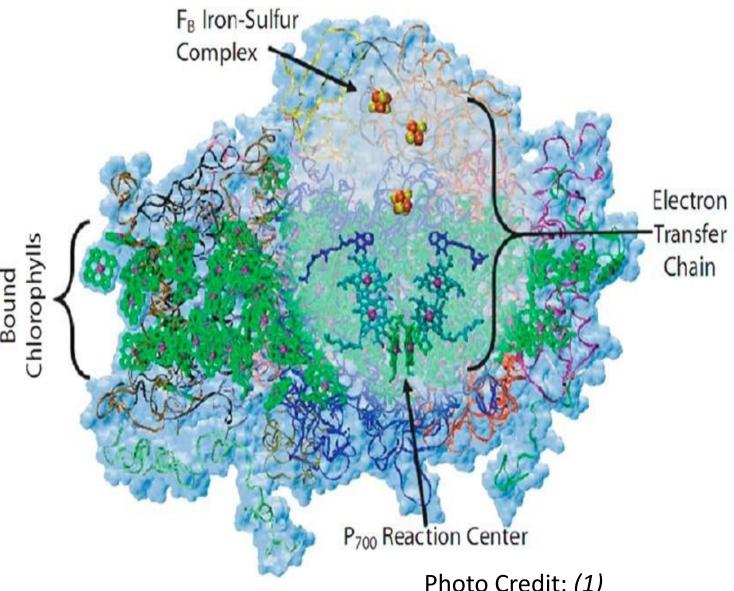


# **Controlling the Orientation of Photosynthetic Protein Assembly on Solid** Surfaces: a Strategy for Improving Bio-derived Solar Cells

## Introduction

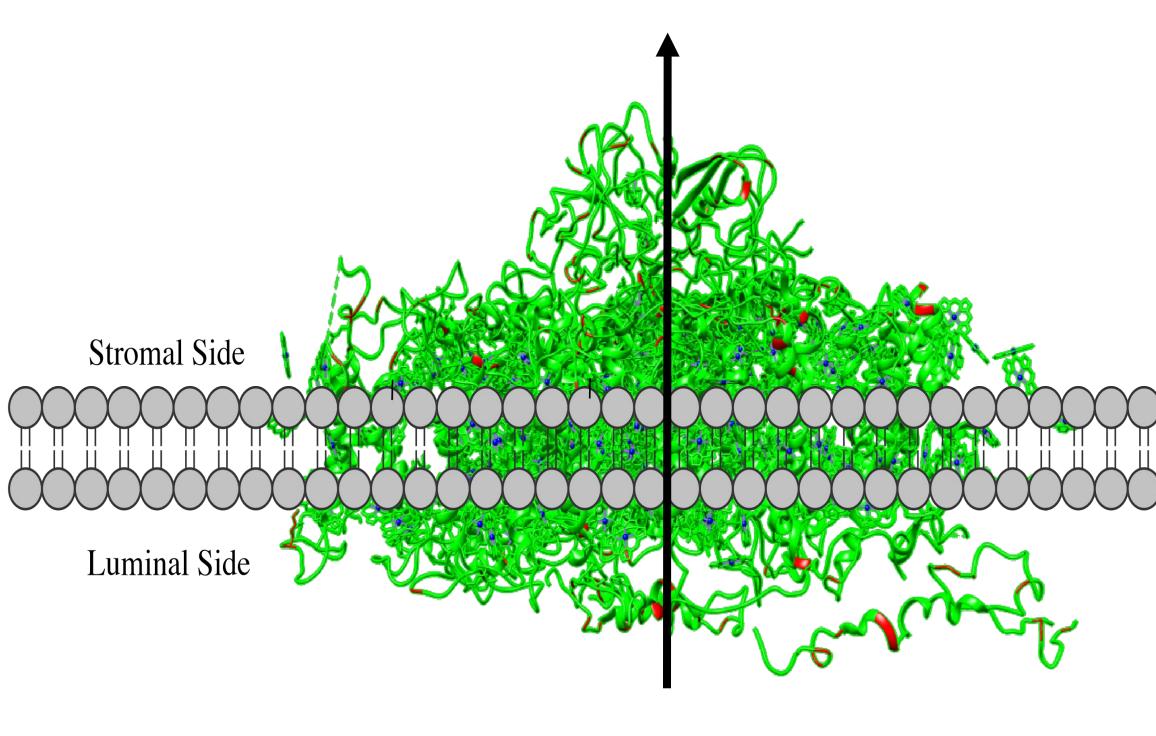
- Photosystem I (PSI) is a membrane-bound protein found in higher order plants that acts as a natural photodiode
- PSI can be used in solar cells as a photodiode which, utilizes light to generate an electron-hole pair



• Bio-derived solar cells can provide remarkably clean energy and utilizing PSI affords an abundant, low cost material for solar cells

### **Natural Orientation of Photosystem I**

In Nature, Photosystem I is oriented uniformly in the thylakoid membrane found in chloroplasts, and operates by shuttling electrons across the membrane unidirectionally



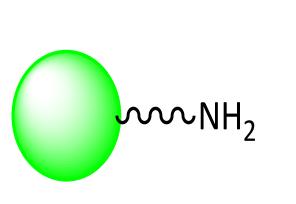
In Vivo **Electron Flow** 

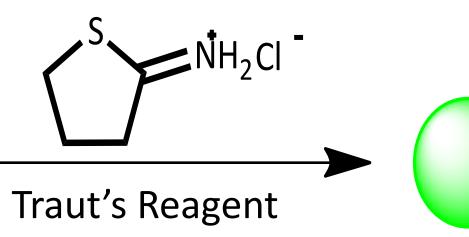
Natural orientation leads to a uniform electron flow across the thylakoid membrane, driving photosynthesis

To achieve maximum current in a solar energy conversion device with PSI, the orientation of PSI must be uniformly controlled

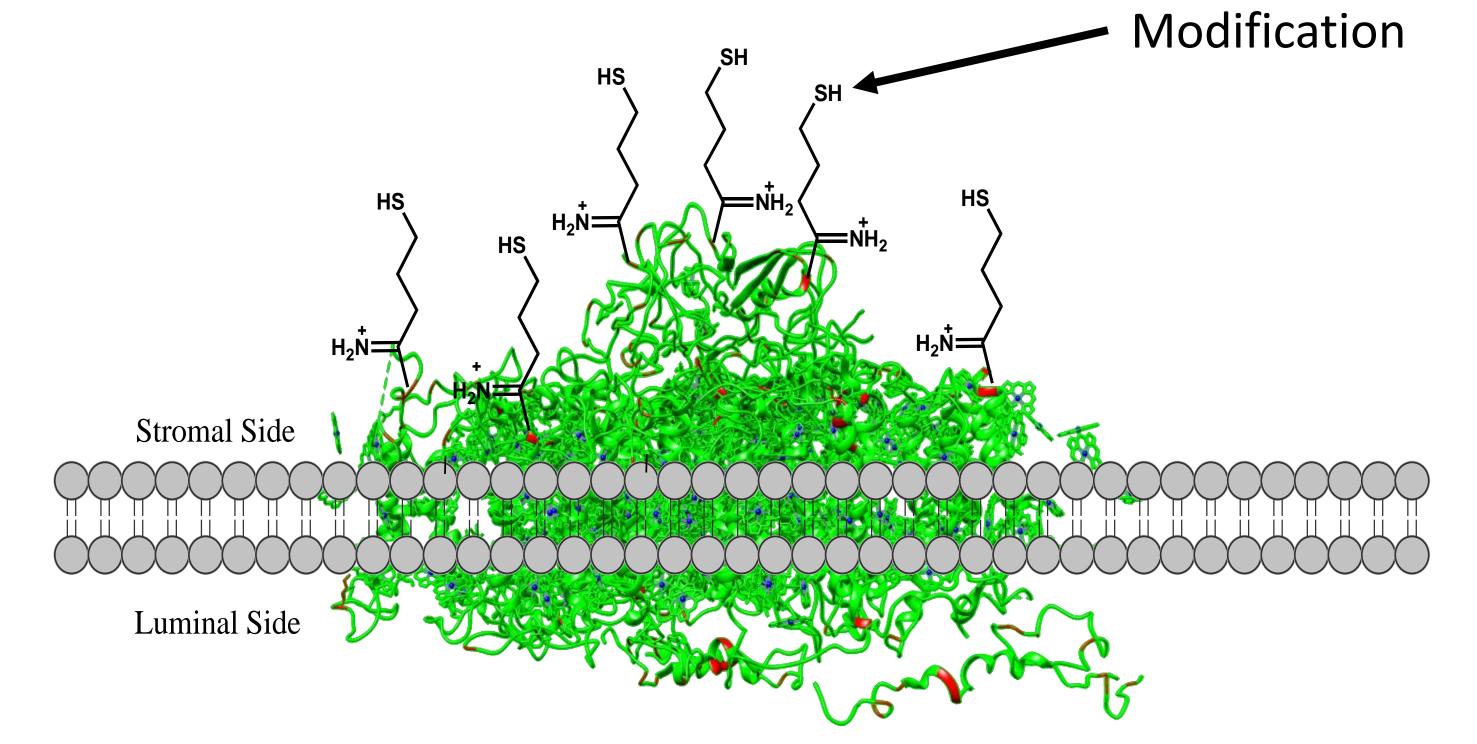
<sup>1</sup>Department of Chemical Engineering, University of Kansas, Lawrence, KS 66045 <sup>2</sup>Department of Chemistry, Vanderbilt University, Nashville, TN 37235

In Situ Modification of Photosystem I





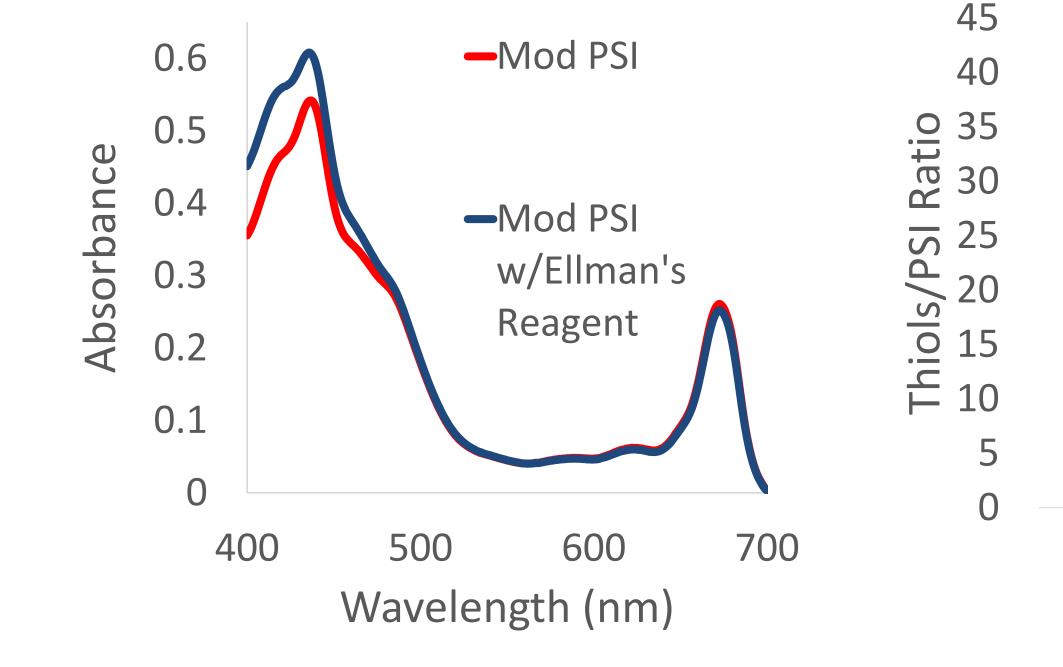
In order to orient PSI, an *in situ* modification was performed using 2-iminothiolane (Traut's Reagent) to modify one side of the protein with the thylakoid membrane acting as a ligand barrier



# Chemical modification with 2-iminothiolane provides a vector for orientation via gold-thiol interactions

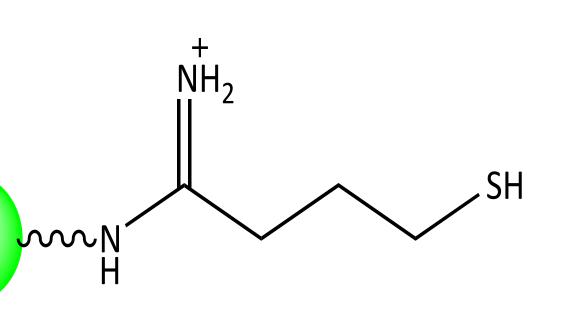
# **Quantifying Chemical Modification**

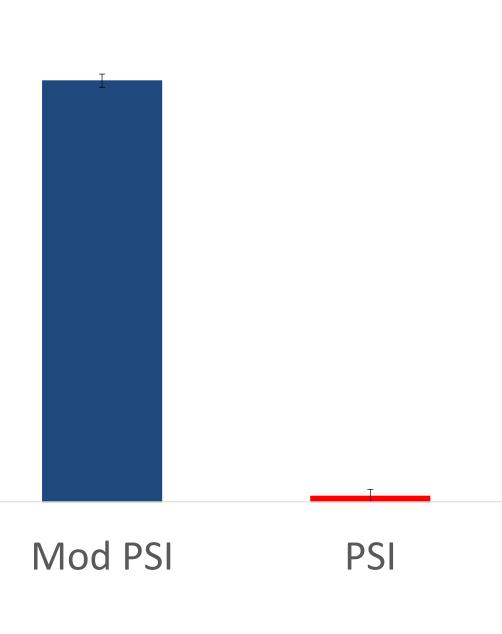
Ellman's Assay was used to quantify the number of new thiols on PSI via a colorimetric change at 412 nm



Quantifying the chemical modification indicates extensive thiolation of PSI, allowing a vector for orientation

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QCM can be utilized to show a preferential binding from thiolated PSI via a mass change on the gold crystal surface

 Sonicating the QCM crystal removes the unmodified PSI indicating non-specific binding

Future QCM experiments with ≥ Trauts modified PSI aim to show stronger substrate binding to gold surfaces **Photochronoamperometric Analysis** 

Electrochemical analysis indicates an increased photocurrent from a modified PSI monolayer

- UV light deactivation provides a control for PSI with similar surface chemistry
- Future research includes optimizing electronic interactions  $\vec{o}$ with Trauts modified PSI

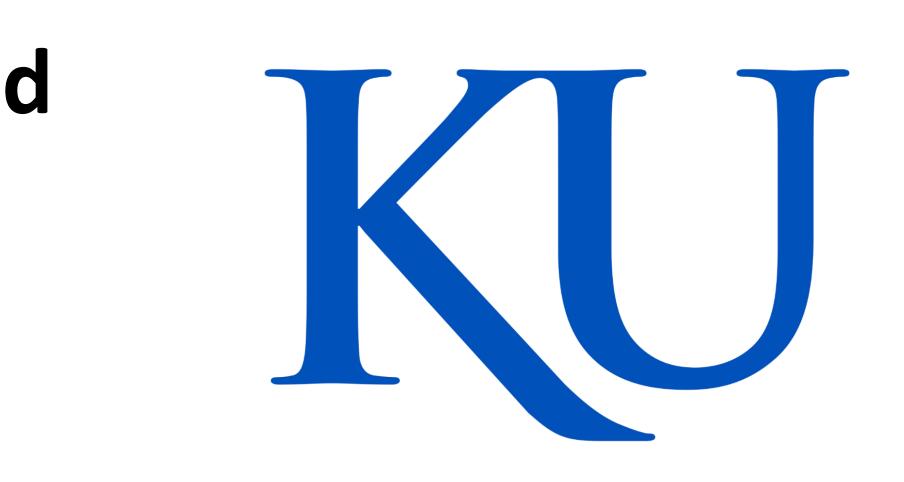
### Conclusions

# **Acknowledgements and References**

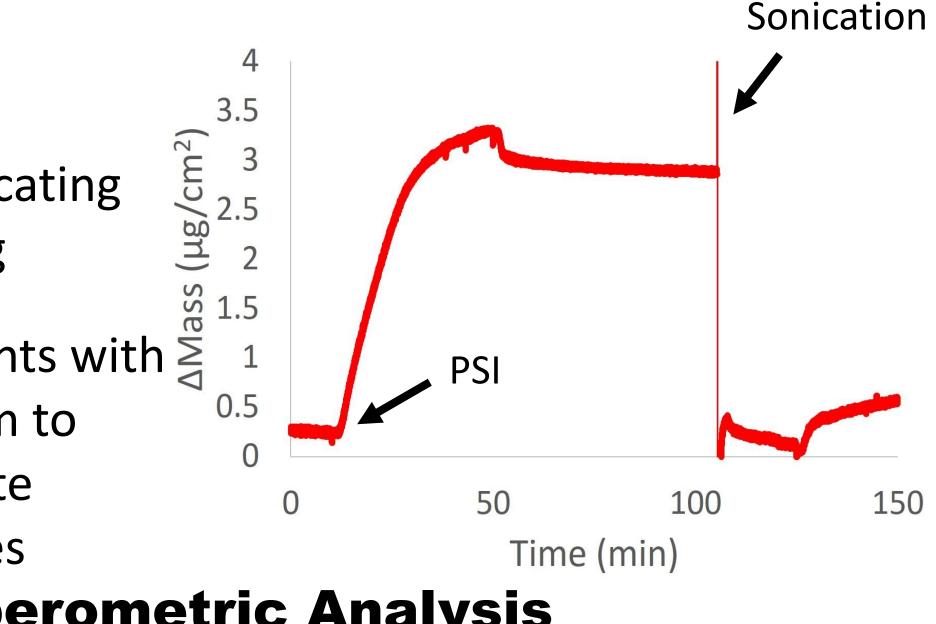
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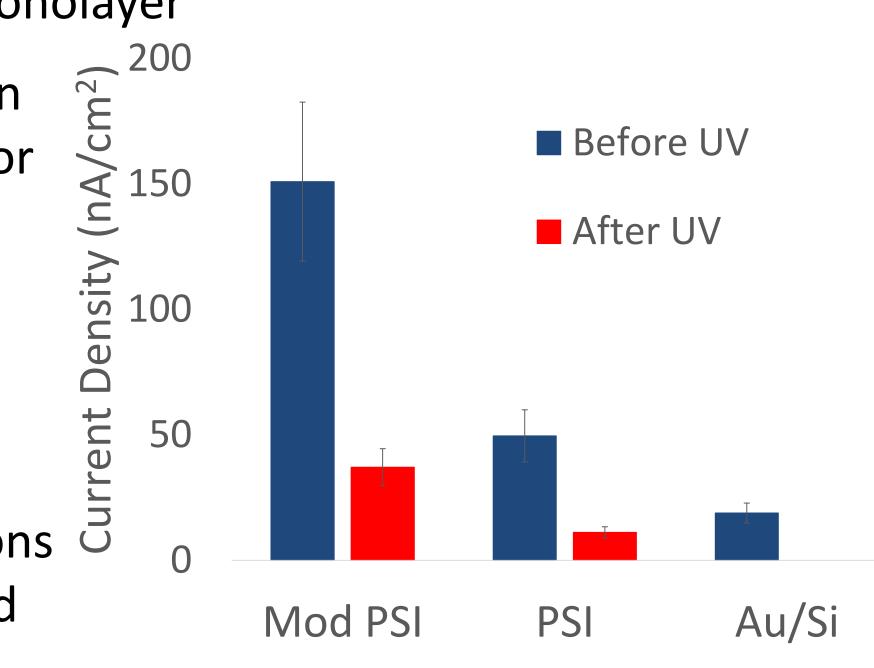


- (1) (2)
- *Chem.* **2007**, *599* (1), 72–78.



# **Quartz Crystal Microbalance (QCM)**





Photosystem I can be modified *in situ* with Traut's Reagent

• Future experiments aim to show that Trauts modified PSI has a stronger gold binding affinity than unmodified PSI

Electrochemical analysis indicates that Trauts modified PSI has increased photocurrent when compared to unmodified PSI



Leblanc, G.; Gizzie, E.; Yang, S.; Cliffel, D. E.; Jennings, G. K. *Langmuir* **2014**, *30* (37), 10990–11001. Ciobanu, M.; Kincaid, H. A.; Lo, V.; Dukes, A. D.; Kane Jennings, G.; Cliffel, D. E. J. Electroanal.