Bridging the Gap: Photosystem I Initiated Polymer Growth For Solid-State Solar Cell Applications

Patrick Wellborn [a, b], Max Robinson [b], David E. Cliffel [c], and G. Kane Jennings [b*]

Department of Chemical Engineering[a], Washington and Lee University, Lexington, VA 24450
Departments of Chemical & Biolmolecular Engineering[b] and Chemistry[c], Vanderbilt University, Nashville, TN 37235

Introduction

Background:

Photosystem I (PSI) is a photocatayltic protein that drives photosynthesis in green plants. Once extracted, it can be placed on an electrode in order to convert light energy into electrical energy within a biohybrid cell.

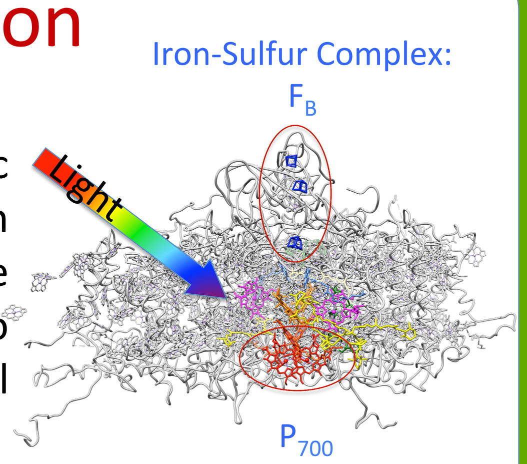
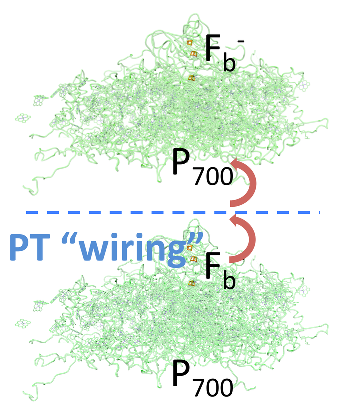


Figure 1: PSI Protein Complex



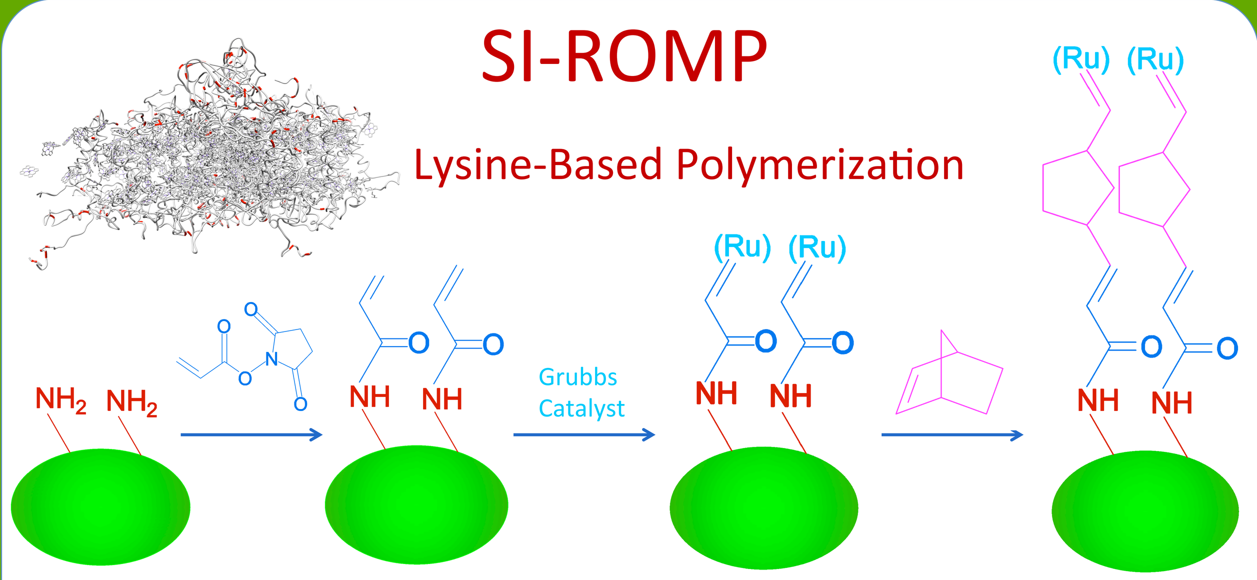
Polymerization off of PSI with a semiconducting polymer, polythiophene (PT), would provide a route to more efficient PSI-PSI electron transport within the active layer of solid-state devices.

Objective:

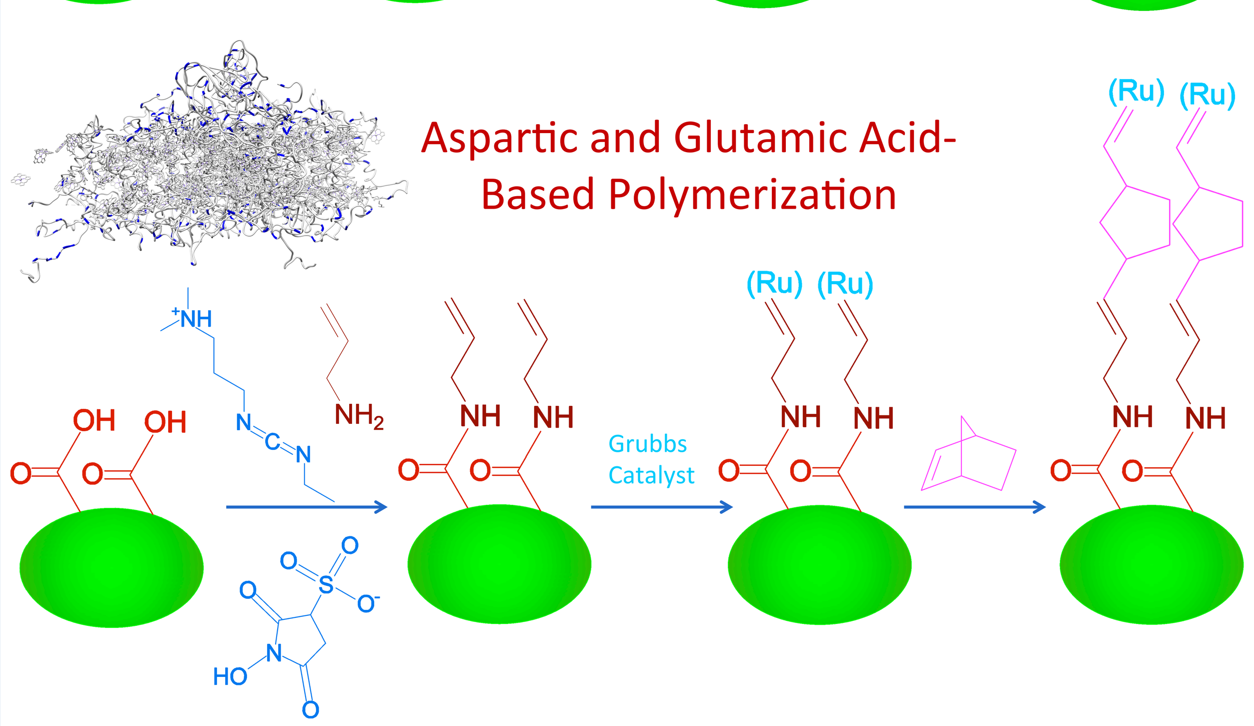
- Grow polymer off of PSI via Surface-Initiated Ring Opening Metathesis Polymerization (SI-ROMP)
- Explore two different polymer attachments to PSI
  1. Lysine-based from Amine termini
  2. Aspartic and Glutamic Acid-based from Carboxylic Acid termini

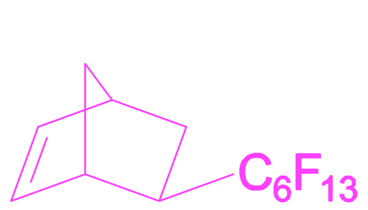
SI-ROMP

Lysine-Based Polymerization



Aspartic and Glutamic Acid-Based Polymerization



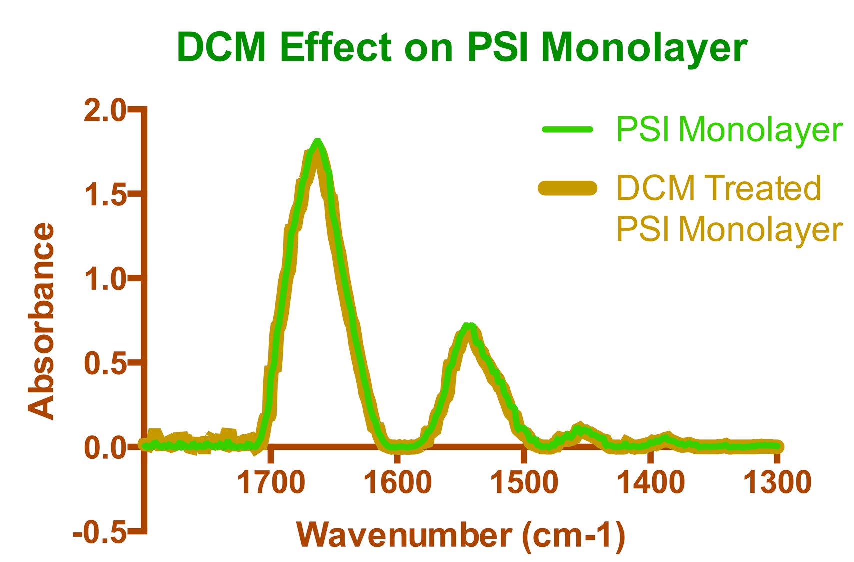


NBF6 monomer

NBF6 is characterized by fast growth kinetics and a unique spectroscopic signature, making it an ideal monomer for a "proof-of-concept" study. It has also been previously tested and proven in Jennings Lab.

Results

DCM Tests:

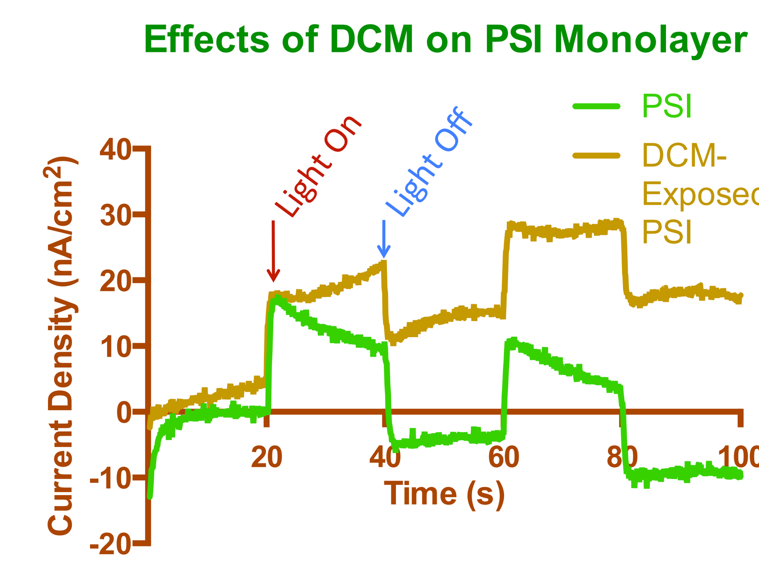


Graph 1: PMIRAS results of PSI Amide Peaks

Graph 1 shows that both the Amide I and Amide II peaks of PSI remain unchanged after exposure to DCM, indicating that the secondary structure of PSI remained intact.

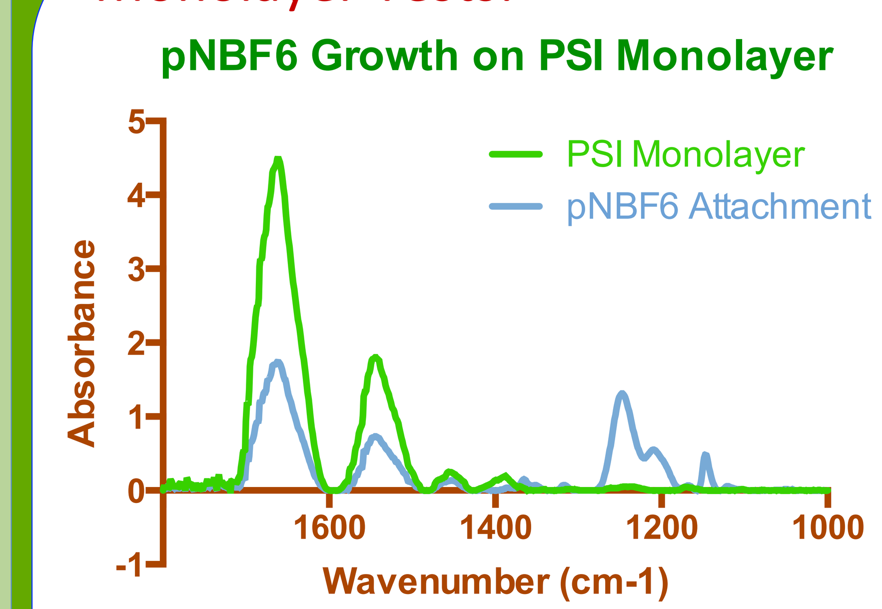
SI-ROMP is most efficient in the organic solvent Dichloromethane (DCM). For DCM testing, PSI monolayers were exposed to two 15 minute intervals of DCM to simulate SI-ROMP preparation.

Graph 2 shows that PSI retains photoactivity after DCM exposure.



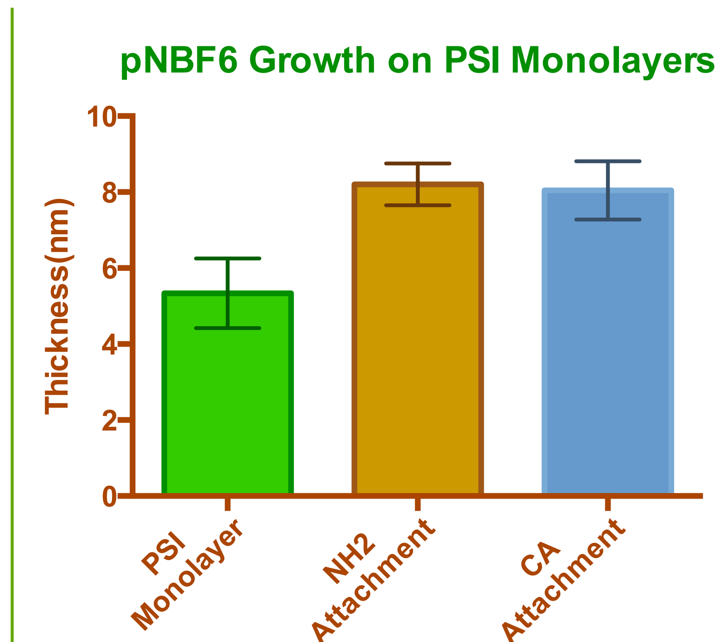
Graph 2: Photochronoamperometry of DCM-Exposed PSI Monolayer

Monolayer Tests:



Graph 3 : PMIRAS results of SI-ROMP progression on PSI

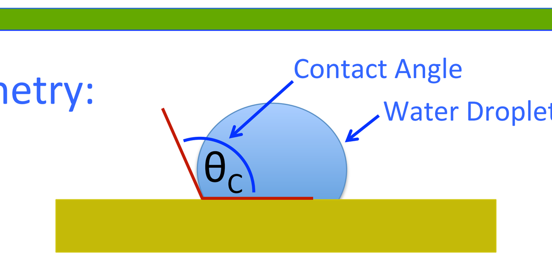
The appearance of C-F stretching peaks from 1300-1100 cm^{-1} verifies the attachment of the NBF6 polymer.



Graph 4: Ellipsometry results of pNBF6 growth off PSI

Both attachment methods show polymer growth off of a PSI monolayer.

Goniometry:



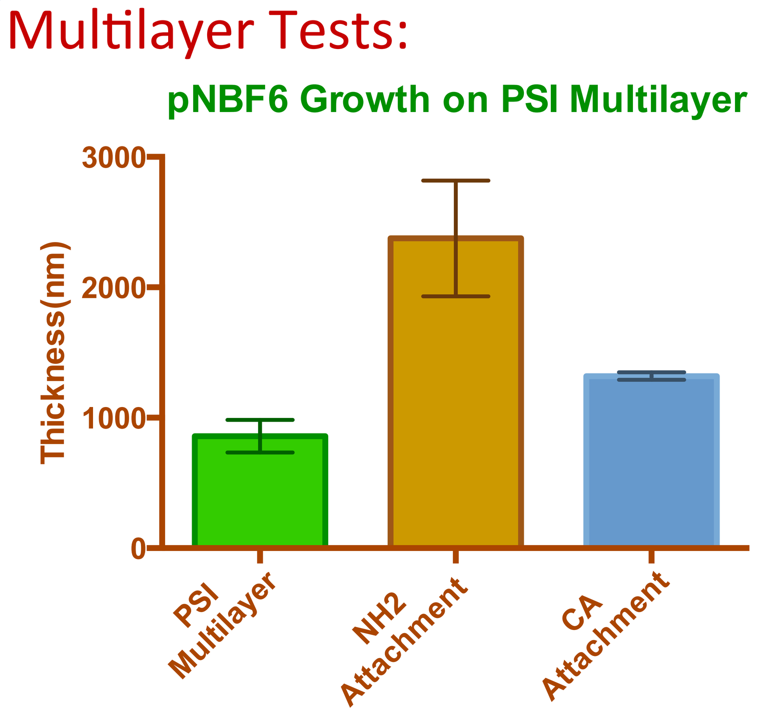
Advancing Contact Angles after SI-ROMP on PSI monolayers

Samples	PSI	NH2 Attachment	CA Attachment
PSI Monolayer	85° ± 1°	96° ± 2°	107° ± 4°
PSI Multilayer	49° ± 1°	160° ± .5°	154° ± .5°

Table 1: Goniometry results of pNBF6 growth off PSI

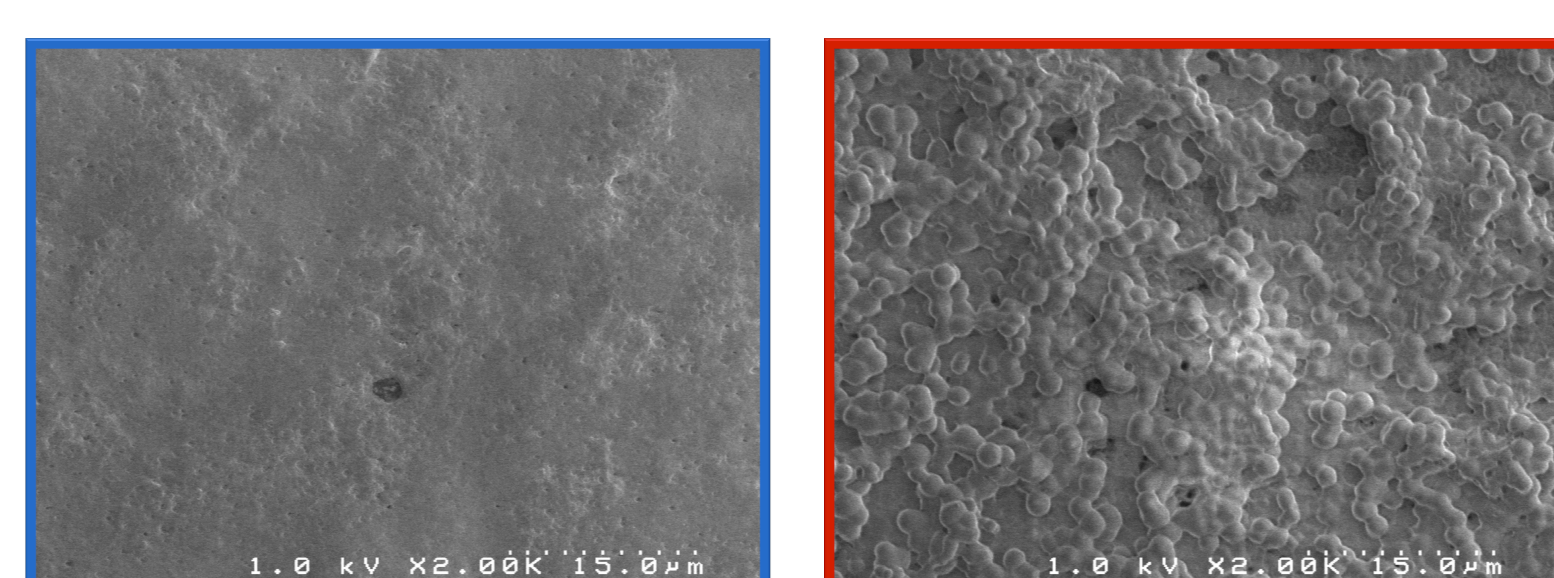
Increased contact angles for both attachment methods indicates polymer attachment to PSI due to the hydrophobicity of C-F bonds within the polymer

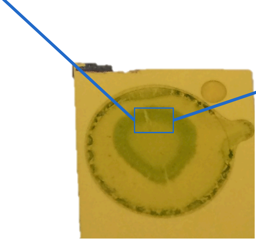
Multilayer Tests:

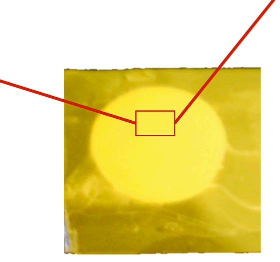


Graph 5: Profilometry results of pNBF6 growth off PSI

Both attachment methods show hundreds of nanometers of average polymer growth on top of the PSI multilayer.







Using images taken from a scanning electron microscope (SEM), it is clear that a rough polymer (pNBF6) film has grown off of the Photosystem I multilayer.

Conclusions

- Successfully polymerized off of PSI via SI-ROMP using two different attachment methods
- Obtained polymer growth from both monolayers and multilayers of PSI
- Characterized polymer films using contact angles, FTIR, ellipsometry, and profilometry
- Discovered that Grubbs Catalyst physisorbs to PSI, effectively growing polymer from the unmodified protein surface
- Attachment methods initiated from terminal amines or terminal carboxylic acids allow for more consistent polymer growth

Future Work

- Synthesis of an anchored polythiophene (PT) monomer to a norbornene backbone, providing for a covalently-wired and highly conjugated polymer matrix for efficient PSI-PSI charge mediation.

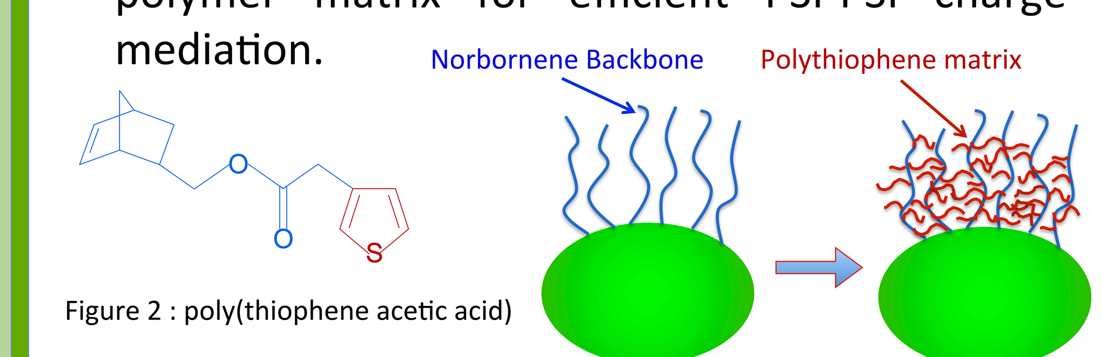


Figure 2 : poly(thiophene acetic acid)

References & Acknowledgments

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[1] Brad Barron et al, "Growth and Structure of Surface-Initiated polyalkylnorbornene Films", *Langmuir* 2007

[2] Christopher Faulkner et al, "Surface-Initiated Polymerization of 5-(Perfluoro-n-alkyl)norbornenes from Gold Substrates", *Macromolecules* 2010