A New Method for Improving Solar Cell Conversion: Side Selective Modification of Photosystem I

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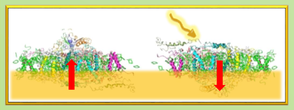
Introduction

Turning to Plants

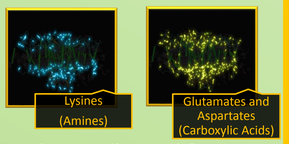
Biohybrid Cells address the problem of resource limitation and low efficiency faced by current solar cells by utilizing the light converting plant protein, Photosystem I (PSI).

The Problem: Film Orientation



PSI binds to electrodes in upright and inverted orientations [1].

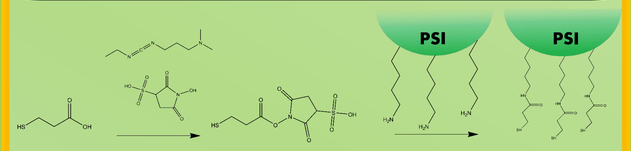
The solution: Side Selective Functionalization



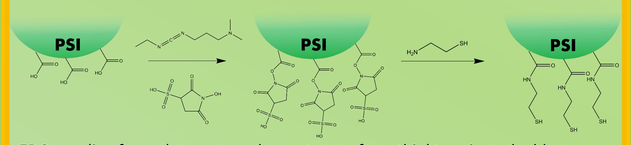
By chemically modifying one side of the protein, we can increase the percentage of upright oriented PSI.

Objectives

1. Functionalization of Photosystem I with electrode binding ligand

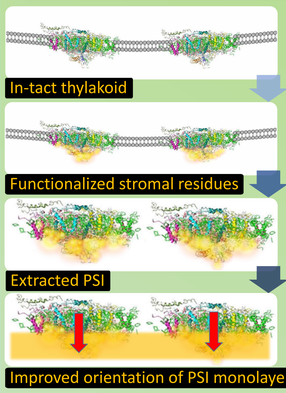


EDC coupling reaction from lysines to form the thiol terminated adduct



EDC coupling from glutamate and aspartate to form thiol terminated adducts

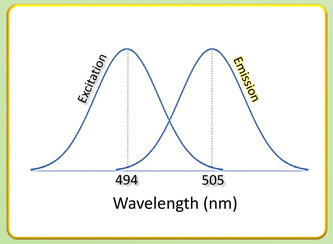
2. **Side Selective** Functionalization for **improved orientation** on electrode



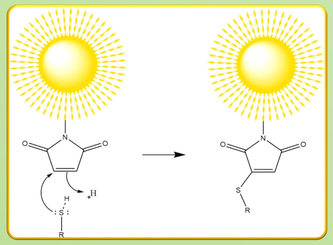
1. Perform EDC coupling on stromal residues adding thiolated ligands
2. Lyse thylakoid membrane with surfactants and purify PSI via column chromatography
3. Deposit Functionalized PSI on gold electrode exploiting the gold-thiol reaction

Methods

Fluorescence Spectroscopy

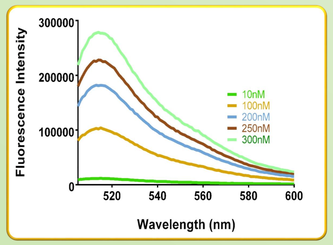


- When we apply light at the excitation maximum wavelength to the fluorophore, its unique chemical properties allow for the **emission of a photon** at a lower energy.

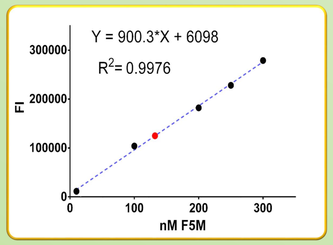


- Fluorescein-5-Maleimide (F5M) has **high selectivity** for thiols.
- Allows for **quantification** of free thiols on PSI

Calibration Curve



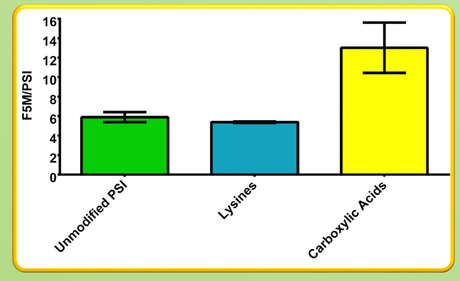
- Spectral overlay of standard F5M solutions for calibration



- The concentrations were found by **linear regression.**
- Example: A **132nM** F5M sample would give **125,000 FI**.

Results and Discussion

Lysines vs Carboxylic Acids

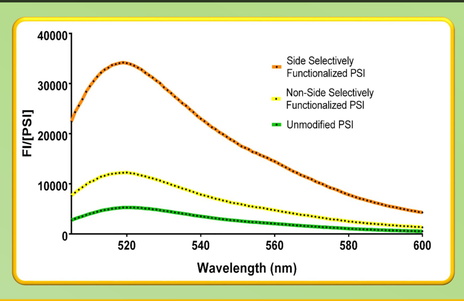


Purpose: To determine which residues works best in our coupling strategy

Samples	Unmodified PSI	Lysines	Carboxylic Acids
F5M/PSI	5.897 ± 0.514	5.390 ± 0.077	13.02 ± 2.58

- Our results show successful functionalization from the activating the surface carboxylic acids. However, no functionalization occurred on the samples that had undergone the coupling reaction from surface lysines.

Side Selective Functionalization



Samples	Unmodified PSI	Non-SSF PSI	SSF PSI
Max FI/PSI	5.30 ± 0.16 x 10^3	1.22 ± 0.03 x10^4	3.42 ± 0.10 x 10^4

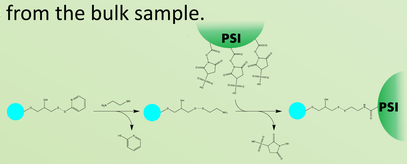
- Unexpectedly, the intensities values for the side selectively functionalized samples were over 3-fold higher than the non-side selectively functionalized sample. This may suggest that the side selective functionalization is the more efficient method.

Conclusions

- Coupling to surface glutamate and aspartates (carboxylic acids) provided successful functionalization on PSI, whereas coupling to surface lysines was unsuccessful.
- Coupling to intact thylakoids using its membrane as a natural barrier allows for side selective functionalization.
- Side selective functionalization provided more adducts per PSI than non-side selective functionalization.

Future Directions

- Perform electrochemical analysis on side-selectively functionalized PSI.
- A new purification method where functionalization occurs in a ligand activated resin could potentially remove unmodified proteins from the bulk sample.



- Different ligand attachments could open up new avenues in biomolecular applications.
  - Aminothiophenol - improved conductivity
  - Multilayer crosslinking
- Complete solar cell development with improved orientation of PSI film.
  - Testing with 1-Sun Illumination

References & Acknowledgments

[1] Ciesielski, P. N.; Cliffel, D. E.; Jennings, G. K. *J. Phys. Chem. A* **2011**, *115*, 3326–3334.

[2] LeBlanc, G.; Gizzie, E.; Yang, S.; Cliffel, D. E.; Jennings, G. K. *Langmuir* **2014**.

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