Synthesis of Polyviologens as Mediators for Photosystem-I-Based Assemblies

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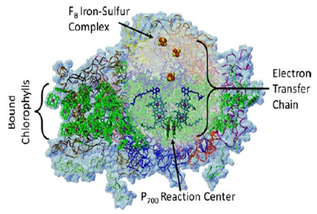
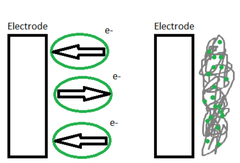
Introduction

Photosystem I
- Integral membrane protein
- Part of electron transfer chain
- Creates charge gradient and allows plant cells to store energy



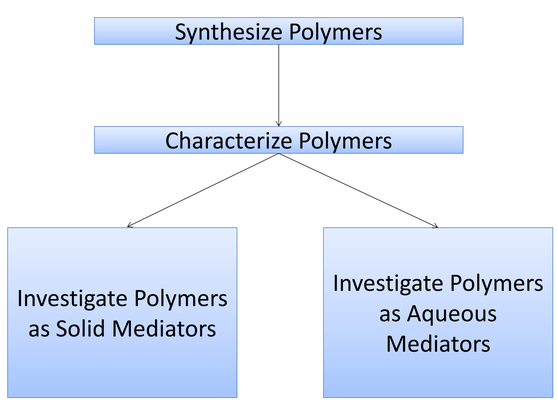
Why is PSI useful for solar technology?
- High quantum efficiency
- Abundant in nature
- Stable



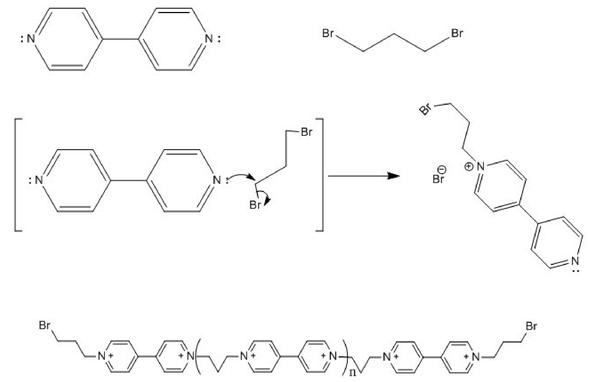
Polymers as mediator allow:
- Enhanced electron transfer
- Reduced directional effects
- Possible 3-D network
- Future work in solid state studies

Previous work includes:
- Usage of aqueous mediators to mimic electron transfer chain
- Embedding of PSI in poly-aniline films
- Creation of thick PSI films

Objective



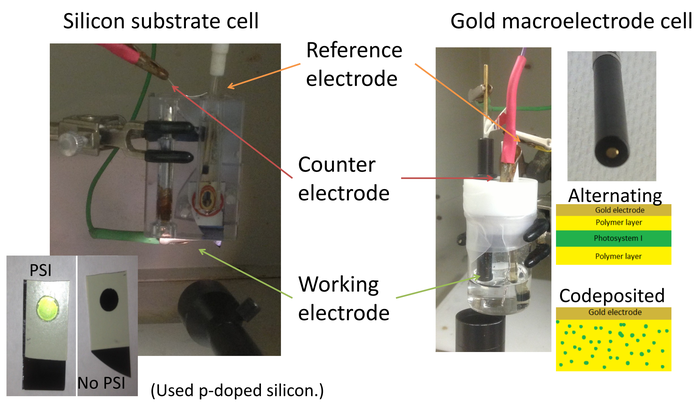
Methods



Reaction utilizes the Menshutkin mechanism and converts a tertiary amine to a quaternary ammonium salt.
Monomers (4,4'-bipyridine and p-dibromoxylene or 1,3-dibromopropane) were dissolved in acetonitrile and stirred throughout reaction.

Polymers created were
- Poly(xylyl viologen) 3.5 day reaction, RT, 62.2% yield
- Poly(propyl viologen) 1 day reaction, refluxed, 2.2% yield

Two Types of Electrochemical Cells



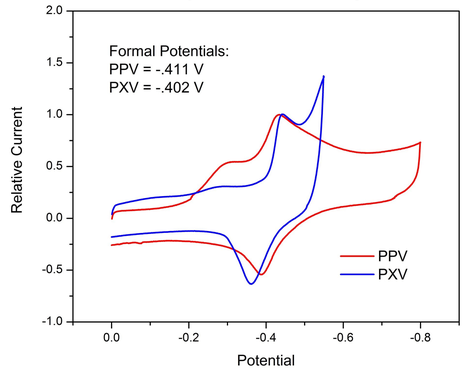
(Used p-doped silicon.)

CVs were run in 100mM KCl solution, generated formal potentials which are unique for each polymer.

i-t curve generation:
- 633 nm high-pass lamp shone on sample
- 100mM KCl, 5mM sodium ascorbate (for Au test), 1 mg/mL polymer
- Held at open-circuit potential
- 20 seconds dark, 20 seconds light, 20 seconds dark

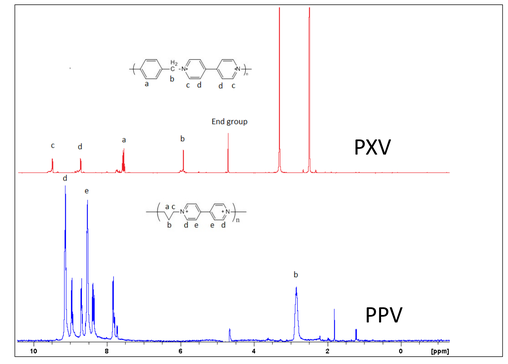
Results

Cyclic Voltammetry



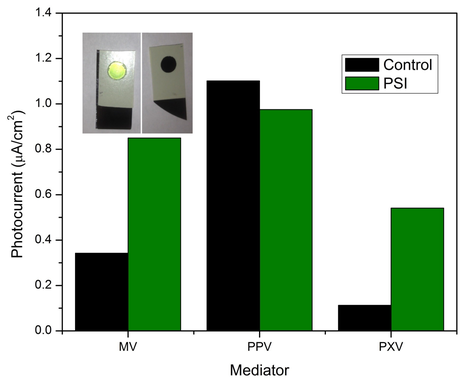
CVs show different curve shapes for each polymer and have different formal potentials.

NMR

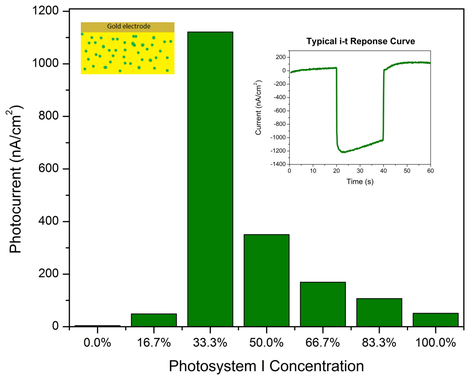


- PPV spectrum isn't clean; suggests reaction did not reach completion
- PXV spectrum clean, confirms molecular structure, gives rough molecular weight of 1.2kD

- PXV did not adhere to gold, and thus could not be used for deposition methods
- Lead to study of performance as aqueous mediator
- Outperformed control and PPV, compared favorably with currently preferred mediator



- PPV adhered well to gold surface
- Codeposition was tested by preparing PPV-PSI solutions in varying concentrations
- Showed increased photocurrents over solely PSI electrodes



Conclusions, Future Directions, and Acknowledgements

- Two polymers were synthesized for use in PSI assemblies
- PXV showed potential for use as an aqueous mediator
- PPV was capable of being codeposited onto gold; resulted in photocurrent improvements over both non-PSI control and layered deposition
- Future work could focus on viability of PPV-PSI codepositions as solid-state mediators for solar cells

- Gizzie, E. A.; LeBlanc, G.; Kane Jennings, G.; Cliffel, D. E. *In preparation for Chemistry of Materials* **2013**.
- LeBlanc, G.; Chen, G.; Gizzie, E. A.; Jennings, G. K.; Cliffel, D. E. *Advanced Materials* **2012**, *24*, 5959–5962.

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