extreme heterogeneity of inorganic/organic interfaces has been a key obstacle to developing a quantitative, molecular-level understanding of such devices.^{6–8} Here we introduce a powerful new technique for studying eT processes at highly heterogeneous interfaces; SMS-EC measures electrochemical behavior one molecule at a time, offering for the first time the distribution of key electrochemical variables, such as the half-wave potential, $E_{1/2}$, not just the ensemble average. SMS-EC is used herein to study the oxidation at an indium tin oxide (ITO) electrode of single molecules of the organic conjugated polymer poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT), used in solar cells and OLEDs.



The experiments employed an electrochemical cell (Figure 1A) with a transparent (ITO) working electrode, a gold counter electrode, and a silver wire quasi-reference electrode (QRE). Potentials relative to a ferrocenium/ferrocene (Fc/Fc⁺) couple internal standard (introduced into the cell after the SMS-EC data were acquired) are about 0.20 ± 0.04 V more negative than those of QRE. The reported potentials herein are relative to QRE. The ITO electrode was spin-coated with thin <5 nm, well-separated polystyrene (PS)/F8BT spots. Dispersion in PS is necessary to suppress F8BT aggregation. The single F8BT molecules (MW = 100 kg/mol, ~4 nm in radius calculated assuming a collapsed conformation (spherical shape), and a density of 0.8 g/mL) were large enough that many span the PS layer and are in simultaneous contact with both the ITO electrode and electrolyte solution. F8BT was present at ~1 molecule/ μm^2 at the interface, allowing for the imaging (Figure 1B) of hundreds of single F8BT molecules by wide-field total internal reflectance fluorescence (TIRF) microscopy using 488 nm excitation.

In a typical experiment, the potential of the working electrode (vs QRE) of a pristine cell was linearly scanned (0–1.5 V) at a scan rate, ν , of 100 mV/s (Figure 1C) while simultaneously measuring the fluorescence intensities, $I_{\text{fl}}(t)$, as a function of time of many single molecules (e.g., Figure 1D). Most $I_{\text{fl}}(t)$ curves exhibit a large intensity drop associated with electrochemical oxidation of F8BT (with a redox potential of about 1.36 V vs Fc/Fc⁺, as determined from separate studies of solutions or films of F8BT in MeCN/0.2 M LiClO₄). Intensity fluctuations due to photon shot noise and photochemical-induced blinking are also apparent in the individual trajectories. On the contrary, when the $I_{\text{fl}}(t)$ curves are

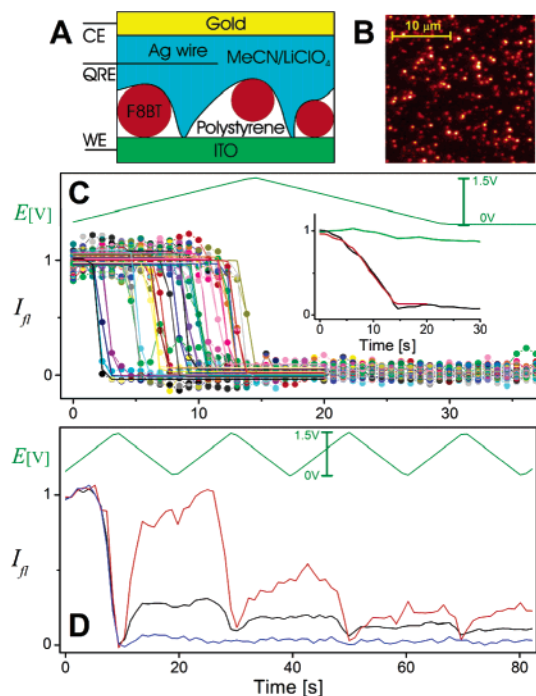


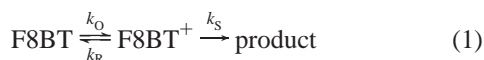
Figure 1. (A) SMS-EC cell configuration. (B) Wide-field TIRF image for a SMS-EC cell. (C) Examples of normalized single-molecule fluorescence intensity trajectories (data points) that were obtained while applying the bias shown by the top green curve, and corresponding fits ($I_{\text{fl}}(t) \approx 1/(1 + \exp((E - E_{1/2,i})/\delta E))$) with a variable $E_{1/2,i}$ for each molecule and a global δE of <0.1 eV. Inset: Ensemble average of 200 trajectories (black curve) and of their corresponding fits (red curve). The green curve shows the ensemble average of 200 trajectories obtained at zero bias. (D) Ensemble average of normalized single-molecule fluorescence intensity trajectories (150 molecules, black curve) and sub-ensembles constructed by selecting individual trajectories with quenching depths smaller than 30% (red line) and larger than 90% (blue line), in the 18–20 s time range. The green curve shows the applied bias.

recorded during the same period of time while applying a constant potential of 0 V, the average fluorescence intensity does not change appreciably (see inset of Figure 1C, green curve). Fluorescence of F8BT molecules and other isolated conjugated polymer molecules is quenched with an efficiency approaching 100% for injection of a single positive charge.^{9,10}

SMS-EC is therefore able to indirectly measure single oxidation events at room temperature, something that is impossible by measuring the current in conventional electrochemistry. By observing the fluorescence, a huge amplification factor is obtained. In fact, the $I_{\text{fl}}(t)$ curves are effectively single-molecule voltammograms for the relevant oxidation reaction.¹¹ Thus, the bias where the normalized $I_{\text{fl}}(t)$ is quenched by 50% is an indirect measure of the electrochemical half-wave potential, $E_{1/2}$, for a reversible (Nernstian) reaction. A small but significant fraction of F8BT molecules (typically 20%) exhibit no evidence of oxidation during the

experiment because these F8BT molecules are not in contact with the ITO electrode.

Figure 1D portrays the ensemble averaged $I_{fl}(t)$ data for ~ 150 molecules recorded with four cycles at $v = 150$ mV/s (black curve). Although the oxidation process is essentially irreversible at slower scan rates, it is partially reversible at this v . The irreversibility of the oxidation for some molecules is assigned to a subsequent chemical reaction (i.e., a EC reaction sequence, e.g., deprotonation or reaction with dioxygen),¹² producing an unknown reacted site in the polymer chain that quenches fluorescence (eq 1).



Here k_O and k_R are the rate constants for oxidation and the reverse reduction reactions, and k_S is the rate constant for the subsequent reaction. This reaction is absent when F8BT is oxidized by an electrode in solid films (pure or diluted with an inert polymer).¹¹ The time scale of this reaction (k_S^{-1}) must be comparable to the period for which the potential significantly exceeds $E_{1/2}$ since a significant fraction of the molecules exhibit reversible oxidation.

Sub-ensemble averaged $I_{fl}(t)$ data for molecules that were reversibly (red curve) oxidized in the first cycle of the potential are shown in Figure 1D. The small fraction of F8BT molecules that survive the first electrical oxidation cycle subsequently react in later cycles. For the reversibly oxidized molecules, the $E_{1/2,i}$ values are narrowly distributed with a standard deviation of 0.2 V, which is close to our experimental resolution, suggesting both a very small spread in $E_{1/2}$ energies for the different conjugated F8BT molecules in the sample and additionally a uniform electrochemical potential at the electrode. In fact, the sub-ensemble data are highly consistent with a calculated curve based on the Marcus theory for electrochemical kinetics using a single $E_{1/2}$ value of 1.5 eV.¹² The calculation, furthermore, strongly suggests that the *chemically* reversible component of oxidation is essentially electrochemically reversible (i.e., in the Nernstian limit).

In contrast, the irreversibly oxidized sub-ensemble (blue curve in Figure 1D) exhibits a broad distribution of $E_{1/2}$ values with some molecules oxidizing at potentials as low as 0.2 V; see Figure 1C. We assign this surprising low potential (0.2–1 V) mode of oxidation to electrochemical oxidation of singlet electronically excited F8BT molecules followed by trapping of the oxidized molecules by eq 1. Figure 2A,B portrays the yield of oxidation-induced quenching as a function of bias with the excitation intensity “on” and “off” during the oxidation step, respectively. The irreversible oxidation of ground state F8BT does not occur measurably until the potential exceeds 1.4 V and continues over this potential with only a small increase in effective rate (as implied from the yield). In contrast, the excited state reaction has a significant rate over a broad potential range, as also seen in separate photoelectrochemical experiments (data not shown).

The photochemical nature of the low potential process is further demonstrated in Figures 2C, where it is shown that the oxidation at 0.6 V requires simultaneous optical irradiation. This is not unexpected since the oxidation of the singlet is energetically favorable above ~ -1.0 V, that is, the difference in the half-wave potential of the ground state oxidation and the energy of the singlet excited state. The oxidation at 1.6 V, however (Figure 2D), occurs readily in the dark.

In summary, a new technique, single-molecule spectroelectrochemistry (SMS-EC), has been used to study the electrochemical

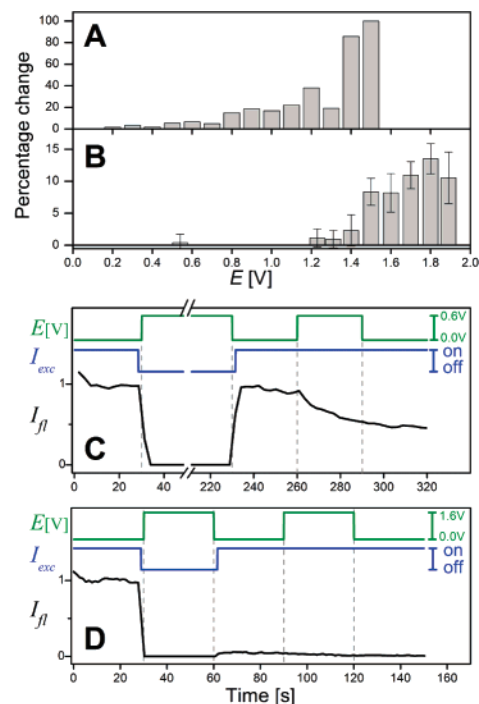


Figure 2. Percent oxidation yield as a function of applied bias with (A) continuous optical irradiation and scanning of the bias, and (B) with alternatively pulsed electrical bias (from $V = 0$) and optical irradiation during the oxidation process. (C) and (D) show the recorded ensemble fluorescence intensity for ~ 200 molecules (black curve) obtained under different combinations of applied potential (green curve) and excitation intensity (blue curve).

oxidation of the conjugated polymer F8BT at an ITO electrode. The results reveal both excited singlet state and ground state oxidation, and furthermore show that the latter process occurs with a narrow distribution of single-molecule half-wave potential values.

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Supporting Information Available: Details on sample preparation and assembly. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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