

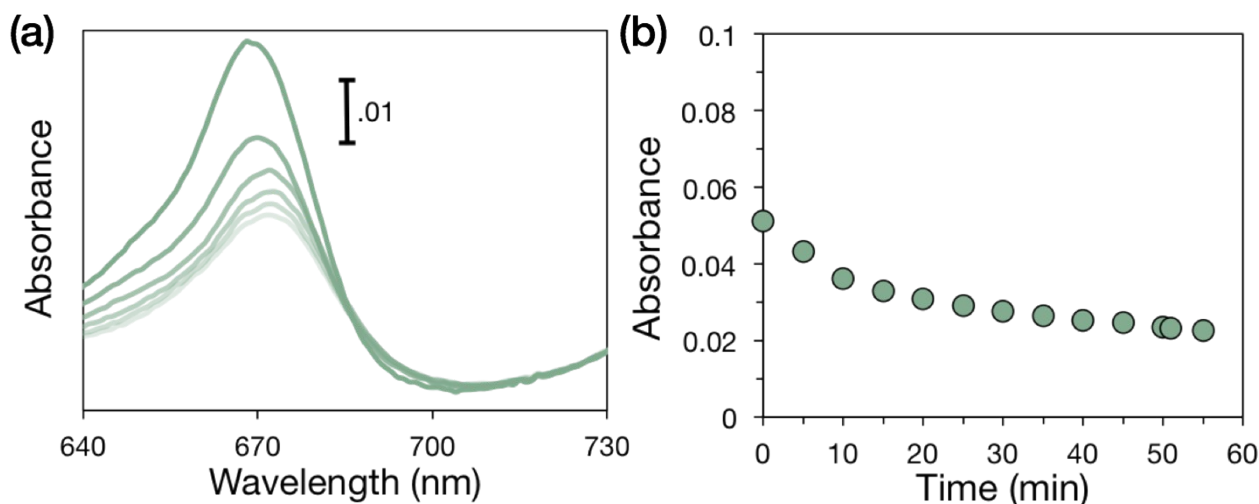
## SUPPLEMENTARY INFORMATION

### Photocatalytic Photosystem I/PEDOT Composite Films Prepared by Vapor-Phase Polymerization

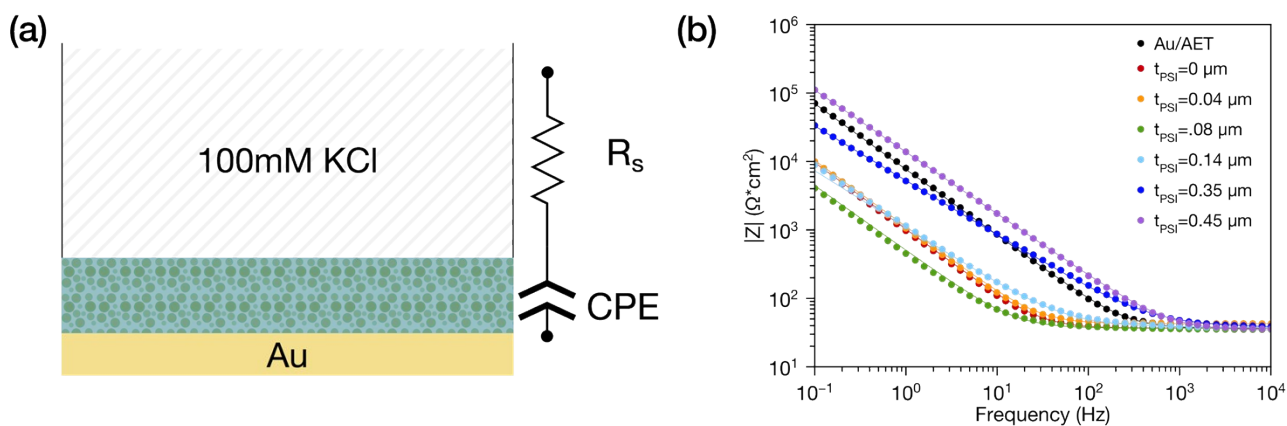
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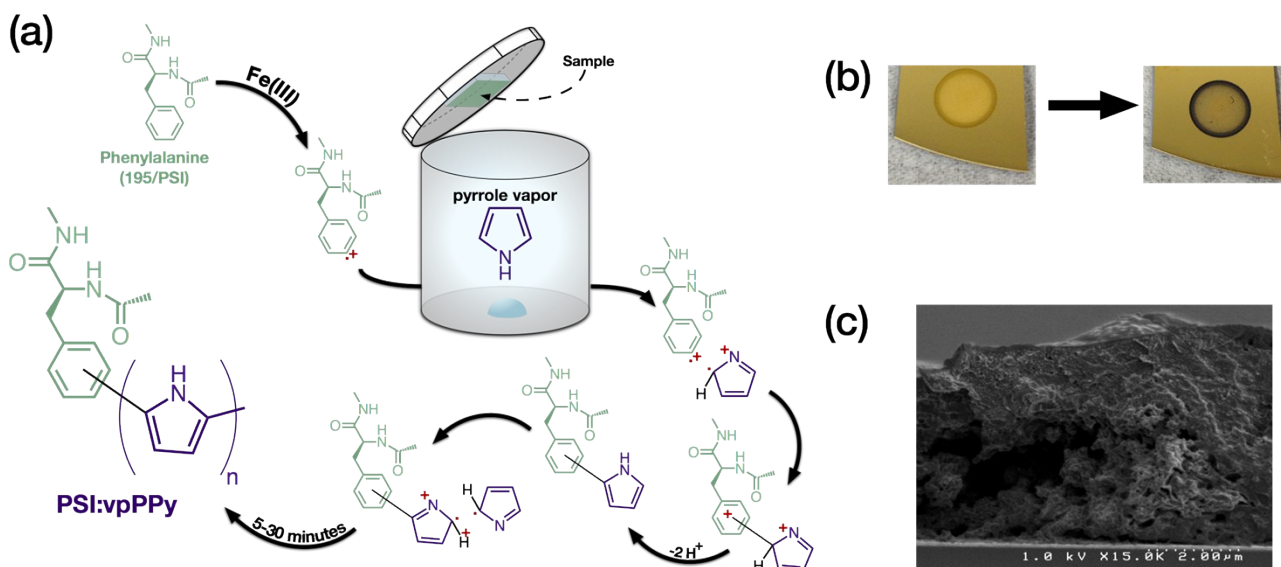
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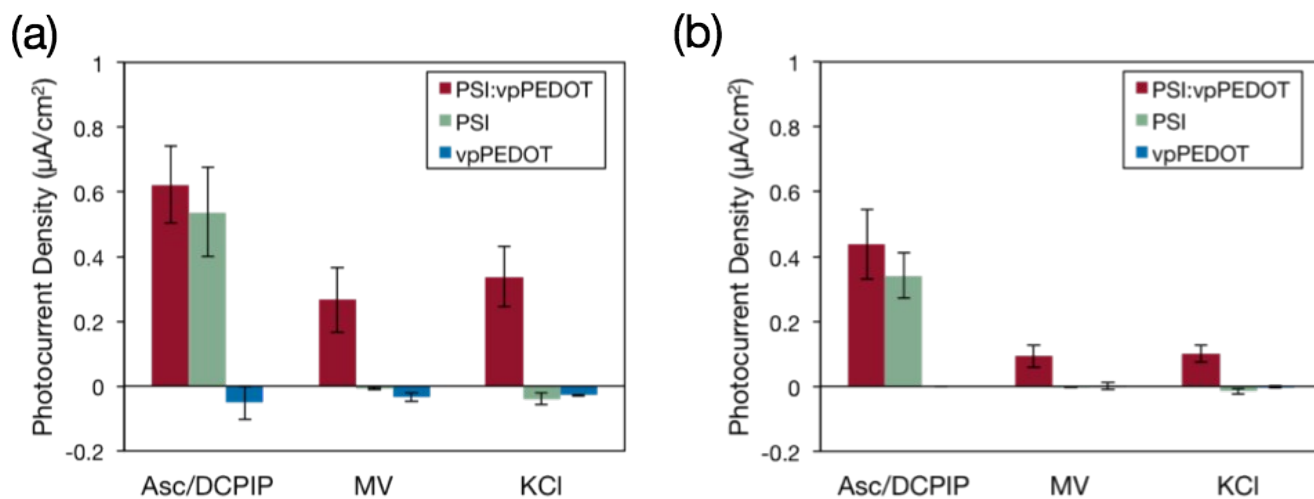
**Figure S1.** (a) Visible absorbance measurements of PSI solutions containing  $\text{FeCl}_3$  reveal transient decay of red absorbance due to peripheral ChlA in PSI proteins. (b) Time-resolved peak red absorbance of a solution containing PSI and  $\text{FeCl}_3$  oxidant demonstrates oxidation of PSI's chlorophyll network before film assembly. The cuvette contained 2450  $\mu\text{L}$  of a 10 mM  $\text{FeCl}_3$  and .025% w/v Triton X-100 solution and 50  $\mu\text{L}$  dialyzed PSI solution.



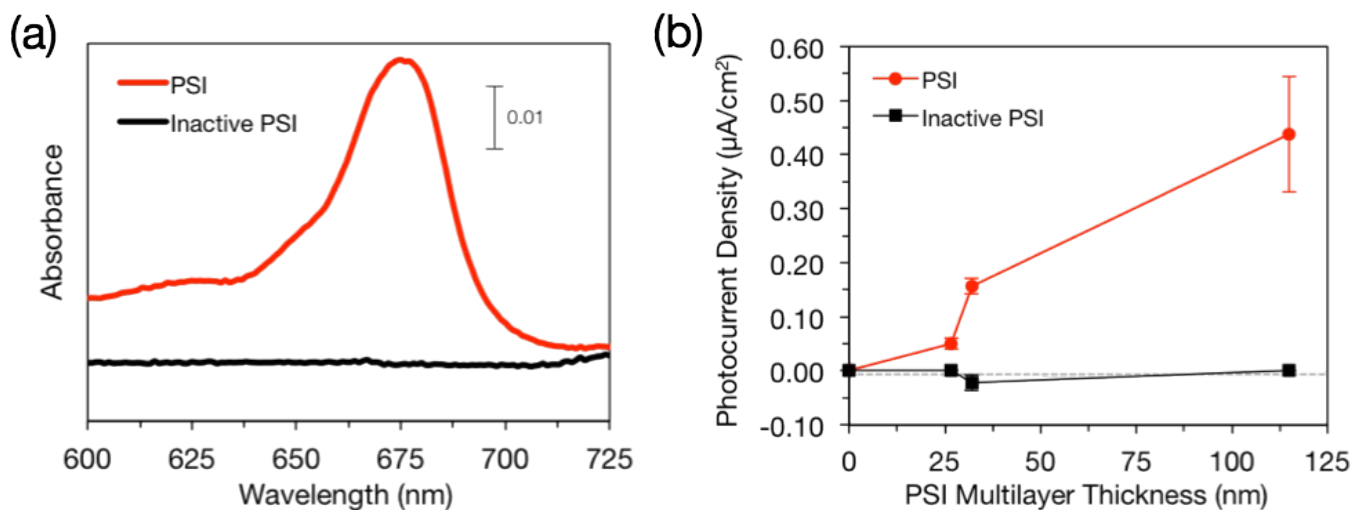
**Figure S2.** (a) EIS spectra of PSI:vpPEDOT films were fit to a series circuit consisting of a resistor corresponding to pure solution resistance and a constant phase element (CPE) which models the pseudocapacitance of incorporated PEDOT. (b) PSI incorporation significantly modifies the pseudocapacitance of a vpPEDOT film. All spectra were collected in 100 mM KCl.



**Figure S3.** (a) We propose that a similar ‘grafting-from’ mechanism applies to vpPPy films grown in the presence of PSI to form PSI:vpPPy. (b) We successfully grew dense PPy from catalyst-replete PSI multilayer films in minutes using our technique. (c) SEM of composite film.



**Figure S4.** Photocurrent measurements were performed on PSI:vpPEDOT ( $t_{\text{PSI}} \sim 300$  nm), PSI ( $t_{\text{PSI}} \sim 300$  nm), and vpPEDOT films prepared on Au/AET electrodes in 20 mM Asc/1 mM DCPIP, 0.5 mM methyl viologen (MV), and with no added redox mediator. All solutions contain 100 mM KCl as supporting electrolyte and were performed in air. Both (a) full spectrum and (b) red light responses indicate that the addition of PSI within a PEDOT scaffold facilitates a photocathodic response.



**Figure S5.** To provide further evidence for PSI-based photocurrent in composite films, PSI:vpPEDOT films were prepared with both active and inactive PSI (inPSI). (a) Solution absorbance comparison of unmodified PSI and inactive PSI prepared by prolonged UV-irradiation of PSI solution. Measurements were collected a mixture of 50  $\mu\text{L}$  inactive/unmodified PSI solution and 2450  $\mu\text{L}$  phosphate buffer (pH 7). (b) Near-zero and cathodic photocurrents are observed for inPSI:vpPEDOT and PSI:vpPEDOT films, respectively, tested under filtered red light in an electrolyte solution containing 20 mM Asc, 1 mM DCPIP, and 100 mM KCl.