Composite Films of Photosystem I Proteins with Substituted Polyanilines

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Photosystem I (PSI)

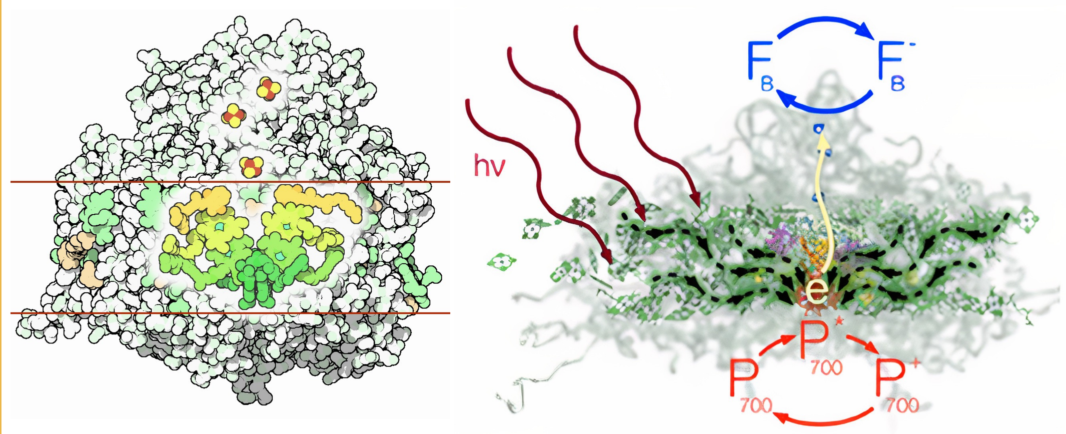


Figure 1: Photosystem I protein complex demonstrating active sites and excitation by light energy (right); visual representation of PSI's electron transfer chain (left). Image credit Maxwell T. Robinson (2017).

- Photoactive multi-subunit protein. complex involved in photosynthesis.
- Nearly perfect quantum yield.
- Oxidizing potential: 490 mV vs SHE.

Substituted Aniline Molecules

- Cyclic voltammetry is used to observe the reduction and oxidation processes of molecular species.

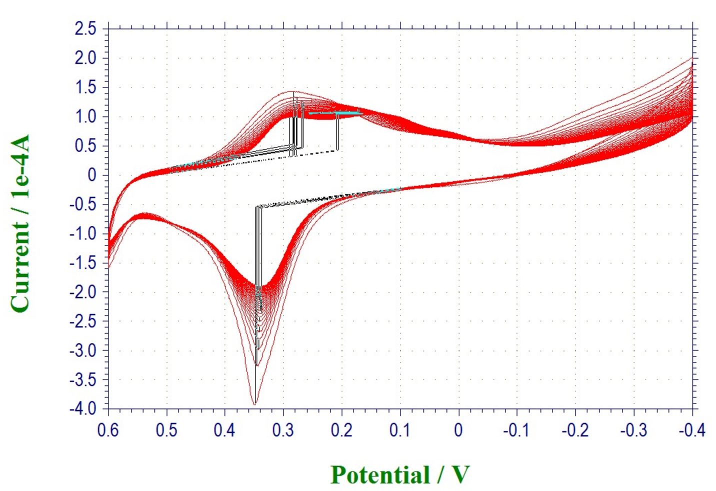


Figure 2: Cyclic voltammetry (CV) graph of the electropolymerization of p-anisidine, with Ag/AgCl as the reference electrode.

- Aniline with a methoxy (OCH_3) group attached at the para and ortho positions.
- Polymerization should result in a conductive polymer.
  - Enhance sensitivity, speed, stability of solar energy conversion devices.

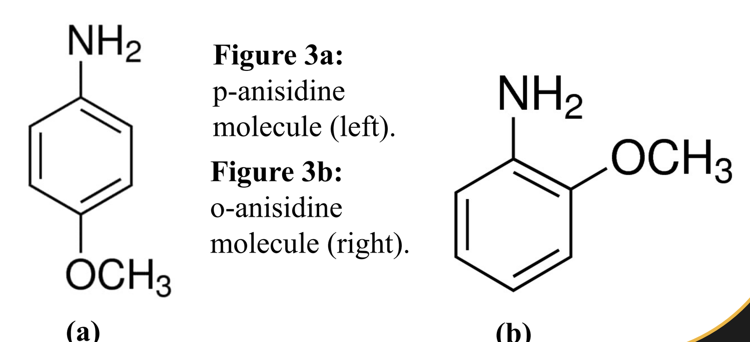
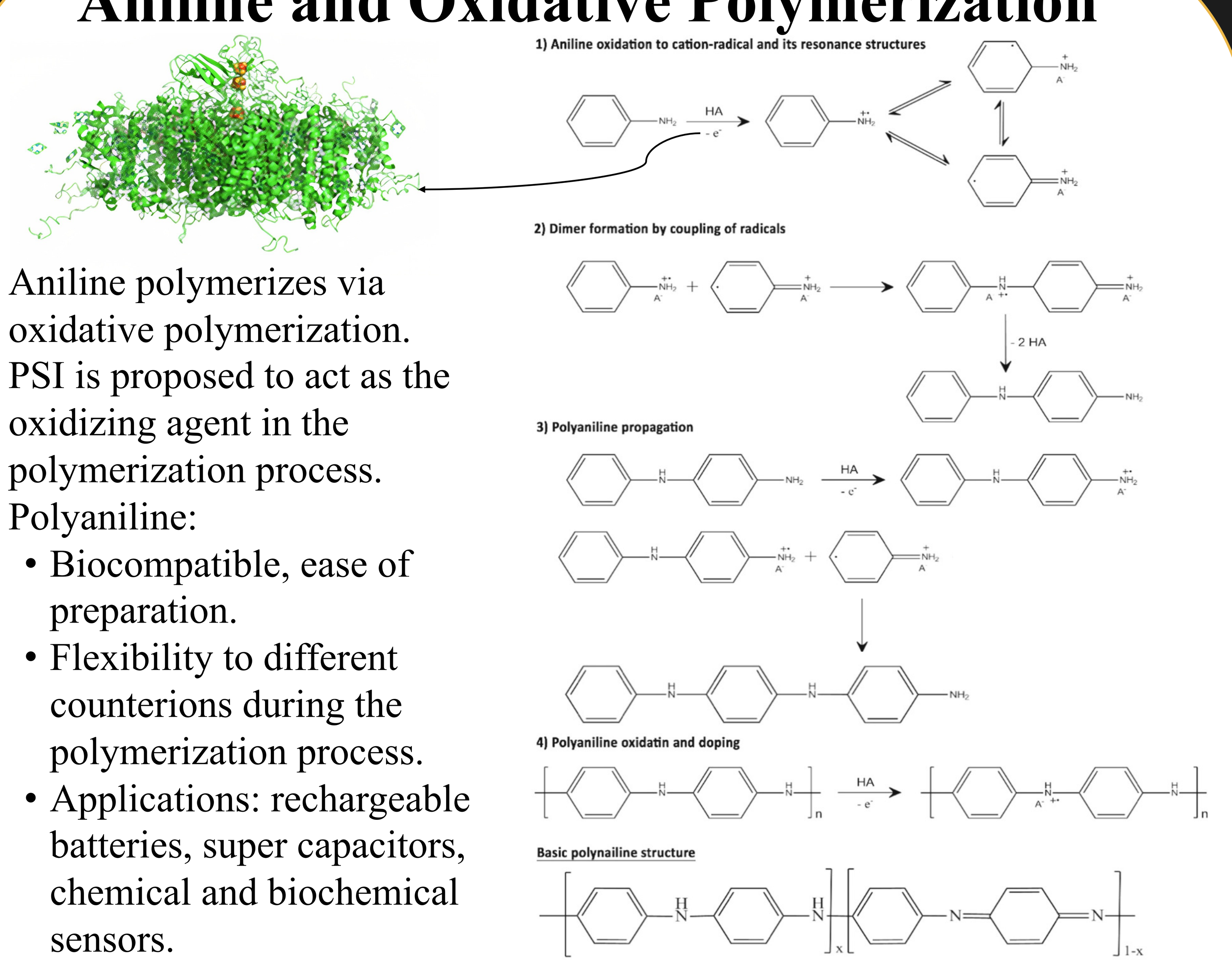


Figure 3a: p-anisidine molecule (left).
Figure 3b: o-anisidine molecule (right).

Aniline and Oxidative Polymerization



- Aniline polymerizes via oxidative polymerization.
- PSI is proposed to act as the oxidizing agent in the polymerization process.
- Polyaniline:
  - Biocompatible, ease of preparation.
  - Flexibility to different counterions during the polymerization process.
  - Applications: rechargeable batteries, super capacitors, chemical and biochemical sensors.

Figure 4. Proposed mechanism of electropolymerization of polyaniline, with PSI acting as an oxidizing agent (reproduced from Korent et al.)

Working Hypotheses

- P_{700} has a sufficiently high oxidizing potential to facilitate polymerization of certain substituted aniline molecules through oxidative radical polymerization.
- The polymers align energetically with the protein and the protein-polymer mixture is conductive and suitable for solar energy conversion applications.

Surface Wettability: Contact Angles

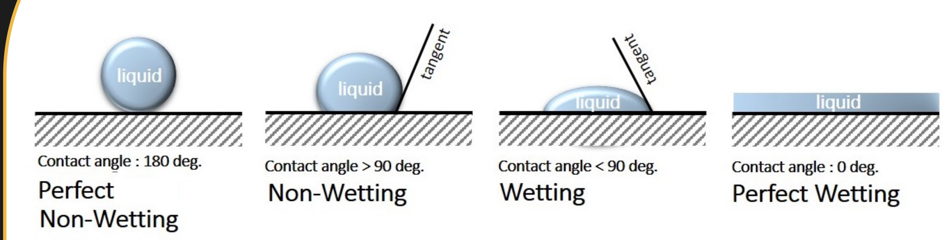


Figure 5: Visualization of different values of contact angles. Image credit CSC Scientific.

	Average Contact Angle (°)
PSI	81 ± 4
10:1 PPA:PSI	53 ± 1
100:1 PPA:PSI	50 ± 2
1,000:1 PPA:PSI	49 ± 2
10,000:1 PPA:PSI	46 ± 1
PPA	31 ± 1

- Contact angles provide information on the hydrophilicity of a surface.
  - θ<90 : hydrophilic.
  - θ >90: hydrophobic.
- The protein-polymer mixtures result in surfaces that exhibit different hydrophilicities.
  - The protein and the polymer were mixed at different ratios to analyze the behavior and characteristics of the resulting films.
  - Overall, the contact angle decreases as the concentration of monomer increases, and the contact angle approaches that of PPA's.

IR Spectroscopy of PPA and PSI films

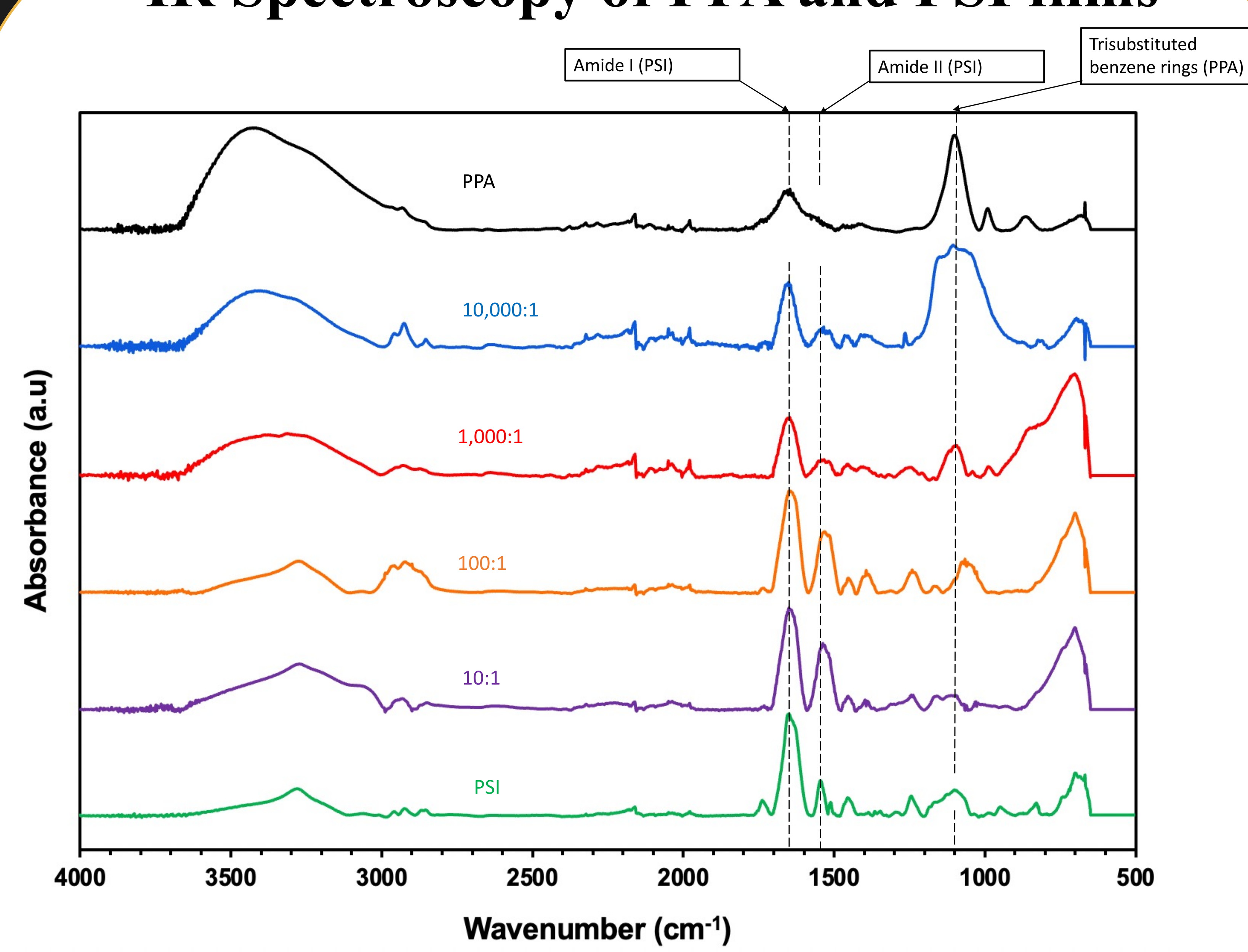


Figure 6: Infrared spectroscopy confirms that when mixed with PSI and irradiated with simulated sunlight, the PPA forms a composite film with the PSI, as shown by PSI's Amide I peak (~1640 cm^{-1}) and PPA's trisubstituted benzene ring peak (~1100 cm^{-1}). There is a positive correlation between the intensity of these peaks and the concentration of monomer mixed in solution.

IR Spectroscopy of POA and PSI films

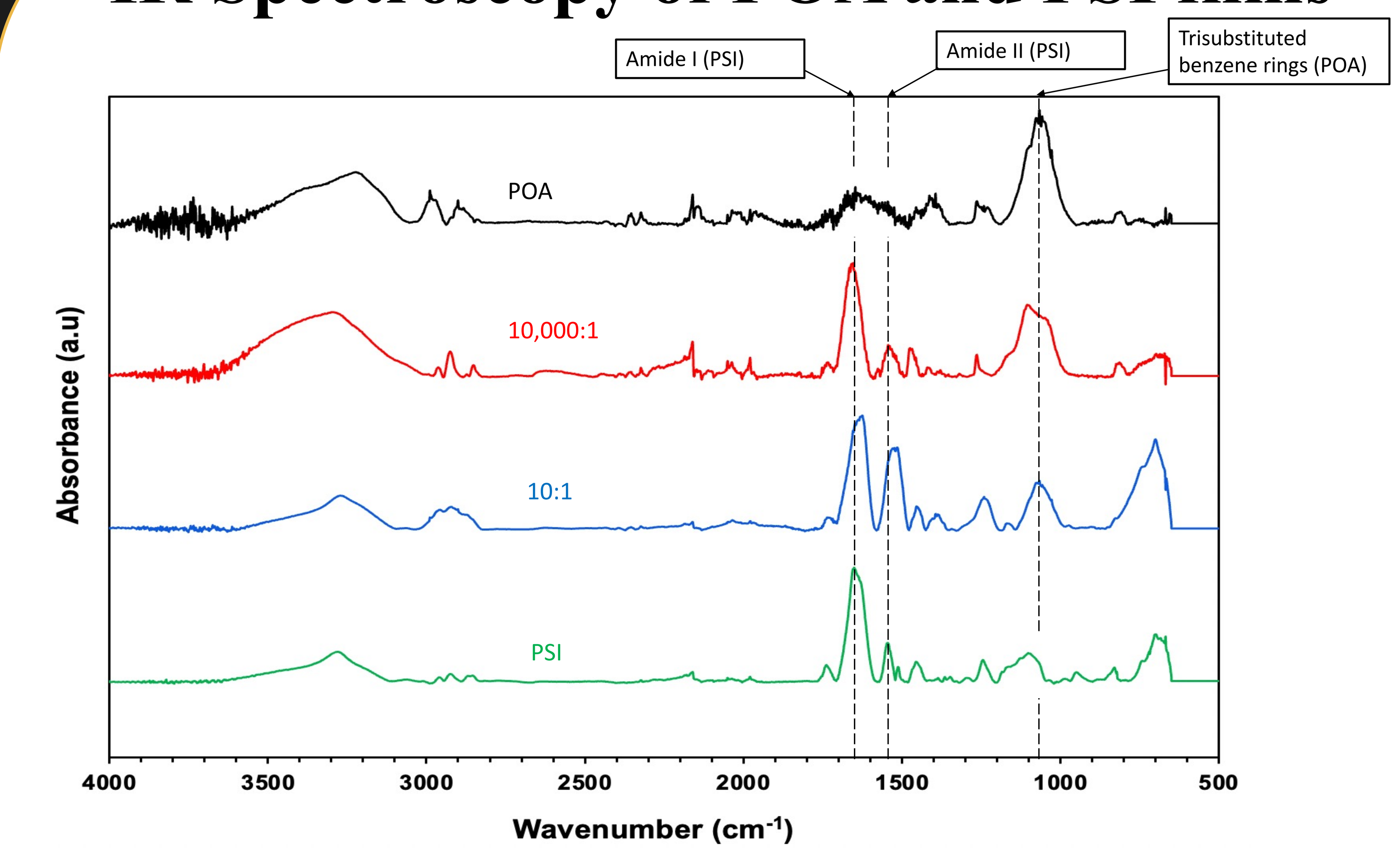


Figure 7: POA films were created at different ratios of POA to PSI. Similar to the PPA:PSI films, the presence of a composite film is demonstrated by the intensity of the Amide I and polymer peaks as the concentration of monomer increases.

Conclusions

- Para- and ortho- methoxyanilines can form composite films with PSI.
- The composite films become more hydrophilic as the ratio of polymer to PSI is increased.
- The amount of polymer observed in the films correlates positively with an increase in ratio of monomer to PSI in solution.

Future Work

- Perform conductivity tests on composite films.
  - Four-point probe measurements
- Characterize the composite material with SDS-PAGE and GPC to determine polymer-protein connectivity and molecular weight.
- Investigate the contribution of chlorophyll a to polymerization.
- Look at other substituted anilines or monomers with higher redox potentials to experiment polymerization feasibility.

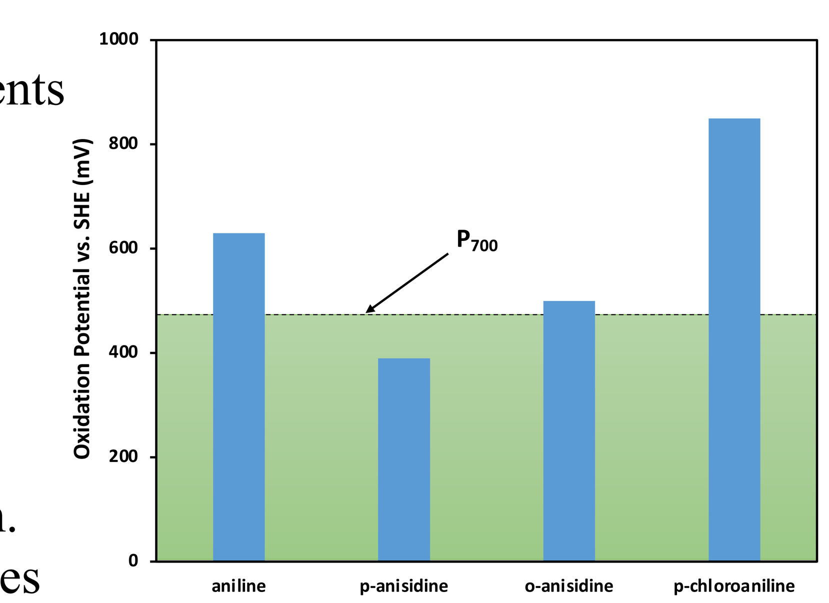


Figure 7: Oxidation Potentials of different substances; the green area represents energetic favorability with P700 (490 mV), ending at the dashed line.

Acknowledgments

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