DEVELOPMENT OF A MOLECULAR OPTOELECTRONIC TRANSUDER

A Thesis
Presented to
The Honors Tutorial College
Ohio University

In Partial Fulfillment
of the Requirements for Graduation
from the Honors Tutorial College
with the degree of
Bachelor of Science in Chemistry

by
Ryan M. O’Donnell
June 2010
This thesis has been approved by

The Honors Tutorial College and the Department of Chemistry & Biochemistry

__________________________
Dr. Jeffrey J. Rack
Associate Professor, Chemistry
Thesis Advisor

__________________________
Dr. Lauren E. H. McMills
Chemistry Director of Studies
Honors Tutorial College

__________________________
Dr. Jeremy Webster
Dean, Honors Tutorial College
**Table of Contents:**

INTRODUCTION .................................................................................................................. 15

EXPERIMENTAL ................................................................................................................ 24

Instrumentation ................................................................................................................ 24

Materials .............................................................................................................................. 25

Room Temperature Ionic Liquids ..................................................................................... 25

  - Synthesis of 1-methyl-1-butyl pyrrolidinium iodide (Pyr4I) .................................. 25
  - Synthesis of 1-methyl-1-butyl pyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr4NTf2) ................................................................. 26
  - Synthesis of 1-butyl-3-methylimidazolium Bromide (BMImBr) ..................... 27
  - Synthesis of 1-Butyl-3-Methylimidazolium Hexafluorophosphate (BMImPF6) ............................................................................................................. 28
  - Synthesis of 1-butyl-3-methyl (BMImNTf2) .......................................................... 29

Ligands ................................................................................................................................ 30

  - Synthesis of 2-(propane-2-sulfanyl)methyl)-pyridine (pyS) ............................. 30
  - Synthesis of 2-(isopropylsulfinyl)methyl)pyridine (pySO) ......................... 31
  - Synthesis of 4,4'-Di(3-thiopropyl)-2,2'-bipyridine (bpySAC) ...................... 32

Ruthenium Complexes ...................................................................................................... 34

  - Synthesis of [Ru(bpy)2(X)]-Silica Nanoparticle Syntheses ............................. 34
  - Synthesis of [Ru(bpy)2(pySO)](PF6) ............................................................... 36
  - Synthesis of [(p-cymene)RuCl2]2 ..................................................................... 37
<table>
<thead>
<tr>
<th>Synthesis of [(p-cymene)Ru(bpy)Cl]Cl</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesis of [Ru(bpy)(pySO)Cl₂]</td>
<td>39</td>
</tr>
<tr>
<td>Synthesis of <a href="OTf">Ru(bpy)(bpySAc)(pySO)</a>₂</td>
<td>40</td>
</tr>
<tr>
<td>Deprotection of <a href="OTf">Ru(bpy)(bpySAc)(pySO)</a>₂ and Attachment to Gold Electrode</td>
<td>41</td>
</tr>
<tr>
<td>Optoelectronic Device Designs</td>
<td>43</td>
</tr>
<tr>
<td>ITO</td>
<td>Ru-Nafion</td>
</tr>
<tr>
<td>FTO</td>
<td>Pt-FTO Design</td>
</tr>
<tr>
<td>FTO</td>
<td>Pt,Pt Design</td>
</tr>
<tr>
<td>Photochemical Cell Switching</td>
<td>47</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>49</td>
</tr>
<tr>
<td>Electrode Modifications</td>
<td>49</td>
</tr>
<tr>
<td>Ruthenium-doped Silica Nanoparticles (Ru-SiO₂ NPs)</td>
<td>50</td>
</tr>
<tr>
<td>Ruthenium-doped Nafion</td>
<td>55</td>
</tr>
<tr>
<td>Ruthenium Attachment via Gold-Thiol Linkage</td>
<td>60</td>
</tr>
<tr>
<td>Self-Contained Molecular Optoelectronic Transducers</td>
<td>63</td>
</tr>
<tr>
<td>ITO</td>
<td>ITO Cell</td>
</tr>
<tr>
<td>FTO</td>
<td>Pt-FTO Cell</td>
</tr>
<tr>
<td>FTO</td>
<td>Pt,Pt Cell Design</td>
</tr>
<tr>
<td>CONCLUSIONS AND FUTURE DIRECTIONS</td>
<td>95</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>96</td>
</tr>
</tbody>
</table>
Table of Figures

Figure 1: Molecular structure of [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ demonstrating photoisomerization between the S-bonded ground state and O-bonded metastable state isomers with relevant chemical information listed.............19

Figure 2: Schematic depicting oxidation (a) in red or reduction (b) in orange of a molecule in solution at an electrode surface. Adapted from reference $^{75}$ twitter

Figure 3. Potential versus time plots for a) cyclic voltammetry and b) differential pulse voltammetry techniques. Adapted from reference $^{75}$. ..................................................21

Figure 4: Expected ECEC square scheme of [Ru(bpy)$_2$(pySO)]$^{2+}$ ..................................................21

Figure 5: Expected photochemical switching of [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ monitored by differential pulse voltammetry (DPV). .................................................................22

Figure 6: Expected graph of O-bonded peak current versus cycle number for a photochemical switching experiment in an ideal molecular optoelectronic transducer.................................................................23

Figure 7: Synthetic scheme for 1-methyl-1-butyl pyrrolidinium iodide (Pyr$_4$I)........25

Figure 8: Synthetic scheme for 1-methyl-1-butyl pyrrolidinium bis(trifluoromethylsulfonylimide (Pyr$_4$NTf$_2$).................................................................26

Figure 9: Synthetic scheme of 1-butyl-3-methylimidazolium bromide (BMIImBr). ...27

Figure 10: Synthetic scheme for BMIImPF$_6$.................................................................28

Figure 11: Synthetic scheme for BMIImNTf$_2$.................................................................29

Figure 12: Synthetic scheme of 2-(propane-2-sulfanyl)methyl)-pyridine (pyS) ligand.30
Figure 13: Synthetic scheme for the oxidation of pyS to pySO. ..........................31
Figure 14: Synthetic scheme for 4,4'-Di(3-chloropropyl)-2,2'-bipyridine..................32
Figure 15: Synthetic Scheme for 4,4'-Di(3-thiopropyl)-2,2'-bipyridine (bpySAc). ....33
Figure 16: Synthetic scheme for [Ru(bpy)\textsubscript{2}(pySO)](PF\textsubscript{6})\textsubscript{2}. ................................36
Figure 17: Synthetic scheme for [(\textit{p}-cymene)RuCl\textsubscript{2}]\textsubscript{2}. ................................37
Figure 18: Synthetic scheme for [(\textit{p}-cymene)Ru(bpy)Cl]Cl. ................................38
Figure 19: Synthetic scheme for [Ru(bpy)(pySO)Cl\textsubscript{2}]. ................................39
Figure 20: Synthetic scheme for [Ru(bpy)(bpySAc)(pySO)](OTf)\textsubscript{2}. ..............40
Figure 21: Deprotection of [Ru(bpy)(bpySAc)(pySO)](OTf)\textsubscript{2} to

[Ru(bpy)(bpySH)(pySO)](OTf)\textsubscript{2}. ..................................................................41
Figure 22: Photographs of the FTO\textbar\textbar Pt-FTO cell construction..................45
Figure 23: Schematic for FTO\textbar\textbar Pt,Pt cell construction. ................................46
Figure 24: Photograph of an unfilled FTO\textbar\textbar Pt, Pt electrochemical cell...........47
Figure 25: Experimental set up for 355 nm and 472 nm laser irradiation for cell
cycling between the S-bonded and O-bonded states of the electrochemical
devices..................................................................................................................48
Figure 26: Optical microscope images of [Ru(bpy)\textsubscript{2}(X)]\textsuperscript{2+} SiO\textsubscript{2} NPs where X is (a)
(CH\textsubscript{3}CN)\textsubscript{2}, (b) CO\textsubscript{3}\textsuperscript{2-}, and (c) (EtOH)\textsubscript{2}. The orange scale bar in the bottom left
corner of the photographs is 10 µm. ..............................................................51
Figure 27: CV of [Ru(bpy)\textsubscript{3}](PF\textsubscript{6})\textsubscript{2}-SiO\textsubscript{2} NPs adhered to ITO glass (red trace) and
blank (blue trace). ..........................................................................................52
Figure 28: CV of [Ru(bpy)$_2$(EtOH)$_2$](PF$_6$)$_2$-SiO$_2$ NPs adhered to ITO glass (red trace) and blank (blue trace). ................................................................. 53

Figure 29: CV of [Ru(bpy)$_2$(pySO)]$^{2+}$-SiO$_2$ NPs adhered to ITO glass (red trace) and blank (blue trace). ................................................................. 53

Figure 30: DPVs of [Ru(bpy)$_2$(pySO)]$^{2+}$-SiO$_2$ NPs adhered to ITO: the blue trace is an unmodified electrode blank, the red trace is the initial scan, and the purple is the second scan which indicates loss of SiO$_2$ NPs on surface. .................. 54

Figure 31: Initial (red) and second (purple) DPVs of [Ru(bpy)$_2$(pySO)]$^{2+}$ attached to a GCE with Nafion. The blue trace is a blank DPV taken with an unmodified GCE. The electrochemistry was performed with a Pt wire counter electrode and a Ag/AgPF$_6$ in CH$_3$CN reference electrode in a 0.1 M TBAPF$_6$ in acetonitrile electrolyte solution. .................................................. 56

Figure 32: DPVs of [Ru(bpy)$_2$(pySO)]$^{2+}$-Nafion modified GCE upon irradiation with 355 nm laser. The red trace was obtained prior to irradiation, the blue after 2 total minutes, the purple after 4.5 minutes, and the green after 9 minutes of total irradiation with 355 nm light. .................................................. 57

Figure 33: CV of [Ru(bpy)$_2$(pySO)]$^{2+}$-Nafion modified ITO before (red) and after (black) irradiation. The blue trace was obtained using unmodified ITO as a blank. ........................................................................................................... 58

Figure 34: CV of [Ru(bpy)$_3$](PF$_6$)$_2$-Nafion modified FTO indicating loss of compound upon each scan. ........................................................................................................... 59
Figure 35: Depiction of the hypothesized self-assembled monolayer of 

\[ \text{[Ru(bpy)(bpySH)(pySO)]}^{2+} \] on a gold electrode surface. ........................................61

Figure 36: \[ \text{[Ru(bpy)(bpySH)(pySO)](OTf)}_{2} \] modified Au electrodes indicating loss of Ru complex upon oxidation of the thiol linkage........................................61

Figure 37: \[ \text{[Ru(bpy)(bpySH)(pySO)]}^{2+} \] modified Au electrode indicating loss of Ru complex upon thiol linker oxidation........................................62

Figure 38: Initial DPV scan of the ITO| \[ \text{[Ru(bpy)_{2}(pySO)]}^{2+} \] -Nafion, \text{Pyr}_{4}\text{NTf}_{2} |ITO cell. Presence of the S-bonded isomer at 2.324 V and the O-bonded isomer at 1.300 V is apparent. .................................................................65

Figure 39: Photochemical switching of an ITO| \[ \text{[Ru(bpy)_{2}(pySO)]}^{2+} \] -Nafion, \text{Pyr}_{4}\text{NTf}_{2} |ITO cell. ..............................................................................66

Figure 40: Photograph of ITO| \[ \text{[Ru(bpy)_{2}(pySO)]}^{2+} \] -Nafion, \text{Pyr}_{4}\text{NTf}_{2} |ITO cell. ......67

Figure 41: Photochemical switching of the ITO| \[ \text{[Ru(bpy)_{2}(pySO)]}^{2+} \] -Nafion, \text{Pyr}_{4}\text{NTf}_{2} |ITO cell: (a) S-bonded isomer, (b) O-bonded isomer. The graphs display the diminishing peak potential current over the duration of the experiment................................................68

Figure 42: CVs of the FTO| BMImPF_{6} |Pt-FTO cell. The traces correspond to different potential windows: red is from 0 to 1.6 V, blue is from 0 to 1.4 V, purple is from 0 to 1.2 V, and green is from 0 to 1.0 V.................................69

Figure 43: DPVs of the FTO| BMImPF_{6} |Pt-FTO cell. The traces correspond to different potential windows: red is from 0 to 1.6 V, blue is from 0 to 1.4 V, purple is from 0 to 1.2 V, and green is from 0 to 1.0 V.................................69
Figure 44: DPVs of FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$ -Nafion, BMImPF$_6$ |Pt-FTO cell. Only the S-bonded isomer was present in the first scan, red trace, while the O-bonded isomer was electrochemically generated during subsequent scans as indicated by the black arrows.

Figure 45: DPVs obtained during the photochemical switching experiment of the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$ -Nafion, BMImPF$_6$ |Pt-FTO cell. Blue traces were obtained after 10 minutes of 355 nm irradiation while the red traces were obtained after 20 minutes of 472 nm irradiation. Peak currents decreased during the course of the experiment.

Figure 46: Photochemical switching of the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$ -Nafion, BMImPF$_6$ |Pt-FTO cell monitored as a function of maximum O-bonded current versus cycle number. Integer values correspond to DPVs obtained after 355 nm irradiation while half values correspond to DPVs taken after 472 nm irradiation.

Figure 47: O-bonded isomer peak stability in a FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$ -Nafion, BMImPF$_6$ |Pt-FTO cell measured by repetitive scanning. The blue, green, purple, and grey traces were obtained in that order. The red trace was obtained after 472 nm irradiation during the photoswitching experiment and is included for comparison.

Figure 48: Initial DPVs of an FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$ |Pt-FTO cell. The initial scan is indicated by the red trace, while the blue and purple traces correspond to the second and third scans, respectively.
Figure 49: Photochemical switching results of an FTO|[Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$|Pt-FTO cell where the blue traces were obtained after 5 minutes of 355 nm irradiation and the red traces were obtained after 10 minutes of 472 nm irradiation. The overall trend was decreasing peak current.

Figure 50: Photochemical switching of an FTO|[Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$|Pt-FTO cell monitored as a function of maximum O-bonded current versus cycle number. Integer values correspond to DPVs obtained after 355 nm irradiation while half values correspond to DPVs taken after 472 nm irradiation.

Figure 51: O-bonded isomer peak stability measured by 10 repetitive DPV scans. The peak current decreased after each successive scan.

Figure 52: Photograph of an FTO|[Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$|Pt-FTO cell. The O-bonded isomer can be seen as the red spot in the center of the reservoir, while the surrounding yellow color is due to the S-bonded isomer.

Figure 53: Initial DPV of an FTO|[Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$|Pt-FTO cell (blue trace) and subsequent formation of the O-bonded isomer upon 60 seconds of 355 nm irradiation (red trace).

Figure 54: Initial DPV and DPVs obtained from photochemical switching of the FTO|[Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$|Pt-FTO cell. Excepting the trace from 0 to 1.2 V with maximum current at 1.044 V, the blue traces depict DPVs taken after 355 nm irradiation (60 s) while the red traces were taken after 472 nm irradiation (3 min). The x-axis has been extended to better demonstrate the
peak shape while the inset is included to depict the photochemical switching data.

Figure 55: Photochemical switching of the FTO \([\text{Ru(bpy)}_2(\text{pySO})]^ {2+}, \text{BMImPF}_6 \mid \text{Pt} \) FTO cell monitored as a function of maximum O-bonded current versus cycle number. Integer values correspond to DPVs obtained after 355 nm irradiation while half values correspond to DPVs taken after 472 nm irradiation.

Figure 56: Bulk three electrode electrochemistry of BMImPF\(_6\), blue trace, and \([\text{Ru(bpy)}_2(\text{pySO})]^ {2+}\) dissolved in BMImPF\(_6\), red trace. Glassy carbon (1 mm diameter) working electrode, Pt wire counter electrode, and Pt wire quasi-reference electrode.

Figure 57: Ten successive DPV scans of the bulk \([\text{Ru(bpy)}_2(\text{pySO})]^ {2+} \) BMImPF\(_6\) solution. The S-bonded peak current diminished as the O-bonded peak current increased. Glassy carbon (1 mm diameter) working electrode, Pt wire counter electrode, and Pt wire quasi-reference electrode.

Figure 58: Ten successive DPV scans of bulk \([\text{Ru(bpy)}_2(\text{pySO})]^ {2+}\) in BMImPF\(_6\). FTO glass working electrode, Pt wire counter electrode, and Pt wire quasi-reference electrode.

Figure 59: Photograph of the FTO \([\text{Ru(bpy)}_2(\text{pySO})]^ {2+}, \text{BMImPF}_6 \mid \text{Pt}, \text{Pt} \) cell after photochemical cycling experiments. Note that the air bubble was present throughout the experiments. The lower left inset indicates the presence of both O-bonded and S-bonded \([\text{Ru(bpy)}_2(\text{pySO})]^ {2+}\) isomers. The electrodes are as follows: green – working; red – counter; reference – white.
Figure 60: Initial DPV scans of the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$|Pt,Pt cell indicating the absence of the O-bonded isomer initially and its subsequent electrochemical generation. Red trace: initial scan; blue trace: second scan; purple trace: third scan with the reduced potential window used for subsequent experiments.

Figure 61: Comparison of the S- and O-bonded isomer peak potentials in BMImPF$_6$ upon the second DPV scan in bulk electrochemistry and FTO| |Pt,Pt cell. Red trace: bulk three electrode configuration with FTO glass working electrode (we), Pt wire counter electrode (ce), and Pt wire quasi-reference electrode (re). Blue trace: 25x magnification of bulk three electrode configuration with 1 mm diameter glassy carbon we, Pt wire ce, and Pt wire re. Black trace: FTO| |Pt,Pt cell.

Figure 62: DPVs obtained from the photochemical cycling experiment of the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$ |Pt,Pt cell. The cell was irradiated with 355 nm light for 60 seconds (~5-6 mJ/pulse), scanned, irradiated with 472 nm light for 3 minutes (~4-7 mJ/pulse), scanned, and repeated for a total of 10 cycles. The red traces are DPV scans taken after 472 nm irradiation and the blue traces are DPV scans taken after 355 nm irradiation. The dashed purple line indicates a proposed threshold current value distinguishing between the two sets. The overall trend is a decrease in peak potential current.

Figure 63: Photochemical switching graph of an FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$ |Pt,Pt cell monitored as a function of maximum O-bonded current versus cycle.
number. Integer values correspond to DPVs obtained after 355 nm irradiation while half values correspond to DPVs taken after 472 nm irradiation. ............87

Figure 64: Photographs of the FTO| [Ru(bpy)$_2$(pySO)$_2$]$^{2+}$, BMImNTf$_2$ |Pt,Pt Cell from April 28th, 2010 before (left) and after (right) irradiation experiments. ............88

Figure 65: Initial DPV scans of the FTO| [Ru(bpy)$_2$(pySO)$_2$]$^{2+}$, BMImNTf$_2$ |Pt,Pt cell indicating the initial lack of O-bonded [Ru(bpy)$_2$(pySO)$_2$]$^{2+}$ and its electrochemical generation upon subsequent scans. Red trace: initial scan; blue trace: second scan indicating formation of O-bonded isomer; purple trace: third scan with reduced potential window for further experiments.........................88

Figure 66: Twenty successive DPV scans of the FTO| [Ru(bpy)$_2$(pySO)$_2$]$^{2+}$, BMImNTf$_2$ |Pt,Pt cell taken after initial electrochemical formation of the O-bonded product. The black arrow indicates the diminishing peak current after each successive scan with no wait time between scans. .........................90

Figure 67: Raw DPV data from the photochemical cycling experiment in the FTO| [Ru(bpy)$_2$(pySO)$_2$]$^{2+}$, BMImNTf$_2$ |Pt,Pt cell. The topmost red trace is the initial DPV scan prior to the irradiation cycling and indicates the absence of O-bonded product. The cell was irradiated with 355 nm light for 60 seconds (~18 mJ/pulse) and a DPV was obtained, blue traces. After 355 nm irradiation, the cell was irradiated with 472 nm light for 3 minutes (~20 mJ/pulse) and a DPV was obtained, red traces. The cell exhibited an overall increase in peak potential and shifting of the peak potential to successively more positive values throughout the cycling experiment. ..................................................90
Figure 68: Raw data from Figure 67 was shifted to a constant peak potential of 0.880 V and the baseline was shifted to obtain zero current at approximately 0.15 V to qualitatively assess the results. Clear delineation can be seen between the mostly O-bonded and mostly S-bonded cycle sets achieved via 355 nm and 472 nm irradiation, respectively.

Figure 69: Photochemical switching graph of the shifted data from the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImNTf$_2$ |Pt,Pt cell monitored as a function of maximum O-bonded current versus cycle number. Integer values correspond to DPVs obtained after 355 nm irradiation while half values correspond to DPVs taken after 472 nm irradiation.

Figure 70: After photochemical switching of the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImNTf$_2$ |Pt,Pt cell, "erasure" of the O-bonded product after 472 nm irradiation was accomplished via 20 successive DPV scans. The black arrow indicates the decrease in peak current from the initial to final scan.

Figure 71: Post-erasure photochemical cycling of the O-bonded isomer in the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImNTf$_2$ |Pt,Pt cell.

Figure 72: "Erasure" of the O-bonded product after 355 nm irradiation was accomplished over 50 successive DPV scans. The black arrow indicates the decrease in peak current from the initial to final scan.
INTRODUCTION

The global demand for faster, more computationally complex, and innovative technologies requires the creation of new, simple devices capable of reliably performing specific functions. In a recent Technology, Entertainment and Design (TED) talk, Prof. George M. Whitesides of Harvard University described the science of simplicity and how much of our complex world is comprised of simpler components. He defines simple things as reliable/predictable, cheap to produce, and stackable such that they can be used as building blocks to create more complex devices. Whitesides illustrated the culmination of complex technologies from simple devices and simple theory. Smart phones are an excellent example as they are simple enough for millions of people to use and are composed of simple components such as cameras, batteries, and LED screens. The individual components themselves are possible only through iterations of simpler technologies all the way down to the transistors and binary code that form the basis of the device's function. The simple devices and theory "stack" to create the complex devices that we rely on in our daily lives.

The aim of this work was the development of a self-contained molecular optoelectronic transducer. Such a device would utilize different wavelengths of light as inputs to effect a chemical change in a molecule that would subsequently be read using electrochemistry. Ideally, the transducer would exhibit characteristics of a simple device and serve as a foundation for more complex technologies. While the complex technologies possible from such a device are purely speculative, one
application could be in molecular computing\textsuperscript{2-7} where standard silicon-based circuitry would be replaced by nanoscale components using a bottom-up construction approach. With the creation of nanoscale lasers\textsuperscript{8-11} and advances in nanofabrication\textsuperscript{12-15} it is possible to envision micro- or nanoscale molecular optoelectronic transducers that could be integrated into current computing, data storage, and telecommunications technologies or used in wholly novel applications.

Molecular switches are regarded as the ideal motif for use in molecular computing applications and data storage as their structure inherently involves two states which can be utilized as the "0" or "OFF" and "1" or "ON" outputs that form the basis of Boolean logic. Current molecular switch research focuses on azobenzenes,\textsuperscript{16-18} diarylethenes/dithienylethenes,\textsuperscript{19-24} fulgides,\textsuperscript{25} spiropyans,\textsuperscript{26-29} tetrathiafulvalenes,\textsuperscript{30} thiophenes,\textsuperscript{31} and interlocked catenanes and rotaxanes.\textsuperscript{32-35} Most of these molecules and their derivatives are photochromic, meaning that their electronic properties and often their molecular structures change when irradiated with light.\textsuperscript{36} Electrochromic materials undergo similar changes as a result of an applied electric charge or other electrochemical perturbation to the molecule.\textsuperscript{37}

The simultaneously photochromic and electrochromic diarylethene\textsuperscript{38-42} and spiropyran\textsuperscript{43} compounds have been utilized in the development of light-induced conductance switching molecular devices. The current densities of the devices can be switched from a low value, OFF, to a high value, ON, after irradiation with ultraviolet light and reversed using visible light. The maximum reported number of photoswitching cycles between the ON and OFF states for this type of experiment was
13 using a diarylethene device. However, the device construction and experimental design is complex. It is furthermore difficult to prove that the photoactive molecules are the cause of the conductance switching and that the molecules retain their switching function when tethered in these devices.

Modified electrodes incorporating spiropyran, phenoxynapthacenequinone, azobenzene, and diarylethene derivatives demonstrated electrochemical current changes upon photochemical switching. These electrodes were typically monitored by cyclic voltammetry over 2 to 4 photoswitching cycles with a maximum of 6 cycles for spiropyran and diarylethene modified electrodes. Furthermore, the electro- and photochemistry were typically performed independently where the electrode was irradiated in open atmosphere and the electrochemistry was obtained using standard, three-electrode bulk electrochemistry.

The ruthenium sulfoxide compounds synthesized by the Rack Group are a suitable class of molecules for incorporation in a molecular optoelectronic transducer as they are simultaneously photochromic and electrochromic. The ruthenium sulfoxide compounds are synthetically simple to prepare making this class of photoswitchable compounds more appealing than those previously mentioned. Irradiating into the metal-to-ligand charge transfer (MLCT) band of ruthenium sulfoxide compounds triggers isomerization from the S-bonded ground state to the O-bonded metastable state. As the electron moves from a ruthenium-based orbital to a bipyridine-based orbital, the Ru$^{II}$ effectively oxidizes to Ru$^{III}$. Hard-soft acid base (HSAB) theory predicts that hard-hard and soft-soft pairings of acids and bases are
preferred compared to hard-soft pairings. In this usage, the hardness or softness of an ion are qualitative assessments of its charge density and electronegativity.\textsuperscript{71-73} Compared to the Ru\textsuperscript{III} hard acid, Ru\textsuperscript{II} acts as a soft acid. Thus, the S-bonded isomer is most stable for Ru\textsuperscript{II} as sulfur is a soft base, while the O-bonded isomer is preferred for Ru\textsuperscript{III} because oxygen is a hard base. Photochromism results as the S-bonded isomer is typically yellow in color while the O-bonded isomer is red. Electrochemical oxidation from Ru\textsuperscript{II} to Ru\textsuperscript{III} triggers the same S$\rightarrow$O isomerization chemistry and reduction from Ru\textsuperscript{III} to Ru\textsuperscript{II} triggers the reverse O$\rightarrow$S isomerization, see Figure 4.

The two-color reversible [Ru(bpy)$_2$(pySO)]$^{2+}$ compound, where bpy is 2,2'-bipyridine and pySO is 2-(isopropylsulfinylmethyl)pyridine, first synthesized by Beth McClure\textsuperscript{74} is unique with regard to the ruthenium sulfoxide compounds in its ability to undergo both O$\rightarrow$S and S$\rightarrow$O photochemical isomerization achieved with different irradiation wavelengths. Irradiation with 355 nm light triggers the O$\rightarrow$S isomerization event with a quantum efficiency ($\Phi_{S \rightarrow O}$) of 0.11(2) and 472 nm light triggers the reverse S$\rightarrow$O isomerization event with quantum efficiency ($\Phi_{S \rightarrow O}$) of 0.027(6) in propylene carbonate, where the experimental error is given in parentheses.\textsuperscript{74} Thus, the isomerization efficiencies should be considered in experimental designs. Concomitant with isomerization is a change in the Ru$^{II/III}$ chemical potential with the S-bonded potential ($E_S$) equal to 1.35 V and the O-bonded potential ($E_O$) equal to 0.75 V in propylene carbonate.\textsuperscript{74} The relevant properties and chemical structure of [Ru(bpy)$_2$(pySO)]$^{2+}$ are highlighted in Figure 1.
Figure 1: Molecular structure of [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ demonstrating photoisomerization between the S-bonded ground state and O-bonded metastable state isomers with relevant chemical information listed.

The oxidation and reduction of a compound can be achieved experimentally following the scheme depicted in Figure 2. Scanning the energy level of electrons in an electrode from an initially positive potential to a more negative final potential will result in oxidation of a compound if the electron energy level passes through the highest occupied molecular orbital (HOMO) of the molecule in solution. The left side of Figure 2 depicts the oxidation of a molecule in solution and the right hand side illustrates the opposite case of reduction, where an electron is added to the lowest unoccupied molecular orbital (LUMO). At the beginning of an electrochemical scan, a small background current will pass dependent upon the experimental set-up. Once the electron energy level of the electrode equals the HOMO or LUMO energy, little current will pass as there is no thermodynamic driving force to encourage electrons to flow. Once the HOMO or LUMO energy level is passed, the molecule will be either
oxidized or reduced, respectively and a large amount of current will flow in the cell before subsequently decreasing back to the background level.

Figure 2: Schematic depicting oxidation (a) in red or reduction (b) in orange of a molecule in solution at an electrode surface. Adapted from reference 75.

Two voltammetric techniques were used in this work, namely cyclic voltammetry (CV) and differential pulse voltammetry (DPV). In cyclic voltammetry, the potential is scanned in either the positive or negative direction, switched to the reverse direction of opposite polarity, and typically repeated twice more in both directions. The second DPV technique is a pulsed method that scans the electrode potential in only one direction and provides better sensitivity compared to CV. Plots of applied current versus time for the two techniques are shown in Figure 3.
Figure 3. Potential versus time plots for a) cyclic voltammetry and b) differential pulse voltammetry techniques. Adapted from reference 75.

The ruthenium sulfoxide compounds follow the ECEC square scheme where two electron-transfer reactions are coupled by two chemical reactions. 75-77 Shown in Figure 4 for [Ru(bpy)$_2$(pySO)]$^{2+}$, the initial Ru$^{II}$ S-bonded isomer electrochemically oxidizes to the Ru$^{III}$ S-bonded isomer at 1.35V in propylene carbonate; undergoes S$\rightarrow$O isomerization with a rate constant $k_{S\rightarrow O}$; electrochemically reduces to the Ru$^{II}$ O-bonded isomer at 0.75 V in propylene carbonate; and finally undergoes O$\rightarrow$S isomerization with a rate constant $k_{O\rightarrow S}$. 74

Figure 4: Expected ECEC square scheme of [Ru(bpy)$_2$(pySO)]$^{2+}$.

As Ru$^{II/III}$ oxidation of the [Ru(bpy)$_2$(pySO)]$^{2+}$ compound is expected to
electrochemically generate the O-bonded isomer, photochemical switching experiments were typically monitored at potentials less than ~1.2V. Figure 5 depicts the DPVs expected from a device based on the [Ru(bpy)$_2$(pySO)]$^{2+}$ photochemistry and electrochemistry. In the "0" state, the majority of the compound would exist as the S-bonded isomer, although a small amount of O-bonded isomer is also expected to be present due to experimental limitations. Similarly, the "1" state would mainly contain the O-bonded isomer with a minimum amount of the S-bonded isomer present. Setting a threshold value for the device would easily allow for determination of its state. Figure 5 illustrates a hypothetical threshold using yellow and red dashed lines for the "0" and "1" states, respectively.

![Figure 5: Expected photochemical switching of [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ monitored by differential pulse voltammetry (DPV).](image)

Ideally, a molecular optoelectronic transducer would switch between the "0" and "1" states an infinite number of times with minimal variation of the peak current in each state. The expected graph of an ideal device switched between the "1" and "0" state using 355 nm and 472 nm irradiation, respectively, is shown in Figure 6. The graph depicts the current change monitored at the O-bonded isomer peak potential over ten Photoswitching cycles. A cycle is defined as a write-read-erase-read cycle.
where the O-bonded isomer is formed with 355 nm irradiation, monitored via DPV, erased with 472 nm irradiation, and again monitored via DPV. Comparison of this ideal graph to those obtained from experimental data allows for qualitative determination of device stability.

Figure 6: Expected graph of O-bonded peak current versus cycle number for a photochemical switching experiment in an ideal molecular optoelectronic transducer.

Compared to molecular switching devices reported in the literature, the molecular optoelectronic transducers discussed below are advantageous in multiple aspects. Several devices are capable of undergoing at least ten photoswitching cycles, operate at ambient conditions, are self-contained, are simple to construct, utilize two wavelengths of light as inputs, and exhibit predictable electrochemical responses for the output.
EXPERIMENTAL

Instrumentation

One dimensional $^1$H-NMR, $^{13}$C-NMR, and two dimensional correlated spectroscopy (COSY) NMR were collected on a 300 MHz Bruker AG spectrometer. Cyclic and differential pulse voltammetry were performed on a CH Instruments CHI730A Electrochemical Analyzer. This workstation contains a digital simulation package as part of the software package to operate the workstation (CHI Version 2.06). Unless otherwise specified, DPVs were obtained using the default program parameters: 0.004 V incremental voltage, 0.05 V amplitude, 0.05 second pulse width, 0.0167 second sampling pulse width, 0.2 second pulse period, and 2 second quiet time. Unless otherwise noted, CVs were obtained using the following parameters: positive initial scan polarity, 0.1 V/s scan rate, 6 sweep segments, 0.001 V sample interval, and 2 second quiet time. Unless otherwise specified, bulk electrochemical measurements were obtained using Pt wire as the counter electrode, Ag/AgPF$_6$ (0.01 M AgPF$_6$ and 0.1 M TBAPF$_6$ in acetonitrile) as the reference electrode, and performed in 0.1 M TBAPF$_6$ in acetonitrile electrolyte solution. Electronic absorption spectra were collected on an Agilent 8453 spectrophotometer. The small-angle x-ray scattering experiments were performed by Congshang Wang and Gang Chen. Laser experiments were performed using a Continuum Surelite Nd:YAG laser, Surelite PSS, and Surelite optical parametric oscillator (OPO) operating at 10 Hz. It should be noted that the irradiation times reported were not corrected for the laser pulse width of ~3.5 ns. Thus
at 10 Hz, the reported time of one minute would correspond to ~2.1 µs of actual irradiation time.

**Materials**

All reagents were purchased from Sigma Aldrich and used as received. The solvents acetone, acetonitrile, chloroform, dichloromethane, diethyl ether, dimethyl formamide (DMF), ethanol, ethyl acetate, hexanes, and methanol were purchased from VWR and used without further purification. Deionized, 18 Ω water was obtained using a Millipore filtration unit. Indium-doped tin oxide (ITO) glass was purchased from Delta Technologies (Stillwater, MN) as 25x25x1.1 mm glass with 4-8 Ω sheet resistances. Fluorine-doped tin oxide (FTO) glass was 2.2 mm thick TEC 7 Glass™ and donated by Pilkington Building Products (Toledo, OH). Platinum wire was obtained from J.Bishop & Co. Platinum Works (Malvern, PA) as 24 gauge wire.

**Room Temperature Ionic Liquids**

**Synthesis of 1-methyl-1-butyl pyrrolidinium iodide (Pyr4I)**

\[
\begin{align*}
\text{N} & \quad + \quad \text{I} \quad \xrightarrow{\text{CH}_3\text{CN}} \quad \text{N}^+ \quad \text{I}^- \\
\text{Figure 7: Synthetic scheme for 1-methyl-1-butyl pyrrolidinium iodide (Pyr4I)}
\end{align*}
\]

The synthesis of 1-methyl-1-butyl pyrrolidinium iodide was achieved through the literature preparation described by MacFarlane et al.\textsuperscript{78} To a 100 mL pear-shaped flask, 8.000 mL (d=0.819, 76.95 mmol) 1-methylpyrrolidine (Aldrich, 97%) was dissolved in 20 mL acetonitrile and purged with N\textsubscript{2} for five minutes prior to the
addition of 10.000 mL (d=1.617, 87.87 mmol) 1-iodobutane (Aldrich, 99%). The reaction mixture was stirred in an ice bath and covered in aluminum foil to avoid decomposition of the light-sensitive iodobutane prior to reaction. The reaction mixture changed from colorless and clear initially to a peach-yellow, clear solution upon completion after approximately three hours. The solvent was removed via rotary evaporation and yielded a solid, white precipitate. Upon removal of the flask from the rotary evaporator, the precipitate immediately re-wetted and regained its peach-yellow color. The liquid was placed under high vacuum to yield a pale yellow, waxy solid.

Yield: 18.2464 g (88.10%). $^1$H NMR (CDCl$_3$, 300 MHz) δ: 3.549 (s, 4H), 3.396 (m, 2H), 3.015 (s, 3H), 2.052 (s, 4H), 1.542 (m, 2H), 1.201 (m, 2H), 0.734 (t, 3H) ppm. COSY.

**Synthesis of 1-methyl-1-butyl pyrrolidinium bis(trifluoromethylsulfonylimide)**

(Pyr$_4$NTf$_2$)

The synthesis of 1-methyl-1-butyl pyrrolidinium bis(trifluoromethylsulfonylimide) (Pyr$_4$NTf$_2$) was achieved via counterion exchange of iodide to NTf$_2$. In a 50 mL beaker, 8.9465 g (33.23 mmol) Pyr$_4$I was dissolved in 10.0 mL deionized water. In a second 50 mL beaker, 5.5720 g (19.41 mmol) lithium...
bis(trifluoromethylsulfonyl)imide (LiNTf₂) was dissolved in 10.0 mL deionized water. The LiNTf₂ solution was mixed into the Pyr₄I solution and stirred for 3 hours. The solution was allowed to phase separate overnight and then the Pyr₄NTf₂ was collected by pipetting the bottom layer from the beaker into a vial. The product was placed under vacuum to remove any excess water and yielded a viscous, light yellow liquid. Attempts to de-color the solution with activated charcoal and filtration through an alumina column were unsuccessful. Yield: 11.6305 g (82.85%). ¹H NMR (d₆-DMSO, 300 MHz) δ: 3.430 (m, 4H), 3.288 (m, 3H), 2.975 (s, 3H), 2.084 (s, 4H), 1.682 (m, 2H), 1.321 (m, 2H), 0.934 (t, 3H) ppm. COSY. ¹³C NMR: (d₆-DMSO, 300 MHz) δ: 125.87, 121.60, 117.34, 113.07, 63.41, 62.97, 47.50, 30.55, 24.88, 21.04, 19.24, 13.34 ppm.

**Synthesis of 1-butyl-3-methylimidazolium Bromide (BMImBr)**

![Synthetic scheme of 1-butyl-3-methylimidazolium bromide (BMImBr).](image)

Figure 9: Synthetic scheme of 1-butyl-3-methylimidazolium bromide (BMImBr).

The synthesis of 1-butyl-3-methylimidazolium bromide was achieved by modifying the literature procedure for 1-butyl-3-methylimidazolium chloride. In a three-necked, 250 mL round bottom flask equipped with a thermometer and magnetic stirring bar, 14.9976 g (0.1826 mol) of N-methylimidazole was diluted in 20 mL acetonitrile. Then 32.4180 g (0.2366 mol) of n-bromobutane was added, stirred, and
heated. The reaction temperature was maintained at 70°C with the use of a hot oil bath temperature controller. The reaction progress was monitored by thin layer chromatography (TLC) in 100% ethyl acetate and KMnO₄ development. The starting materials developed as a bright yellow spot on the TLC plate which was not visible upon completion. The originally colorless solution appeared amber in color after completion and was cooled to room temperature. The solvent was removed on a vacuum line to afford a viscous liquid which was placed in a freezer overnight. The final product removed from the round bottom flask was a waxy solid that was ground with a mortar and pestle and placed into vials for storage. Yield: 39.1273 g (97.8%).

\(^1\text{H NMR (CDCl}_3, 300 \text{MHz}) \delta: 10.266 \text{ (s, 1H), 7.606 \text{ (s, 1H), 7.479 \text{ (s, 1H), 4.268 \text{ (t, 2H), 4.054 \text{ (s, 1H), 1.834 \text{ (m, 2H), 1.294 \text{ (m, 2H), 0.878 \text{ (t, 3H) ppm.}}}}}

**Synthesis of 1-Butyl-3-Methylimidazolium Hexafluorophosphate (BMImPF₆)**

\[ \text{BMImBr} + \text{NaPF}_6 \xrightarrow{\text{H}_2\text{O}} \text{BMImPF}_6 \]

Figure 10: Synthetic scheme for BMImPF₆

The synthesis of 1-butyl-3-methylimidazolium hexafluorophosphate (BMImPF₆) was accomplished by modifying the preparation reported by Dupont et al.\(^9\) To a 100 mL round bottom flask, 18.1692 g (82.92 mmol) BMImBr was dissolved in 15 mL deionized water and stirred before adding 15.1771 g (90.4 mmol) NaPF₆. After the reaction solution stirred for 2 hours, a two-layer phase separation became apparent. The top, yellow layer was separated via separatory funnel and
washed three times with 5 mL portions of deionized water. Addition of colorless AgNO₃ crystals to the aqueous layer resulted in instantaneous precipitation of a yellow precipitate, indicating the presence of bromide ions. A control test performed with deionized water and AgNO₃ only dissolved the crystals with no precipitate formation. The obtained product was redissolved in 10 mL of dichloromethane, 3.6585 g MgSO₄ was added to remove any remaining water, and the solution was filtered to remove the MgSO₄. The solvent was removed via rotary evaporator to yield a highly viscous, pale yellow solid. Yield: 20.5578 g (87.24%). ¹H NMR (CD₂Cl₂, 300 MHz) δ: 8.400 (s, 1H), 7.292 (s, 2H), 4.119 (t, 2H), 3.872 (s, 3H), 1.823 (m, 2H), 1.329 (m, 2H), 0.919 (t, 3H) ppm. ¹³C NMR (CD₂Cl₂, 300 MHz) δ: 136.07, 124.16, 122.80, 50.33, 36.6, 32.20, 19.74, 13.49 ppm.

**Synthesis of 1-butyl-3-methyl (BMImNTf₂)**

![Synthetic scheme for BMImNTf₂](image)

The synthesis of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (BMImNTf₂) was achieved by the same counterion exchange synthesis used for BMImPF₆ except with 9.4216 g (42.997 mmol) BMImBr and 12.7496 g (44.410 mmol) lithium bis(trifluoromethylsulfonyl) imide. Yield: 13.8203 g (76.74%).
$^1$H NMR (CD$_2$Cl$_2$, 300 MHz) δ: 8.579 (s, 1H), 7.302 (s, 2H), 4.140 (t, 2H), 3.897 (s, 3H), 1.831 (m, 2H), 1.345 (m, 2H), 0.938 (t, 3H) ppm. $^{13}$C NMR (CD$_2$Cl$_2$, 300 MHz) δ: 136.27, 124.26, 122.91, 120.40 (q), 50.49, 36.79, 32.38, 19.82, 13.48 ppm.

Ligands

**Synthesis of 2-(propane-2-sulfanylmethyl)-pyridine (pyS)**

![Synthetic scheme of 2-(propane-2-sulfanylmethyl)-pyridine (pyS) ligand.](image)

Figure 12: Synthetic scheme of 2-(propane-2-sulfanylmethyl)-pyridine (pyS) ligand.

The synthesis of the 2-(propane-2-sulfanylmethyl)-pyridine (pyS) was prepared following a literature procedure.$^{74}$ In a 100 mL round bottom flask equipped with a magnetic stirrer, 1.6495 g (6.522 mmol) of 2-(bromomethyl)pyridine was dissolved in 50 mL acetonitrile. Then 0.5223 g (13.06 mmol) of sodium hydroxide and 730 μL (d = 0.816 g/mL, 0.596 g, 7.82 mmol) of 2-propanethiol were added to the solution, stirred, and brought to reflux for 2 hours and 45 minutes. The reaction was removed from heat and placed in a freezer overnight. The solution was stripped to dryness via rotary evaporation and subsequently redissolved in 15 mL of deionized water. The aqueous solution was extracted into 100 mL and then 50 mL of chloroform. The aqueous layer appeared yellow and the combined organic layers appeared orange. The organic layer was dried over MgSO$_4$, filtered, and the solvent was then removed via rotary evaporation. Yield: 1.0518 g (96.4%). $^1$H NMR (CD$_3$CN,
300 MHz) δ: 8.460 (d, 1H), 7.701 (t, 1H), 7.390 (d, 1H), 7.197 (t, 1H), 3.843 (s, 2H),
2.886 (m, 1H), 1.224 (d, 6H) ppm.

Synthesis of 2-(isopropylsulfinylmethyl)pyridine (pySO)

\[
\begin{align*}
\text{Oxidation of the pyS ligand to pySO followed McClure's literature procedure.}^{74} \\
\text{In a 100 mL round bottom flask equipped with a magnetic stirrer, 1.0518 g (6.288 mmol) of pyS was dissolved in 18 mL MeOH and 14 mL deionized H}_2\text{O and}
\end{align*}
\]

stirred at room temperature. Separately, 1.3496 g (6.310 mmol) of sodium periodate
was dissolved in 20 mL deionized H\textsubscript{2}O and added dropwise to the pyS solution over 5
minutes. The solution color changed from red-orange to yellow accompanied by
precipitation of a white solid. The solution was stripped to dryness via rotary
evaporation and subsequently redissolved in 40 mL deionized H\textsubscript{2}O. The aqueous
solution was extracted into three portions of chloroform, the first of which was 40 mL
and colored while the subsequent two were 25 mL each and colorless. The organic
layers were combined, dried over magnesium sulfate, and the chloroform was
removed via rotary evaporation to yield a dark red oil. Yield: 1.0765 g (93.4%).

\[
\begin{align*}
{}^1\text{H NMR (CDCl}_3, 300 \text{MHz}) \delta: 8.543 (s, 1H), 7.649 (t, 1H), 7.340 (d, 1H), 7.203 (t, 1H),
\end{align*}
\]
4.025 (q, 2H), 2.782 (m, 1H), 1.280 (m, 6H) ppm. \(^{13}\)C NMR (CDCl\(_3\), 300 MHz) \(\delta\):
151.55, 149.89, 136.95, 125.45, 123.06, 56.64, 49.56, 16.44, 14.38 ppm.

**Synthesis of 4,4'-Di(3-thiopropyl)-2,2'-bipyridine (bpySAc)**

![Synthetic scheme for 4,4'-Di(3-chloropropyl)-2,2'-bipyridine.](image)

Figure 14: Synthetic scheme for 4,4'-Di(3-chloropropyl)-2,2'-bipyridine.

The 4,4'-di(3-thiopropyl)-2,2'-bipyridine (bpySAc) was synthesized by modifying two separate literature procedures\(^{80-81}\) to create a novel bipyridine derivative. All glassware and needles were dried in an oven prior to use. To a 100 mL two-necked round bottom flask equipped with a stirring bar, 20 mL dry THF was added via syringe. The apparatus was placed under 2.0 mL of diisopropylamine (d=0.722, 14.3 mmol) was added, the mixture was stirred and then cooled to -78°C in a dry ice/acetone bath. Once cooled, 5.60 mL of \(n\)-butyllithium (1.99 M, 11.1 mmol) was added and stirred for 10 minutes. The dry ice/acetone bath was then removed and stirred for another 10 minutes at room temperature before the solution was placed back into the dry ice/acetone bath. In a separate 50 mL round bottom flask, 0.9245 g (5.018 mmol) of 5,5'-dimethyl-2,2'-bipyridine (dmb) was dissolved in 25 mL dry THF. The dmb solution was added to the cold LDA solution via cannula. The initially colorless solutions immediately changed to an intensely dark brown-green color. The solution
was stirred at -78°C for one hour and then 1.25 mL (d=1.723, 15.0 mmol) 1-bromo-2-chloroethane was added and stirred at room temperature for seven hours. The solution color changed to yellow/orange and a white solid precipitated. The reaction solution polarity was changed with the addition of 10 mL of saturated NaCl brine solution. The organic layer was washed with three 20 mL portions of dichloromethane, combined, and washed with three 20 mL portions of brine. The organic layer was subsequently dried with MgSO₄ and the yellow filtrate stripped to dryness via rotary evaporator to yield a brown precipitate. Yield: 1.3199 g (85.06%).

**¹H NMR (CDCl₃, 300 MHz)**

δ: 8.584 (d, 2H), 8.268 (s, 2H), 7.171 (d, 2H), 3.562 (t, 4H), 2.885 (m, 4H), 2.177 (d, 4H) ppm.

**¹³C NMR (CDCl₃, 300 MHz)**

δ: 156.42, 150.97, 149.42, 124.24, 121.42, 44.11, 33.08, 32.57 ppm.

![Figure 15: Synthetic Scheme for 4,4'-Di(3-thiopropyl)-2,2'-bipyridine (bpySAc).](image)

In a 250 mL round bottom flask equipped with a magnetic stir bar, 1.6506 g (14.45 mmol) potassium thioacetate was dissolved in 85 mL dry DMF along with 1.1256 g (3.640 mmol) 4,4'-Di(3-chloropropyl)-2,2'-bipyridine. The solution was heated at ~75°C using a hot oil bath overnight (17 hours). The solution was concentrated to ~ 5 mL by placing it under high vacuum for ten hours and afforded an
oily precipitate. The oily precipitate was redissolved in 70 mL dichloromethane, washed with three 5 mL portions of H₂O, dried with MgSO₄, and concentrated via rotary evaporation to a red-orange oil. The measured yield was greater 100% and attributed to DMF that could not be removed. ^1H NMR (CDCl₃, 300 MHZ) δ: 8.560 (d, 2H), 8.242 (s, 2H), 7.141 (d, 2H), 2.906 (t, 4H), 2.771 (t, 4H), 2.328 (d, 6H), 1.973 (m, 4H) ppm. ^13C NMR (CDCl₃, 300 MHz) δ: 195.67, 155.94, 151.64, 149.12, 124.14, 121.53, 34.47, 30.75, 30.24, 28.63 ppm.

Ruthenium Complexes

Synthesis of [Ru(bpy)₂(X)]-Silica Nanoparticle Syntheses

X: bpy, (CH₃CN)₂, (EtOH)₂, CO₃²⁻, or pySO

The general procedure for preparing SiO₂ encapsulated [Ru(bpy)₂(X)] nanoparticles ([Ru(bpy)₂(X)]-SiO₂ NPs), where X is bpy, (CH₃CN)₂, (EtOH)₂, CO₃²⁻, or pySO, is described below and is a modification of a literature preparation. The (CH₃CN)₂, (EtOH)₂, and CO₃²⁻ compounds were previously synthesized by Nick Mockus and the bpy by Christine Schultz. In a conical test tube equipped with a magnetic stir bar, 3.54 mL of Triton X-100, 15.0 mL of cyclohexane, 3.6 mL of hexanol, and 680 µL of deionized water were vigorously stirred. After several minutes of stirring, 160 µL of 0.1M [Ru(bpy)₂(X)] aqueous solution, 200 µL tetraethyl orthosilicate, and 120 µL of ammonium hydroxide were added. The reaction solution was stirred overnight, after which time 40 mL of acetone was added to the reaction mixture to promote disruption of the suspension and accumulation of the nanoparticles. Aliquots of the nanoparticles were added to 1.5 mL centrifuge tubes and
were obtained using a long-stem, glass Pasteur pipette to extract approximately 1-2 mL of the \([\text{Ru}(\text{bpy})_2(\text{X})]\)-SiO\(_2\) rich solution that accumulated at the bottom of the reaction vessel. The samples were centrifuged for 10 minutes, the supernatant removed via pipette, and more sample was added. This procedure was repeated in triplicate for each synthesis and resulted in 15-20 mg, or greater, of \([\text{Ru}(\text{bpy})_2(\text{X})]\)-SiO\(_2\) NPs. After the centrifugation collection, the samples were washed prior to analysis. First, absolute ethanol was added to the 1.25 mL gradation mark on the centrifugation tube. Then samples were sonicated for 5 minutes to resuspend the NPs and excess \([\text{Ru}(\text{bpy})_2(\text{X})]\) in the solvent. The samples were subsequently sonicated for 10 minutes and the supernatant was removed with a disposable, glass Pasteur pipette. Deionized water was added to the 1.25 mL gradation mark of the centrifuge tube and sonicated for another 5 minutes. The samples were again centrifuged for 10 minutes and the supernatant was removed. This washing process was repeated two more times for a total of three wash cycles per sample, after which the supernatant would run clear and colorless.

The Ru-SiO\(_2\) NPs were attached to ITO glass electrodes using Villemure's Method\(^8\) where 100 \(\mu\)L of a mixture of Ru-SiO\(_2\) NPs and polystyrene (PS) dissolved in THF was deposited onto 1"x1" ITO glass electrodes and dried for use as working electrodes. The mixture compositions were as follows: 2.9 mg Ru-SiO\(_2\) NPs and 5.1 mg PS in 0.580 mL THF for X = (EtOH)\(_2\); 13.1 mg Ru-SiO\(_2\) NPs and 3.5 mg PS in 2.620 mL THF for X = CO\(_3\)^{2-}; 14.3 mg Ru-SiO\(_2\) NPs and 2.9 mg PS in 2.86 mL THF for X = bpy; and 26.5 mg Ru-SiO\(_2\) NPs and 1.0 mg PS in 1.000 mL THF for X =
pySO. Future preparation of this type of solution would be best carried out by first dissolving a known amount of polystyrene into a large volume of THF and subsequently adding the Ru-SiO$_2$ NPs.

**Synthesis of [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$**

![Synthetic scheme for [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$.](image)

Figure 16: Synthetic scheme for [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$.

The synthesis of [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ was reported by McClure in 2009.$^{74}$ In a 100 mL round bottom flask equipped with a magnetic stirrer, 0.1894 g (364.0 μmol) of [Ru(bpy)$_2$Cl$_2$]·2 H$_2$O was dissolved in 30 mL absolute ethanol along with 0.0829 g (452.3 μmol, 1.2 equivalents) pySO and 0.2877 g (1.138 mmol, 3.1 equivalents) AgPF$_6$. The solution was stirred and refluxed overnight (18.5 hours). The reaction was considered complete via UV-Vis monitoring of the peak at $\lambda_{\text{max}} \sim 370$ nm. The reaction solution was cooled to room temperature and placed in a freezer for approximately three hours to fully precipitate the AgCl byproduct. The AgCl was removed by vacuum filtration through a fine frit and rinsed with methanol and acetonitrile. The filtrate was collected and stripped to dryness via rotary evaporation. The solid was redissolved in approximately 2 mL of absolute ethanol and approximately 2 mL diethyl ether was added to precipitate out product. The precipitate
was vacuum filtered on a medium frit, rinsed with diethyl ether, and air dried to afford a yellow-orange powder. Yield: 0.2586 g (80.1%).

**Synthesis of [(p-cymene)RuCl₂]₂**

![Chemical structure of [(p-cymene)RuCl₂]₂](image)

Figure 17: Synthetic scheme for [(p-cymene)RuCl₂]₂.

To synthesize trisheteroleptic compounds, the [(p-cymene)RuCl₂]₂ dimer was synthesized. In a 250 mL round bottom flask equipped with a magnetic stir bar, 1.7459 g (7.744 mmol) of ruthenium (III) chloride hydrate was dissolved in 100 mL of absolute ethanol and 7.000 mL (d=0.85, 43.68 mmol) of α-phellandrene was added. The dark brown solution was stirred and refluxed for 3 hours at which time the solution appeared deep red. The reaction mixture was removed from heat and the solvent was reduced to one quarter of its original volume using a rotary evaporator. Approximately 10 mL of diethyl ether was added to the solution, to precipitate the product, which was placed in the freezer overnight. The reaction solution was filtered on a 30 mL fine frit to obtain a red, microcrystalline precipitate of [(p-cymene)RuCl₂]₂ which was rinsed with ether and air-dried on the frit. Yield: 1.5846 g (66.83%). ¹H NMR (CD₃CN, 300 MHZ) δ: 5.464 (d, 4H), 5.297 (d, 4H), 2.906 (m, 2H), 2.185 (s, 6H), 1.310 (d, 12H) ppm.
Synthesis of [(p-cymene)Ru(bpy)Cl]Cl

Figure 18: Synthetic scheme for [(p-cymene)Ru(bpy)Cl]Cl.

In a 250 mL round bottom flask equipped with a magnetic stir bar, 0.6592 g (1.076 mmol) of [(p-cymene)RuCl₂]₂ was dissolved in 100 mL of CH₃CN along with 0.3730 g (2.388 mmol) of 2,2'-bipyridine. The reaction mixture was stirred and refluxed under nitrogen for 12 hours. The solution was removed from heat, stripped to dryness via rotary evaporation, and redissolved in absolute ethanol. A few milliliters of diethyl ether were added to effect slight precipitation of the product which was then placed in the freezer overnight. The precipitate was filtered on a fine frit and washed with diethyl ether to afford an orange powder of the [(p-cym)Ru(bpy)Cl]Cl product. Yield: 0.9274 g (93.16%). ¹H NMR (CD₃CN, 300 MHz) δ: 9.368 (d, 2H), 8.346 (d, 2H), 8.176 (t, 2H), 7.692 (t, 2H), 5.943 (d, 2H), 5.744 (d, 2H), 2.643 (m, 1H), 2.197 (s, 3H), 1.017 (d, 6H) ppm.
Synthesis of [Ru(bpy)(pySO)Cl$_2$]

Figure 19: Synthetic scheme for [Ru(bpy)(pySO)Cl$_2$].

In a 10 mL round bottom flask equipped with a magnetic stir bar, 0.2117 g (457.8 µmol) of [(p-cym)Ru(bpy)Cl]Cl was dissolved in 1.25 mL DMF along with 0.0840 g (458.3 µmol) of pySO ligand. The solution was stirred and brought to reflux overnight. The reaction was stopped, cooled to room temperature, and placed in the freezer for four hours after the addition of 20 mL of acetone. The reaction solution was filtered through a fine frit, washed with diethyl ether and absolute ethanol and air dried to afford the [Ru(bpy)(pySO)Cl$_2$] precipitate. $^1$H NMR (CD$_3$CN, 300 MHz) δ: 9.878 (d, 1H), 9.776 (d, 1H), 8.278 (d, 1H), 8.214 (d, 1H), 8.002 (t, 1H), 7.883 (m, 2H), 7.774 (d, 1H), 7.714 (d, 1H), 7.599 (t, 1H), 7.489 (t, 1H), 7.249 (t, 1H), 5.075 (d, 1H), 4.609 (d, 1H), 3.975 (q, 1H), 1.343 (d, 3H), 0.664 (d, 3H) ppm.
Synthesis of [Ru(bpy)(bpySAc)(pySO)](OTf)₂

In a 50 mL round bottom flask equipped with a magnetic stir bar, 111.0 mg (217.0 mmol) of [Ru(bpy)(pySO)Cl₂] was dissolved in 25 mL acetonitrile along with 123.0 mg (478.7 mmol) silver triflate (AgOTf). The reaction was stirred and refluxed under nitrogen for three and a half hours and considered complete when the growth of the UV-Vis peak at λ_max ~ 425 nm stabilized. The reaction solution was filtered through a fine frit to filter off 22.0 mg (153.6 mmol) AgCl precipitate and collected in a 100 mL round bottom flask. The solvent was removed via rotary evaporator and a small amount of product was removed for NMR characterization. ¹H NMR (CDCl₃, 300 MHZ) δ: 9.142 (d, 1H), 9.041 (d, 1H), 8.438 (d, 1H), 8.392 (d, 1H), 8.232 (t, 1H), 8.143 (t, 2H), 7.849 (d, 2H), 7.746 (t, 1H), 7.670 (t, 1H), 7.484 (t, 1H), 5.039 (d, 1H),
4.670 (d, 1H), 3.429 (m, 1H), 2.478 (s, 3H), 2.245 (s, 3H), 1.316 (d, 3H), 0.920 (d, 3H) ppm.

The [Ru(bpy)(CH$_3$CN)$_2$(pySO)](OTf)$_2$ was left in the 100 mL round bottom flask and redissolved in 50 mL EtOH. The bpySAc starting material was added, 100.3 mg (258.4 mmol), and the reaction mixture was refluxed under nitrogen for five and a half hours. The reaction was monitored by the shift of the UV-Vis peak at $\lambda_{\text{max}}$ ~ 344 nm to $\lambda_{\text{max}}$ ~ 360 nm. The reaction solution volume was reduced by half, diethyl ether was added to facilitate precipitation of the product, and the solution was placed in a freezer overnight. The product was filtered through a fine frit and found to be sticky rather than powder-like so it was washed with ~10 mL diethyl ether. Yield: 60.7 mg (24.8% overall).

**Deprotection of [Ru(bpy)(bpySAc)(pySO)](OTf)$_2$ and Attachment to Gold Electrode**

![Figure 21: Deprotection of [Ru(bpy)(bpySAc)(pySO)](OTf)$_2$ to [Ru(bpy)(bpySH)(pySO)](OTf)$_2$.](image)

The first method for deprotection of the [Ru(bpy)(bpySAc)(pySO)](OTf)$_2$ and attachment to the gold-coated ITO electrode surface was performed simultaneously. Two gold-coated ITO glass were cleaned by immersion in hot piranha (3:1
H$_2$SO$_4$/H$_2$O$_2$) solution and rinsed with H$_2$O and EtOH. The two electrodes were subsequently immersed in a 1 mM solution of [Ru(bpy)(bpySAc)(pySO)](OTf)$_2$ in acetonitrile along with 60 µL of NH$_3$OH and heated in a 60°C water bath for three hours. The electrodes were removed and rinsed with acetonitrile prior to use in electrochemical experiments.

The second deprotection and attachment method utilized sodium thiomethoxide$^{85}$ to deprotect the [Ru(bpy)(bpySAc)(pySO)](OTf)$_2$ compound. In a 50 mL round bottom two-necked flask equipped with a magnetic stir bar, 35.7 mg (31.7 mmol) [Ru(bpy)(bpySAc)(pySO)](OTf)$_2$ was placed under N$_2$. In a separate vial, 6.8 mg (97 mmol) of NaSMe was dissolved in 5 mL of dry MeOH and then added to the [Ru(bpy)(bpySAc)(pySO)](OTf)$_2$. The solution was stirred and heated in a 50°C water bath. After two hours, 1.5 mL of 0.1 M HCl (aq.) was added to the flask along with 3 mL H$_2$O. The organic layer was extracted into three 10 mL portions of dichloromethane and washed with 10 mL brine solution. The intensely red colored organic layers were dried over MgSO$_4$, filtered, and concentrated via rotary evaporation to yield a deep red oil. Diethyl ether was added to precipitate the compound as a powder. Yield: 4.0 mg (12%). The product was dissolved in 3.6 mL CD$_3$CN in an attempt to obtain $^1$H-NMR characterization which was unsuccessful.

One piece of gold-plated FTO was placed in a 10 mL beaker along with the NMR solution and heated for three hours in a 60°C water bath. The electrode was subsequently rinsed with acetonitrile to remove excess compound prior to electrochemical experiments.
**Optoelectronic Device Designs**

The fluorine-doped tin oxide (FTO) glass was cleaned by sonicating several 1"x1" squares in a saturated solution of sodium hydroxide and isopropanol for 1 hour. The glass squares were subsequently sonicated in solutions of acetonitrile and acetone, dried, and stored for later use. Immediately prior to cell construction, the FTO glass was rinsed with acetone and dried with a Kimwipe. Pt-FTO electrodes were prepared by sputtering Pt onto the cleaned FTO glass by Dr. Martin Kordesch.

The nomenclature method used below is such that a device listed as FTO|Ru, BMImPF$_6$ |Pt,Pt indicates that FTO functions as the working electrode which sandwiches a ruthenium compound dissolved in the BMImPF$_6$ ionic liquid against two Pt wires, one which serves as the counter electrode and the other as the reference electrode.

**ITO| Ru-Nafion |ITO Design**

The ITO|Ru-Nafion |ITO design consists of one 1"x1" piece of ITO glass as the working electrode and another 1"x1" piece of ITO glass serving as both the counter and reference electrode with a single piece of Parafilm used as a spacer in between the two pieces of ITO glass. The working electrode was prepared by depositing 40 µL of a 15 mg / mL solution of [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ in Nafion-117 into a hole punched out of the Parafilm spacer on top of the ITO glass and dried under Ar for one hour. Sufficient Pyr$_4$NTf$_2$ ionic liquid was pipetted onto the Ru-Nafion surface, approximately 100 µL, to fully wet the surface. The other piece of ITO glass was carefully placed on top of the working electrode in a sandwich cell fashion.
and held in place with binder clips; no heat was used to seal the cell. Excess ionic liquid was removed via capillary wicking with Kimwipes prior to electrochemical experiments.

**FTO|Pt-FTO Design**

To construct the FTO|Pt-FTO cell, two pieces of 2”x2” Parafilm were hole-punched with a standard, ¼” single-hole punch and placed on top of the FTO glass working electrode. A small rectangle was cut out with a utility knife to facilitate electrolyte introduction, see Figure 22. The Pt-FTO glass, which served as both the counter and reference electrodes, was sandwiched against the Parafilm spacer with binder clips and heated to melt the Parafilm. The cell was allowed to cool to room temperature before the ionic liquid electrolyte was added via vacuum back-filling. The cell was placed in a vacuum desiccator with a drop of ionic liquid placed above the electrolyte inlet hole in the Parafilm. Once under vacuum, the ionic liquid would displace the air in the reservoir. Additional ionic liquid was added to the cell and placed under vacuum until the reservoir was completely filled and free of air bubbles.

If a solution of Ru complex in Nafion 117 was used, the two pieces of Parafilm would first be melted to the FTO working electrode, then 35 µL of the Ru-Nafion 117 solution would be deposited into the Parafilm reservoir. Once the Nafion layer dried, after approximately two hours, the electrolyte inlet rectangle would be cut from the Parafilm and construction would proceed as described above, see Figure 22.
FTO$|\text{Pt}$ Design

To construct the FTO$|\text{Pt,Pt}$ cell, ten 2"x2" pieces of Parafilm were cut and hole-punched with a standard $\frac{1}{4}$" single-hole punch. Three sheets were placed on top of a 0.5"x1" piece of microscope slide glass and cut to size, see Figure 23. Two Pt wires were pressed into the Parafilm to serve as the counter and reference electrodes and the remaining seven sheets of Parafilm were placed on top of the Pt wires. The large amount of Parafilm was necessary to ensure that the Pt wires did not contact the FTO working electrode. A small rectangle was cut out of the Parafilm for ionic liquid introduction using a utility knife. The conductive side of the FTO glass was offset with respect to the microscope glass backing and pressed onto the Parafilm, see Figure 23.
Figure 23: Schematic for FTO|Pt, Pt cell construction.

The cell was heated with a heat gun until the Parafilm changed from translucent/opaque to transparent/clear at which time slight pressure was applied with a pair of forceps to seal the cell. Care should be taken to ensure that the Pt wires are fully enveloped with Parafilm and that no gaps exist between the Parafilm spacer and the glass to eliminate electrolyte leakage. Pressure was removed once the Parafilm regained its translucent appearance and then allowed to cool to room temperature. Once cooled, any number of ruthenium and electrolyte combinations could be introduced into the reservoir, see Figure 24. Typically, 35 µL of an 8 mM solution of [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ dissolved in either BMImPF$_6$ or BMImNTf$_2$ was micropipetted into the reservoir and the whole cell was placed under vacuum in a vacuum desiccator to remove air bubbles.
Figure 24: Photograph of an unfilled FTO|Pt,Pt electrochemical cell. The FTO conductive glass is closest to the viewer followed by seven pieces of Parafilm, the two platinum wires, three more pieces of Parafilm, and a piece of microscope slide glass.

**Photochemical Cell Switching**

For irradiation experiments, the electrochemistry was performed on the laser table with the sample mounted on a post to restrict movement. The working, counter, and reference electrodes were attached to the sample and the CH Instruments 730A EChem Analyzer, with care taken not to disturb the contacts during the experiment. The 472 nm laser beam was obtained by using the 355 nm third-harmonic of a Nd:YAG laser which was picked out using the Surelite PSS, tuned to 472 nm with the use of the OPO, and used to directly irradiate the sample, shown in Figure 25. Unless noted otherwise, the cells were irradiated through the working electrode.
Figure 25: Experimental set up for 355 nm and 472 nm laser irradiation for cell cycling between the S-bonded and O-bonded states of the electrochemical devices.

The 355 nm beam used for irradiation was rerouted around the OPO with the use of two stationary prisms and two movable prisms, shown in Figure 25. Because the 472 nm beam required no movement of parts, the irradiation spot size was consistent throughout individual experiments, while the necessary movement of prisms for 355 nm irradiation resulted in less precise positioning of the spot size. Typically the laser power for 355 nm irradiation was set to 1.00 kV for power intensities of ~15-20 mJ/pulse and for 472 nm irradiation the laser power was set to 1.30 kV for power intensities of ~18-23 mJ/pulse. The power of the incident laser beam was measured directly in front of the sample several times throughout an experiment and was generally found to fluctuate by 1-2 mJ/pulse.
RESULTS AND DISCUSSION

Development of the molecular optoelectronic transducer required many different approaches to accomplish the goal of creating a self-contained device capable of utilizing light as an input to effect an electrochemical change as the output. To date, several modified electrodes have been developed that are capable of utilizing photochemical switching to effect an electrochemical output.\textsuperscript{44-55} These electrodes are typically irradiated out of solution and monitored using standard, three electrode bulk electrochemistry. Furthermore, only 2 to 4 photoswitching cycles are typically reported with a maximum of 6 reported for modified electrodes using spiropyran\textsuperscript{45} and diarylethene\textsuperscript{52} derivatives. The electrode modification attempts and molecular optoelectronic devices described here were inspired by dye sensitized solar cell designs that gradually became tailored to the specific function desired.

Electrode Modifications

While initially developing the device, it was believed that high sensitivity obtained using a minimal amount of compound was an ideal characteristic. Attempts were made to adhere the photoactive compound directly to the electrode surface to fulfill this goal. This approach was also favored as it was hypothesized that cell stability would be greatest with an attachment scheme, as opposed to free compound dissolved in an electrolyte, because diffusion of the compound to and from the electrode surface would be minimized.
Ruthenium-doped Silica Nanoparticles (Ru-SiO$_2$ NPs)

The first electrode modification method was an adaptation of work done by Dong, Wang, and coworkers using silica nanoparticles (SiO$_2$ NPs) doped with ruthenium compounds.$^{82,91-92}$ Previous work focused on [Ru(bpy)$_3$]$^{2+}$ because of its electrogenerated chemiluminescence properties and application as a sensor for detecting organic molecules in aqueous solutions. The ruthenium compounds incorporated into SiO$_2$ NPs in this work include [Ru(bpy)$_3$]$^{2+}$, [Ru(bpy)$_2$(EtOH)$_2$]$^{2+}$, [Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$, [Ru(bpy)$_2$(CO$_3$)]$^{2+}$, and [Ru(bpy)$_2$(pySO)]$^{2+}$. While the [Ru(bpy)$_2$(pySO)]$^{2+}$ compound is the sole photochromic/electrochromic material of the five studied, the others could be worked with under normal light conditions which aided in the method development. The three photographs in Figure 26 were obtained using an optical microscope and are representative of the ruthenium doped SiO$_2$ NPs. Using the freely available ImageJ image processing software,$^{93-94}$ it is possible to correlate the pixel size in the image to the known distance using the orange, 10 µm scale bar in the bottom left corner of each photograph. Then, the diameters of the different NPs may be approximated using the software. The smallest particles were found to have sub-micrometer diameters in the three images shown, with the largest diameters on the order of 3-4 µm for the [Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$ clusters visible in Figure 26 (c). Small-angle X-ray scattering (SAXS) measurements provided by Congshang Wang and Dr. Gang Chen determined that the approximate diameters were 48 nm for [Ru(bpy)$_3$]$^{2+}$, 27 and 48 nm for [Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$, 26 and 47 nm for [Ru(bpy)$_2$(CO$_3$)]$^{2+}$, and 42 nm for [Ru(bpy)$_2$(EtOH)$_2$]$^{2+}$. The diameters were
Figure 26: Optical microscope images of $[\text{Ru(bpy)}_2(X)]^{2+} \text{SiO}_2$ NPs where $X$ is (a) (CH$_3$CN)$_2$, (b) CO$_3^{2-}$, and (c) (EtOH)$_2$. The orange scale bar in the bottom left corner of the photographs is 10 µm.

approximations based on assumptions that the electron density of the dye solution was 30% greater than water and that the silica shell thickness was 2 nm and could be more precisely defined by determining the actual values. However, the approximate diameters are in relatively good agreement with the 40-60 nm diameters reported in the literature which were measured by transmission electron microscopy (TEM). It is hypothesized that the smaller 26 and 27 nm diameters obtained were due to silica nanoparticles that did not contain any ruthenium compound which could be verified experimentally by preparing undoped SiO$_2$ NPs. Although the Ru-SiO$_2$ NPs appear to be on the micrometer scale in Figure 26 this is likely due to agglomeration of the NPs into clusters upon their removal from solvent. The SAXS measurements were obtained in solution while the optical microscope images were obtained using dried samples. Finally, TEM or scanning electron microscopy (SEM) measurements could improve the precision of the diameter measurement and provide greater physical detail of the Ru-SiO$_2$ NPs.

Nevertheless, the electrochemical properties of the ruthenium doped SiO$_2$ NPs were of most interest and attached to ITO glass using Villemure’s Method$^{83}$ for electrochemistry experiments. Electrochemistry of the Ru-SiO$_2$ modified ITO
electrodes are shown in Figure 27 through Figure 30 with sensitivities of $5 \times 10^{-6}$ A/V. The supporting electrolyte was a 0.05 M aqueous Na$_2$SO$_4$ solution, the counter electrode was a Pt wire, and the reference electrode was Ag/AgCl in saturated, aqueous KCl solution. The CV of the [Ru(bpy)$_3$](PF$_6$)$_2$-SiO$_2$ NPs adhered to ITO glass is shown as the red trace in Figure 27 along with the blank, blue trace, where unmodified ITO glass was used as the working electrode. Similarly, CVs of [Ru(bpy)$_2$(EtOH)$_2$](PF$_6$)$_2$ and [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ SiO$_2$ NPs adhered to ITO glass are shown as red traces in Figure 28 and Figure 29, respectively.

![Image](image-url)

Figure 27: CV of [Ru(bpy)$_3$](PF$_6$)$_2$-SiO$_2$ NPs adhered to ITO glass (red trace) and blank (blue trace).
Figure 28: CV of [Ru(bpy)$_2$(EtOH)$_2$](PF$_6$)$_2$-SiO$_2$ NPs adhered to ITO glass (red trace) and blank (blue trace).

Figure 29: CV of [Ru(bpy)$_2$(pySO)]$^{2+}$-SiO$_2$ NPs adhered to ITO glass (red trace) and blank (blue trace).

The [Ru(bpy)$_3$](PF$_6$)$_2$ modified electrode exhibited reversible behavior with an anodic peak ($E_{pa}$) at 1.136 V and cathodic peak ($E_{pc}$) at 1.052 V. The electrode modified with [Ru(bpy)$_2$(EtOH)$_2$](PF$_6$)$_2$ exhibited $E_{pa1} = 0.541$ V, $E_{pa2} = 0.733$ V, $E_{pc1} = 0.656$ V, and $E_{pc2} = 0.419$ V. The electrode of most interest, the [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ SiO$_2$ NP modified electrode exhibited reversible behavior for
the O-bonded isomer, seen in Figure 29, with \( E_{pa} = 0.829 \) V and \( E_{pc} = 0.758 \) V. The S-bonded isomer was experimentally verified using another modified electrode by DPV in 0.1 M TBAPF\(_6\) in acetonitrile solution with the same counter and reference electrodes used previously, shown in Figure 30. The O-bonded isomer was attributed to the peak at 0.896 V and the S-bonded isomer to the peak at 1.696 V, however it should be noted that both of these potentials were higher than the expected potentials. It is clear from the second scan, the purple trace, that some of the Ru-SiO\(_2\) NPs dissolved from the electrode surface into the bulk solution. This hypothesis was visually verified by noting the lack of NPs on the electrode surface and coloration of the previously colorless electrolyte solution.

The Ru-SiO\(_2\) NPs were successfully synthesized and exhibited good electrochemical properties, albeit that the [Ru(bpy)\(_2\)(pySO)]\(^{2+}\) -SiO\(_2\) NP potentials were slightly positive from the expected values. However, the presence of water inside
the SiO$_2$ shell and the removal of the Ru-SiO$_2$ NP layers from the electrode surface were disconcerting for the long-term success of the project. Ideally, the solvent surrounding the photoactive species would be more photochemically robust and the attached particles would remain stable for repeated electrochemical measurements.

**Ruthenium-doped Nafion**

The instability of the ruthenium doped SiO$_2$ NP modified electrodes prompted research into a less complex attachment method. The anionic polymer Nafion-117 was chosen due to the dicaticonic charge of the [Ru(bpy)$_2$(pySO)]$^{2+}$ compound which should electrostatically bind to the polymer and remain close to the electrode surface as a result.$^{95-99}$ Literature reports of stable, modified electrodes using [Ru(bpy)$_3$]$^{2+}$-doped Nafion films in aqueous solutions indicated that the attachment method increased the detection sensitivity of electrochemical sensors.$^{98}$ The electrochemistry in this work was not performed in aqueous solutions, but the stability and electrostatic binding of Nafion lead to its choice as a suitable polymer for electrode modification.

The [Ru(bpy)$_2$(pySO)]$^{2+}$ was attached to a 3 mm diameter glassy carbon electrode (GCE) by pipetting 20 µL of 15 mg [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ / 1 mL Nafion-117 onto the surface. Electrochemistry was performed with sensitivities of 5x10$^{-5}$ A/V. The first and second DPVs of the Ru-Nafion modified electrode are shown in Figure 31 as red and purple traces, respectively, with the blank of an unmodified glassy carbon electrode shown in blue. It is notable that large amounts of current were obtained from the modification and that electrochemical generation of the O-bonded isomer occurs as indicated by the appearance of the 0.716 V peak in the second scan.
The peak potentials of 1.284 V for the S-bonded isomer and 0.716 V for the O-bonded isomer were comparable to the expected values.

Figure 31: Initial (red) and second (purple) DPVs of [Ru(bpy)$_2$(pySO)]$^{2+}$ attached to a GCE with Nafion. The blue trace is a blank DPV taken with an unmodified GCE. The electrochemistry was performed with a Pt wire counter electrode and a Ag/AgPF$_6$ in CH$_3$CN reference electrode in a 0.1 M TBAPF$_6$ in acetonitrile electrolyte solution.

After the initial scans, the electrode was removed from the bulk electrochemistry solution and irradiated with 355 nm light for approximately two minutes. Figure 32 shows the irradiation results of the [Ru(bpy)$_2$(pySO)]$^{2+}$-SiO$_2$ modified GCE. The red trace in Figure 32 is the same as the second DPV shown in Figure 31 and was obtained prior to irradiation. The effect of continued 355 nm irradiation was experimentally determined by taking DPVs after two minutes (blue), four and a half minutes (purple), and after seven minutes (green) of total irradiation time.
Figure 32: DPVs of [Ru(bpy)$_2$(pySO)]$^{2+}$-Nafion modified GCE upon irradiation with 355 nm laser. The red trace was obtained prior to irradiation, the blue after 2 total minutes, the purple after 4.5 minutes, and the green after 9 minutes of total irradiation with 355 nm light.

The drastic, unexpected feature of the experiment was the growth of a peak at 1.032 V whose peak current increased after each irradiation. Concomitant with the current increase at 1.032 V was the decrease in the S-bonded current at 1.284 V, while the O-bonded peak current at 0.716 V initially increased and subsequently decreased. The electrode was not fully dried prior to irradiation experiments and the [Ru(bpy)$_2$(pySO)]$^{2+}$ compound is known to undergo photo-induced ligand substitution. Thus as the sulfoxide unit photochemically isomerized, residual acetonitrile could bind to the ruthenium forming a new, undesired complex. This hypothesis is supported by the Ru$^{II/III}$ potential of [Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$ which is equal to 1.076 V. The 44 mV difference is attributed to not knowing the undesired complex's structure as well as different experimental conditions, i.e. the
[Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$ data was obtained with an unmodified glassy carbon electrode and dissolved in bulk solution.

The photochemical experiment was repeated, however ITO glass was used for the modified working electrode instead of glassy carbon. The electrochemistry experiments were obtained with sensitivities of 5x10$^{-4}$ A/V. The initial CV of the modified electrode exhibited O-bonded peak potentials of $E_{pa1} = 0.848$ V and $E_{pc1} = 0.680$ V with S-bonded potentials of $E_{pa2} = 1.456$ V and $E_{pc2} = 1.295$ V, see the red trace in Figure 33. Shown along with the initial CV is the blue trace of a blank obtained using unmodified ITO as the working electrode. The current difference between the blank and the modified electrode shows the drastic current increase resulting from surface modification.

![Figure 33: CV of [Ru(bpy)$_2$(pySO)]$^{2+}$-Nafion modified ITO before (red) and after (black) irradiation. The blue trace was obtained using unmodified ITO as a blank.](image)

The [Ru(bpy)$_2$(pySO)]$^{2+}$-Nafion modified ITO electrode was then irradiated with 355 nm light for approximately five minutes. After irradiation, a third peak with $E_{pa} = 1.196$ V and $E_{pc} = 0.998$V was present. Thus, the intermediate peak consistently
appeared after 355 nm irradiation and is most likely attributed to photo-triggered ligand substitution of [Ru(bpy)$_2$(pySO)](PF$_6$)$_2$ with acetonitrile.

The results of the [Ru(bpy)$_2$(pySO)]$^{2+}$-Nafion modified electrodes were promising because a consistent baseline was present throughout the experiments, large amounts of current were obtained, and photochemical isomerization was successful, albeit with the caveat of possible photo-triggered ligand substitution. The ligand substitution issue prompted a search for non-coordinating electrolytes suitable for use in a device with propylene carbonate and ionic liquids chosen as the most appealing replacements.

While Nafion modified ITO electrodes generally worked well, there were still issues with dissolution of the ruthenium compound out of the polymer membrane into the bulk electrolyte, resulting in current loss. Figure 34 depicts the loss of [Ru(bpy)$_3$](PF$_6$)$_2$ and Nafion from the FTO electrode as evidenced by the loss in current for the red trace.

![Figure 34: CV of [Ru(bpy)$_3$](PF$_6$)$_2$-Nafion modified FTO indicating loss of compound upon each scan.](image-url)
The electrochemistry was performed with sensitivities of $1 \times 10^{-4}$ A/V. The blue trace was a blank obtained using unmodified FTO for the working electrode. The current loss may be due to one of two reasons. The first cause could be total dissolution of the Nafion polymer from the electrode surface and into the bulk electrolyte. Alternatively, the ruthenium compound could be dissolving out of the Nafion polymer and into the bulk electrolyte. The second cause is considered the more likely of the two and might be abated in future experiments by thoroughly washing the electrode with the electrolyte solution to remove excess ruthenium compound that is not electrostatically bound to the Nafion. Alternatively, the electrodes could be prepared by first depositing the Nafion onto the electrode surface and then soaking the Nafion modified electrode in a ruthenium solution prior to use.

**Ruthenium Attachment via Gold-Thiol Linkage**

To combat the loss of ruthenium compound from the electrode, direct chemical modification of the electrode surface was investigated. A gold-thiol linkage approach was initially pursued due to previous literature reports of self-assembled monolayers of thiol-containing compounds onto gold electrodes for electrochemical purposes. Particularly useful were the two reviews of photoactive compounds attached to metal surfaces by Browne and the more general review of metal surface attachment by Cao et al. Many reports use a mixture of long chain alkane thiols and the photoactive compound with the thiol linker, however
[Ru(bpy)(bpySH)(pySO)](OTf)$_2$ was solely used for gold electrode modification in this study and the hypothesized self-assembled monolayer is shown in Figure 35.

Figure 35: Depiction of the hypothesized self-assembled monolayer of [Ru(bpy)(bpySH)(pySO)]$^{2+}$ on a gold electrode surface.

The electrochemistry of the [Ru(bpy)(bpySH)(pySO)](OTf)$_2$ modified gold electrode was obtained with sensitivities of $5 \times 10^{-4}$ A/V. The initial traces in Figure 36 are shown in red and indicate that the ruthenium complex did indeed attach to the gold surface. Unfortunately, subsequent scans of the electrode indicate that the peak current drastically diminishes, see first the blue, then green traces. The black traces are blank DPVs of unmodified gold-coated ITO glass and indicate that the broad peak centered around 0.5 V is inherent to the gold electrodes used.

Figure 36: [Ru(bpy)(bpySH)(pySO)](OTf)$_2$ modified Au electrodes indicating loss of Ru complex upon oxidation of the thiol linkage.
The electrochemical results using a different gold modification approach were similar to those shown in Figure 36. The red trace in Figure 37 indicates the initial scan of the electrode while the blue and green are from the second and third scans, respectively. The black trace was obtained using an unmodified, gold-coated ITO electrode as the blank.

![Graph showing electrochemical results](image)

Figure 37: [Ru(bpy)(bpySH)(pySO)]^{2+} modified Au electrode indicating loss of Ru complex upon thiol linker oxidation.

Upon further review of the literature, it was found that gold-thiol bonds oxidize between 0.8 and 1.0 V\textsuperscript{108-110} dependent upon the experimental conditions and the molecular structure. This suggests that the self assembled monolayer of [Ru(bpy)(bpySH)(pySO)]^{2+} is stripped from the electrode surface after the initial scan. Continued use of gold-thiol modified electrodes may be possible if only the O-bonded isomer is monitored, but a potential window below 0.8 V is less than ideal for these specific experiments because of the background current with $E_p = 0.5$ V and the expected O-bonded isomer peak potential of 0.75 V. Alternatively, photochemical
switching of [Ru(bpy)(bpySH)(pySO)]^{2+} could be studying using scanning tunneling microscopy or transmission electron microscopy techniques as opposed to electrochemical methods. One possible solution to avoid the gold-thiol oxidation is to synthesize a [Ru(X)(bpySH)(pySO)]^{2+} complex where X is an electron-donating ligand that would shift the O-bonded potential to less positive values. Rather than relying on the gold-thiol linkage, the more electrochemically robust silyl group^{53,111}
could be used to anchor the ruthenium pySO compound to either ITO or FTO glass. Similarly, carboxylate-TiO_2 linkage like those employed in dye sensitized solar cells (DSSCs)^{87,112-113} may be useful for anchoring a [Ru(bpy)(bpy')(pySO)]^{2+} compound to the conductive glass where bpy' is 4,4-dicarboxy-2,2'-bipyridine.

**Self-Contained Molecular Optoelectronic Transducers**

The desire to create self-contained devices for use as molecular optoelectronic transducers stemmed from the need to create a stable, reproducible device. Bulk electrochemistry was deemed undesirable because of solvent evaporation and irradiation issues. Constructing small devices allowed for precise placement of the electrodes and minimized or eliminated their movement during experiments. Cell construction also lent control over the volume size of the sample, an important aspect for irradiation experiments due to the diameter of the laser beam. The results of the different cell designs are detailed below in chronological order of creation.

**ITO|ITO Cell**

The first cell construction was a modified dye-sensitized solar cell design where the photoactive compound is held in close contact with the working electrode in
a two-electrode sandwich cell configuration.\textsuperscript{86-89} Typical dye sensitized solar cells (DSSCs) are comprised of an FTO working electrode coated with colloidal TiO\textsubscript{2} which is sensitized by soaking the electrode in a solution of dye. The counter/reference electrode is comprised of Pt coated FTO glass and the cell is held together either with binder clips or Surlyn heat-shrink polymer.\textsuperscript{87} In DSSCs, the colloidal TiO\textsubscript{2} increases the surface area coverage of the dye and anchors the dye to the electrode surface. In this work, the sandwich cell principle was retained with two pieces of ITO glass serving as the working and counter/reference electrodes which were separated with a Parafilm spacer and held together with binder clips. Rather than TiO\textsubscript{2}, Nafion was employed to modify the working electrode surface.

The initial DPV scan, shown in Figure 38, indicated the presence of both S-bonded and O-bonded isomers with peak potentials of 2.324 and 1.300 V, respectively. The following electrochemistry was obtained with sensitivities of 5x10\textsuperscript{-6} A/V. The peak potentials for the cell are markedly more positive than expected and may be attributed to the use of ITO as both the reference and counter electrode. The peaks are also notably broad which may be due to the large amount of [Ru(bpy)\textsubscript{2}(pySO)]\textsuperscript{2+} used and the Nafion polymer.
Figure 38: Initial DPV scan of the ITO[[Ru(bpy)$_2$(pySO)]$^{2+}$-Nafion, Pyr$_4$NTf$_2$|ITO
cell. Presence of the S-bonded isomer at 2.324 V and the O-bonded isomer at 1.300 V
is apparent.

Photochemical switching of the cell was achieved using 2 minute irradiation times
with 355 nm light for S$\rightarrow$O conversion and 6 minute irradiation times with 472 nm
light for O$\rightarrow$S conversion. The cell was switched between the S-bonded and O-
bonded isomers for a total of six cycles. The DPVs obtained during the photochemical
switching experiment are overlaid in Figure 39. The blue traces are DPVs taken after
355 nm irradiation and the red traces were taken after 472 nm irradiation.
Figure 39: Photochemical switching of an ITO|([Ru(bpy)$_2$(pySO)])$^{2+}$-Nafion, Pyr$_4$NTf$_2$|ITO cell. The cell was irradiated with a 355 nm laser for 2 minutes, blue traces, followed by irradiation with a 472 nm laser for 6 minutes, red traces, for a total of six cycles. The cell exhibited an overall trend of decreasing peak potential current.

The peak potential currents decreased over the duration of the experiment for both the S-bonded and O-bonded isomers. The peak potentials drifted to consistently more positive values after the initial cycle, ranging from 1.288 to 1.427 V for the O-bonded peak and 2.240 to 2.388 V for the S-bonded peak. Full S$\rightarrow$O conversion was not achieved and may be due to a combination of the short irradiation times as well as irradiation of only a fraction of the photoactive compound, seen in Figure 41. The red spot in the center of the photograph is indicative of the O-bonded isomer and demonstrates the spot size of the 355 nm laser beam, while the yellow ring around the red spot is indicative of unisomerized S-bonded complex. The green alligator clip was attached to the working electrode while the red and white clips were attached to the counter/reference electrode.
Figure 40: Photograph of ITO\([\text{Ru(bpy)}_2\text{(pySO)}]^2+\)-Nafion, Pyr$_4$NTf$_2$|ITO cell. Formation of the O-bonded isomer is indicated with a red arrow and the S-bonded isomer is indicated with a yellow arrow. Full conversion to the O-bonded species did not occur due to the spot size of the laser beam. The working electrode is connected to the green alligator clip with the counter/reference electrode connected to the red and white alligator clips.

Plotting the peak current versus cycle number allows for critical evaluation of the device's ability to repetitively switch between the S-bonded and O-bonded isomers. The peak currents for both the S-bonded and O-bonded isomers are shown in Figure 41 and the overall decrease in peak current is readily visible in the data. The decreasing current is attributed to electrolyte leakage from the cell. The device results were difficult to reproduce due to highly variable cell seals and inconsistent peak potentials, necessitating a new cell design. However, the results were encouraging because they demonstrated the viability of a molecular optoelectronic device based on the photochemistry of [Ru(bpy)$_2$(pySO)]$^2+$. 
Figure 41: Photochemical switching of the ITO| [Ru(bpy)$_2$(pySO)]$^{2+}$ -Nafion, Py$_4$NTf$_2$ |ITO cell: (a) S-bonded isomer, (b) O-bonded isomer. The graphs display the diminishing peak potential current over the duration of the experiment.

**FTO| Pt-FTO Cell**

The original device design was modified to improve the seal to prevent leakage and to incorporate a Pt electrode which would serve as a more robust counter/reference electrode. Incorporation of a piece of Pt-FTO glass scored across the middle to effectively create independent counter and reference electrodes proved unsuccessful,\textsuperscript{114} but employing the Pt-FTO glass as both the counter/reference electrode exhibited desirable properties. The FTO|Pt-FTO cell response was investigated by filling a cell solely with BMImPF$_6$ ionic liquid to serve as a blank. The CVs obtained with different potential windows ranging from 0 to 1.0 V and 0 to 1.6 V are shown in Figure 42.
Figure 42: CVs of the FTO|BMImPF_6|Pt-FTO cell. The traces correspond to different potential windows: red is from 0 to 1.6 V, blue is from 0 to 1.4 V, purple is from 0 to 1.2 V, and green is from 0 to 1.0 V.

Similarly, DPVs of the cell were obtained using the same potential windows and are shown in Figure 43. The CVs and DPVs were obtained with sensitivities of 1x10^{-6} A/V for the red, blue, and purple traces and 5x10^{-7} A/V for the green traces. The important features of these electrochemical measurements are the lack of impurities in the cell and the onset of electrolyte charging around 1.2 V.

Figure 43: DPVs of the FTO|BMImPF_6|Pt-FTO cell. The traces correspond to different potential windows: red is from 0 to 1.6 V, blue is from 0 to 1.4 V, purple is from 0 to 1.2 V, and green is from 0 to 1.0 V.
The first FTO|\([\text{Ru(bpy)}_2(\text{pySO})]^{2+}\)-Nafion, BMImPF$_6$|Pt-FTO cell was repetitively scanned from 0 to 1.6 V using DPV with sensitivities of 5x10$^{-6}$ A/V. The initial scan, the red trace in Figure 44, exhibited an S-bonded isomer peak potential of 1.376 V and no O-bonded isomer. The black arrows indicate the decreasing S-bonded peak current upon successive scanning and the increasing current at the 0.456 V peak attributed to be the O-bonded isomer. While the S-bonded peak potential remains relatively constant, the O-bonded peak shifts from 0.456 V to 0.620 V over the six successive scans. The peaks are notably broad, which may be attributed to inclusion of \([\text{Ru(bpy)}_2(\text{pySO})]^{2+}\) into the Nafion layer. The photochemical switching ability of the cell was assessed by irradiating the sample for 10 minutes with the 355 nm laser followed by 20 minute irradiation with the 472 nm laser.

![Figure 44: DPVs of FTO|\([\text{Ru(bpy)}_2(\text{pySO})]^{2+}\)-Nafion, BMImPF$_6$|Pt-FTO cell. Only the S-bonded isomer was present in the first scan, red trace, while the O-bonded isomer was electrochemically generated during subsequent scans as indicated by the black arrows.](image)

Figure 45 shows the DPVs obtained after 355 nm irradiation, blue, and 472 nm irradiation, red. The peak currents decreased over the duration of the experiment,
which can be seen in Figure 46. The stability of the O-bonded isomer peak was assessed after the photochemical cycling experiment by repetitively scanning from 0 to 1.0 V, so as to avoid electrochemical isomerization. The peak current and peak potential exhibited negligible change, seen in Figure 47, where the blue, green, purple, and grey traces were the repetitive scans taken after 355 nm irradiation and the red trace was taken after 472 nm irradiation and included for comparison. The peak stability is attributed to the use of Nafion such that the [Ru(bpy)_2(pySO)]^{2+} is held close to the electrode surface and cannot diffuse away.

![Figure 45: DPVs obtained during the photochemical switching experiment of the FTO| [Ru(bpy)_2(pySO)]^{2+} -Nafion, BMImPF_6 |Pt-FTO cell. Blue traces were obtained after 10 minutes of 355 nm irradiation while the red traces were obtained after 20 minutes of 472 nm irradiation. Peak currents decreased during the course of the experiment.](image-url)
Figure 46: Photochemical switching of the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$ -Nafion, BMImPF$_6$ |Pt-FTO cell monitored as a function of maximum O-bonded current versus cycle number. Integer values correspond to DPVs obtained after 355 nm irradiation while half values correspond to DPVs taken after 472 nm irradiation.

Figure 47: O-bonded isomer peak stability in a FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$ -Nafion, BMImPF$_6$ |Pt-FTO cell measured by repetitive scanning. The blue, green, purple, and grey traces were obtained in that order. The red trace was obtained after 472 nm irradiation during the photoswitching experiment and is included for comparison.
To investigate the utility of the Nafion, an FTO \([\text{Ru(bpy)}_2\text{(pySO)}]^2+\), BMImPF$_6$ |Pt-FTO cell was constructed. The DPVs for the cell were obtained using 5x10$^{-6}$ A/V sensitivities, with the initial scans shown in Figure 48. Interestingly, this cell exhibited a broad peak at 2.252 V upon the first scan and four peaks upon subsequent scans: $E_{pa_1} = 0.596$ V, $E_{pa_2} = 1.116$ V, $E_{pa_3} = 1.376$ V, and $E_{pa_4} = 2.356$V. The peak at 2.356 V was attributed to the S-bonded isomer and the peak at 1.376 V was attributed to the O-bonded isomer. The peaks were assigned as such even with the 1.00 V and 0.36 V differences for the S-bonded and O-bonded isomer potentials compared to the expected values, respectively, because of the photochemical switching experiment results. The source of the other two peaks remains unknown, but may simply be impurities. Figure 49 shows the photochemical switching results with DPVs obtained after 5 minutes of 355 nm irradiation, blue traces, and after 10 minutes of 472 nm irradiation, red traces. Clear delineation between the two irradiation wavelength sets can be seen in the data and the overall trend was a decrease in the peak current, visible in Figure 50.
Figure 48: Initial DPVs of an FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$ |Pt-FTO cell. The initial scan is indicated by the red trace, while the blue and purple traces correspond to the second and third scans, respectively.

Figure 49: Photochemical switching results of an FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$ |Pt-FTO cell where the blue traces were obtained after 5 minutes of 355 nm irradiation and the red traces were obtained after 10 minutes of 472 nm irradiation. The overall trend was decreasing peak current.
Figure 50: Photochemical switching of an FTO| [Ru(bpy)₂(pySO)]^{2+}, BMImPF₆ |Pt-FTO cell monitored as a function of maximum O-bonded current versus cycle number. Integer values correspond to DPVs obtained after 355 nm irradiation while half values correspond to DPVs taken after 472 nm irradiation.

The stability of the O-bonded isomer peak was investigated by 10 repetitive DPV scans with the results shown in Figure 51. Unlike the stable peak current obtained for the FTO| [Ru(bpy)₂(pySO)]^{2+} -Nafion, BMImPF₆ |Pt-FTO cell, the peak current decreased after each successive scan for the FTO| [Ru(bpy)₂(pySO)]^{2+}, BMImPF₆ |Pt-FTO cell. Curiously, the peak at 1.104 V was not present after the first scan, but was present in a DPV taken four hours later.
Figure 51: O-bonded isomer peak stability measured by 10 repetitive DPV scans. The peak current decreased after each successive scan.

The cell functioned as an optoelectronic transducer, however the peak potentials were cause for concern due to the more positive than expected values, so a second cell was constructed to assess the reproducibility of the cell design. Figure 52 is a photograph of the second FTO | Pt-FTO cell filled with ~8 mM [Ru(bpy)$_2$(pySO)$_2$]$^{2+}$ dissolved in BMImPF$_6$ ionic liquid, taken after photochemical switching. The red, O-bonded isomer is visible in the center portion of the cell while the yellow, unisomerized S-bonded compound can be seen in the rest of the reservoir. The Pt-FTO can be seen functioning as the counter/reference electrode while the FTO connected to the green alligator clip is the working electrode. To avoid electrochemical generation of the O-bonded isomer, the potential window was set from 0 to 1.2 V. A small peak at 0.344 V was present in the initial DPV scan, shown in the blue trace of Figure 53, and upon 60 second irradiation with the 355 nm laser a peak at 1.044 V appeared, the red trace in Figure 53. Even though the 1.044 V was
more positive than the expected value of 0.75 V, it was attributed to the O-bonded isomer and the peak potential difference was attributed to the lack of a reference electrode in the cell.

Figure 52: Photograph of an FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$ |Pt-FTO cell. The O-bonded isomer can be seen as the red spot in the center of the reservoir, while the surrounding yellow color is due to the S-bonded isomer.

Figure 53: Initial DPV of an FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$ |Pt-FTO cell (blue trace) and subsequent formation of the O-bonded isomer upon 60 seconds of 355 nm irradiation (red trace).
Photochemical switching of the cell was achieved using 60 second irradiation times for 355 nm S→O conversion and 3 minute irradiation times for 472 nm O→S conversion. The DPVs were obtained from 0.6 to 1.2 V at sensitivities of $1 \times 10^{-6}$ A/V throughout the switching experiment. Over the duration of the experiment, the peak potential of the O-bonded isomer shifted to more positive potentials spanning the range of 1.088 to 1.200 V. The DPVs should have been obtained from 0.6 up to 1.4 or 1.6 V in order to see the full peak shape. The DPVs are shown in Figure 54 on an extended x-axis to better represent the peak shape and also given as an inset to show the clear delineation between the DPVs taken after 355 nm irradiation, blue traces, and those taken after 472 nm irradiation, red traces. A plot of the maximum peak current versus the cycle number, shown in Figure 55, illustrates that the cell displayed relatively good current consistency between cycles, particularly after cycle number three onward. It is unknown as to why the peak potential drifted to more positive potentials throughout the experiment.
Figure 54: Initial DPV and DPVs obtained from photochemical switching of the FTO\([\text{Ru(bpy)}_2(\text{pySO})]^2^+\), BMImPF$_6$ Pt-FTO cell. Excepting the trace from 0 to 1.2 V with maximum current at 1.044 V, the blue traces depict DPVs taken after 355 nm irradiation (60 s) while the red traces were taken after 472 nm irradiation (3 min). The x-axis has been extended to better demonstrate the peak shape while the inset is included to depict the photochemical switching data.

Figure 55: Photochemical switching of the FTO\([\text{Ru(bpy)}_2(\text{pySO})]^2^+\), BMImPF$_6$ Pt-FTO cell monitored as a function of maximum O-bonded current versus cycle number. Integer values correspond to DPVs obtained after 355 nm irradiation while half values correspond to DPVs taken after 472 nm irradiation.
The FTO|Pt-FTO cell design functioned reasonably well producing the desired electrochemical response during photochemical switching experiments. The peak potentials were vastly improved, i.e. closer to the expected values from bulk electrochemistry, compared to the ITO|ITO cell design. Other improvements from the previous design were the use of the heat-shrink capabilities of Parafilm to seal the cell for electrolyte leakage prevention; the smaller device size which requires half of the materials compared to the ITO|ITO cell; and greater control over the photoactive compound reservoir which is useful for tailoring the amount of sample that is irradiated by the laser. The biggest downfall of the cell was the irreproducibility of the peak potentials which meant that photochemical switching was required to assign peak potentials to the isomers or any impurities present.

**FTO|Pt,Pt Cell Design**

The need for a reference electrode in the cell was readily apparent after the FTO|Pt-FTO experiments to increase the reproducibility and reliability of the device. The plan was to fully assess the bulk electrochemistry in ionic liquid and transfer that knowledge to a self-contained device. To investigate the role of a reference electrode in the cell, bulk electrochemistry was performed on the BMImPF$_6$ ionic liquid and an ~8 mM [Ru(bpy)$_2$(pySO)]$^{2+}$ in BMImPF$_6$ solution. In a standard, one-compartment cell, the DPV of BMImPF$_6$ was obtained using a 1 mm diameter glassy carbon working electrode, a Pt wire counter electrode, and a Pt wire quasi-reference electrode. The same electrodes were then used to obtain a DPV of [Ru(bpy)$_2$(pySO)]$^{2+}$ in BMImPF$_6$ solution, shown in Figure 56 along with the BMImPF$_6$ blank. The
sensitivities of the DPVs for these experiments were $1 \times 10^{-6}$ A/V. The electrochemistry exhibited two peaks attributed to impurities were found in the BMImPF$_6$ blank at 0.860 and 1.060 V and electrolyte charging which began at approximately 1.8 V. Even in the presence of slight impurity, the peak potentials for the S-bonded, 1.268 V, and O-bonded, 0.660 V, isomers were comparable to the expected values of 1.35 and 0.75 V, respectively. Successive DPV scans taken with zero wait time between scans exhibited diminishing S-bonded current and increasing O-bonded current, see Figure 57. Similar behavior occurred when the working electrode was changed to a 0.5"x1" piece of FTO glass, used to simulate the electrochemical conditions in a device, which is shown in Figure 58. The increase in O-bonded current indicates electrochemical generation of the O-bonded isomer after oxidation of the S-bonded isomer.

![Figure 56: Bulk three electrode electrochemistry of BMImPF$_6$, blue trace, and [Ru(bpy)$_2$(pySO)]$^{2+}$ dissolved in BMImPF$_6$, red trace. Glassy carbon (1 mm diameter) working electrode, Pt wire counter electrode, and Pt wire quasi-reference electrode.](image)

Figure 57: Ten successive DPV scans of the bulk \([\text{Ru(bpy)}_2(\text{pySO})][\text{BMImPF}_6]\) solution. The S-bonded peak current diminished as the O-bonded peak current increased. Glassy carbon (1 mm diameter) working electrode, Pt wire counter electrode, and Pt wire quasi-reference electrode.

Figure 58: Ten successive DPV scans of bulk \([\text{Ru(bpy)}_2(\text{pySO})][\text{BMImPF}_6]\) in \(\text{BMImPF}_6\). FTO glass working electrode, Pt wire counter electrode, and Pt wire quasi-reference electrode.

Based upon the results of the bulk electrochemistry, a new cell was designed. Comprised of a piece of FTO glass as the working electrode, two Pt wires serving as the counter and quasi-reference electrodes, and ten total sheets of Parafilm spacer. A photograph of the cell, Figure 59, was taken upon completion of the photochemical
switching experiment. The working electrode is shown connected to the green alligator clip while the Pt wire counter electrode is connected to the red clip and the Pt wire reference electrode is connected to the white clip. The inset in the photograph is a magnified portion of the cell labeled to indicate the presence of the S-bonded and O-bonded isomers after the experiment. The air bubble seen in the lower left corner of the reservoir was present and consistent throughout the experiment and did not seem to cause any detrimental effects.

Figure 59: Photograph of the FTO\([\text{[Ru(bpy)}_{2}\text{(pySO)}]^{2+}, \text{BMImPF}_{6}]\text{Pt,Pt cell after photochemical cycling experiments. Note that the air bubble was present throughout the experiments. The lower left inset indicates the presence of both O-bonded and S-bonded } [\text{Ru(bpy)}_{2}\text{(pySO)}]^{2+}\text{ isomers. The electrodes are as follows: green – working; red – counter; reference – white.}

The initial DPV scan of the cell did not indicate the presence of any O-bonded isomer, as seen in the red trace of Figure 60, although the S-bonded isomer was present at 1.240 V. Successive scanning through the S-bonded peak created O-bonded isomer, as expected from the previous results, and can be seen at 0.572 V. To avoid electrochemical generation of the O-bonded isomer during the photochemical switching experiment, the scan range was changed to 0.2 to 0.8 V. The sensitivities for these initial scans were $1 \times 10^{-5}$ A/V.
Figure 60: Initial DPV scans of the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$|Pt,Pt cell indicating the absence of the O-bonded isomer initially and its subsequent electrochemical generation. Red trace: initial scan; blue trace: second scan; purple trace: third scan with the reduced potential window used for subsequent experiments.

The peak potentials of the S-bonded and O-bonded [Ru(bpy)$_2$(pySO)]$^{2+}$ isomers are shown in Figure 61 for the bulk electrochemistry experiments and the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$ |Pt,Pt cell. The blue trace is a 25x magnification of the bulk electrochemistry using the glassy carbon working electrode, the red trace is from the FTO glass working electrode bulk electrochemistry, and the black trace is from the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$ |Pt,Pt cell. The peak potentials show good agreement and indicate improvement compared to previous cell designs.
Figure 61: Comparison of the S- and O-bonded isomer peak potentials in BMImPF$_6$ upon the second DPV scan in bulk electrochemistry and FTO|Pt,Pt cell. Red trace: bulk three electrode configuration with FTO glass working electrode (we), Pt wire counter electrode (ce), and Pt wire quasi-reference electrode (re). Blue trace: 25x magnification of bulk three electrode configuration with 1 nm diameter glassy carbon we, Pt wire ce, and Pt wire re. Black trace: FTO|Pt,Pt cell.

The cell was photochemically switched between the O-bonded and S-bonded states using irradiation times of 60 seconds with 5-6 mJ/pulse power for the 355 nm O$\rightarrow$S conversion and 3 minutes with 4-7 mJ/pulse power for the 472 nm S$\rightarrow$O conversion. The DPVs taken during the experiment are shown in Figure 62 along with a proposed threshold value for determining whether the cell exists in the "0" S-bonded or "1" O-bonded state. The notable features of this data set are that the peak potential remains relatively constant, varying from 0.744 to 0.764V, and that the background currents remain consistent throughout the experiment. The only detrimental aspect of this data is that the O-bonded peak current decreases for both the 355 nm and 472 nm data sets. Interestingly, the 355 nm data set decreases to a greater extent than the 472 nm data set which rules out electrolyte leakage as a cause for the decreasing current. Perhaps the greater experimental error for the 355 nm laser irradiation as compared to
the 472 nm irradiation is the major cause. This decreasing current trend is visible in the photochemical switching graph shown in Figure 63.

Figure 62: DPVs obtained from the photochemical cycling experiment of the FTO| [Ru(bpy)₂(pySO)]²⁺, BMImPF₆ |Pt,Pt cell. The cell was irradiated with 355 nm light for 60 seconds (~5-6 mJ/pulse), scanned, irradiated with 472 nm light for 3 minutes (~4-7 mJ/pulse), scanned, and repeated for a total of 10 cycles. The red traces are DPV scans taken after 472 nm irradiation and the blue traces are DPV scans taken after 355 nm irradiation. The dashed purple line indicates a proposed threshold current value distinguishing between the two sets. The overall trend is a decrease in peak potential current.
Figure 63: Photochemical switching graph of an FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImPF$_6$ |Pt,Pt cell monitored as a function of maximum O-bonded current versus cycle number. Integer values correspond to DPVs obtained after 355 nm irradiation while half values correspond to DPVs taken after 472 nm irradiation.

The FTO| |Pt,Pt cell was also investigated using BMImNTf$_2$ as the ionic liquid electrolyte because of concern that the PF$_6^-$ anion might photochemically degrade to F$^-$ and PF$_5$. Photographs of the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImNTf$_2$ |Pt,Pt cell are shown in Figure 64 before and after irradiation experiments. The indicative yellow color of the S-bonded isomer is visible in the before picture while the red colored O-bonded isomer is visible in the after picture. The decreased viscosity of the BMImNTf$_2$ is apparent in the photograph as the O-bonded isomer has diffused throughout the reservoir shown in Figure 64 compared to the small amount of diffusion present in the BMImPF$_6$ cell shown in Figure 59. The BMImPF$_6$ ionic liquid is almost six times more viscous than the BMImNTf$_2$ ionic liquid with viscosity values of 308 and 52 mPa·s, respectively.\textsuperscript{115}
The initial DPV scan exhibited a peak potential of 1.560 V for the S-bonded isomer, while the second scan exhibited peak potentials of 1.492 V for the S-bonded isomer and 0.724 V for the O-bonded isomer. The initial DPV scans are shown in Figure 65 along with the third scan, which is representative of the potential window scanned in subsequent experiments.

The stability of the electrochemically generated O-bonded current was assessed by taking 20 consecutive DPV scans from 0.0 to 1.2 V with no wait time between scans and sensitivity of $1 \times 10^{-6}$ V/A. Figure 66 depicts the diminishing O-
bonded current which reaches a stable, zero current after approximately 15 consecutive scans. The initial peak current of $-1.079 \times 10^{-6}$ A, monitored at 0.744 V, reached a minimum value of $-2.656 \times 10^{-7}$ A after the final DVP scan. This indicates that the electrochemically generated isomer diffuses away from the electrode surface as a result of successive scanning. The cell was then photochemically switched between the O-bonded and S-bonded states with 60 second 355 nm irradiation (~18 mJ/pulse) and with 3 minutes of 472 nm irradiation (~20 mJ/pulse), respectively. The results of the photoswitching experiment are shown in Figure 67 where the topmost red trace indicates the initial DPV of the cell prior to irradiation, the blue traces were taken post 355 nm irradiation, and the remaining red traces were obtained following 472 nm irradiation. A threshold current value of $-1.6 \times 10^{-6}$ A is indicated with a dashed purple line. The cell exhibited successful switching between the two states, but peak potential drift was an issue. The peak potential drifted a total of 308 mV over the duration of the experiment from 0.876 to 1.184 V.
Figure 66: Twenty successive DPV scans of the FTO| \([\text{Ru(bpy)}_2(\text{pySO})]^2^+\), BMImNTf₂|Pt,Pt cell taken after initial electrochemical formation of the O-bonded product. The black arrow indicates the diminishing peak current after each successive scan with no wait time between scans.

Figure 67: Raw DPV data from the photochemical cycling experiment in the FTO| \([\text{Ru(bpy)}_2(\text{pySO})]^2^+\), BMImNTf₂|Pt,Pt cell. The topmost red trace is the initial DPV scan prior to the irradiation cycling and indicates the absence of O-bonded product. The cell was irradiated with 355 nm light for 60 seconds (~18 mJ/pulse) and a DPV was obtained, blue traces. After 355 nm irradiation, the cell was irradiated with 472 nm light for 3 minutes (~20 mJ/pulse) and a DPV was obtained, red traces. The cell exhibited an overall increase in peak potential and shifting of the peak potential to successively more positive values throughout the cycling experiment.
One possible cause of the peak potential drift was leakage of the ionic liquid along the silver wires, which was noted after the experiment. As the electrolyte traveled down the wires, it effectively decreased the resistance of the cell thereby increasing the potential according to Ohm's Law of V=IR, assuming that the current remained consistent. The BMImPF$_6$ may have not exhibited this leakage due to its greater viscosity.\textsuperscript{115} Assuming that leakage caused the peak potential drift, the raw data shown in Figure 67 was shifted to a constant peak potential of 0.880 V and baseline shifted to a minimum current of zero amperes, see Figure 68. The constant potential of 0.880 V was chosen from the peak potential after the first irradiation. The corrected DPVs show that the O-bonded peak maintains consistent

![Figure 68: Raw data from Figure 67 was shifted to a constant peak potential of 0.880 V and the baseline was shifted to obtain zero current at approximately 0.15 V to qualitatively assess the results. Clear delineation can be seen between the mostly O-bonded and mostly S-bonded cycle sets achieved via 355 nm and 472 nm irradiation, respectively.](image-url)
shape throughout the photoswitching experiment. The peak current increased during the experiment for both the 355 nm and 472 nm irradiation data sets and is depicted by the red and blue arrows in Figure 68 and the photochemical switching graph shown in Figure 69.

After the ten cycles of the photochemical switching experiment, the O-bonded current stability was assessed via successive DPV scans and is shown in Figure 70. Similar results were obtained compared to the initial "erasure" experiment, where the current decreased after each scan, Figure 66, but the O-bonded peak persisted even after 20 scans.
Figure 70: After photochemical switching of the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImNTf$_2$ |Pt,Pt cell, "erasure" of the O-bonded product after 472 nm irradiation was accomplished via 20 successive DPV scans. The black arrow indicates the decrease in peak current from the initial to final scan.

After the erasure, the cell was again cycled with 355 nm irradiation and 472 nm irradiation, Figure 71. The topmost red trace depicts the cell after erasure, the blue traces were obtained after 355 nm irradiation, and the remaining red traces were obtained after 472 nm irradiation.

Figure 71: Post-erasure photochemical cycling of the O-bonded isomer in the FTO| [Ru(bpy)$_2$(pySO)]$^{2+}$, BMImNTf$_2$ |Pt,Pt cell.
After the final 355 nm irradiation, the cell was again erased via 50 successive DPV scans. Similar to the results in Figure 70, the O-bonded current decreased but the O-bonded peak was not fully erased even after the 50th scan. The current decreased below the $-1.6 \times 10^{-6}$ A threshold, shown as a gray dashed line, after 10 DPV scans. This indicates that the O-bonded isomer diffuses away from the electrode surface upon successive DPV scans and that the Ru-doped Nafion attachment method should be examined to see if it can stabilize the peak current.

![Graph showing DPV scans](image)

Figure 72: "Erasure" of the O-bonded product after 355 nm irradiation was accomplished over 50 successive DPV scans. The black arrow indicates the decrease in peak current from the initial to final scan.

The FTO|Pt,Pt cell design functions as the best self-contained molecular optoelectronic device compared to all of the previous designs. The peak potentials occur near the expected values and are reproducible between separate device constructions. The ability to reliably switch the device between the mostly O-bonded and mostly S-bonded states photochemically at least ten times is promising and performs better than the diarylethene-modified ITO electrode reported in the
literature. The BMImPF$_6$ and BMImNTf$_2$ data have their advantages where the BMImPF$_6$ device demonstrated excellent stability of the O-bonded peak potential and peak shape while the BMImNTf$_2$ device exhibited close to ideal current switching but peak potential drift. The simplest cell modification that should result in improvement would be to grind the conductive FTO coating off of the working electrode in areas that are not involved in the electrochemistry. Similarly, the use of smaller diameter Pt wires would decrease the amount of materials required for the device as well as its physical size.

CONCLUSIONS AND FUTURE DIRECTIONS

A molecular optoelectronic transducer based on [Ru(bpy)$_2$(pySO)]$^{2+}$ was developed and is capable of utilizing light as an input to trigger two-color reversible photochromism in the molecule which can be read electrochemically. The devices are constructed and operated in ambient environmental conditions making them simple to create and use. Capable of undergoing at least 10 Write-Read-Erase-Read cycles, they surpass the maximum of 6 similar cycles reported for spiropyran and diarylethene modified electrodes.

Future research could pursue device miniaturization, working electrode modification with surface attachment of a [Ru(bpy)$_2$(pySO)]$^{2+}$ derivative, and incorporation of another photochromic/electrochromic compound to create the foundation for a molecular logic gate. A long-term goal is the non-trivial task of synthesizing new two-color photoreversible ruthenium sulfoxide compounds for greater device options.
REFERENCES


