SUPPLEMENTARY INFORMATION

An Electrochemical Reaction-Diffusion Model of the Photocatalytic Effect of Photosystem I Multilayer Films

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Extraction of Values for ϕ_R and ϕ_O From Extended Chronoamperometry Scans

To establish values for ϕ_R and ϕ_O, a least squares fitting routine was applied to a numerical model established within the MATLAB partial differential equation solver, *pdepe* (Figure S1). The boundary conditions were (1) Butler-Volmer kinetics at the electrode surface (x=0) and (2) zero flux condition at the length of the cell $\left(\frac{dC_i}{dx} = 0\right)$, which was made long enough (2000 μm) such that concentrations were not altered at the far boundary for any applied potential used. Within the control volume, we formulated two regions. First, within the PSI film ($0 < x \leq H$), a modified version of Fick's second law was applied that included ϕ_i. No reactive term associated with PSI/mediator electron transfer reactions, $r_{v,i}$, was included since the measurements were conducted in the dark. Second, the bulk electrolyte ($x > H$) was modeled using Fick's second law. The fitting routine utilized *fminsearch* to search for values of ϕ_R and ϕ_O that minimized the error between experimental and modeled chronoamperometry curves (90 s duration) at various applied bias (-200 mV, -100 mV, -50 mV, -10 mV, 10 mV, 50 mV, 100 mV, 200 mV). The fit is accurate, as evident in the first 100 s of chronoamperometry in Figure 6a of the main text.

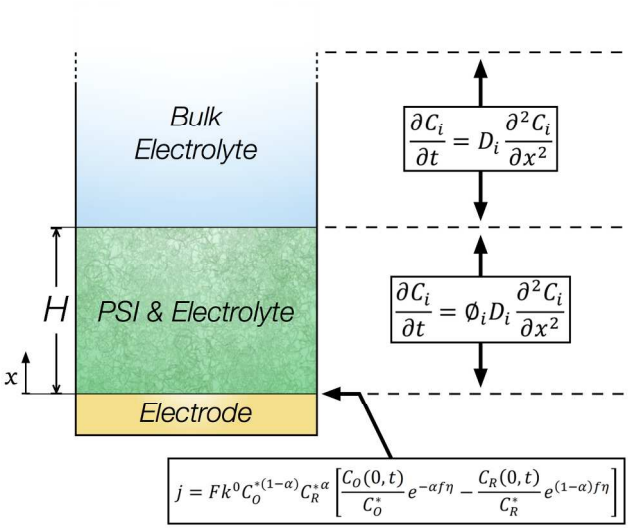

Figure S1. Layout and pertinent equations for model used to extract values of ϕ_i. Extended chronoamperometry at various applied bias of PSI multilayer films on Au/AET electrodes was performed to establish an experimental value for ϕ_R and ϕ_O which relate constraints on the diffusion coefficient due to free volume reduction and electrostatic interactions incurred by the dense protein film on the diffusion of redox ions, R and O. All tests were performed with a 650 nm-thick PSI multilayer film atop a Au/AET electrode that was immersed in an electrolyte containing 0.1 mM R, 0.1 mM O, 100 mM KCl, and 5 mM tris (pH 8.0). All tests were performed in the dark.

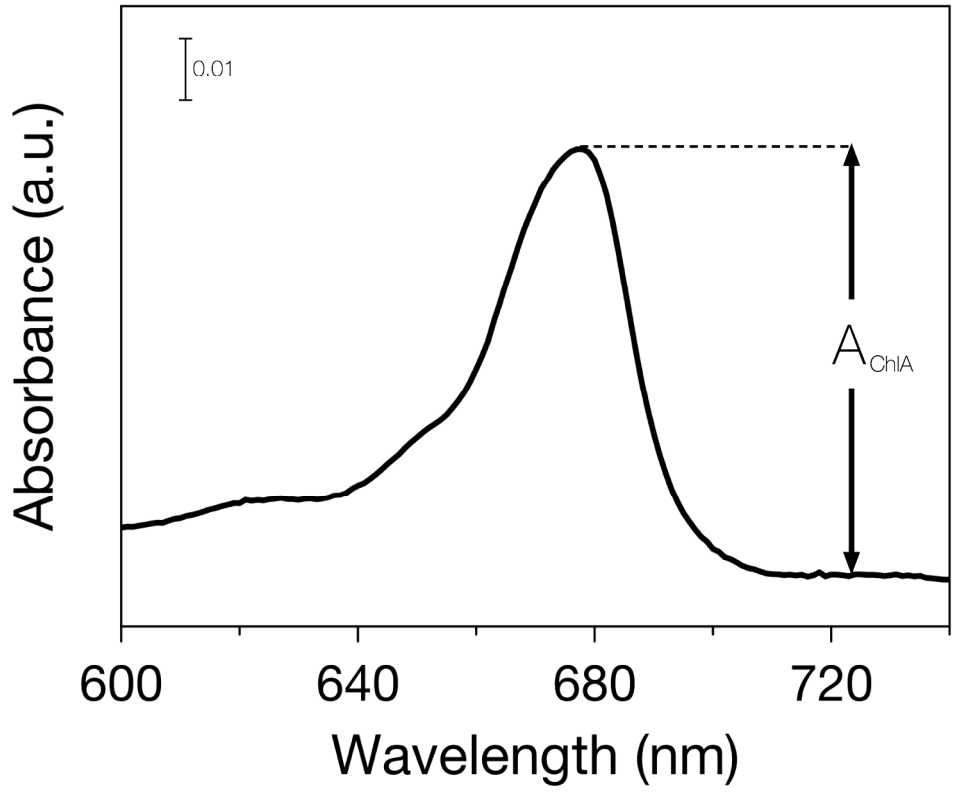

Figure S2. The concentration of chlorophyll in a PSI multilayer film, C_{chl}, was established *via* spectrophotometry of solutions used in drop casting by applying the Beer-Lambert Law to the absorbance peak of ChlA at 680 nm for PSI solutions that were diluted 50x. Above, we find this absorbance is 0.07, which equates to 84 mM in an undiluted PSI solution.

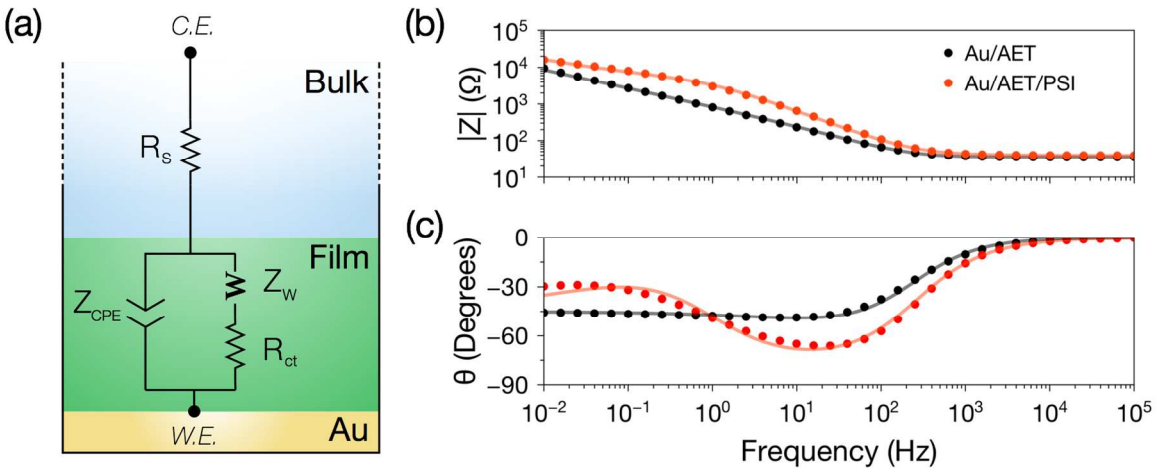

Figure S3. (a) A Randles circuit model was used to determine the standard rate constant, k^0, of a Au/AET electrode coated by a PSI multilayer film. Plots of (b) magnitude and (c) phase angle versus frequency of a Au/AET electrode and a Au/AET/PSI electrode reveal significant differences. Bare electrodes have low R_{ct}, which is indicative of high k^0 (~.1 cm/s). The addition of a PSI multilayer occludes both the surface and the immediately surrounding volume of the electrode and thus incurs a significant increase in R_{ct} and corresponding increase in k^0 (5.0×10^{-4} cm/s). All EIS measurements were conducted using an aqueous electrolyte incorporating 0.1 mM $Fe(CN)_6^{4-}$, 0.1 mM $Fe(CN)_6^{3-}$, 100 mM KCl, and 5 mM tris (pH 8.0).

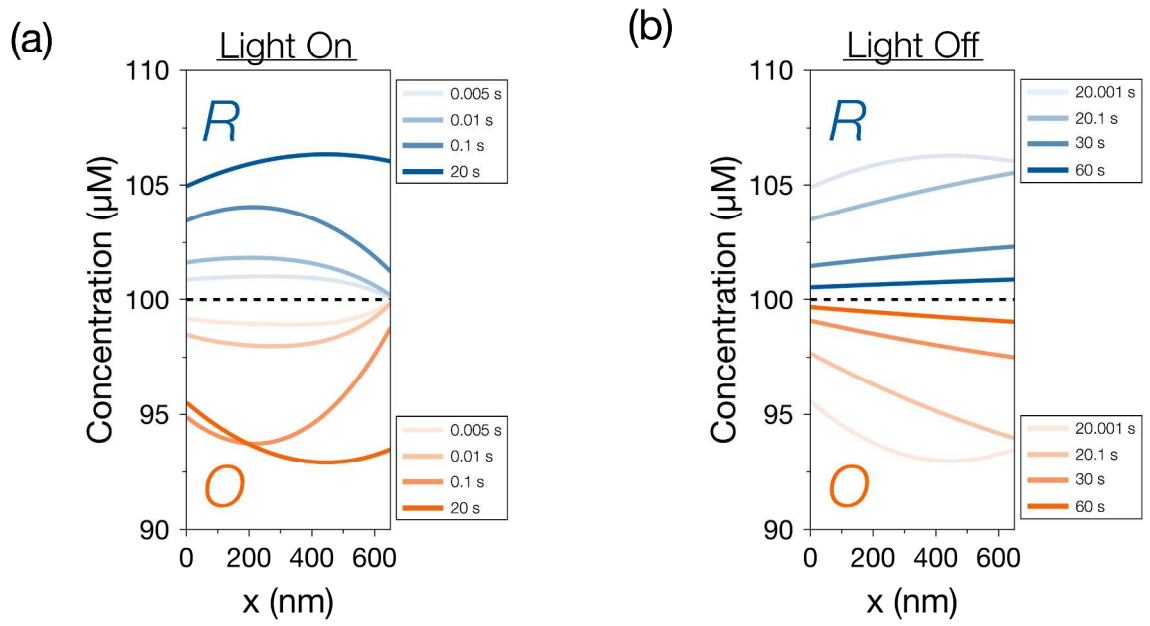

Figure S4. Simulated concentration profiles of mediators—R and O—within a PSI multilayer film during a photochronoamperometric experiment. (a) Simulated mediator concentration profiles during illumination. (b) Simulated mediator concentration profiles after the light source is turned off. The data in this figure was generated from the fitted model presented in Figure 5 of the main text. The thickness of the PSI multilayer film is 0.65 μm, C_R^* = 0.1 mM, and C_O^* = 0.1 mM.