Supporting Information

Polyviologen as Electron Transport Material in Photosystem I-Based Biophotovoltaic Cells

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A. Calculation of the Fermi Level of p-Type Silicon:

The Fermi level of doped silicon can be calculated from the manufacturer specified resistivity. The carrier mobility, μ_p, is first expressed as a function of resistivity.[1] A function for carrier mobility with respect to carrier concentration has been empirically derived by Masetti et. al. and varies between dopants and dopant concentrations.[2] The empirical relation chosen is valid for boron doped silicon where $10^{14}\ cm^{-3} < p < 10^{20}\ cm^{-3}$. These two equations can be solved for carrier mobility and set equal to solve for carrier concentration. Next, the carrier concentration is used to determine the shift in the Fermi level from that of intrinsic silicon. In p-type semiconductors the Fermi level is shifted more negative, or lower in energy, by the addition of holes via doping. Classical semiconductor statistics determines the magnitude of this Fermi level shift.[1] Note that the Fermi level of intrinsic silicon, $E_{intrinsic}$, was estimated based on relating the work function for (100) silicon, $4.91\ eV\ vs\ vacuum$,[3] to the valence band and the energy at half of the band gap, $1.14\ eV$.

Calculation:

1. Express carrier mobility as a function of the resistivity:[1]

$$\rho = \frac{1}{\sigma} = \frac{1}{nq\mu_p}$$

$$\mu_p = \frac{1}{nq\rho}$$

- The resistivity, ρ, of the silicon wafers used in this work ranges from 1-10 $\Omega.cm$ and an average value of 5.0 $\Omega.cm$ was chosen for this calculation.

2. Express carrier mobility as a function of carrier concentration empirically:[2]

$$\mu_p = \mu_o e^{-p_c/p} + \frac{\mu_{max}}{1 + \left(\frac{p}{C_R}\right)^{\alpha}} - \frac{\mu_1}{1 + \left(\frac{C_S}{p}\right)^{\beta}}$$

For boron doped silicon:

$\mu_o = 44.9\ cm^2/(V \times s)$
$\mu_{max} = 470.5\ cm^2/(V \times s)$
$\mu_1 = 29.0\ cm^2/(V \times s)$
$C_R = 2.23 \times 10^{17}\ cm^{-3}$
$C_S = 6.10 \times 10^{20}\ cm^{-3}$
$p_c = 9.23 \times 10^{16}\ cm^{-3}$
$\alpha = 0.719$

$\beta = 2.00$

3. Set these equations equal and solve for carrier concentration (p):

$$\frac{1}{p \times -1.60 \times 10^{-19}\, C \times 5.0\, \Omega.cm} = 44.9 \times e^{-9.23 \times 10^{16}/p} + \frac{470.5}{1 + \left(\frac{p}{2.23 \times 10^{17}}\right)^{0.719}} - \frac{29.0}{1 + \left(\frac{6.10 \times 10^{20}}{p}\right)^{2.00}}$$

$$p = 2.76 \times 10^{15}\, cm^{-3}$$

4. Calculate the Fermi level from carrier concentration for a p-type semiconductor:[1]

$$E_{Fermi} = E_{intrinsic} - kTln\left(\frac{p}{n_{intrinsic}}\right)$$

Where:

$^*E_{intrinsic} = -4.34\, eV$
$k = 8.61 \times 10^{-5}\, eV/K$
$T = 300\, K$
$n_{intrinsic} = 1.5 \times 10^{10}\, cm^{-3}$

*Estimated based on the work function of (100) Si. The work function is related to the energy required to remove an electron from the valence band. The band gap of silicon was taken to be 1.14 eV.[3]

$$E_{Fermi} = -4.34\, eV - (8.61 \times 10^{-5} \frac{eV}{K} \times 300\, K) ln\left(\frac{2.76 \times 10^{15}\, carriers/cm^3}{1.5 \times 10^{10}\, carriers/cm^3}\right)$$

$$E_{Fermi} = -4.65\, eV\, vs.\, vacuum$$
$$E_{Fermi} = -(-4.65\, eV\, vs.\, vacuum) - 4.44 = 0.21\, V\, vs.\, SHE$$

B. ^{1}H-NMR Characterization of poly(p-xylylviologen):

^{1}H-NMR spectrum was collected using a Bruker 400 MHz spectrometer. The spectrum (Figure S1) shows four proton peaks, which correspond to the four distinct proton types in the structure. Peak a (δ 7.65 ppm) represents four equivalent protons belonging to the xylyl group in the repeating unit. Peaks b (δ 9.17 ppm) and c (δ 8.56 ppm) represent the protons in the aromatic bipyridine system. Peak d (δ 6.00 ppm) represents the protons on the methyl groups linking the two bipyridines. Peaks a, b, c, and d all integrate to account for approximately the same relative number of protons. The number average molecular weight (M_n) was calculated from the integrated ^{1}H-NMR peaks. The peaks corresponding to chain termini were identified as peaks e and f, which arise from a bipyridine group ending the chain. The integrations for these signals were normalized to 2 (the number of equivalent protons for each termini group). This normalization resulted in an integration value of about 48 for peaks a, b, and c, all of which correspond to 4 equivalent protons.

Based on the calculated ratios, the synthesized poly(p-xylylviologen) sample contains an average chain length of 12 repeating units. With a molecular weight of 260 g/mol for each repeating unit, the synthesized product has an approximate M_n of 3200 Da.

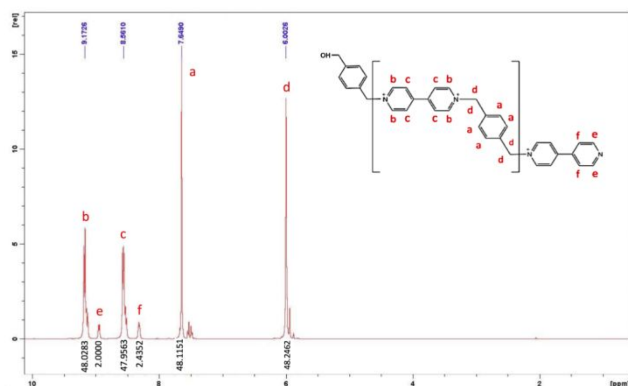

Figure S1. ^{1}H-NMR spectrum of poly(p-xylylviologen) with assigned peaks.

C. *Absorbance spectra of Photosystem I (PSI) and Poly(p-xylylviologen) (PxV):*

The absorption spectra of deposited thin films of PSI and PxV on glass (Figure S2) show that PxV does not competitively absorb with PSI. PSI absorbs strongly in the red (680 nm) and blue (430 nm) regions, whereas the PxV film absorbs in the green (550 nm) and orange (610 nm) regions.

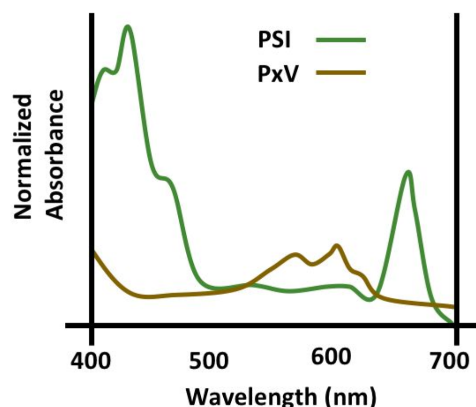

Figure S2. Absorbance spectra of PSI and PxV deposited on glass. PSI film thickness is around 0.4 µM and PxV film thickness is around 0.2 µM.

D. *Solid-state device fabrication:*

Solid-state p-Si/PSI/PxV/ITO devices were assembled as outlined in Figure S3. Lightly (boron) p-doped silicon (p-Si) substrates (1-10 Ohm-cm) were purchased from

University Wafer (Boston, MA). Each substrate was masked with electrochemical masking tape (Gamry) to yield an exposed area of 1 cm^2. The substrates were modified with PSI protein and PxV polymer as described in the experimental section. The devices were completed with a conductive ITO film on flexible PET (Resistivity: 60 Ω/square, Sigma-Aldrich) to act as the device anode. This was accomplished by resting the flexible ITO on the mask such that it was bridging the exposed area on the substrate but without contacting it. In order to control the exact surface area of the contact, a small piece of transparent PET contact spacer (0.283 mm^2) was pressed onto ITO/PET layer, forcing the ITO to contact the PxV surface. For control devices, ITO was contacted on the PSI or bare p-Si surface using the same method. Structural support was provided by sandwiching the entire device stack between two pieces of borosilicate glass (1 mm thickness) and binding the system together with clamps in order to make secure electrical contact without short-circuiting.

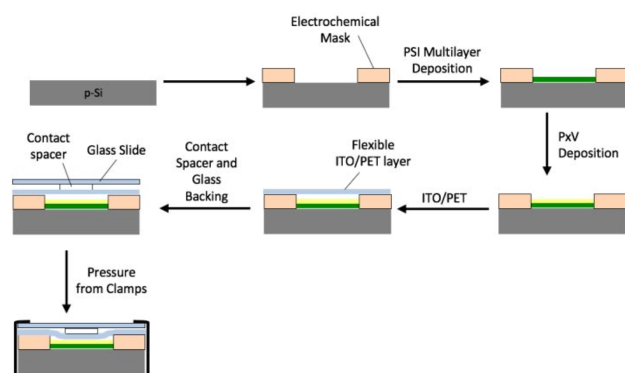

Figure S3. Solid-state p-Si/PSI/PxV device fabrication scheme.

E. Inactive PSI absorbance and photocurrent density performance:

To provide further support for PSI-based photocurrent density, solid-state p-Si/PSI/PxV devices were prepared both with active and inactive PSI extracts. Inactive PSI was prepared by heating of the PSI extract to 80° Celsius. Absorbance measurements were collected from active and inactive PSI solutions in phosphate buffer (pH 7). Inactive PSI spectrum does not have the characteristic 680 nm absorption peak that active PSI possesses. Photochronoamperometry measurements were taken as described in the experimental section. The p-Si/PSI/PxV devices made from active PSI generated 30 times more photocurrent density than the devices made with inactive PSI. This further supports our hypothesis that PSI is the main photoactive component of these solar devices.

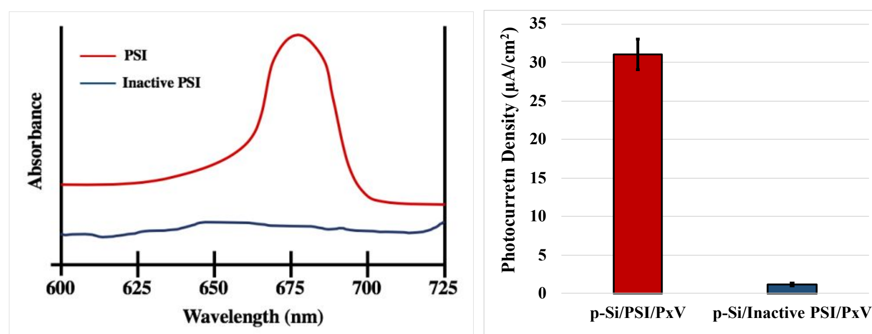

Figure S4. Absorbance spectra of solutions of active and inactive PSI in phosphate butte (pH=7) (left) and photocurrent density comparison of p-Si/PSI/PxV devices made with active and inactive PSI solution (right).

F. *Current-voltage (I-V) analysis of HF-treated (etched) p-Si devices:*

I-V analysis under both dark and calibrated solar illumination for p-Si/PxV control device and p-Si/PSI/PxV device are given. These devices use hydrofluoric acid (HF) treated lightly p-doped silicon substrates. The short circuit current density (J_{SC}) of the etched p-Si/PSI/PxV device is 80 μA/cm^2, the open-circuit voltage (V_{OC}) is 210 mV and the external efficiency is calculated to be 0.0059%.

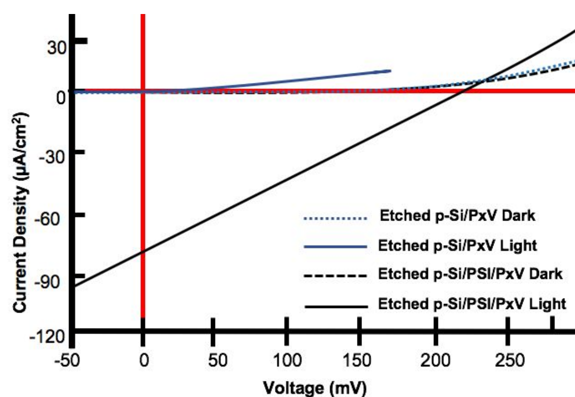

Figure S5. Current-Voltage (i-V) analysis of solid-state p-Si/PSI/PxV (black) and p-Si/PxV (blue) devices made with HF-treated (etched) lightly p-doped silicon substrates. Samples were tested under 1 sun illumination and in the dark.

References:

1) Kittel, C.; Kroemer, H. *Thermal Physics,* 2nd ed.; W. H. Freeman and Company: New York, 1980.

2) Masetti, G.; Severi, M.; Solmi, S. Modeling of Carrier Mobility Against Carrier Concentration in Arsenic-, Phosphorous-, and Boron-Doped Silicon. *IEEE Trans. Electron Devices.* **1983,** 30(7), 764-769.

3) Lide, D. R. *CRC Handbook of Chemistry and Physics,* 88th ed.; CRC Press: Florence, 2007.