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Extraction of PPIX from Brown Eggshells for Use in Dye-Sensitized Solar Cells

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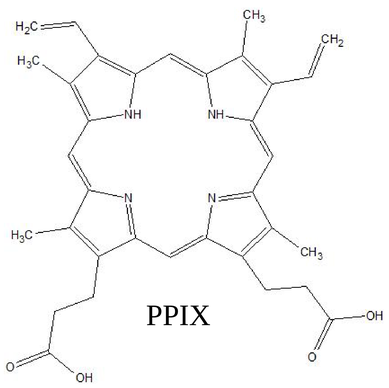
Introduction

Dye-sensitized solar cells (DSSC) are a possible alternative to traditional solar energy technologies. Organic dyes such as porphyrins seem to be an especially promising option as a sensitizer due to their characteristic Soret band and smaller Q-bands in the visible spectrum. Protoporphyrin IX (PPIX) is a naturally occurring porphyrin found in sources such as hemoglobin, chlorophyll, and brown eggshells. PPIX exhibits a typical porphyrin absorbance spectrum, and the carboxylic acid substituents make it ideal for direct attachment to the TiO_2 of the DSSC.

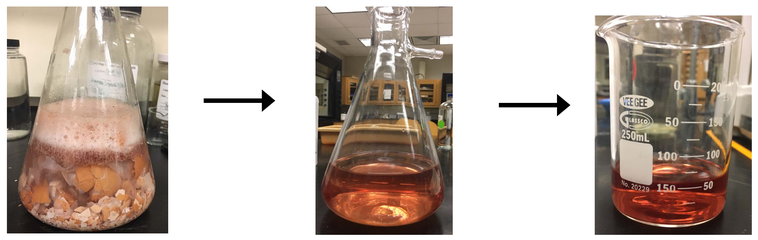


The purpose of the research project is to extract PPIX at a high enough concentration from brown eggshells that it can be purified using a fast protein liquid chromatography system (FPLC) and used as a sensitizer in DSSCs. This semester's work has focused on optimizing a purification method for the PPIX and using the FPLC to automate the process. Because the core of the extracted PPIX has no metal, the secondary goal of this research is to place different metals in the core in order to determine which metal maximally intensifies the Soret and Q-bands in the panchromatic solar energy spectrum.

Experimental

Part 1: Extraction

- 2M HCl and ethyl acetate added to brown eggshells until CO_2 production stopped
- Filtered using Buchner funnel, filter paper, and silica
- Organic layer separated, washed, and dried with anhydrous magnesium sulfate
- Ethyl acetate solvent evaporated off using rotary evaporator



Part II: Purification

- PPIX extract was purified on silica column using ethyl acetate to methanol elution gradient mobile phase.
- Eluent passed through 390 µL flow cell cuvette, and the absorbance at 280 nm and 400 nm was monitored on the Cary-50 spectrometer using a kinetics program.
- High performance liquid chromatography (SpectraSYSTEM) was used with C18 reverse phase column and silica column. Mobile phase of 60/40 methanol/water was used.

Part III: Pharmacia FPLC (circa 1985) Repair

- Detector was tested at various sensitivity settings.
- Silica column, reverse stationary phase, and magnesium silicate stationary phases were tested using various elution gradients of ethanol, methanol, water, and ethyl acetate as mobile phases.
- Blue dye, tyrosine, and PPIX extract were tested on the instrument with the three stationary phases.

Part IV Metalation[6]

- 150 mL of PPIX unpurified extract in ethyl acetate was refluxed for 30 minutes at 70 °C.
- 3.5 mmoles of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$, $NaC_2H_3O_2$, $KC_2H_3O_2$ and 1.25 mmoles of $Mg(C_2H_3O_2)_2$ were dissolved in 25 mL of methanol and slowly added to the PPIX solution. These solutions, and a control solution of PPIX with 25 mL of methanol, refluxed at 65 °C for two hours.

Results and Discussion

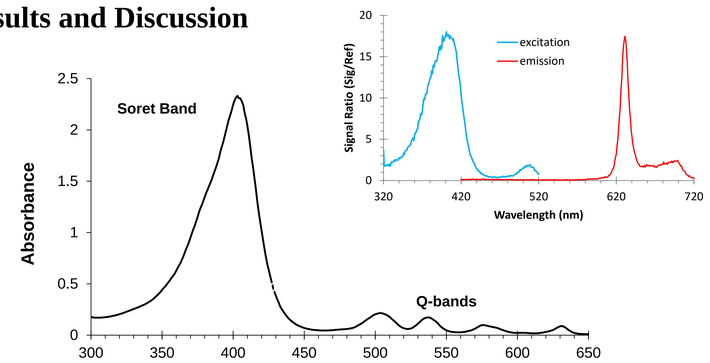


Figure 1. UV-vis absorbance spectrum of a PPIX extract showing Soret band (406 nm) and four Q-bands (504, 537, 576, 630 nm). Inset is a fluorescence spectrum of PPIX (λ_{ex}=408 nm; λ_{em}= 631, 697 nm). Absorbance and fluorescence spectra confirms presence of PPIX.[4]

Table 1. UV-Vis absorbance shifts in Soret and Q-bands following metalation of PPIX. Spectra obtained directly after metalation process.

Sample	Soret max (nm)	Shift	Peak Height (abs)	Hyper-chromism Ratio	Q-bands (nm)			
PPIX	417	none	.018	1	490	544	587	644
PPIX-Zn	417	none	.382	21	-	546	583	-
PPIX-K	403	blue	.164	9	-	531	570	-
PPIX-Na	402	blue	.040	2	493?	-	572	-
PPIX-Mg	404	blue	.038	2	505?	-	591	-

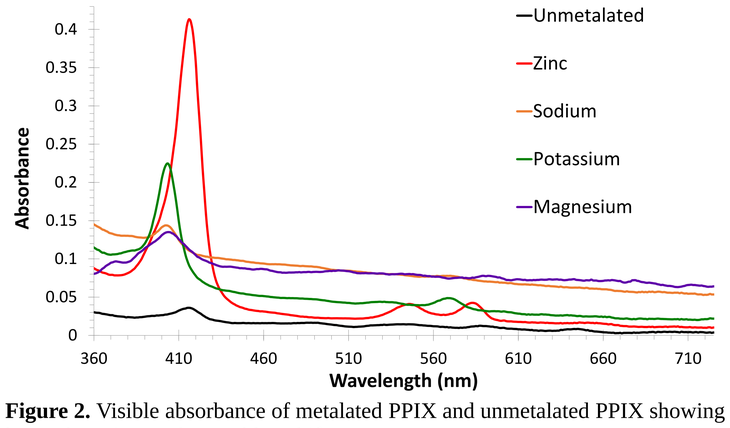


Figure 2. Visible absorbance of metalated PPIX and unmetalated PPIX showing hyperchromism and some blue-shifts.

Figure 3. Image of Pharmacia Liquid Chromatography Controller 500 with fraction collector (FPLC system).

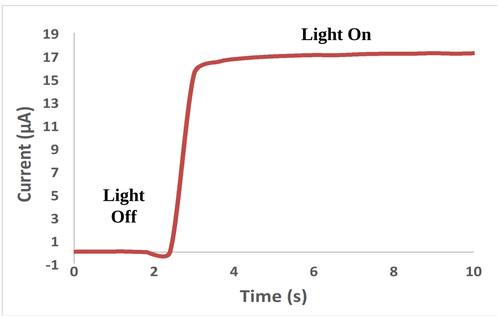


Figure 4. Time dependent photocurrent graph showing current with white light LED source of PPIX unpurified extract on TiO_2 DSSC. Current measured using cyclic voltammeter across 600 seconds and plateaued at 17 µA.

Conclusions

- Protoporphyrin IX was successfully extracted from brown eggshells based on the comparison of fluorescence and absorbance spectra to literature values (Figure 1).
- NMR results (not shown) confirm presence of material other than PPIX in extract. Results from both the Cary 50 flow cell cuvette and HPLC (not shown) indicate a reverse phase stationary phase is most effective in separation of the components of the extract.
- While theoretically still a useful instrument for automation of the purification process, detector tests on the FPLC system have shown inconsistent results (Figure 3).
- PPIX successfully attached to a TiO_2 DSSC and held current for ten minutes, providing support for PPIX as a potential sensitizer dye (Figure 4).
- Metalation of PPIX shows hyperchromism, suggesting that PPIX may have higher power conversion efficiencies when metalated.

Acknowledgments

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