

Photo-induced Polarization in Light-sensitive Dye Monolayers Measured by Electrical Impedance Spectroscopy

A Major Qualifying Project Report

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Abstract

Metal Porphyrin complexes are used in dye sensitized solar cells due to their electrochemical properties. Zinc Protoporphyrin IX was placed into ITO slides in an attempt to validate the hypothesis that photo-reactive monolayers display polarization effects in response to stimulation. The project looked for alterations in the electrochemical profile of the material as measured by electrical impedance spectroscopy.

Acknowledgements

I would like to thank Mr. Alexander Carl for instructing me on the use of the x-ray photoelectron spectroscopy machine and the software to use it.

I would also like to thank Dr. Roghi Kalan, PhD. for instruction on the use of both the glovebox and the potentiostat.

I would like to thank Worcester Polytechnic Institute and the Department of Chemistry and Biochemistry for their commitment to undergraduate research.

Finally I would like to thank Professor Ronald Grimm most of all for his guidance in this project, his role as a mentor, and his time spent instructing and educating me throughout the course of the project.

1. Introduction

Our society is more and more dependent on small electronics in our daily lives, in our medical care, and in our luxury purchases. Thin film monolayers have the potential to advance the level of sophistication and complexity our devices are capable of, however, they are not a fully understood media in terms of their electrochemical properties.

In order to progress our society's ability to use electronic devices, technological leaps and bounds must be made. In order for these leaps and bounds to even be feasible, a better understanding of the photo-voltaic and electrochemical properties of thin films is required.

This endeavor was undertaken in order to explore potential electrochemical behavior of thin film monolayers on conductive substrates in response to light, and in doing so to advance knowledge about the field and encourage future progress.

2. Background

Many monolayers on conductive media undergo electrochemical changes in response to stimulation by light. A proposed explanation for some of these electrochemical changes is a polarization effect across the surface of the monolayer. The purpose of this project is to evaluate this potential polarization change by observing changes in surface dipoles of deposited monolayers as noted by changes in the capacitance of the monolayer in response to light.

For this project, Indium doped Tin-Oxide (ITO) slides were prepared with monolayers deposited on the functionalized surface. The application of these monolayers was verified via XPS (X-ray Photoelectron Spectroscopy) and their electrochemical properties were observed using Impedance Spectroscopy.

The end purpose of this project is to examine a possible phenomenon in monolayer electrochemistry and to use the conclusions drawn to further evaluate the photosensitivity of these systems.

2.1 Metal Porphyrins

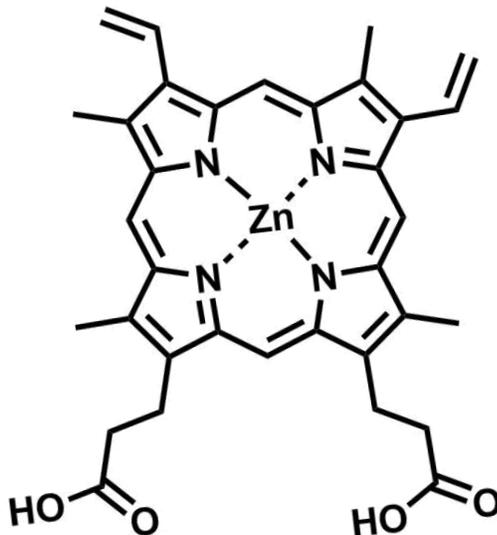


Figure 1: Zinc Protoporphyrin IX

Metal Porphyrins are frequently used in dye sensitized solar cells due to their photo-voltaic properties. This project focused on Zinc Protoporphyrin IX (featured above) due to its readily available carboxylic acid ends which facilitate deposition onto ITO. Protoporphyrin IX is a precursor for hemes as well as chlorophyll in biological processes.^[1] In Zinc Protoporphyrin IX a zinc is added to the center of the ring, binding directly to two of the Nitrogen's in the central ring and complexing with the other two.

2.2 X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a spectroscopic technique that is used to evaluate the surface composition of a material quantitatively. XPS can be used to identify components of a material surface and to determine how much of these components are present. The XPS is

operated at ultra-high vacuum with pressures in the order of 10^{-9} millibar. The XPS works by reflecting x-rays at an angle specific to the individual machine (90° in the case of the XPS located in Gateway Park). These x-rays stimulate the surface of the material and cause photoelectrons to be emitted in correspondence to the binding energy of the deposited elements, as measured in electron-Volts (eV). The counts of photoelectrons measured by the XPS at each given binding energy are directly quantitatively linked to the amount deposited at the surface. By comparing the area under the curve of the peaks of deposited materials along with their sensitivity factors at 90° , the XPS can be used to examine coverage of a surface in fractions of a monolayer or to verify the empirical formula of the deposited chemicals. [2]

2.3 Monolayer Impedance

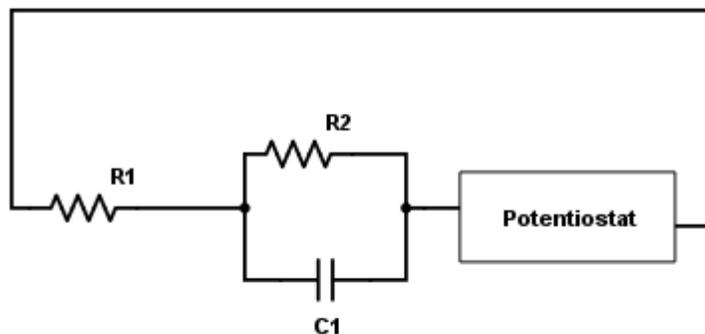


Figure 2: Impedance Circuit

Monolayers deposited on conductive substrates can act as capacitors in circuits. At low frequencies the capacitor does reset and so acts as a break in the circuit, forcing the current to pass through both resistor one and resistor two. At higher frequencies, however, the capacitor acts as a short and the current bypasses resistor two entirely. The impedance of the monolayer is a measurement of the opposition to current passed through the system and is a complex ratio of the voltage and current in an alternating current system. Impedance acts as an extension of

system resistance to AC systems and has both magnitude and phase. The measured impedance of a system featuring a monolayer on conductive substrate is a product of the resistance of the system at different frequencies.

2.4 Impedance Spectroscopy and Nyquist Impedance

Electrochemical Impedance Spectroscopy (EIS) is the quantitative analysis of the electric properties of a sample as a function of frequency. EIS can be used to characterize the nature of a sample (e.g. verifying monolayer deposition) as well as to observe changes in the dipole moment of a sample in response to stimulation. As system impedance is a complex measurement, there are multiple possible graphical representations of the data collected. Nyquist Impedance is one such representation which uses the real component of the transfer function for the x-axis and the imaginary component for the y-axis. Using fitting software the data from a Nyquist Plot can be used to find the resistance values of a circuit as well as other electrical components, including capacitance.

3. Experimental

3.1 RCA-1/RCA-2 Cleaning of ITO

In order to prepare the ITO slides for use they were treated via RCA-1/RCA-2. To remove residual organics, a solution was made up of 35.0 mL deionized water, 7.0 mL aqueous ammonium hydroxide (NH_4OH , 29% by weight of NH_3), and 7.0 mL aqueous hydrogen peroxide (H_2O_2 , 30% by weight). ITO was placed into this solution which was brought to approximately 75 °C for ten minutes. After this, the ITO was rinsed with 18-megohm water and then added to a solution of 42.0 mL deionized water, 7.0 mL hydrochloric acid (HCl , 37% by weight), and 7.0 mL aqueous hydrogen peroxide (H_2O_2 , 30% by weight) at 75 °C for approximately ten minutes. The ITO was then removed from solution, rinsed with 18-megohm water, dried via dry argon gas, and finally stored in a sealed, dry container.

3.2 Application of Silane Monolayers

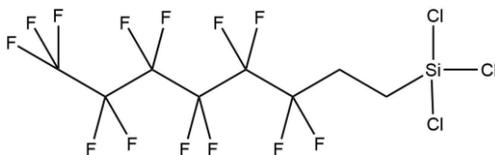


Figure 3: Trichloro(1H,1H,2H,2H-perfluorooctyl)silane

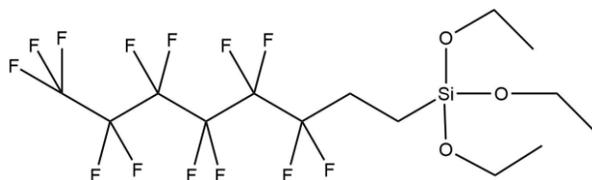


Figure 4: 1H,1H,2H,2H-Perfluorooctyltriethoxysilane

Before work with Zinc Protoporphyrin, monolayers of fluorinated silanes were deposited on ITO practice on instruments and to prepare for the actual final monolayer. Two drops of

Trichloro(1H,1H,2H,2H-perfluorooctyl)silane were added to a small plastic petri dish which was sealed with a piece of ITO next to the drops for five seconds. The ITO was then rinsed with toluene to dislodge any excess silane and prevent polymerization on the surface. The slide was then dried with argon gas. Similarly, 1H,1H,2H,2H-Perfluorooctyltriethoxysilane was diluted to one tenth in ethanol, and then two drops of the dilute solution was added to a petri dish with a clean piece of ITO and let sit while covered for five seconds. The slide was then washed with toluene and dried with argon.

3.3 Deposition of Protoporphyrin IX Monolayer

Protoporphyrin IX was deposited on the surface based on a modified procedure based on that found in Havare et al.^[3] Clean ITO was washed successively with deionized water, acetone, and 2-propanol and then dried with argon gas. The cleaned ITO was treated in an oxygen plasma cleaner for ten minutes to activate the surface. Immediately after plasma cleaning, the slide was dipped into a centrifuge tube containing 2 mM solution of Protoporphyrin IX dissolved in 1:1 DMF (Dimethylformamide):Methanol, completely covering the slide in the solution for 48 hours to ensure a closely packed monolayer. After this, the slide was removed from solution and rinsed with methanol and dried with argon.

3.4 Addition of Zinc to Protoporphyrin on ITO Surface

Zinc was added to the center of the deposited Protoporphyrin. A solution was prepared by dissolving 0.001 g of zinc chloride ($ZnCl_2$) to 10.0 mL methanol under vacuum. The protoporphyrin treated ITO was added to this solution for two hours before being removed, rinsed with methanol, and dried with argon.

3.5 Verification of Zinc Addition via XPS

The addition of zinc to the functionalized surface was verified via XPS. The sample of ITO was run before zinc addition to verify the presence of the protoporphyrin on the surface. Nitrogen and Indium were used as fitting peaks for coverage. The sample was run again after zinc addition to verify the presence of zinc within ring structures, and not as zinc plating or attachment via chlorine. The comparative areas of zinc and nitrogen were used alongside their sensitivity factors at 90° (3.354 for Zn and 0.477 for N) to verify stoichiometric ratios of the two elements.^[4]

3.6 Impedance Measurements of Surfaces

The treated slide of ITO was introduced into a glove box and added to an electrochemical cell containing Ferrocene/Ferrocenium in acetonitrile to form a circuit (seen above in figure two). Using the potentiostat and the EC-Lab software function PEIS, the impedance character of the material was recorded by scanning frequencies from 10 mHz to 1 MHz. This data was taken both in darkness and with a light focused on the sample and Nyquist Plots of each were fitted with the model of $R_1 + R_2/C$ in order to the capacitance of the material.

4. Results and Discussion

Unfortunately, while monolayer impedance was achieved and verified, the data does not support the polarization hypothesis for this particular material. While further testing of new samples may yield slightly different results, the difference in capacitance between the sample in the light and dark was not significant enough to validate the polarization conclusion. The capacitance of the material remains relatively constant around 6 μF in both light and dark (see Table 1, below and Figures 5, 6 below and 12-17, Appendix B).

param.	sel.	sign	value	unit	dev.
R1	<input checked="" type="checkbox"/>	+/-	328.7	Ohm	0.985 2
C2	<input checked="" type="checkbox"/>	+/-	6.261e-6	F	33.95e-9
R2	<input checked="" type="checkbox"/>	+/-	291.3	Ohm	1.353

Figure 5: Resistivity and Capacitance Fitting Without Light

param.	sel.	sign	value	unit	dev.
R1	<input checked="" type="checkbox"/>	+/-	376.9	Ohm	1.058
C2	<input checked="" type="checkbox"/>	+/-	5.655e-6	F	19.62e-9
R2	<input checked="" type="checkbox"/>	+/-	303.9	Ohm	1.392

Figure 6: Resistivity and Capacitance Fitting With Light

Run	Capacitance Without Light (μF)	Capacitance With Light (μF)	Change in Capacitance(Dark to Light) (μF)
1	6.621	5.655	-.996
2	6.161	6.123	+.038
3	5.672	5.535	-.137
Average	6.151	5.771	-.380

Table 1: Capacitance in Light and Dark

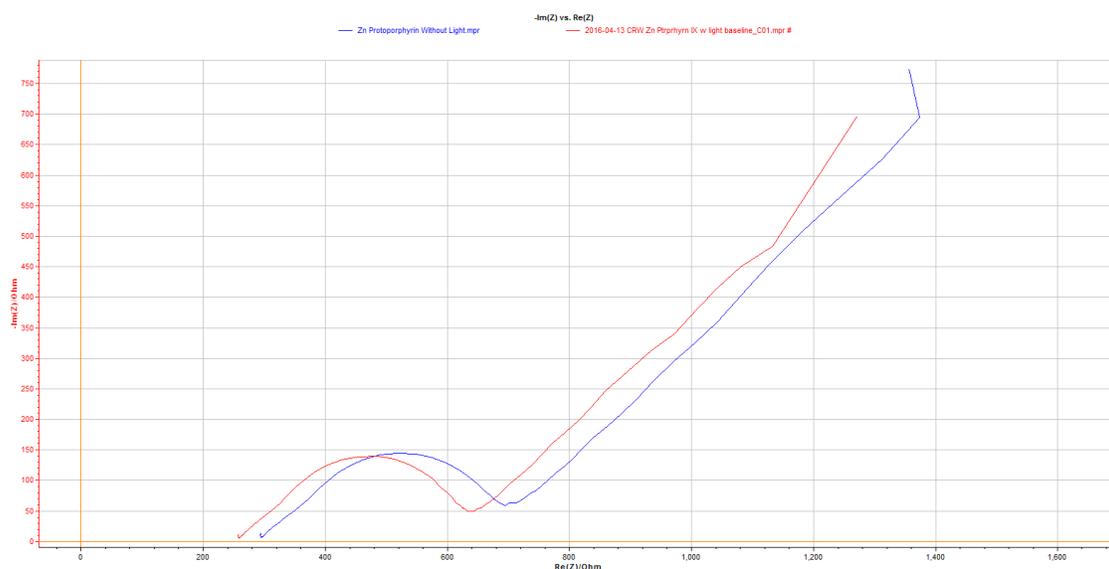


Figure 7: Overlaid Nyquist Plots With and Without Light

The applied layer of Zinc Protoporphyrin IX did behave consistently as a monolayer on conductive media, but there was not enough of a change in capacitance to justify the polarization conclusion. It is unlikely that any errors in execution of the synthetic procedure are to blame, as the process was verified to have attached Zinc Protoporphyrin. It is more likely that either the material itself, or the method of attachment prevented the hypothesized polarization from occurring. Connecting the monolayer to the substrate via a linkage assembly like APTMS, which is commonly used in similar set-ups, may provide a more stable connection to the ITO than simply relying on the carboxylic acid terminations of Protoporphyrin IX to connect to the surface.

5. Conclusion

While the project was unable to verify and support the hypothesis that this particular monolayer undergoes a polarization effect, it is possible that other materials would display the expected interactions. The original goal of the project may be unfulfilled but that does not prevent the project from being picked back up in the future using different materials.

5.1 Other Potential Materials

Other materials could exist that would be better suited for any future attempts at this project. For example, the magnesium complex version of Protoporphyrin IX is produced during photosynthesis and could be more likely to display charge effects in response to light. The Cobalt Protoporphyrin IX complex might also be a useful alternative, as its bulky center is sterically hindered by an attached chlorine from staying planar with the Protoporphyrin ring, and so may behave somewhat differently in response to light. Future attempts at this project may benefit from verifying the existence of any photo response in their chosen material before attempting to look for changes in the surface dipole.

6. References

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2. John F. Watts, J. W. (2003). *An Introduction to Surface Analysis by XPS and AES*. West Sussex: John Wiley and Sons.
3. Havare, A.K., Can, M., Demic, S., Okur, S., Kus, M., Aydın, H., Yagmurcukardes, N. and Tari, S., "Modification of its surface using aromatic small molecules with carboxylic acid groups for OLED applications", *Synthetic Metals*, Vol. 161, No. 21, (2011), 2397-2404.
4. Appendix E: Atomic Sensitivity Factors at 90°. (1979). In C. Wagner, & G. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy : A Reference Book of Standard Data for Use in X-Ray Photoelectron Spectroscopy*. Eden Prairie, Minn. : Physical Electronics Division, Perkin-Elmer .

Appendix A: XPS Spectra

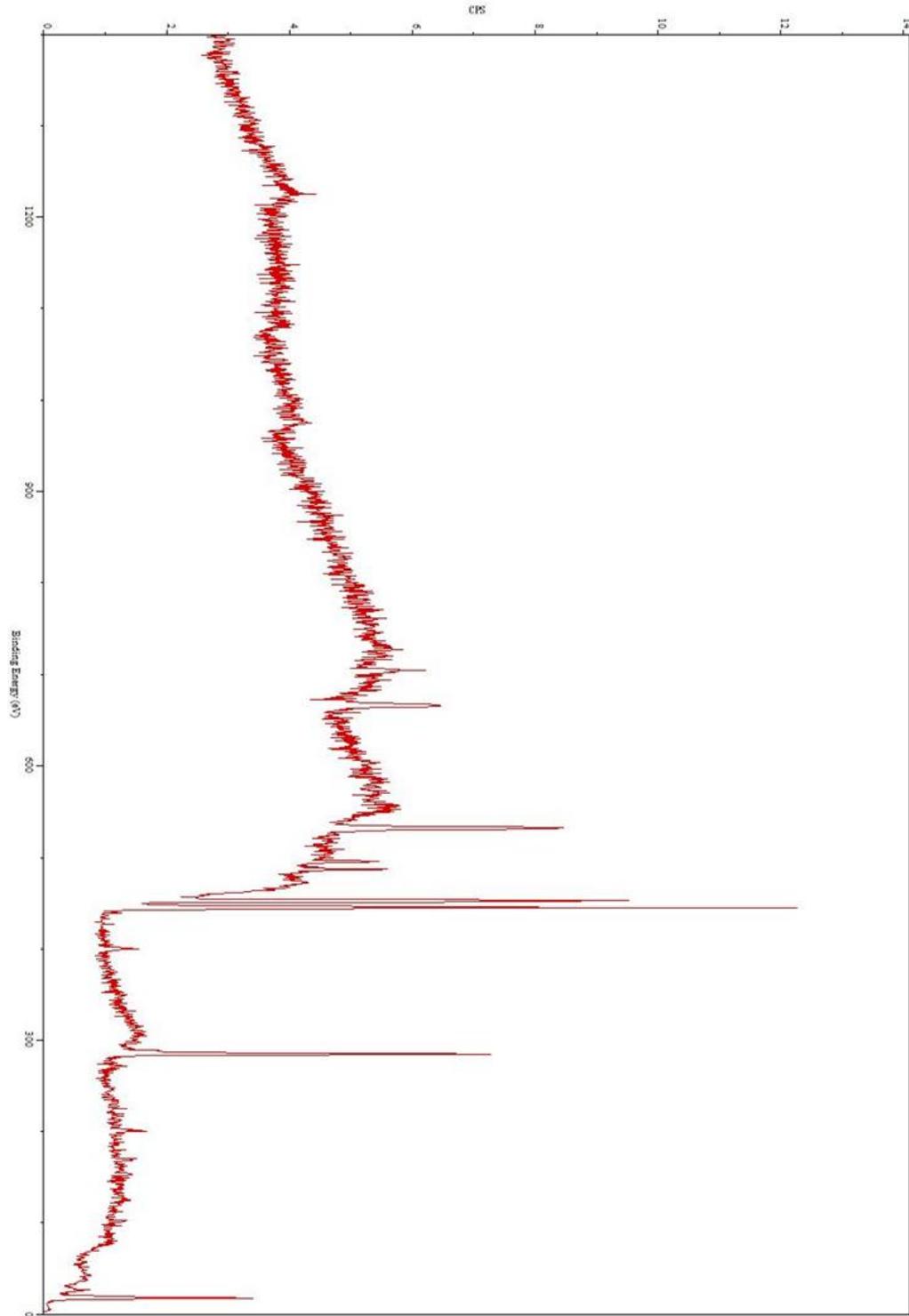


Figure 8: XPS Survey of Protoporphyrin IX on ITO

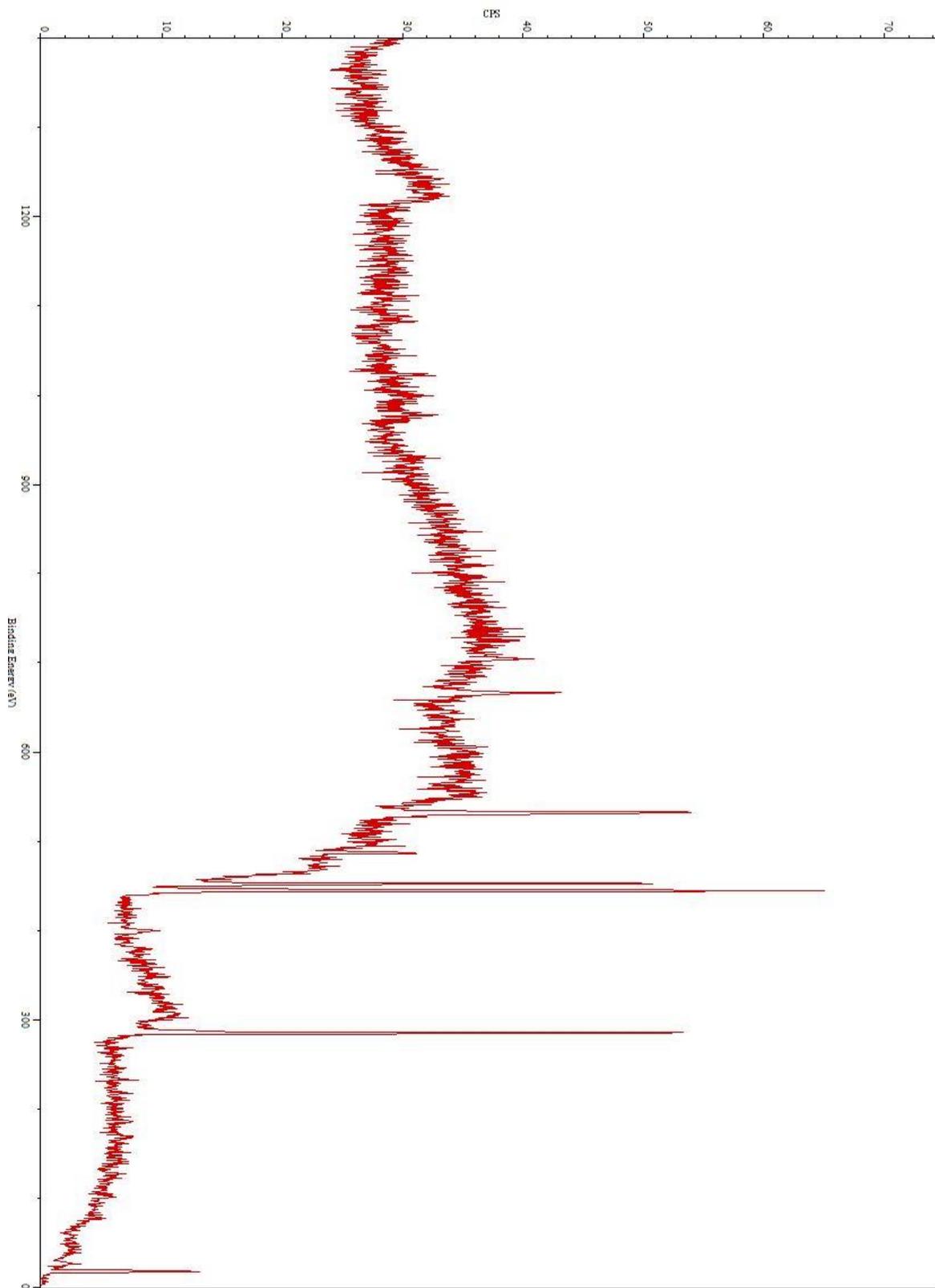
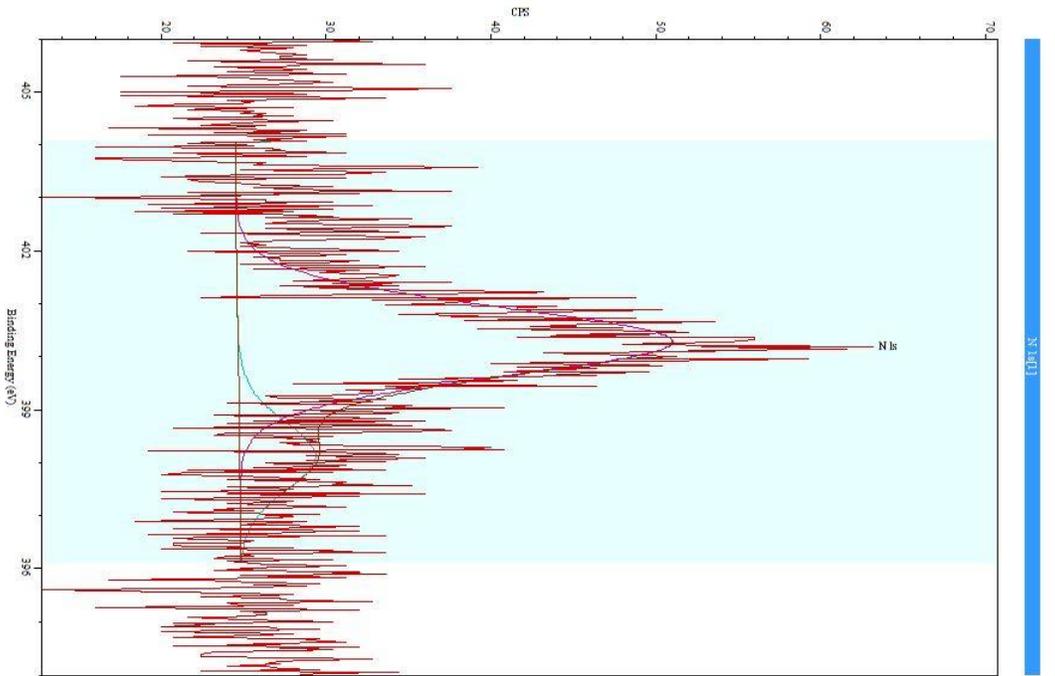


Figure 9: XPS Survey of Zinc Protoporphyrin IX on ITO



Quantification Parameters

Regions: Components | Data Editor | Report Spec. | RPT Report

N 1s [1] [RMS = 141.407, D. of F. = 311] [Fit: RSF = 1.9555] [E]

Component	A	B
Name	N 1s	N 1s
R.S.F.	1.8	1.8
Line Shape	GL(20)	GL(20)
Area	Area = 43.8	7.6
Area Constr.	0.0 - 100000.0	
Width	Width = 1.0	1.53493
Width Constr.		A * 1
Position	398.1249	406.394
Pos Constr.	N 1s	N 1s
Tag	1	1
Comp Index	0.0000	0.0000
Asymmetry / ...	95.22	14.78
% Concentr.		

Etch Time	N 1s	Zn 2p3/2	In 3d5
0	N 1s [1]	Zn 2p3/2	In 3d5 [3]

Figure 10: Zinc Protoporphyrin Nitrogen Peak and Fitting

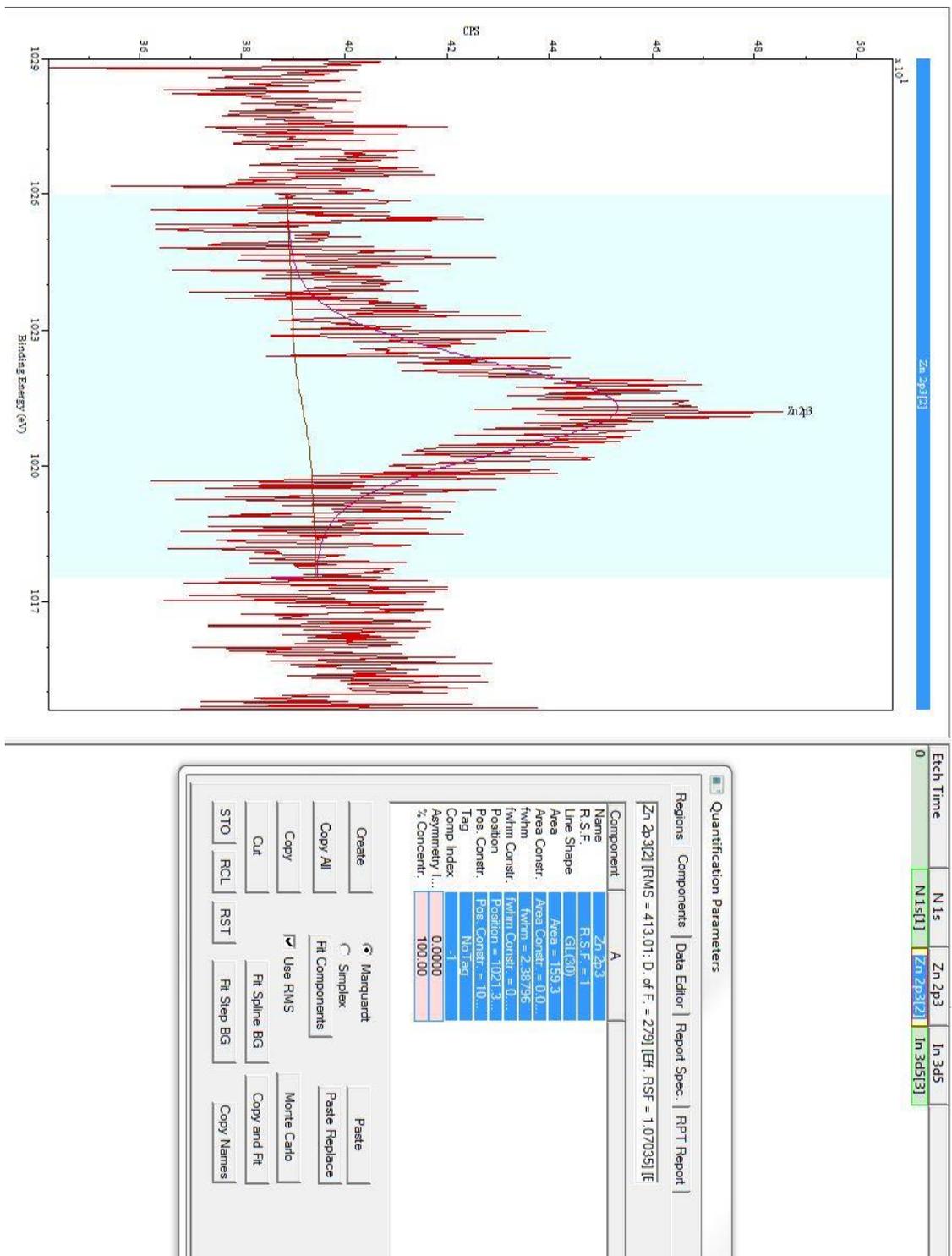


Figure 11: Zinc Protoporphyrin Zinc Peak and Fitting

Appendix B: Impedance Spectra

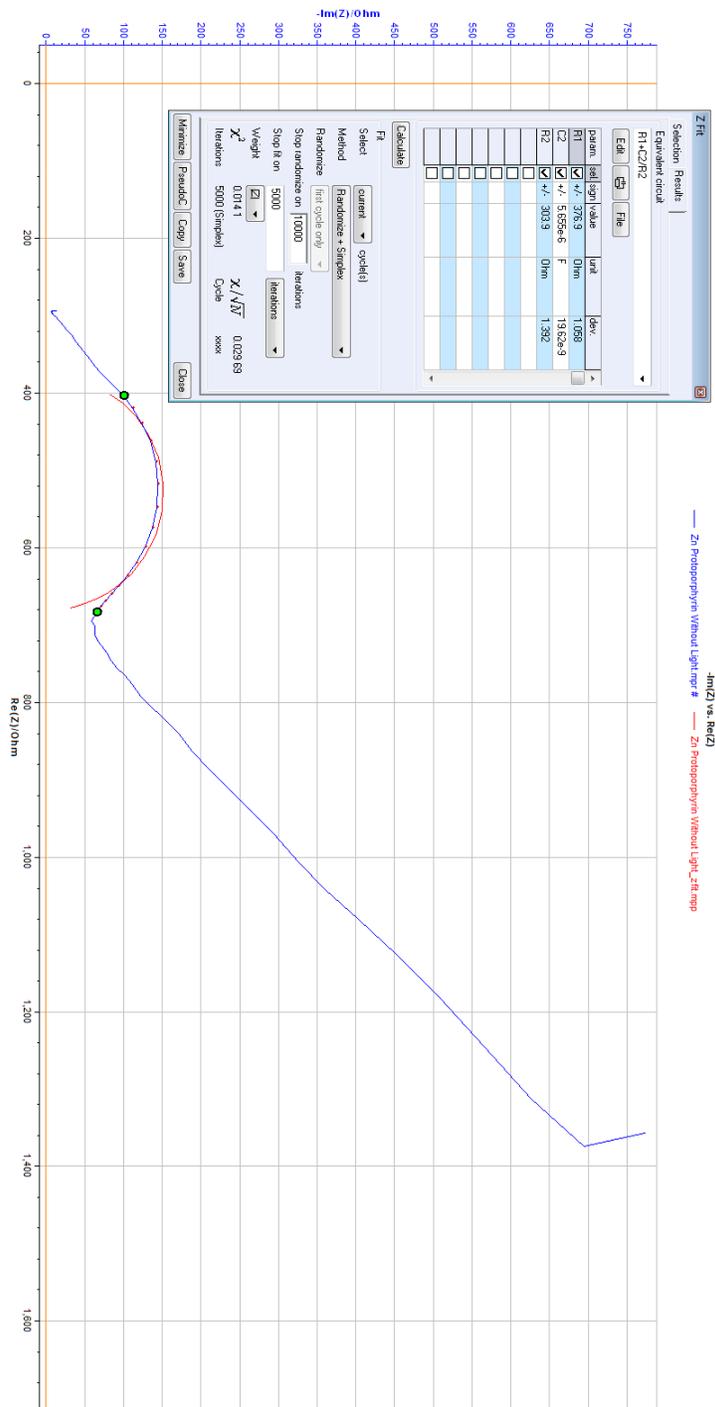


Figure 12: Nyquist Impedance without Light Run 1

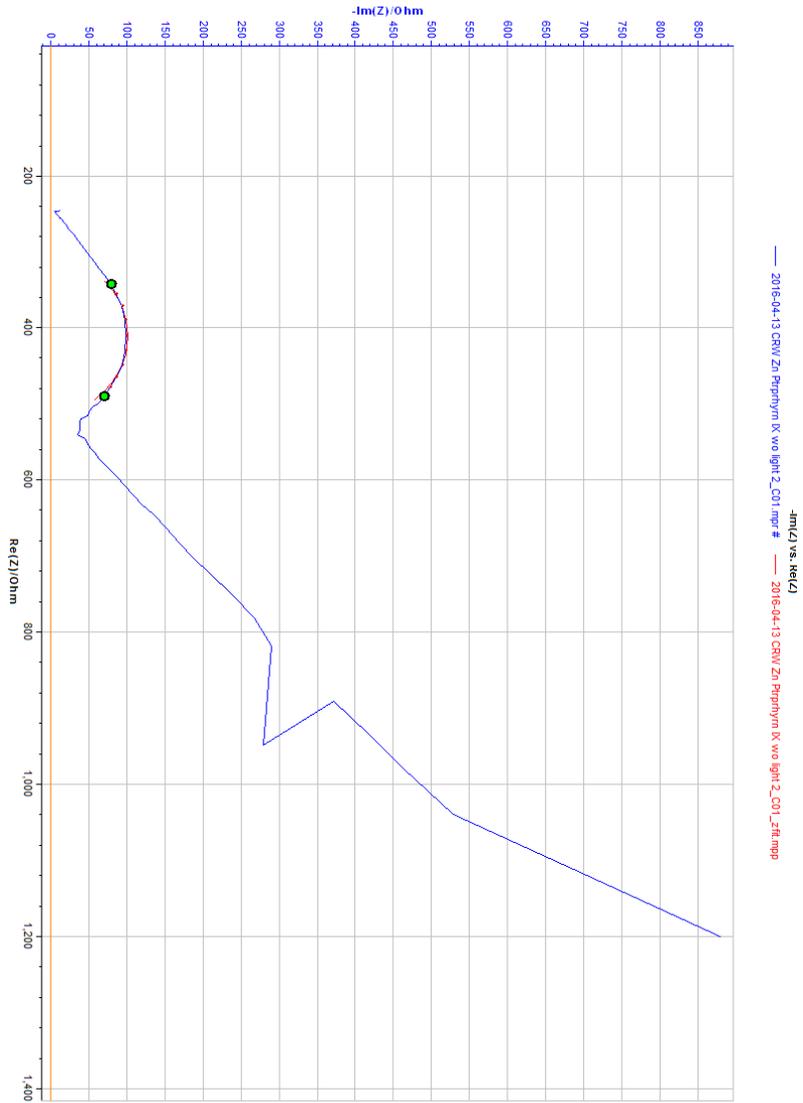
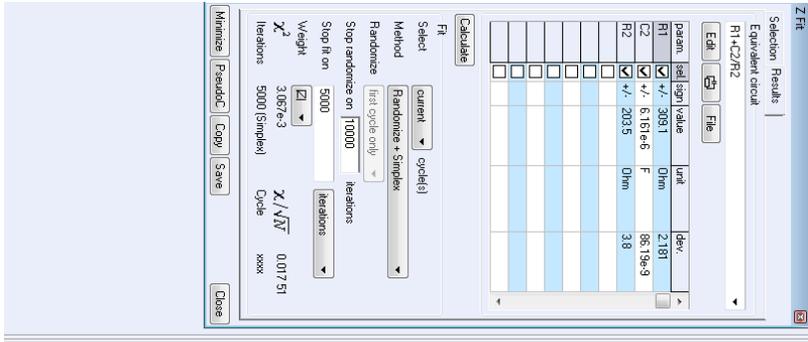


Figure 13: Nyquist Impedance without Light Run 2

ZFit

Selection Results

Equivalent circuit

R1+C2/R2

Param	Est. Ign	Value	Unit	Dev
R1	<input checked="" type="checkbox"/>	370.6	Ohm	1.332
C2	<input checked="" type="checkbox"/>	5.672e-6	F	9.53e-9
R2	<input checked="" type="checkbox"/>	247.4	Ohm	2.029
	<input type="checkbox"/>			

Calculate

Fit

Select cycles(s)

Method iterations

Randomize iterations

Stop randomize on 10000 iterations

Stop fit on 5000 iterations

Weight χ^2 χ/\sqrt{I} 0.028

Iterations 5000 (Steady) Cycle xxx

Minimize

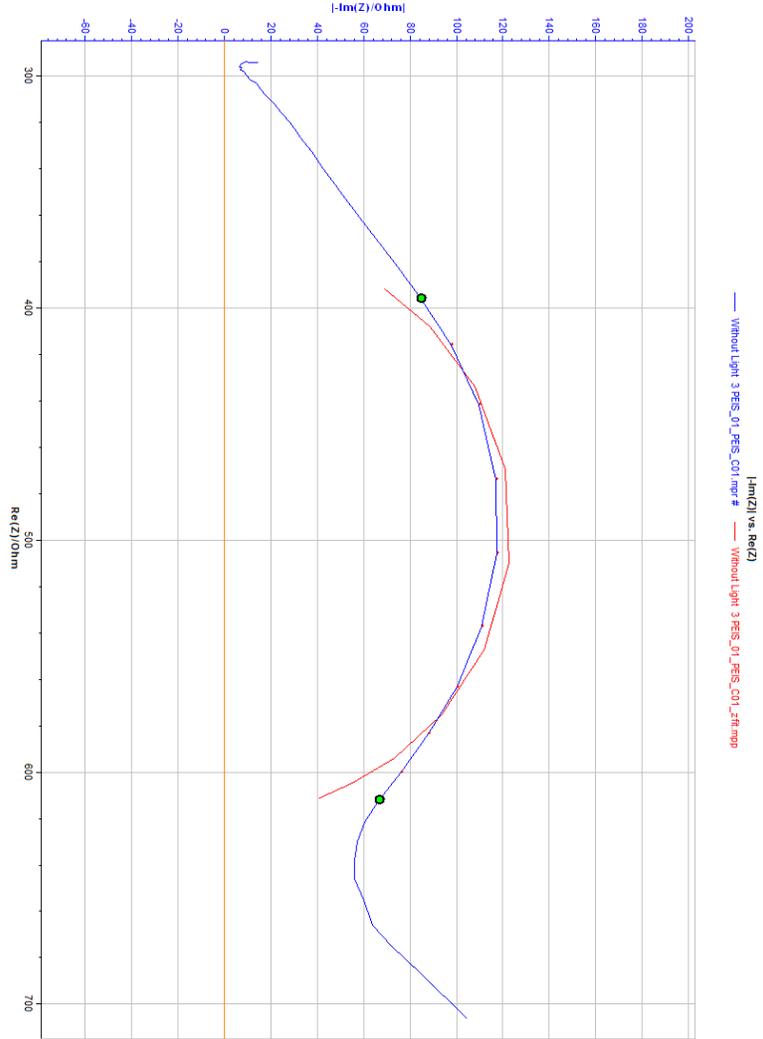


Figure 14: Nyquist Impedance without Light Run 3

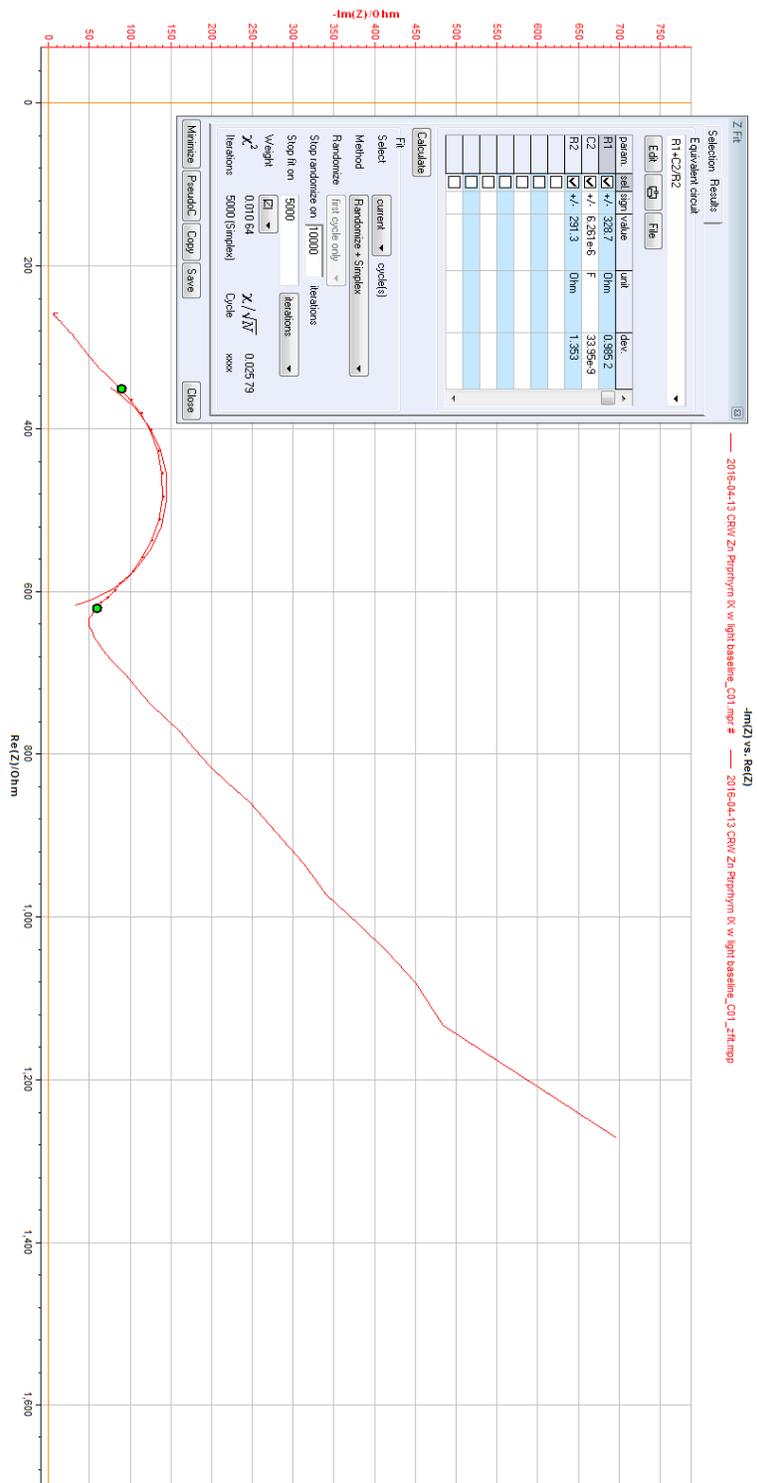


Figure 15: Nyquist Impedance with Light Run 1

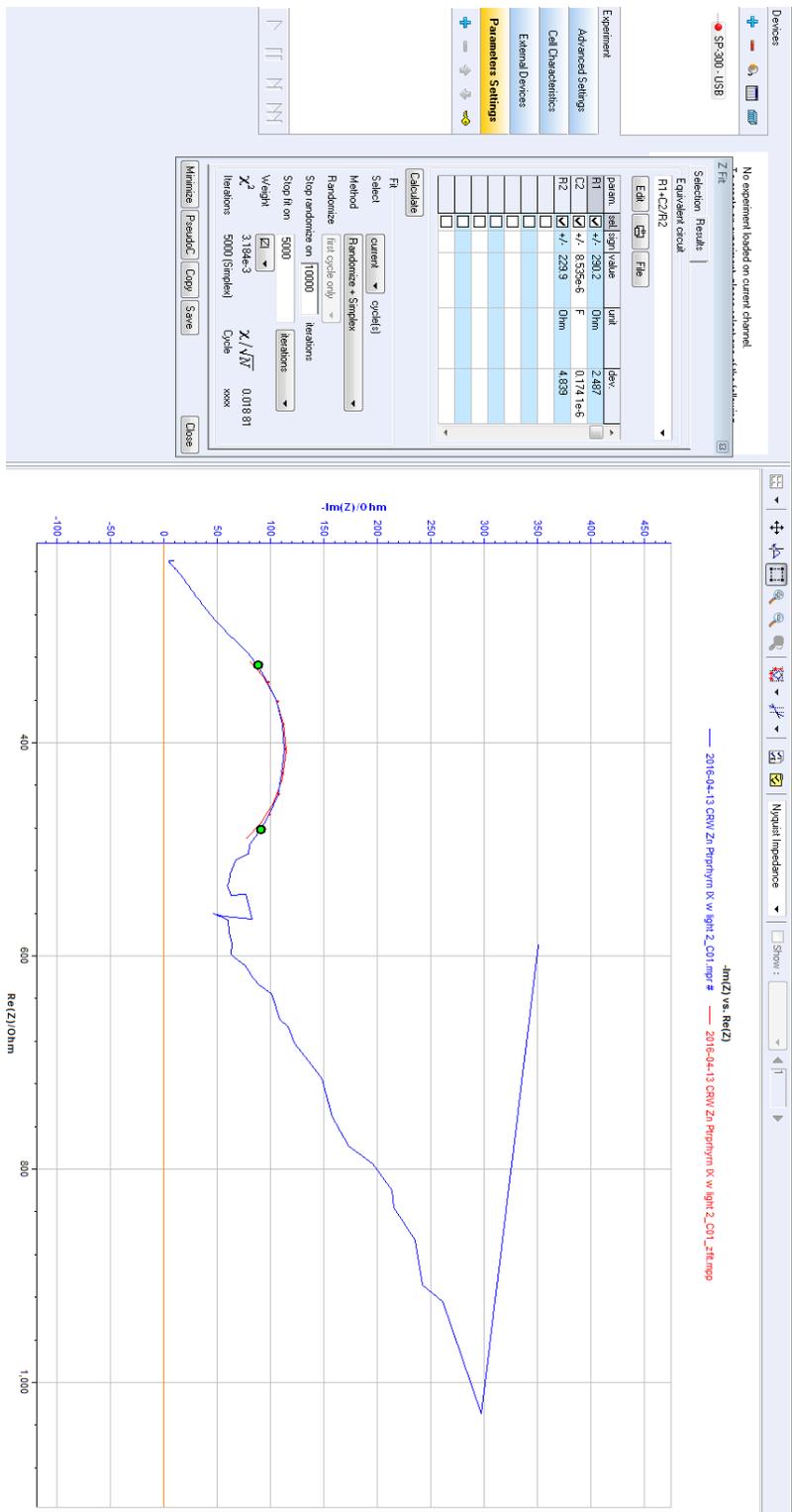


Figure 16: Nyquist Impedance with Light Run 2

Z Fit

Selection Results

Equivalent circuit: R1+C2/R2

param.	sel	sign	value	unit	dev.
R1	<input checked="" type="checkbox"/>	+	370.9	Ohm	1.308
C2	<input checked="" type="checkbox"/>	+	5.55e-6	F	55.07e-9
R2	<input checked="" type="checkbox"/>	+	257.4	Ohm	202

Calculate

Fit

Select: current cycle(s)

Method: Randomize + Simplex

Randomize: first cycle only

Stop randomize on: 10000 iterations

Stop fit on: 5000 iterations

Weight: χ^2

Weight: 7.58e-3

χ^2 : 0.02753

Iterations: 5000 (Simplex) Cycle: xxxxx

Buttons: Minimize, Random, Copy, Save, Close

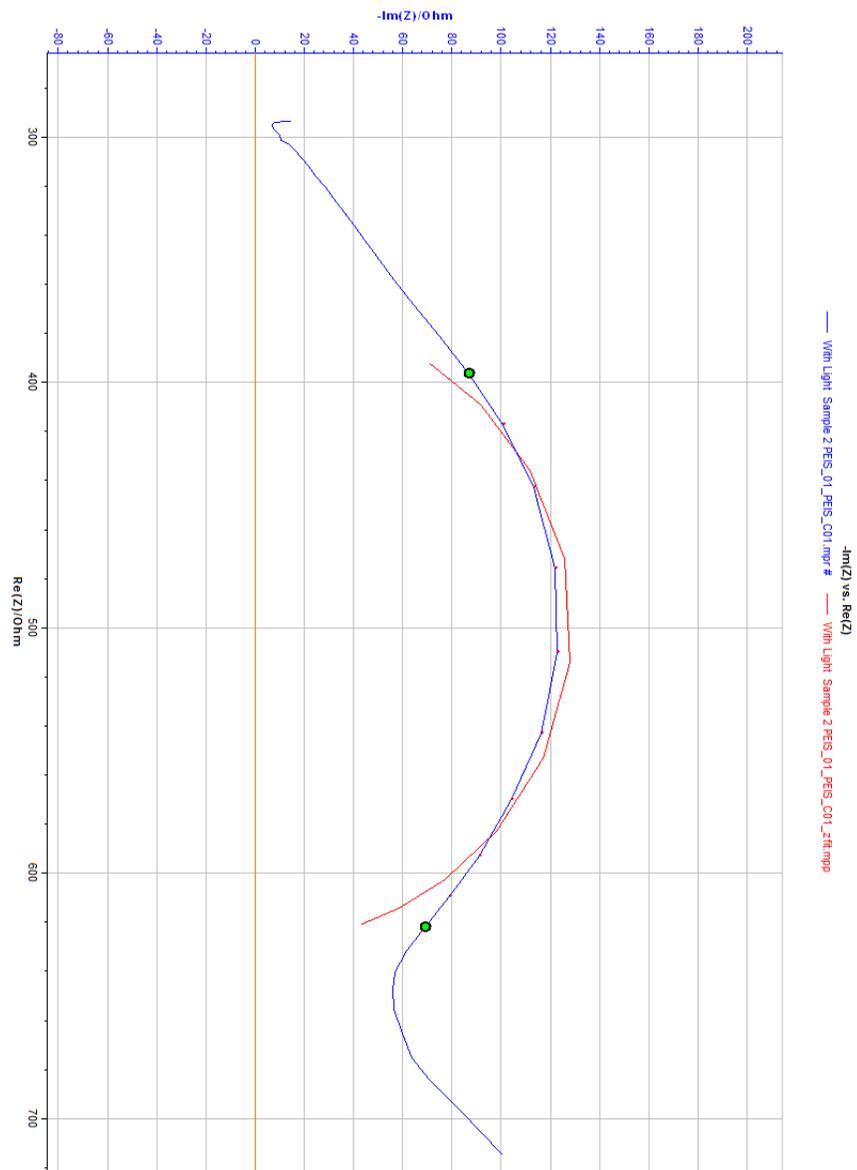


Figure 17: Nyquist Impedance with Light Run 3