Ru,Rh,Ru Supramolecular Photocatalysts within Nafion® Membranes: Ion-exchange, Photoelectrolysis and Electron Transfer Processes

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Abstract

Perfluorosulfonate ionomers, such as Nafion® have been shown to demonstrate a profound affinity for large cationic complexes, and the study of polymer-bound cations may provide insight regarding Nafion® morphology by contrasting molecular size with existing models. The trimetallic complex, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$, is readily absorbed by ion exchange into Na$^+$-form Nafion® membranes under ambient conditions. The dimensions of three different isomers of the trimetallic complex are estimated to be: 23.6 Å × 13.3 Å × 10.8 Å, 18.9 Å × 18.0 Å × 13.7 Å, and 23.1 Å × 12.0 Å × 11.4 Å, yielding an average molecular volume of $1.2 \times 10^3$ Å$^3$. At equilibrium, the partition coefficient for the ion-exchange of the trimetallic complex into Nafion® from a DMF solution is $5.7 \times 10^3$. Furthermore, the total cationic charge of the exchanged trimetallic complexes counterbalances 86 ± 2% of the anionic SO$_3^-$ sites in Nafion®. The characteristic dimensions of morphological models for the ionic domains in Nafion® are comparable to the molecular dimensions of the large mixed-metal complexes. Surprisingly, SAXS analysis indicates that the complexes absorb into the ionic domains of Nafion® without significantly changing the ionomer morphology. Given the profound affinity for absorption of these large cationic molecules, a more open-channel model for the morphology of perfluorosulfonate ionomers is more reasonable, in agreement with recent experimental findings. In contrast to smaller monometallic complexes, the time-
dependent uptake of the large trimetallic cations is biexponential. This behavior is attributed to a fast initial ion-exchange process on the surface of the membrane, accompanied by a slower, transport-limited ion-exchange for sites in the interior of the ionomer matrix.

The development of Nafion®/[(bpy)₂Ru(dpp)₂RhBr₂]⁵⁺ modified electrodes is also described for both FTO electrodes and materials made from electrospun carbon mats. The [(bpy)₂Ru(dpp)₂RhBr₂]⁵⁺ complexes behave as photocatalytic hydrogen production catalysts in the Nafion® membrane. Furthermore, a second bulk photoelectrolysis experiment with the Nafion®/[(bpy)₂Ru(dpp)₂RhBr₂]⁵⁺/FTO electrodes shows an enhancement of catalytic activity compared to the first photoelectrolysis experiment. This enhancement is attributed to halide loss following the first reduction process. Lastly, electrospun carbon nanofiber mats behave as electron donor materials for [(bpy)₂Ru(dpp)₂RhBr₂]⁵⁺/Nafion® membranes.
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List of Abbreviations

\( \nu = \) frequency
\( h = \) Planck’s Constant, \( 6.626 \times 10^{-34} \) J
\( \lambda = \) wavelength
\( c = \) speed of light, \( 3.00 \times 10^8 \) m/s
\( E = \) energy
\( \text{bpy} = 2,2'\)-bipyridyl
\( \text{Me}_2\text{bpy} = 4,4'\)-dimethyl-2,2'-dipyridyl
MLCT = metal-to-ligand charge transfer
HOMO = highest occupied molecular orbital
LUMO = lowest unoccupied molecular orbital
\( \tau = \) emission excited state lifetime
\( \Phi = \) quantum yield of emission
GS = ground state
LA = light absorber
ED = electron donor
ER = electron relay
C = catalyst
TEOA = triethanolamine
EDTA = ethylenediaminetetraacetic acid
MV = methylviologen
PEC = photoinitiated electron collector
HP = porphyrin sensitizer
PBDCI = perylene bis(carboximide)
dpb = 2,3-bis(2-pyridyl)benzoquinoxaline
dpq = 2,3-bis(2-pyridyl)quinoxaline
dpp = 2,3-bis(2-pyridyl)pyrazine
TEA = triethylamine
phen = 1,10-phenanthroline
Ph₂phen = 4,7-diphenyl-1,10-phenanthroline
'Bubpy = 4,4'-di-tert-butyl-2,2'-dipyridyl
tatpp = tetraazatetrapyridopentacene
tatpq = tetraazatetrapyridoquinone
DMA = dimethylaniline
TON = turnover number
PSS = sulfonated polystyrene
TEM = transmission electron microscopy
EW = equivalent weight
PTFE = poly(tetrafluoroethylene)
SAXS = small angle X-ray scattering
SANS = small angle neutron scattering
NMR = nuclear magnetic resonance
PAN = poly(acrylonitrile)
HPLC = high performance liquid chromatography
LF = ligand field
NHE = normal hydrogen electrode
DMF = dimethylformamide
PFCB = perfluorocyclobutane ionomer
PVDF = polyvinylidene difluoride
TBA = tetrabutylammonium
FTO = fluorine doped tin oxide
TGA = thermogravimetric analysis
CV = cyclic voltammetry
LSV = linear sweep voltammetry
LED = light emitting diode
IPA = isopropanol
ICTAS = Institute for Critical Technology and Applied Science
NCFL = Nanoscale Characterization and Fabrication Laboratory
XPS = X-ray Photoelectron Spectroscopy
SEM = scanning electron microscopy
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Chapter 1. Introduction

1.1 Motivation

With increasing global energy consumption, the energy expense for the extraction of finite fossil fuels increases. Additionally, global public concern is elevated regarding the effects of pollutants released from burning fossil fuels. There is a growing need for clean, renewable energy sources.

Renewable energy sources include: hydroelectricity, tides and ocean currents, geothermal sites, wind energy and solar energy. Considering the potential instantaneous output of these renewable energy sources, Figure 1.1 clearly demonstrates that there is significantly more available energy from the sun compared to the other sources. To further emphasize this point, the amount of depicted instantaneous solar energy available (20TW) is the quantity calculated from the sun striking 0.16% of the Earth’s surface with 10% energy conversion efficiency. The other energy sources illustrate a theoretical maximum of the available energy on the entire planet.\(^1\) In 2005, the instantaneous yearly averaged energy consumption rate for the Earth was 13 TW. It is evident that harnessing solar energy has the potential to satisfy the world’s energy requirements.\(^2\)
Figure 1.1 Comparison of the potential instantaneous energy available from renewable energy sources. *Covering 0.16% of the total land on earth with 10% efficiency. Figure adapted from reference 2.

Considering the immense quantity of energy radiated by the sun, the challenge becomes harnessing that energy with the goal of replacing current fossil fuel sources. Solar irradiation is discontinuous and dispersed; therefore it is necessary to store the sun’s energy for use when direct sunlight is unavailable. In nature, plants and algae absorb light and store energy in the form of chemical bonds through the process of photosynthesis. Remarkably, even fossil fuels are an example of solar energy storage in chemical bonds through the process of photosynthesis.³

Photosynthesis is essential to the biological process in which the process of energy flow sustains life. A simplified diagram of the energy flow through the biological process is outlined in Figure 1.2. Through an elaborate progression involving light absorption, charge separation, water splitting, and proton/electron transfer processes; the photosynthetic process is ultimately capable of storing solar energy in chemical bonds. In photosynthesis, the two main reactions of interest are water splitting and CO₂ reduction. The photosynthetic dark reactions produce sugars and other organic compounds that make up biomass, edible plants and (over millions of years)
fossil fuels. The water splitting reaction (Equation 1.1) is of particular interest in the development of an artificial photosynthetic process for solar energy harvesting.\textsuperscript{4-7}

\[ 2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \quad \text{Equation 1.1} \]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Simplified diagram representing the biological process. Upon irradiation from the sun, photosynthetic light reactions split H\textsubscript{2}O to produce, H\textsuperscript{+}, e\textsuperscript{-}, and O\textsubscript{2}. Protons and electrons can react with CO\textsubscript{2} in dark reactions to form sugars and other organic molecules that compose biomass, edible plants (food) and fossil fuels. People and animals can consume this food and with O\textsubscript{2} the respiration process can extract the energy stored in the chemical bonds of the organic molecules. Water is formed after respiration and the process can be repeated. Figure adapted.\textsuperscript{3}}
\end{figure}

In the photosynthetic process, H\textsuperscript{+} and e\textsuperscript{-} transfer processes aide in the transfer of energy to store solar energy in the form of chemical bonds in organic molecules. The process of converting light energy into usable chemical energy has been termed “artificial photosynthesis” and has been a subject of considerable interest for a number of researchers.\textsuperscript{5,7-19} For the purpose
of artificial photosynthesis, rather than storing energy in organic molecules, there has been considerable research focused on water splitting reactions, and particularly on the water reduction half reaction for H\textsubscript{2} production (Equation 1.2 and Equation 1.3).\cite{7,19} When compared to other common hydrocarbon fuels, H\textsubscript{2} has the highest specific energy of combustion.\cite{20} This is demonstrated in Table 1.1 with the power density of H\textsubscript{2} compared to gasoline, diesel fuel, coal and methane.\cite{20} It is important to note that although H\textsubscript{2} is a high power density fuel by mass, it is difficult to condense, and the power per volume is actually lower than some hydrocarbon fuels.\cite{7} Fortunately, the power density of hydrogen is not the only attractive feature for its utilization as a fuel source.

\[
4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2 \quad -0.41 \text{ V} \quad \text{Equation 1.2*}
\]

\[
2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 2 \text{H}_2 \quad -1.23 \text{ V} \quad \text{Equation 1.3}
\]

*pH = 7 and 25 °C*

There is a growing concern about the effects of pollutants in the atmosphere generated from the combustion of hydrocarbon fuel sources. The combustion products of hydrocarbons are H\textsubscript{2}O and CO\textsubscript{2}. With the absence of carbon, the combustion of H\textsubscript{2} produces only H\textsubscript{2}O. Figure 1.3 represents the cyclic nature of solar water splitting and hydrogen combustion, which could ease concerns about atmospheric pollutants.
Table 1.1 Power density of hydrogen compared to common hydrocarbon fuels.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Power Density (kWh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>30.1</td>
</tr>
<tr>
<td>Gasoline</td>
<td>13.3</td>
</tr>
<tr>
<td>Diesel</td>
<td>12.6</td>
</tr>
<tr>
<td>Coal</td>
<td>9.0</td>
</tr>
<tr>
<td>Methane</td>
<td>15.5</td>
</tr>
</tbody>
</table>

Figure 1.3 Representation of the cyclic nature of solar water splitting and hydrogen combustion.

The goal of harnessing clean, renewable energy may be accomplished through solar water splitting. Water splitting is a complicated process that requires the cooperation of several factors, including light absorption, charge separation and the ability to collect multiple oxidizing/reducing equivalents. Considerable research in the field is focused on the reduction half reaction with a focus on hydrogen production for hydrogen fuel.\textsuperscript{1,21-23} The isolation and
collection of oxygen is not practically necessary since there is sufficient O\(_2\) in the atmosphere to sustain H\(_2\) combustion. However, recent research has focused on O\(_2\) production from water with the ultimate goal of using the electrons formed in the water oxidation process to drive the water reduction process.\(^{24}\) The requirements for photocatalytic water reduction, strategies and examples will be considered below.

1.2 Photoinduced Hydrogen Production

Photochemical reactions are initiated when a quantum of electromagnetic energy (a photon) in the infrared, visible or UV region, is absorbed by a molecule, resulting in the excitation of an electron to a higher energy level.\(^{25}\) In order to achieve solar water splitting, a sufficient amount of energy is required in order to at least overcome the thermodynamic free energy barrier for the water splitting process. For a multi-electron process, water splitting requires 1.23 eV (\(\lambda \approx 1000\) nm) (Equation 1.3). The homolytic process, which involves the formation of H\(^+\) and OH\(^+\), requires significantly more energy than the multi-electron process (~5 eV).\(^{26}\) As seen in Figure 1.4, the energy required for the water splitting reaction is available from the sun.

Fortunately for species that require water to survive, water splitting does not occur spontaneously in sunlight to a significant degree. Therefore, in order to split water with sunlight, it is necessary to introduce the light energy in another way, such as with a photocatalytic system. There are several requirements that must be met in order to achieve water splitting with such a system. First, efficient light absorption is necessary at an energy that is ample for driving the water splitting reaction. Upon excitation, the excited state lifetime must long enough to transfer
the absorbed energy and generate a charge-separated state. Finally, since water splitting is most efficient through a multi-electron process, multiple reducing or oxidizing equivalents must be collected and transferred to water. For hydrogen production via water reduction multiple reducing equivalents must be collected and transferred to water.

\[ 2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 2 \text{H}_2 \text{ } \text{Equation 1.3} \]

\[ -1.23 \text{V} \]


*Figure 1.4* Solar Irradiance spectra calculated for Blacksburg, VA on June 30, 2015 at 12:00 pm using: https://www.pvlighthouse.com.au/calculators/solar%20spectrum%20calculator/solar%20spectrum%20calculator.aspx. The colorful spectrum is the solar irradiance on the ground and the black spectrum is the irradiance at the top of the atmosphere. The dotted blue line represents the thermodynamic energy required for solar water splitting (1000 nm). The arrow points toward higher energy to indicate the region of the solar irradiance spectra that has sufficient thermodynamic energy to achieve the water splitting reaction.

### 1.2.1 Ruthenium Polypyridyl Complexes

A photosensitizer is a molecule that can induce chemical change upon excitation with light.\(^{25,27}\) Ruthenium(II) tris-2,2'-bipyridyl (Ru(bpy)\(_3\))\(^{2+}\)*(Figure 1.5a)* was first suggested for its potential as a photosensitizer in photocatalytic water splitting systems by Creutz and Sutin in
Since this initial suggestion, Ru(bpy)$_3^{2+}$ has become a common photosensitizer for photo-induced charge transfer reactions due to its light absorbing, excited state and stable, reversible redox properties.\textsuperscript{16-18,30-35} The Ru(bpy)$_3^{2+}$ molecule absorbs strongly in the visible region through a metal-to-ligand charge transfer (MLCT) transition ($\lambda_{\text{max}}=450$ nm, $\varepsilon=13,000$ M$^{-1}$cm$^{-1}$ in acetonitrile (CH$_3$CN)) (Figure 1.5b).\textsuperscript{5,36} Upon excitation, an electron in the highest occupied molecular orbital (HOMO), which is predominantly metal in character (Ru d$\pi$) is excited to the lowest unoccupied molecular orbital (LUMO), which is predominantly ligand in character (bpy $\pi^*$). In this spatially separated excited state, the [Ru(bpy)$_3$]$^{2+}$ is both more easily oxidized and reduced than in the ground state. The simplified orbital diagram in Figure 1.7 demonstrates the excitation, and oxidation and reduction processes in the excited state.

\textbf{Figure 1.5} a) [Ru(bpy)$_3$]$^{2+}$ chemical structure. b) Electronic absorbance spectrum of Ru(bpy)$_3^{2+}$ in CH$_3$CN. Results are consistent with reported values.\textsuperscript{5,31}
The lowest energy absorbance by Ru(bpy)$_3^{2+}$ will promote an electron into the $^1$MLCT excited state. The $^1$MLCT state relaxes to the lower energy $^3$MLCT state, through an electron spin flip, on the femtosecond timescale (Figure 1.6). Following excitation, the $^*$Ru(bpy)$_3^{2+}$ complex can undergo excited state quenching by electron transfer, typically on the nanosecond timescale. The excited electron is located on the bpy ligand, however it moves between the three equivalent bpy ligands on the picosecond timescale. The long lifetime of Ru(bpy)$_3^{2+}$ ($\tau = 600$ ns in CH$_3$CN, 400 ns in water) allows the complex to undergo intramolecular charge transfer reactions under the appropriate conditions. The oxidation to Ru(bpy)$_3^{3+}$ and reduction to Ru(bpy)$_3^{3+}$ are reversible processes, allowing the molecule to shuttle multiple electrons under visible light irradiation.

![Figure 1.6](image.png)

**Figure 1.6** Basic Orbital diagram representing a MLCT transition in which a complex is first excited to a $^1$MLCT excited, which relaxes to a more stable $^3$MLCT excited state.
Figure 1.7 Basic orbital diagrams of the Ru(bpy)$_3^{2+}$ excitation, and oxidation and reduction in the excited state. The hole left by the excited electron makes the complex easier to reduce in the excited state. Additionally, the excited electron is more easily oxidized in the excited state.

Ruthenium polypyridyl complexes exhibit phosphorescence upon excitation with UV or visible light. Upon excitation, the $^3\text{MLCT}$ state decays back to the ground state by radiative (photon emission), or non-radiative decay (inter and intramolecular quenching) processes. These processes are represented in the simplified state diagram, shown in Figure 1.8. Emission spectroscopy is used to probe the excited state of luminescent molecules. Specifically, the quantum yield of emission and the lifetime of emission can be used to probe excited state reactivity in the presence of an excited state quencher. The quantum yield of emission ($\Phi$) is a ratio of photons emitted to photons absorbed and can also be expressed as the rate constant of radiative decay over all the rate constants that deactivate the excited state. The quantum yield is expressed for a phosphorescent system in Equation 1.4. The lifetime of emission ($\tau$) can be expressed as one over all the rate constants that deactivate the emissive excited state. The lifetime of radiative decay for Ru(bpy)$_3^{2+}$ and other similar compounds is shown in Equation .
1.5. The emission wavelength, lifetime, and quantum yield can provide information about the local environment of luminescent compounds including Ru(bpy)$_3^{2+}$.  

\[
\Phi = \frac{k_p}{k_p + k_{nr}} \quad \text{Equation 1.4}
\]

\[
\tau = \frac{1}{k_p + k_{nr}} \quad \text{Equation 1.5}
\]

**Figure 1.8** State diagram representing the different processes that occur in a phosphorescent system such as [Ru(bpy)$_3^{2+}$. The excitation with a photon is represented by $h\nu$, the rate constant for nonradiative decay from the $^1$MLCT excited state is $k_{nr}$, intersystem crossing is $k_{isc}$, the rate constant for radiative decay from the $^3$MLCT excited state is represented by $k_p$ and the nonradiative decay rate constant from the $^3$MLCT excited state is represented by $k_{nr'}$.  


1.2.2 Multi-Component Hydrogen Production

Following the initial suggestion that Ru(bpy)$_3^{2+}$ could be a suitable photosensitizer for photocatalytic water reduction, several multi-component systems with Ru(bpy)$_3^{2+}$ light absorbers were reported. Figure 1.9 demonstrates a general representation of the processes that occur in a multicomponent hydrogen production system. The same processes shown in the diagram are represented in Equation 1.6-Equation 1.9. Upon excitation with light, the $^3$MLCT excited state of Ru(bpy)$_3^{2+}$ is populated. The excited $^3$Ru(bpy)$_3^{2+}$ reduces the electron relay by donating an electron from the bpy $\pi^*$ orbital, as demonstrated in Figure 1.7. The electron relay then transfers an electron to the catalyst. The Ru(bpy)$_3^{3+}$, is reduced by sacrificial electron donor and the oxidation state is regenerated. This process must be repeated twice in order to collect two electrons on the catalyst and drive the two-electron water reduction reaction.

![Diagram of multi-component hydrogen production system](image)

**Figure 1.9** Generic representation of a multi-component water reduction system, where a chromophore is excited with light. A sacrificial electron donor reduces the excited molecule. The reduced chromophore reduces an electron relay, which donates and electron to the catalyst. Water reduction occurs following the collection of two reducing equivalents at the catalytic center. The process is shown twice to emphasize the necessity of collecting two electrons at the catalyst in order to drive the two-electron water reduction process.
\[
\begin{align*}
\text{LA} + \text{hv} & \rightarrow \text{LA}^* & \text{Equation 1.6} \\
\text{LA}^* + \text{ER} & \rightarrow \text{LA}^+ + \text{ER}^- & \text{Equation 1.7} \\
\text{LA}^+ + \text{ED} & \rightarrow \text{LA} + \text{ED}^+ & \text{Equation 1.8} \\
\text{ER}^- + \text{C} & \rightarrow \text{ER} + \text{C}^- & \text{Equation 1.9}
\end{align*}
\]

The multi-component systems described all use Ru(bpy)$_3^{2+}$ as the chromophore.\textsuperscript{41-45} The sacrificial electron donors used include triethanolamine (TEOA),\textsuperscript{41,43,45} ascorbate,\textsuperscript{44} and ethylenediaminetetraacetic acid (EDTA)\textsuperscript{42}. The electron relays included Rh(bpy)$_3^{3+}$,\textsuperscript{41,43,45} and methylviologen (MV)\textsuperscript{42}. In several cases, K$_2$PtCl$_4$, or K$_2$PtCl$_6$,\textsuperscript{41,43,45} was added to the photolysis solution as a catalyst, however it was determined that the active catalyst was colloidal Pt.\textsuperscript{45} Finally, mixed Pt and Au catalyst mixtures were successful multi-electron collectors for water reduction photocatalysis in multi-component systems.\textsuperscript{42} It was demonstrated that the electron relay could be bypassed, and direct reduction of a Co(II) macrocycle catalyst or Eu(II) catalyst by the Ru(bpy)$_3^{2+}$ photosensitizer occurred.\textsuperscript{44}

In the systems with Rh(bpy)$_3^{3+}$ electron relays, hydrogen was not produced in the absence of the Pt catalyst.\textsuperscript{45} This could be in part due to the fact that the Rh(bpy)$_3^{3+}$ is coordinatively saturated by the bpy ligands.\textsuperscript{29} However, upon reduction, the Rh(bpy)$_3^{2+}$ ligand is known to undergo a geometry change from octahedral to square planar, accompanied by loss of the bpy ligand (Equation 1.10).\textsuperscript{45} This square planar Rh(bpy)$_2^{2+}$ complex could potentially undergo oxidative addition to form a Rh(bpy)$_2$H$_2^{+}$, which has been shown to undergo photochemical H$_2$ loss upon UV irradiation.\textsuperscript{46} Considering that no H$_2$ is produced in the absence of Pt, it is likely that the disproportionation of Rh(bpy)$_3^{2+}$ and Rh(bpy)$_2^{2+}$ (Equation 1.11) is more favorable than
oxidative addition under these conditions.\textsuperscript{45} Furthermore, following disproportionation, \( \text{Rh(bpy)}_2^+ \) is known to dimerize, which, for every dimer formed, removes two Rh-metals from the available \( \text{Rh(bpy)}_3^{3+}/\text{Rh(bpy)}_3^{2+} \) complexes available for reversible redox as electron relays.\textsuperscript{47}

\[
\text{Rh(bpy)}_3^{2+} \rightarrow \text{Rh(bpy)}_2^{2+} + \text{bpy} \quad \text{Equation 1.10}
\]

\[
\text{Rh(bpy)}_3^{2+} + \text{Rh(bpy)}_2^{2+} \rightarrow \text{Rh(bpy)}_3^{3+} + \text{Rh(bpy)}_2^+ \quad \text{Equation 1.11}
\]

While multi-component systems that use a \( \text{Ru(bpy)}_3^{2+} \) photosensitizer have demonstrated that it is possible to photocatalytically produce \( \text{H}_2 \) by water reduction, the systems are hindered by several factors. All of the necessary electron transfer reactions are dependent on the diffusion of the individual components through the solution and their collision while in the proper excited/oxidation state. Undesirable back-electron transfer and side electron transfer reactions further limit these systems.\textsuperscript{48-50}

\subsection*{1.3 Supramolecular Photochemical Devices}

Supramolecular photochemistry, as described by Balzani, is when individual components of a system are brought together into a single molecule. The individual properties of each component of a supramolecular system would be retained, enabling the molecule to function as a complex molecular device.\textsuperscript{51} Furthermore, since the individual components would retain their properties, sub-unit modification could tune the properties of the photochemical device. Considering the constituents of a multi-component photocatalytic system (Figure 1.9), one can imagine combining those components into a single photochemical device, shown in Figure 1.10.
The device would retain the necessary properties of a photocatalytic system, including light absorption, directed electron transfer and the ability to collect multiple electrons.\textsuperscript{16,29}

\begin{figure}[h!]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Diagram of a supramolecular photochemical device, which could be designed by combining the components of a multi-component photocatalytic water reduction system (Figure 1.9) into a single molecular device, while retaining the individual properties of each of the components.}
\end{figure}

1.3.1 Photoinitiated Electron Collectors (PECs)

A photoinitiated electron collector will undergo progressive light absorption and electron transfer events, which will eventually lead to localized charge accumulation. The development of photoinitiated electron collectors for photochemical water reduction requires that the molecule absorb sufficient light and the excited electrons undergo directed electron transfer events that lead to charge accumulation at a single site. This will result in two reducing equivalents being stored on a molecular device. Relatively few molecules have been successful at collecting multiple reducing equivalents at a single position.\textsuperscript{29,52-55}

The donor-acceptor-donor structure shown in Figure 1.11 is one of the first reported molecules capable of collecting multiple reducing equivalents upon several excitation/electron transfer events.\textsuperscript{55} The complex contains two porphyrin sensitizers (HP) and a perylene
bis(carboximide) (PBDCI) electron collector. The HP-PBDCI-HP molecule behaves as a PEC by first exciting the HP donors with high intensity laser pulses. The HP-PBDCI-HP collects two reducing equivalents following two excitation/electron transfer events where the sensitizers are excited *HP-PBDCI-HP* followed by the first electron transfer event to produce HP^+^-PBDCI^-HP. A second electron transfer event produces the doubly reduced HP^+^-PBDCI^-2-HP^+. The doubly reduced excited state decays in 5 ns, while the singly reduced state decays in 120 ps. This PEC is a fundamentally important molecule, in that it demonstrates multiple electron collection on a single molecule. However, due to the high intensity light required for excitation and the low stability of the complex over time, it is not practically significant for water reduction catalysis.\(^{29,52,55}\)

![Figure 1.11 Structure of a photoinitiated electron collector with a porphyrin sensitizer (HP) and a perylene bis(carboximide) (PBDCI) electron collector.](image)

The Brewer Group published the first photoinitiated electron collector capable of collecting multiple reducing equivalents upon excitation with low intensity light in 1994 (Figure 1.12).\(^{56}\) The complex had terminal bpy ligands coordinated to two terminal Ru metals, with 2,3-bis(2-pyridyl)benzoquinoxaline (dpb) bridging ligands to an Ir center (\([\{(bpy)2Ru(dpb)\}2IrCl2]^{5+}\)).\(^{56}\) Upon irradiation with visible light (1000 W Xe arc lamp) in the
presence of an electron donor, two reducing equivalents are collected on the dpb bridging ligands. This is the first complex exhibiting that it is possible to coordinate two light absorbing units with low intensity excitation in a single molecule.

![Complex](image)

**Figure 1.12** First reported supramolecular photoinitiated electron collector: \([\{\text{bpy}\}_2\text{Ru(dpbb)}\}_2\text{IrBr}_2]^{5+}\)

Shortly after the publication of the first photoinitiated electron collector, the Brewer group published a series of trimetallic complexes with variations on the central metal and the bridging ligands (Figure 1.13). Of these nine complexes, four behaved as photoinitiated electron collectors and two collected electrons on the central metal. The electron collecting complexes are the three molecules with a Rh central metal

\([\{\text{bpy}\}_2\text{Ru(dpbb)}\}_2\text{RhCl}_2]^{5+}\), \([\{\text{bpy}\}_2\text{Ru(dpq)}\}_2\text{RhCl}_2]^{5+}\), and \([\{\text{bpy}\}_2\text{Ru(dpbb)}\}_2\text{RhCl}_2]^{5+}\) and the \([\{\text{bpy}\}_2\text{Ru(dpbb)}\}_2\text{IrCl}_2]^{5+}\) complex (Figure 1.12). The two complexes that collected electrons on the central metal were the Rh-based \([\{\text{bpy}\}_2\text{Ru(dpbb)}\}_2\text{RhCl}_2]^{5+}\), and \([\{\text{bpy}\}_2\text{Ru(dpq)}\}_2\text{RhCl}_2]^{5+}\). The differences in photoinitiated electron collection was explained through differences in orbital energetics, and in the case of the dpb bridging ligand, the ability of the molecule to collect multiple electrons was attributed to the fused aromatic rings and increased conjugation, stabilizing the \(\pi^*\) orbital by delocalization (Figure 1.13c).^{56,57}
Figure 1.13 Chemical structures of trimetallic Ru, M, Ru complexes published by the Brewer Group. M = Os, Ir, Rh, with dpp (a), dpq (b), and dpb (c) bridging ligands.

The relative orbital energetics, determined by the observed electrochemical potentials are represented in (Figure 1.14). The Os compounds were unique in that the HOMO was Os-based (Figure 1.14b). In order for complexes of this architecture to function as photochemical devices, it is important for the desired light absorber to be the HOMO. Although the Os complexes of this architecture are not functioning photochemical electron collectors, the knowledge that the Os can behave as a lower energy light-absorbing HOMO has led the Brewer
Group to the development of several mixed-metal complexes for exploitation in both photocatalytic water reduction and photodynamic therapy.\textsuperscript{58-76}

The Ir metal reduction is not observed in the electrochemical window of these complexes, leading to the conclusion that the reduction lies outside of the electrochemical window (\textsim\textasciitilde2 V vs. NHE), significantly higher in energy than the bridging ligands (Figure 1.14a). Therefore, the HOMO of these Ru,Ir,Ru complexes is assigned as Ru based, and the LUMO is bridging ligand based. The ability of the \{ (bpy)\textsubscript{2}Ru(dpb)\}\textsubscript{2}IrCl\textsubscript{2}\textsuperscript{5+} complex to collect electrons is attributed to the conjugated character of the bridging ligand, allowing for the electrons to be more delocalized and stabilizing the dpb $\pi^*$ orbitals.\textsuperscript{56,57}

The Ru,Rh,Ru trimetallic complexes are distinctive from the Ir and Os metal centered complexes in that there is an orbital inversion between the bridging ligands and central Rh, from the dpb to the dpq and dpp ligands. As seen in Figure 1.14c, for the \{ (bpy)\textsubscript{2}Ru(dpb)\}\textsubscript{2}RhCl\textsubscript{2}\textsuperscript{5+} complex, the dpb bridging ligand is the LUMO, while the Rh is the LUMO for the dpq and dpp bridging ligands in the \{ (bpy)\textsubscript{2}Ru(dpq)\}\textsubscript{2}RhCl\textsubscript{2}\textsuperscript{5+} and \{ (bpy)\textsubscript{2}Ru(dpp)\}\textsubscript{2}RhCl\textsubscript{2}\textsuperscript{5+} complexes. Of the nine trimetallic complexes in this study, these two Ru,Rh,Ru complexes are the only ones that collect electrons on the central Rh. Since these complexes are capable of collecting multiple electrons on a single metal center, they are the most promising for use as photoinitiated molecular devices for water reduction and hydrogen production.
Figure 1.14 Representation of the orbital energetics of Ir (a), Os (b), and Rh(c) complexes with dpp (black), dpq (blue) and dpb (pink) bridging ligands, determined by comparison of the electrochemical redox potentials of the complexes. The filled blocks represent orbitals that are filled in the ground state, while the hollow blocks represent unfilled orbitals in the ground state.

The PECs developed by the Brewer Group pioneered the development of heteropolymetallic complexes for photoinitiated electron collection.52 Following the publication of the above photoinitiated electron collectors, several modified Ru polypyridyl complexes that functioned as photochemical electron collectors were developed.53,54,77-80 These complexes were inspired by combined development of the Ru light absorbers first shown in the Brewer Group PECs and the ability to collect multiple reducing equivalents on a conjugated organic ligand, demonstrated by both Brewer56,57 and Wasielewski55.

MacDonnell published diruthenium compounds with 1,10-phenanthroline (phen) terminal ligands and tetraazatetrapyridopentacene (tatpp) (Figure 1.15a) or tetraazatetrapyridoquinone (tatpq) (Figure 1.15b) bridging ligands. Upon photolysis in the presence of a triethylamine (TEA) electron donor, the complex with a tatpp bridge collects two reducing equivalents while the tatpq collects four electrons. The PEC in these complexes is coupled with protonation, where two of the pyridine nitrogens on the tatpp are protonated. On the tatpq complex, two pyridine
nitrogens on the bridging ligand are protonated in addition to protonation of the two oxygens. Upon exposure to air, these complexes can be re-oxidized and the electron collection process is reversible upon returning the complexes to an inert atmosphere.\textsuperscript{53,54,77,80}

Figure 1.15 Dinuclear ruthenium complexes published by MacDonnell.\textsuperscript{53,77,80}

1.3.2 Supramolecular Complexes for Hydrogen Production

In 2007, the Brewer Group reported the first supramolecular complex for hydrogen production via water reduction photocatalysis with the $\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhCl}_2^{5+}$ complex.\textsuperscript{81} Upon excitation at 470 nm, in the presence of a sacrificial electron donor, the Ru chromophores undergo a MLCT transition from the Ru dπ HOMO to the lowest lying ligand π* orbital (dpp).\textsuperscript{82} Following the photoinduced excitation, the dimethylaniline (DMA) sacrificial electron donor reduces the recently vacated Ru dπ orbital. Finally, the Rh LUMO collects two reducing
equivalents from the two Ru light absorbing units. Upon reduction, the Rh center undergoes a
genometry change from octahedral to square planar, characteristic of Rh(I) $d^8$ metal
complexes. The geometry changed is associated with the loss of the labile halide
ligands. Upon ligand loss, coordination sites for water become available and water catalysis can
occur. It is suggested that the catalyst is activated upon ligand loss and photoinitiated electron
transfer processes propagate the catalytic cycle. 

Figure 1.16 Representation of the initial electron transfer events, which generate the square
planar [{(bpy)$_2$Ru(dpp)}$_2$Rh]$^{5+}$ complex, and promote water reduction.

Following the publication of the first Ru,Rh,Ru trimetallic complex,
[{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$]$^{2+}$, for photocatalytic hydrogen production, several Ru,Rh,Ru
trimetallic complexes with systematic variations of the terminal ligands and non-chromophoric bridging ligands were published (Figure 1.17). Upon variation of the halides, the bromide analogues consistently have higher turnovers for photocatalytic hydrogen production than the chloride counterparts. This is reasonable considering that bromide ligands are more labile than chloride ligands and halide loss is necessary for catalyst activation (Figure 1.16). Furthermore, the \[\{\text{(bpy)}_2\text{Ru(dpp)}\}_2\text{Rh(OH)}_2\] complex produces higher turnover numbers (TON) \(\frac{\text{mol } H_2}{\text{mol complex}}\) than either the \[\{\text{(bpy)}_2\text{Ru(dpp)}\}_2\text{RhCl}_2\] or \[\{\text{(bpy)}_2\text{Ru(dpp)}\}_2\text{RhBr}_2\] complexes (OH\(^-\) = 83 ± 6 TON; Br\(^-\) = 45 ± 4 TON; Cl\(^-\) = 30 ± 4 TON). It is suggested that that ion pairing between the photocatalytic complexes and the halides play an important role in photocatalysis and the presence of halides in solution could be detrimental to the photocatalysis.
Figure 1.17 Ru,Rh,Ru trimetallic complexes published by the Brewer Group, demonstrating systematic variation of the terminal ligands from bpy→phen→Ph₂phen→Me₂phen and variation of the non-chromophoric ligands on the Rh from Cl⁻→Br⁻→OH⁻.

Out of all of the Ru,Rh,Ru trimetallic complexes presented in Figure 1.17, the complex with the highest catalytic turnovers was the [(Ph₂phen)₂Ru(dpp)]₂RhCl₂]⁵⁺ with 610 turnovers in 20 h. Additionally, out of several Ru,Rh bimetallic complexes synthesized by the Brewer Group (Figure 1.18), the bimetallic complex containing Ph₂phen terminal ligands, [(Ph₂phen)₂Ru(dpp)Rh(Ph₂phen)Cl₂]³⁺, was the only one that was an active catalyst for hydrogen production. The Ru,Rh bimetallic complex with bpy terminal ligands on the Ru and a 4,4'-di-tert-butyl-2,2'-dipyridyl (tBubpy) terminal ligand on the Rh (Figure 1.18a),
[(bpy)$_2$Ru(dpp)Rh('Bubpy)Cl$_2$]$^{3+}$, undergoes photoinitiated electron collection, however the complex does not produce H$_2$, because the sterically accessible Rh metal forms a Rh-Rh dimer, blocking the available coordination sites for H$_2$ production.\(^91\) Furthermore, the Ru,Rh [(phen)$_2$Ru(dpp)Rh(bpy)Cl$_2$]$^{3+}$ bimetallic (Figure 1.18b) does not produce H$_2$, while the [(Ph$_2$phen)$_2$Ru(dpp)Rh(Ph$_2$phen)Cl$_2$]$^{3+}$ (Figure 1.18c) complex underwent 49 ± 4 TONs in 20 h under identical photolysis conditions.\(^92\) The enhancement in photocatalytic H$_2$ production of the trimetallic, [(Ph$_2$phen)$_2$Ru(dpp)]$_2$RhCl$_2$]$^{5+}$ and observation of H$_2$ production in the bimetallic, [(Ph$_2$phen)$_2$Ru(dpp)Rh(Ph$_2$phen)Cl$_2$]$^{3+}$ complexes compared to other less sterically bulky Ru,Rh,Ru trimetallic and Ru,Rh bimetallic complexes strongly imply the importance of steric protection in these complexes. With this knowledge, it is reasonable to hypothesize that further protection of these complexes; perhaps by incorporation a polymer matrix could enhance catalytic performance.

**Figure 1.18** Bimetallic complexes a) [(bpy)$_2$Ru(dpp)Rh('Bubpy)Cl$_2$]$^{3+}$ b) [(phen)$_2$Ru(dpp)Rh(bpy)Cl$_2$]$^{3+}$ c) [(Ph$_2$phen)$_2$Ru(dpp)Rh(Ph$_2$phen)Cl$_2$]$^{5+}$
1.4 Catalysis with Polymer Support

The integration of a polymer support with a catalytic system could be advantageous for a variety of reasons, several of which are eloquently outlined by Abe and Kaneko. A polymer support could cause catalysts to be dispersed throughout the membrane, preventing undesired coalescence that could be detrimental to the catalysis. In the case of cationic catalysts, the inclusion of these catalysts in an anionic membrane could lead to the formation of molecular aggregates in which the catalytic performance is significantly altered compared to homogenous catalysis. Furthermore, the limitation of solubility for a catalyst could be alleviated by incorporation in an ionomer such as Nafion®. Although Nafion® is a water insoluble ionomer, the ionic aggregates are known to swell with water, therefore, catalytic activity of a water insoluble catalyst could be explored in an aqueous environment upon ion-exchange with a Nafion® membrane. Finally, the diffusion of catalysts bound to a polymer membrane could be significantly hindered, which could be advantageous for the prevention of undesirable side-electron transfer and back-electron transfer events. Limited diffusion may also prevent desirable electron transfer events from occurring, and a necessary balance must be achieved to optimize catalytic activity.

A particularly relevant example highlighting the benefits of polymerization with catalysis is demonstrated by the oxidative electropolymerization of a series Rh(III) complexes on Pt and glassy carbon electrodes. For the electropolymerized compound, electrocatalytic H₂ production via proton reduction was observed following reduction of the complex to the Rh(I) oxidation state. Catalysis was not observed for the complexes in solution. Since Rh catalysts are
known to dimerize, it is likely that the observed differences in catalytic activity between the solution and electropolymerized complexes occur because the polymer prevents Rh dimerization and subsequent catalyst deactivation.\textsuperscript{47,91}

1.4.1 Ion-containing Polymers and Ru(bpy)\textsubscript{3}\textsuperscript{2+} Luminescence Studies

The electronic absorption and emission spectroscopy of Ru polyazine complexes can provide information about local environments through solvatochromism. A red shift is observed in more polar solvents due to stabilization of the MLCT excited state, while a blue shift is observed in non-polar solvents due to destabilization.\textsuperscript{97,98} Due to the stable redox properties, high molar absorptivity, intense luminescence, solvatochromic sensitivity and cationic nature of Ru(bpy)\textsubscript{3}\textsuperscript{2+}, the molecule has been utilized to probe local environments in anionic polymer systems.\textsuperscript{33-35,99-113} While the intention of many of these studies was to gain a better understanding of the environment inside polymer membranes, these studies also provide vital information that could lead to enhancement of photocatalytic systems for incorporating Ru polypyridyl light absorbers.

1.4.1.1 Sulfonated polystyrene and Ru(bpy)\textsubscript{3}\textsuperscript{2+}

The interaction between sulfonated polystyrene (PSS) (\textbf{Figure 1.19a}) and Ru(bpy)\textsubscript{3}\textsuperscript{2+} is significantly different than the interactions between Ru(bpy)\textsubscript{3}\textsuperscript{2+} and other polyelectrolytes such as poly(vinyl sulfonate) (\textbf{Figure 1.19b}) and polyacrylate (\textbf{Figure 1.19c}).\textsuperscript{101-104,114} The difference in intermolecular interactions between the PSS and Ru(bpy)\textsubscript{3}\textsuperscript{2+} is attributed to a hydrophobic interaction in addition to the electrostatic interaction between the anionic side chains and the
cationic Ru(bpy)$_3^{2+}$. The hydrophobic interaction is similar to the solubility concept of “like dissolves like” where the charged nonpolar Ru(bpy)$_3^{2+}$ could be considered more soluble in the more hydrophobic PSS compared to the other less polar polyvinylsulfonate and polyacrylate polyelectrolytes. Additionally, it is feasible that π-stacking contributes to the hydrophobic interaction between Ru(bpy)$_3^{2+}$ and polystyrene.$^{115}$ The hydrophobic interaction in PSS, compared to the other polyelectrolytes where only electrostatic interactions contribute to the complex-polymer interactions was verified by increasing the ionic strength of a solution containing the polyelectrolyte and Ru(II) complex. The solution containing PSS was not affected by the change in ionic strength, while the other polyelectrolytes were, verifying that electrostatic interactions are not the only interactions contributing to Ru(bpy)$_3^{2+}$ and PSS interactions.$^{114}$ The hydrophobic interaction between PSS and Ru(bpy)$_3^{2+}$ was used to explain an increases in luminescence for Ru(bpy)$_3^{2+}$ in PSS that does not occur in the other polyelectrolytes.$^{34,99-104,114}$

![Figure 1.19 Chemical structures of a) sulfonated polystyrene b) polyvinylsulfonate c) polyacrylate](image-url)
The increase in luminescence for Ru(bpy)$_3^{2+}$ complexes in PSS was observed in organic and aqueous solutions under both inert and air saturated solutions.$^{34,99,102,104,116,117}$ With this knowledge, the [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$]$^{5+}$ complex was studied for photocatalytic hydrogen production in aqueous solutions under inert and air saturated conditions with and without PSS present (Table 1.1).$^{118}$ Remarkably, there was a significant increase in H$_2$ production in the presence of a PSS solution in both air saturated and inert atmospheres. There was more H$_2$ produced under an inert atmosphere than in air-saturated solutions in the presence of PSS. However, there was still more H$_2$ produced in the air-saturated PSS solutions than solutions without PSS. Air-saturated solutions without PSS present did not produce H$_2$.$^{118}$ This noteworthy result was attributed to the poor solubility of O$_2$ in the region where there would be a high concentration of ions.$^{102}$ This is supported by the cryo-TEM image shown in Figure 1.20, where it is appears as if the PSS has formed clusters with the [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$]$^{5+}$ complex. These clusters would presumably be formed in inverse-micelle type structures where the anionic -SO$_3^-$ groups would aggregate around the cationic trimetallic complexes. The hydrophobic styrene rings also likely play an important role in the formation of these aggregates and they certainly play a role in protecting the trimetallic [{(bpy)$_2$Ru(dpp)}$_2$RhCl$_2$]$^{5+}$ photocatalytic complex from external quenchers.$^{101-104,114,118}$
Table 1.2 TON after 10 h of photolysis for 65 µM of \([(\text{bpy})_2\text{Ru(dpp)}_2\text{RhCl}_2]^{5+}\) in either air or Ar purged aqueous solutions in the presence and absence of PSS, with 1.1 M ascorbate buffered (pH = 4). Table adapted.

<table>
<thead>
<tr>
<th>Photolysis Solution</th>
<th>Purge</th>
<th>TON (10 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 mM PSS in H$_2$O</td>
<td>Ar</td>
<td>46 ± 2</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Ar</td>
<td>15 ± 1</td>
</tr>
<tr>
<td>2.5 mM PSS in H$_2$O</td>
<td>air</td>
<td>30 ± 1</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>air</td>
<td>none detected</td>
</tr>
</tbody>
</table>

Figure 1.20 Cryo TEM of PSS and \([(\text{bpy})_2\text{Ru(dpp)}_2\text{RhCl}_2]^{5+}\) in aqueous solutions. This image was copied.

1.4.1.2 Luminescent studies of Ru(bpy)$_3^{2+}$ in Nafion®

A similar effect with an increase in luminescence intensity observed upon the addition of a PSS solution to Ru(bpy)$_3^{2+}$ solutions is observed when Nafion® “solutions” are added to Ru(bpy)$_3^{2+}$ solutions. The luminescent intensity of aqueous solutions of Ru(bpy)$_3^{2+}$ increased until a roughly stoichiometric equivalent (2 -SO$_3^-$ : 1 Ru(bpy)$_3^{2+}$) of Na$^+$-form Nafion®
“solution” was added, at which point the luminescent intensity remained constant upon further additions.\textsuperscript{34,105} Furthermore, the $\lambda_{\text{max}}$ of emission was used to probe the polarity of the local environment inside of solid Nafion\textsuperscript{®} films by exploiting the concept of solvatochromism.\textsuperscript{33,35} The $\lambda_{\text{max}}$ of emission for Ru(bpy)$_3^{2+}$ was observed to red-shift with increased loading of Ru(bpy)$_3^{2+}$ (Table 1.3), indicating that the polarity of the environment surrounding the Ru(bpy)$_3^{2+}$ increases with an increase in Ru(bpy)$_3^{2+}$ concentration. Additionally, the $\lambda_{\text{max}}$ of emission blueshifts for up to 1 month after the initial loading.\textsuperscript{35} This luminescence evidence indicates that the “hydrophobic effect” has a significant contribution to the interactions between Nafion\textsuperscript{®} and Ru(bpy)$_3^{2+}$, similar to the interactions between PSS and Ru(bpy)$_3^{2+}$.\textsuperscript{33-35,102}

<table>
<thead>
<tr>
<th>[Ru(bpy)$_3^{2+}$] (%)*</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>[Ru(bpy)$_3^{2+}$] (%)*</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
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</thead>
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<td>0.03</td>
<td>597</td>
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</tr>
<tr>
<td>0.05</td>
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<td>602</td>
</tr>
<tr>
<td>0.07</td>
<td>600</td>
<td>0.80</td>
<td>603</td>
</tr>
<tr>
<td>0.1</td>
<td>600</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Percent of $-\text{SO}_3^-$ sites occupied by [Ru(bpy)$_3^{2+}$].

\textbf{1.5 Nafion\textsuperscript{®}}

Nafion\textsuperscript{®} is a cation-conducting, electrically insulating, perfluorosulfonated ionomer membrane that has a high affinity for large, hydrophobic, cationic compounds (Scheme 1.1).\textsuperscript{94,119} Since many catalysts and photosensitizers based on transition metals are often large cationic complexes bearing organic ligands, the inherent affinity of Nafion\textsuperscript{®} for such complexes makes it...
an ideal substrate for the immobilization of these complexes. For example, ruthenium complexes have been widely used as photoactive species and catalysts in Nafion® membranes for a variety of applications, including platinum and TiO₂ catalyzed H₂ production, O₂ evolution, photocurrent generation in the presence of a semiconductor, photoinduced methyl viologen radical cation formation, and sulfide to sulfoxide oxidation using a lead ruthenate pyrochlore catalyst. Manganese and iron catalysts have also shown enhanced electrocatalytic activity in Nafion®. These studies have demonstrated that the immobilization of photosensitizers in Nafion® can enhance photo-induced electron transfer processes by limiting intermolecular quenching and vibrational relaxation of photoexcited molecules. Moreover, Nafion® membranes may also prevent the decomposition of absorbed catalysts, resulting in enhanced catalytic performance and stability.

\[
\begin{align*}
\text{OCF}_2\text{CFOCF}_2\text{CF}_2\text{SO}_3^- \quad \text{X}^+ \\
\left[(\text{CFCF}_2)(\text{CF}_2\text{CF}_2)_{m}\right]_n \\
\text{CF}_3
\end{align*}
\]

Scheme 1.1 Chemical structure of Nafion®.
1.5.1 Catalysis in Nafion® Membranes

Some of the features of Nafion® that are appealing for use as a support for catalysis include the mechanical stability and insolubility of the film in a variety of solvents. This insolubility and mechanical stability is attributed to the semicrystalline backbone of the ionomer.\textsuperscript{94,129-131} In films cast from Nafion® suspensions, a thermal treatment is necessary in order for the crystallites to form and maintain the desirable insolubility and mechanical integrity of the film.\textsuperscript{131,132}

Nafion® has been studied as a support for catalytic and electrocatalytic reactions.\textsuperscript{120,121,126,133-170} However, there are a large number of instances, particularly among researchers who traditionally focus on catalysis, where Nafion® is cast at room temperature and the thermal treatment is not performed.\textsuperscript{121,136,137,139-142,146,148,150-152,155,156,164,165,169} In these examples, important and beneficial properties of Nafion® membranes are not being attained to their full potential. In situations where Nafion® is not heated to a temperature sufficient for forming crystallites, the films are brittle as opposed to tough and flexible. Additionally, loading of larger cations that require the Nafion® film to be swollen is impossible, as the film will fall apart in these high swelling conditions. This presents significant and avoidable challenges in handling Nafion® membranes and highlights the necessity of understanding the chemistry of the polymer in addition to understanding the catalysis.
Figure 1.21 Representation of a Nafion® film with a semicrystalline backbone (blue), ionic aggregates (grey) and counter ion X⁻ (green).

1.5.2 Nafion® Morphology and Proposed Dimensions

Nafion® is a random copolymer consisting of a tetrafluoroethylene backbone and sulfonate terminated perfluorovinylether side chains (Scheme 1.1). The ion exchange capacity of Nafion® membranes can be described in terms of the equivalent weight (EW), defined as the mass of the dry polymer per mole of sulfonate groups. For the H⁺-form of Nafion®, the equivalent weight is related to m as, \( \text{EW} = 100m + 446 \), and for an 1100 EW membrane, \( m = 6.6 \) (on average). Due to the phenomenon of ionic aggregation, Nafion® consists of at least two distinct morphological regions: a hydrophobic region encompassing the polytetrafluoroethylene (PTFE) backbone and a hydrophilic region containing the ionic side-chains. The semi-crystalline hydrophobic region of the ionomer provides the mechanical stability of the membrane while the hydrophilic domains contain ionic aggregates that impart the membrane with unique transport properties related to ion conductivity and permselectivity. There are numerous models for the ionic domains of Nafion®. These models are based upon results from small angle X-ray (SAXS) and neutron scattering (SANS), water uptake, water and ion transport, uniaxial strain, and NMR results.
An early model for Nafion® morphology is the cluster-network model proposed by Gierke and coworkers (Figure 1.22a).\textsuperscript{171,172} This model consists of spherical clusters, 4 nm in diameter, interconnected by 1 nm channels. The 1 nm channels are included in order to account for the continuous pathway for transport between clusters and high permselectivity (i.e. preferential transport of cations) observed for Nafion® membranes. The characteristic dimensions of the 4 nm clusters were rationalized from SAXS and water absorption measurements; however, there is no experimental evidence to account for the 1 nm channels between clusters.
Figure 1.22 a) The cluster-network model with 4nm spheres connected with 1nm channels b) Fibrillar ribbon model with ribbon like fibrils consisting of the fluorocarbon backbone which bundle together to form aggregates 4-5 nm in diameter c) Cylindrical water channel model with 1.8-3.4 nm diameter parallel cylindrical aggregates. The red dots represent the terminal sulfonate groups on the perfluoroether side chains (black lines) of Nafion®.
Due to the inconsistency of the cluster-network model with scattering data over a wide range of scattering angles and orientation under uniaxial strain, alternative models for the morphology of Nafion® have been proposed. Rubatat and coworkers describe a fibrillar model, where, in solvated films, cylindrical or ribbon-like clusters of semicrystalline fluorocarbon chains are surrounded by ionic groups, constituting rod-like aggregates (Figure 1.22b).\textsuperscript{175,183} Another more recent model is the parallel cylindrical water channel model by Schmidt-Rohr et al.\textsuperscript{174} This model consists of cylindrical aggregates forming parallel channels of water ranging in diameter from 1.8 nm to 3.4 nm with an average diameter of 2.4 nm (Figure 1.22c).

\textbf{1.6 Polymer Modified Electrodes}

Nafion® is perhaps best known as a proton exchange membrane for fuel cell applications.\textsuperscript{94,184-195} The ionomer has also been used as a separator membrane for cation transport in electrocatalytic cells.\textsuperscript{196} Additionally, and particularly relevant to this study, Ru(bpy)\textsubscript{3}\textsuperscript{2+} supported in Nafion® for polymer modified electrodes has been the subject of significant interest.\textsuperscript{106,108,109,111,112,123,197-200} These studies provide a basis for the analysis of electron transport properties in Nafion® membranes.

The electrochemistry in polymer-modified electrodes can be significantly altered compared to solution state properties.\textsuperscript{108,197} One significant difference between the electrochemistry of Ru(bpy)\textsubscript{3}\textsuperscript{2+} in a Nafion® polymer modified electrode in comparison to the solution state is the difference between the anodic and cathodic peak values for reversible couples (\(\Delta E_p\)). In a Nafion® film, \(\Delta E_p\) for the reversible Ru(bpy)\textsubscript{3}\textsuperscript{2+}/Ru(bpy)\textsubscript{3}\textsuperscript{3+} couple is 120-170 mV, opposed to a \(\Delta E_p\) near 59 mV observed in the solution state.\textsuperscript{197} This large peak
separation that deviates from the 59 mV separation (Equation 1.12) can be attributed to differences in the apparent diffusion of the Ru(bpy)$_3^{2+}$ vs. Ru(bpy)$_3^{3+}$. The apparent diffusion is attributed to a combination of the Ru(bpy)$_3^{2+}$/Ru(bpy)$_3^{3+}$ mass transport to the electrode surface through the Nafion® ionic aggregates, “electron hopping” electron transfer events, and counter ion migration.$^{108,197,201-203}$ The apparent diffusion coefficients for the Ru(bpy)$_3^{2+}$ ($D_2$) and Ru(bpy)$_3^{3+}$ ($D_3$) are on the order of $10^{-9}$ cm$^2$/s, the exact rate of these coefficients varied between experiments and were accepted as an order of magnitude value, however, between experiments the ratio was consistent with $D_2/D_3 \approx 2$.$^{197}$ The apparent diffusion is dependent on the oxidation state of the Ru(bpy)$_3^{2+}$/Ru(bpy)$_3^{3+}$ complex. This result suggests that the molecule diffuses through the anionic aggregates faster when it is in the +2-oxidation state as opposed to the +3-oxidation state.

\[
\Delta E_p = \frac{0.059}{n} \ V \quad \text{Equation 1.12}
\]

The apparent diffusion is independent of the loading concentration and whether the complex was loaded prior to casting the film on an electrode, or loaded after the casting process.$^{108}$ This result is significant for the preparation of polymer modified electrodes considering there are substantial advantages to loading the complex prior to the casting process. These advantages include more careful control over the concentration of complex : SO$_3^-$ ratio; and elimination of loading complications after casting, such as the need for a high swelling solvent.

Furthermore, the amount of electroactive species was increased in cases where the Nafion®-modified electrode was used, compared to bare electrodes under the same conditions.$^{108}$
Therefore, for electrocatalytic purposes, the concentration of a catalyst at an electrode surface can be increased by loading the complex in a Nafion® membrane on an electrode surface. This knowledge has led to the application of Nafion® membranes for electrocatalysis.\textsuperscript{204}

\textbf{1.7 Carbon Fibers as Electron Donor Materials}

An ideal sacrificial electron donor would irreversibly donate an electron, and then diffuse away from the acceptor molecule, ceasing to perform further reactions they may be detrimental to the catalytic process. Unfortunately, the use of molecular sacrificial electron donors for catalysis frequently results in the formation of highly reactive free radical species that lead to side reactions, resulting in decreased catalytic function.\textsuperscript{48-50} Sacrificial electron donor materials can be considered the “Achilles’ heel” of catalytic reduction processes.

Additional limitations with sacrificial electron donors are realized when considering catalysis in an ionic membrane material, such as Nafion®. There is added complexity concerning the changing oxidation states of electron donors. As Nafion® is an anionic membrane with a higher affinity for more positive materials and electron donation makes the donor more positive, electron donation of a sacrificial donor could result in the donor having a higher affinity for Nafion® after the donation process. This could make the cycling of electron donors to propagate catalysis even more limiting than it is in the solution state.

Carbon materials as electron donors have an advantage over molecular sacrificial electron donors in that any radicals formed are delocalized throughout the conjugated sp\textsuperscript{2}-carbon backbone. Carbon nanotubes have been demonstrated to behave as radical scavengers.\textsuperscript{205} Furthermore, a solid material in conjunction with an ionomer membrane could alleviate the
limitation associated with an increase in the affinity of molecular donors for an anionic membrane following the donation process. Nitrogen doped carbon nanotube and graphene quantum dot materials have demonstrated electron donor capabilities.\(^{206-210}\)

Polyacrylonitrile (PAN) has been proven to perform as a precursor for the formation of carbon sp\(^2\)-type materials, classically used for the formation of carbon fiber mats.\(^{211-213}\) Recently, the technique of electrospinning has been shown to produce long nanofibers through electrostatic force.\(^{214}\) Electrospun PAN solutions form nanofibrous PAN which can be converted to an sp\(^2\) carbon structure by following the oxidation and carbonization process previously reported for the development of larger diameter carbon materials for carbon fiber fabric shown in and Scheme 1.2. The initial step in the process requires heating in the presence of air to oxidize the PAN to form nitrogen containing six-membered rings. The carbonization process is more elusive and the mechanism for the formation of the carbon fibers is not well established. The evolution of H\(_2\), N\(_2\), and HCN is observed at high temperatures (400-1300 °C) (Scheme 1.3), and the resulting carbonized structure consists of a mixture of 5 and 6-membered rings.\(^{215,216}\)

![Scheme 1.2 Representation of PAN oxidation](image)
Scheme 1.3 Scheme of the suggested carbonization processes for oxidized PAN at different temperatures.

### 1.8 Project Summary

#### 1.8.1 Thesis Statement

The purpose of this project was to study the interactions between Nafion® membranes and trimetallic Ru,Rh,Ru photocatalytic hydrogen production catalysts, to ascertain information
about both the polymer membrane and the electron transfer interactions that lead to hydrogen production within the ionomer membrane.

1.8.2 Summary

In this study, Nafion® is used as a matrix to host photocatalytic complexes. This ionomer has been shown to demonstrate a remarkable affinity for large hydrophobic cationic molecules, and as such, it is an ideal, thin film substrate for immobilizing large metal complexes. Given the unique ionic domain morphology of Nafion® and the large dimensions of the mixed-metal complexes used in this study, it is important to evaluate the size dependent absorption behavior of this guest-host system. Ultimately, this behavior is expected to provide critical insight into the effect of polymer-complex interactions on photocatalytic behavior of the immobilized metal complexes within the ionic domains. Moreover, this uptake behavior may provide useful insight into the true morphology of Nafion®.

Additionally, Nafion®/[{(bpy)2Ru(dpp)}2RhBr2]5+ modified high surface area electrodes were developed in order to perform photocatalytic experiments without the added complication of a molecular sacrificial electron donor. Linear sweep voltammetry, bulk electrolysis and bulk photoelectrolysis experiments over very long times were performed in order to better understand how the interactions between the trimetallic, [{(bpy)2Ru(dpp)}2RhBr2]5+ and Nafion® membrane affected photocatalytic hydrogen production.

Finally, in an attempt to develop high surface area Nafion®/[{(bpy)2Ru(dpp)}2RhBr2]5+ modified electrodes from electrospun carbon mats, it was discovered that the mats were behaving
as electron donating materials. Several experiments were performed to confirm and explain this result. This discovery could be incredibly useful for the future of photocatalytic materials.

1.9 References


Braslavsky, S. E. In Pure and Applied Chemistry 2007; Vol. 79, p 293.


(46) Yan, S. G.; Brunschwig, B. S.; Creutz, C.; Fujita, E.; Sutin, N. Reversible Formation of Bis(2,2'-bipyridine)rhodium(III) Dihydride from Bis(2,2'-bipyridine)rhodium(I) and Dihydrogen. Direct Transfer of Dihydrogen from Rhodium(III) Dihydride to Rhodium(I). J. Am. Chem. Soc. 1998, 120, 10553-10554.


(59) Milkevitch, M.; Brauns, E.; Brewer, K. J. Spectroscopic and Electrochemical Properties of a Series of Mixed-Metal d6,d8 Bimetallic Complexes of the Form \{(bpy)2M(Bl)PtCl2\}2+ (bpy = 2,2'-Bipyridine; Bl = dpq (2,3-Bis(2-pyridyl)quinoxaline) or dpb (2,3-Bis(2-pyridyl)benzoquinoxaline); M = OsIl or RuIl). *Inorg. Chem.* 1996, *35*, 1737-1739.


(110) Ghosh, P. K.; Bard, A. J. Polymer films on electrodes. Part XV. The incorporation of tris(2,2'-bipyridine)ruthenium(2+) into polymeric films generated by electrochemical polymerization of 2,2'-bipyrazine (bpz) and tris(2,2'-bipyrazine)ruthenium(2+). *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1984**, *169*, 113-128.


Yao, G. J.; Onikubo, T.; Kaneko, M. Photoresponsive bilayer membranes composed of tris(2,2'-bipyridine)ruthenium(2+) and methylviologen-containing layers sandwiched between ITO electrodes. *Electrochim. Acta* 1993, 38, 1093-1096.


Chapter 2. Synthesis and Characterization

2.1 Introduction

The trimetallic complexes, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$ and [{(Me$_2$bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$ were synthesized via a building block approach following previously reported procedures with slight modifications.$^{57,87}$ Both complexes contain two terminal ruthenium ions, each chelated by two 2,2'-bipyridine (bpy) or 4,4'-dimethyl-2,2'-dipyridyl (Me$_2$bpy) terminal ligands and a 2,3-bis(2-pyridyl)pyrazine (dpp) bridging ligand. The dpp ligands are, in turn, coordinated to a central rhodium ion, which is also coordinated by two bromides.$^{85,87}$ The complexes were characterized by electronic absorbance, emission and electrochemistry and compared to the previously reported results.$^{57,87,217}$ The trimetallic Ru,Rh,Ru complexes used in this study are of particular importance due to their ability to catalyze the light activated production of hydrogen from water.$^{81,85,87}$ Each coordinated Ru moiety acts as a light absorber. In the presence of a sacrificial electron donor, electron transfer to the Rh center occurs via a photoinduced metal to ligand charge transfer (MLCT) transition to the dpp bridging ligand, followed by electron transfer to the Rh. Upon reduction, the Rh(III) complex undergoes a rearrangement from octahedral geometry to square planar geometry, accompanied by loss of the halide ligands. Consequently, water reduction catalysis occurs at the Rh center.$^{85,87}$
2.2 Experimental

2.2.1 Materials

cis-dichlorobis(2,2'-bipyridyl)ruthenium(II) dihydrate ((bpy)$_2$RuCl$_2$$•$2H$_2$O), 2,2'-bis(2-pyridyl)pyrazine (dpp), 4,4'-dimethyl-2,2'-dipyridyl, ruthenium trichloride hydrate (RuCl$_3$$•$xH$_2$O) from Sigma Aldrich, rhodium(III) bromide hydrate (RhBr$_3$$•$H$_2$O), spectrophotometric grade dimethylformamide and spectrophotometric grade acetonitrile from Alfa Aesar, HPLC grade dimethylformamide, HPLC grade acetonitrile and HPLC grade dichloromethane from Spectrum Chemical Manufacturing Corporation, and diethyl ether from Fisher Scientific.

2.2.2 Synthesis of $\left\{\text{(bpy)}_2\text{Ru(dpp)}\right\}_2\text{RhBr}_2^{5+}$

The trimetallic complex $\left\{\text{(bpy)}_2\text{Ru(dpp)}\right\}_2\text{RhBr}_2\text{(PF}_6\text{)}_5$ was synthesized via a modified approach to the previously reported synthesis.$^{85}$ In order to form the trimetallic, $\left\{\text{(bpy)}_2\text{Ru(dpp)}\right\}_2\text{RhBr}_2\text{(PF}_6\text{)}_5$ product, it was necessary to first synthesize the monometallic, $\left\{\text{(bpy)}_2\text{Ru(dpp)}\right\}^{2+}$ complex (Scheme 2.1).

![Scheme 2.1 Reaction scheme for the synthesis of [(bpy)$_2$Ru(dpp)]Cl$_2$ from ((bpy)$_2$RuCl$_2$$•$2H$_2$O) and a dpp bridging ligand.](image)
Following the synthesis of the \([(\text{bpy})_2\text{Ru(dpp)}]^{2+}\) complex, the \([(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2\)^{5+} complex was synthesized following the previously reported procedure with a modified purification (Scheme 2.2). The dried crude product was redissolved in a minimum amount of \(\text{CH}_3\text{CN}\) and passed through a syringe filter before loading on a Sephadex LH-20 gel column, for size exclusion chromatography. The column was run with a 2:1 EtOH:CH\(_3\)CN solvent mixture. The dark purple band, corresponding to the larger \([(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2)(\text{PF}_6)_5\) complex eluted first with an obvious separation from the orange band, which is indicative of the smaller \([(\text{bpy})_2\text{Ru(dpp)}](\text{PF}_6)_2\) complex. Fractions of the purple band were collected and monitored by electronic absorbance and emission to reduce the possibility of contamination of the \([(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2](\text{PF}_6)_5\) complex by the \((\text{bpy})_2\text{Ru(dpp)}](\text{PF}_6)_2\). Fractions of the \([(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2](\text{PF}_6)_5\) complex were combined was reduced to 5-10 mL by rotary evaporation. The remaining solution was added to \(~100\) mL of \(\text{Et}_2\text{O}\) to precipitate the \([(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2](\text{PF}_6)_5\) complex. The dark purple solid was collected on a fine frit (4.0-5.5 µm), washed with \(\text{H}_2\text{O}, \text{EtOH}\), then \(\text{Et}_2\text{O}\) and placed in an oven to dry at 50 °C.

2 X \[
\begin{array}{c}
\text{N} \quad \text{N} \\
\text{N} \quad \text{N} \\
\text{N} \quad \text{N}
\end{array}
\]
\[(\text{PF}_6)_2\] + \(\text{RhBr}_3 \cdot \text{H}_2\text{O}\)

\[
\begin{array}{c}
\text{N} \quad \text{N} \\
\text{N} \quad \text{N} \\
\text{N} \quad \text{N}
\end{array}
\]
\[(\text{PF}_6)_5\]

\[
\begin{array}{c}
\text{N} \quad \text{N} \\
\text{N} \quad \text{N} \\
\text{N} \quad \text{N}
\end{array}
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\text{N} \quad \text{N} \\
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\text{N} \quad \text{N} \\
\text{N} \quad \text{N}
\end{array}
\]

Scheme 2.2 Reaction scheme for the synthesis of \([(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2](\text{PF}_6)_5\) from \((\text{bpy})_2\text{Ru(dpp)}](\text{PF}_6)_2\) and \(\text{RhBr}_3 \cdot \text{H}_2\text{O}\).
2.2.3 Synthesis of [{(Me$_2$bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$

The [{(Me$_2$bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$ complex was synthesized by modifying previously reported syntheses, replacing the reported terminal ligands with 4,4'-dimethyl-2,2'-dipyridyl (Me$_2$bpy) ligands.\cite{83,85,88,217,218} This synthesis was achieved in three steps, first producing the (Me$_2$bpy)RuCl$_2$ “starting material,” followed by the monometallic, [{(Me$_2$bpy)$_2$Ru(dpp)}](PF$_6$)$_2$, complex and finally the trimetallic, [{(Me$_2$bpy)$_2$Ru(dpp)}$_2$RhBr$_2$](PF$_6$)$_5$, complex.

2.2.3.1 (Me$_2$bpy)$_2$RuCl$_2$

The (Me$_2$bpy)$_2$RuCl$_2$ complex was synthesized (Scheme 2.3) by modifying the previously reported synthesis of (bpy)$_2$RuCl$_2$.\cite{218} To begin, 2.23 g (12.1 mmol) of 4,4'-dimethyl-2,2'-dipyridyl (Me$_2$bpy), 2.00 g (7.66 mmol) of RuCl$_3$·xH$_2$O and 3.25 g (76.6 mmol) of LiCl were added to a 100 mL round bottom flask with 30 mL of DMF. The RuCl$_3$·xH$_2$O was a black powder, the Me$_2$bpy had a light yellow color and the LiCl was colorless. The slight excess of RuCl$_3$ was used to drive the formation of the (Me$_2$bpy)$_2$RuCl$_2$ complex, opposed to the undesirable [(Me$_2$bpy)$_3$Ru]Cl$_2$ product. The ten-fold excess of LiCl was added to hinder dissociation of the labile chloride ligands by Le Chatelier’s principle. The reaction began as a red-brown color and was heated to reflux for 6 h. The color changed to a dark purple within the first hour of refluxing. After 6 h, the solution was allowed to cool to room temperature. The cooled solution was precipitated in ~100 mL of a saturated LiCl solution in H$_2$O. The dark purple solid collected on a medium fritted glass funnel and washed with water, followed by Et$_2$O. The collected solid was then dissolved in a minimum amount of acetone and syringe filtered before loading on a methanol activated alumina column. The column was run with a 4:1
CH$_2$Cl$_2$:acetone solvent system. The first band was dark purple and was the desired (Me$_2$bpy)$_2$RuCl$_2$ product. The second bright orange band was attributed to the undesired tris-substituted [(Me$_2$bpy)$_3$Ru]Cl$_2$, which was discarded. The remaining solvent was removed by rotary evaporation and the dark purple solid was redissolved in a minimum amount of CH$_2$Cl$_2$. The CH$_2$Cl$_2$ solution was added to ~100 mL of Et$_2$O where it reprecipitated. The dark purple product was filtered, washed with water until the filtrate was clear and dried with Et$_2$O.

\[
2 \times \begin{array}{c}
\text{N} \\
\text{N}
\end{array} + \text{RuCl}_3 \cdot x \text{H}_2\text{O} \xrightarrow{10 \times \text{LiCl}} \begin{array}{c}
\text{N} \\
\text{N} \\
\text{N} \\
\text{N}
\end{array}
\]

**Scheme 2.3** Reaction scheme for the formation of (Me$_2$bpy)$_2$RuCl$_2$ from Me$_2$bpy and RuCl$_3$$\cdot$xH$_2$O

2.2.3.2 [(Me$_2$bpy)$_2$Ru(dpp)](PF$_6$)$_2$

The synthesis of [(Me$_2$bpy)$_2$Ru(dpp)](PF$_6$)$_2$ was achieved by combining (Me$_2$bpy)$_2$RuCl$_2$ with dpp in a modified version of previously reported syntheses (**Scheme 2.4**). To begin 0.9792 g (1.812 mmol) of the dark purple (Me$_2$bpy)$_2$RuCl$_2$ and 0.8011 g (3.420 mmol) of the light orange dpp ligand were added to a 100 mL round bottom flask with 30 mL of a 2:1 EtOH:H$_2$O solvent mixture. The excess dpp bridging ligand was added to minimize the formation of the undesired [(Me$_2$bpy)$_2$Ru(dpp)]$^{2+}$ complex. The solution was heated to reflux for 3 h 15 min. The color began to change from the dark purple to orange before reflux was reached. The solution cooled to room temperature and the crude product was immediately metathesized to the PF$_6$ salt by precipitating the reaction mixture in ~200 mL of water solution.
saturated with K(PF$_6$). The precipitate was collected a fine (4.0-5.5 µm) porous glass fritted funnel via vacuum filtration, washed with water until the filtrate was clear, followed by an EtOH wash and dried with Et$_2$O. The resulting product was placed in a desiccator overnight.

To purify the complex, the crude product was dissolved in a minimum amount of CH$_3$CN and syringe filtered before loading on a methanol activated alumina column. The original solvent composition was 2:3 CH$_3$CN:Toluene and an excellent separation was achieved. The initial yellow band was unreacted dpp, the second orange band, [(Me$_2$bpy)$_2$Ru(dpp)](PF$_6$)$_2$ complex and the final purple band, was the undesired bimetallic, [{(Me$_2$bpy)$_2$Ru}$_2$(dpp)](PF$_6$)$_4$. After the initial separation, the polarity of the solvent composition was increased in order to speed of the elution time of the desired product. Since the product was moving very slowly through the column, the solvent ratio was altered from the initial 2:3 CH$_3$CN:toluene, to 1:1 CH$_3$CN:toluene, to 2:1 CH$_3$CN:toluene and finally to 100% CH$_3$CN. After collecting the desired product (orange band) the solution was removed by rotary evaporation and the product was dissolved in a minimal amount of CH$_3$CN and flash precipitated in about 20× volume of Et$_2$O. The solid was collected on a medium porous glass fritted funnel, washed with water until the filtrate was clear, and dried with Et$_2$O. The [(Me$_2$bpy)$_2$Ru(dpp)](PF$_6$)$_2$ product was stored in a desiccator.
Scheme 2.4 Reaction scheme for the synthesis of \((\text{Me}_2\text{bpy})_2\text{Ru(dpp)}\)(Cl)\(_2\) from \((\text{Me}_2\text{bpy})_2\text{RuCl}_2\) and dpp.

2.2.3.3 \[((\text{Me}_2\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_3\](PF\(_6\))

The \[((\text{Me}_2\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_3\](PF\(_6\)) complex was synthesized through the modification of a previously reported synthesis. To begin, 0.3001 g (0.3020 mmol) of the \[((\text{Me}_2\text{bpy})_2\text{Ru(dpp)})_2\](PF\(_6\)) complex and 0.0602 g (0.1518 mmol) of \text{RhBr}_3\(\cdot3\text{H}_2\text{O}\) were added to a 100 mL round bottom flask with 30 mL of mixed 2:1 EtOH:H\(_2\)O solvent. The solution was heated to reflux. The mixture of the orange \[((\text{Me}_2\text{bpy})_2\text{Ru(dpp)})_2\](PF\(_6\)) complex and the black \text{RhBr}_3\(\cdot3\text{H}_2\text{O}\) produced a dark red-orange solution, which turned to a purple color within 1 h of reflux. The solution was refluxed for 2.25 h, then cooled to room temperature. The reaction mixture was precipitated in 100 mL of 0.06 M NH\(_4\)PF\(_6\) in H\(_2\)O. The precipitate was collected on a fine porous glass fritted funnel, washed with water until the filtrate was colorless and dried with Et\(_2\)O. The product was redissolved in a minimum amount of hot 95 % ethanol, then placed in a freezer to reprecipitate. The solid was vacuum filtered, washed with water and dried with Et\(_2\)O.
Scheme 2.5 Reaction scheme for the synthesis of \([(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2\](\text{PF}_6)_5\) from \([(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}](\text{PF}_6)_2\) and \text{RhBr}_3\cdot\text{H}_2\text{O}.

2.2.4 Electronic Absorbance

All electronic absorption experiments described in this chapter were performed with a Hewlett-Packard 8452A diode array spectrophotometer (2 nm resolution). All molar absorptivity experiments were repeated in triplicate for each complex. All dilutions and solutions for molar absorptivity were carefully prepared with volumetric glassware and all masses were greater than 12 mg and weighed on an analytical balance. Serial dilutions were performed in order to generate a series of absorbance values at a particular wavelength (\(\text{MLCT}_{\text{max}}\)) that followed Beer-Lambert Law behavior (\(0.1 \leq A \leq 1.0\)). A calibration curve, plotting absorbance vs. concentration was prepared to determine the molar absorptivity at a particular wavelength using the Beer-Lambert Law.

2.2.5 Emission

Steady-state luminescence measurements were performed with a Quanta Master Model QM-200-45E from Photon Technologies International Inc. The excitation source was a 150 W Xe-Arc lamp and the spectra were detected with a thermoelectrically cooled Hamamatsu 2650
photomultiplier tube. The detector is 90° from the excitation source. All solutions were deaerated by bubbling Ar through the 1 cm quartz cuvette equipped with a screw top and septum.

### 2.2.6 Electrochemistry

Cyclic voltammetry and square wave voltammetry for the \([\text{(Me}_2\text{bpy)}_2\text{Ru(dpp)}]^{2+}\) complex was performed on a three-electrode BASi Epsilon Potentiostat with a Pt disc working electrode, Ag/AgCl reference electrode and a Pt wire auxiliary electrode with 1.0 M tetrabutylammonium hexfluorophosphate (Bu$_4$NPf$_6$) in spectrophotometric grade solvent. Cyclic voltammetry was performed at 100 mV/s, beginning at 0.0 V vs. Ag/AgCl and scanning oxidatively first.

The cyclic voltammetry and square wave voltammetry for all other complexes was performed on a 5-electrode PAR (Princeton Applied Research) 2273 Potentiostat/galvanostat. A Pt disc working electrode, Ag/AgCl reference electrode and a Pt wire auxiliary electrode was used. The red lead corresponded to the auxiliary electrode and was connected appropriately. The grey lead was the “sense” electrode and was connected to the working electrode with the green working electrode lead. The white lead corresponded to the reference electrode and was connected to the Ag/AgCl reference electrode. The black lead was the “ground” lead and was not connected to anything. All experiments were performed in 0.1 M Bu$_4$NPf$_6$ in distilled CH$_3$CN. The Ag/AgCl reference electrode was tested against ferrocene/ferrocenium to ensure the correct reference potential was entered into the software.
2.2 Results and Discussion

2.2.1 Electrochemical Methods

The electrochemical characterization of these complexes was performed with cyclic voltammetry (CV) and square wave voltammetry (SWV) experiments. A general waveform for cyclic voltammetry is shown in Figure 2.1a. This technique provides information about the reversibility of redox processes in addition to the number of electrons transferred by integrating the area under the waves. A waveform for square wave voltammetry is shown in Figure 2.1b, and the method provides information about the number of electrons transferred for reversible processes, with enhanced sensitivity and background suppression. The enhanced sensitivity and background suppression increase the accuracy of the integration, however no information can be obtained about the reversibility of the couples.

![Figure 2.1 a) Representation of potential sweep vs. time for cyclic voltammetry. b) Representation of potential pulse vs. time for square wave voltammetry](image)
2.2.2 \([(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2\)^{5+}

The \([(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2\)^{5+} complex is a previously reported compound and the characterization was compared to the published results in order to verify the identity of the monometallic, \([(\text{bpy})_2\text{Ru(dpp)}]^{2+}\), synthetic precursor and trimetallic, \([(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2\)^{5+}, complex. During the purification process, the identity of the unreacted dpp was verified by electronic absorbance and confirmed by the lack of a MLCT transition around 450 nm. The electronic absorbance spectrum of \([(\text{bpy})_2\text{Ru(dpp)}]\)(\text{PF}_6)_2 is shown in Figure 2.2. The lowest energy transition is assigned to the Ru→dpp MLCT, with the Ru→bpy MLCT at slightly higher energy. The ligand field transitions follow a similar trend, with the dpp π→π* transition at a lower energy than the bpy π→π* transition.\(^{82}\)

![Figure 2.2](image)

**Figure 2.2** Electronic absorption spectrum of \([(\text{bpy})_2\text{Ru(dpp)}]\)(\text{PF}_6)_2 in CH\(_3\)CN. The lowest energy transition is assigned as the Ru→dpp MLCT, with the Ru→bpy MLCT at higher energy. Ligand field transitions are in the UV region with the dpp π→π* transition at lower energy than the bpy π→π* transition.
The electronic absorbance and cyclic voltammetry of the \[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\](PF$_6$)$_5$ complex was compared to previously published results and was found to be consistent.\textsuperscript{57,85,87} As seen in Figure 2.3 compared to Figure 2.2 the lowest energy Ru→dpp MLCT transition has shifted to lower energy, consistent with coordination of the Rh metal to the dpp bridging ligand.

In addition, the cyclic voltammogram in Figure 2.4 is consistent with previously published results where the first oxidation is the reversible Ru(III/II) couple and the first reduction is two irreversible, overlapping one-electron reductions of Rh(III/II/I), followed by more negative reversible one-electron reductions of the ligands. These results are representative of a Ru-based HOMO and Rh-based LUMO.\textsuperscript{57}

\textbf{Figure 2.3} Electronic absorbance spectrum of the \[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\](PF$_6$)$_5$ complex in CH$_3$CN the lowest energy transition is assigned to the Ru→dpp MLCT, with the Ru→bpy MLCT at higher energy and the UV-region dominated by ligand field transitions with the bpy \(\pi\rightarrow\pi^*\) transition at higher energy than the dpp \(\pi\rightarrow\pi^*\) transition.
Figure 2.4 Cyclic voltammogram of the \{[(bpy)_2Ru(dpp)]_2RhBr_2\}(PF_6)_5 complex in 0.1 M TBA+(PF_6−) in CH_3CN. The scan began from the open circuit (OC) voltage (~500 mV vs. NHE) and was scanned at 100 mV/s to positive potential, the potential was switched at 2.0 V vs. NHE, and switched again at −1.2 V vs. NHE before returning to the OC voltage.

The most significant modification to the synthesis was the use of size exclusion chromatography opposed to recrystallization of the \{[(bpy)_2Ru(dpp)]_2RhBr_2\}(PF_6)_5 complex in methanol. As seen in Figure 2.5, the emission of the \{(bpy)_2Ru(dpp)](PF_6)_2 impurity is present after purification by reprecipitation (Figure 2.5a), while there is no observable emission of \{(bpy)_2Ru(dpp)](PF_6)_2 in the \{[(bpy)_2Ru(dpp)]_2RhBr_2\}(PF_6)_5 complex after purification by LH20 size exclusion chromatography (Figure 2.5b). This evidence suggests that the separation of the \{[(bpy)_2Ru(dpp)]_2RhBr_2\}(PF_6)_5 and \{(bpy)_2Ru(dpp)](PF_6)_2 complexes was improved by size exclusion chromatography.
Figure 2.5 Comparison in the emission spectra of [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$ in neat DMF (orange) and as an impurity in trimetallic [(bpy)$_2$Ru(dpp)]$_2$RhBr$_2$](PF$_6$)$_5$ complexes (green). a) shows the emission spectra after purification by reprecipitation, while b) shows the emission after purification by LH20 size exclusion chromatography. The emission of the [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$ impurity in the [(bpy)$_2$Ru(dpp)]$_2$RhBr$_2$](PF$_6$)$_5$ complex is apparent in (a), but is not observed in (b).

In order to perform experiments in Chapter 3 (pg. 82) in which the concentration of the [(bpy)$_2$Ru(dpp)]$_2$RhBr$_2$](PF$_6$)$_5$ complex in mixed DMF and CH$_3$CN solvents was determined by electronic absorbance, it was necessary to express the molar absorptivity of the [(bpy)$_2$Ru(dpp)]$_2$RhBr$_2$](PF$_6$)$_5$ complex in DMF and compare it to the molar absorptivity of the [(bpy)$_2$Ru(dpp)]$_2$RhBr$_2$](PF$_6$)$_5$ complex in CH$_3$CN (Figure 2.6). As expected, due to the solvatochromic effect, there is a slight blue shift in the MLCT$_{max}$ in DMF due to destabilization of the excited state by DMF. The isosbestic point at 480 nm was used to determine the concentration of the [(bpy)$_2$Ru(dpp)]$_2$RhBr$_2$](PF$_6$)$_5$ complex in mixed CH$_3$CN and DMF solutions.
2.2.3 [(Me$_2$bpy)$_2$Ru(dpp)]RhBr$_2$\(^{5+}\)

2.2.3.1 (Me$_2$bpy)$_2$RuCl$_2$

Following the synthesis and purification of the (Me$_2$bpy)$_2$RuCl$_2$ complex (Scheme 2.3), there is the possibility of forming the undesired [(Me$_2$bpy)$_3$Ru]Cl$_2$ complex. In order to verify that the latter species was removed during the purification process, emission spectroscopy on the dark purple (Me$_2$bpy)$_2$RuCl$_2$ was performed. Since the [(Me$_2$bpy)$_3$Ru]Cl$_2$ complex should have similar properties to Ru(bpy)$_3^{2+}$ and other tris-substituted Ru species, the tris-substituted species should exhibit intense emission from 600-700 nm upon excitation at 450 nm if it is present.$^{35,32}$

Figure 2.7 clearly demonstrates that upon excitation at 450 nm, there is no distinct emission signal above the noise. Therefore, it can be concluded that there is not a significant amount of [(Me$_2$bpy)$_3$Ru]Cl$_2$ present in the (Me$_2$bpy)$_2$RuCl$_2$ “starting material.”
Upon excitation at 450 nm, there is no observed emission for the (Me$_2$bpy)$_2$RuCl$_2$ complex, indicating that there is not a significant amount of [(Me$_2$bpy)$_3$Ru]Cl$_2$ present after the purification process.

The identity of the [(Me$_2$bpy)$_2$Ru(dpp)](PF$_6$)$_2$ complex was verified by cyclic voltammetry and square wave voltammetry. Consistent with the [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$ complex, the cyclic voltammogram of [(Me$_2$bpy)$_2$Ru(dpp)](PF$_6$)$_2$, the first oxidation at 1.5 V vs. NHE is attributed to the reversible Ru(III/II) couple. The reversible reduction at −0.9 V vs. NHE is attributed to a dpp (0/−) reduction, followed by more negative reversible one-electron ligand reductions (Figure 2.8). These redox couples are consistent with a Ru-based HOMO and ligand-based LUMO. Since the integration of the current responses for each couple in the square wave voltammetry are very close to each other, it can be determined that each of the couples are
one-electron processes and the ratio of Ru:dpp is 1:1, consistent with the formation of the 

\[ (\text{Me}_2\text{bpy})_2\text{Ru}(\text{dpp})(\text{PF}_6)_2 \] complex.

Figure 2.8 Cyclic voltammogram of \((\text{Me}_2\text{bpy})_2\text{Ru}(\text{dpp})(\text{PF}_6)_2\) complex in 0.1 M Bu$_4$NPF$_6$ electrolyte in CH$_3$CN. The first oxidation at 1.5 V vs. NHE is assigned a reversible Ru(III/II) couple. The first reduction is assigned to a reversible dpp 0/− reduction at −1.3 V vs. NHE. The subsequent reductions are assigned as ligand reductions. The scan was started at 0.0 V vs. Ag/AgCl and scanned in the positive direction first at a scan rate of 100 mV/s. The potential was switched at 2.0 V vs. NHE and −1.8 V vs. NHE.
Figure 2.9 Square wave voltammetry of [(Me₂bpy)₂Ru(dpp)](PF₆)₂. As in Figure 2.8, the first oxidation is assigned to the reversible Ru(III/II) couple, the first reduction is assigned to dpp 0/− and subsequent ligand reductions follow.

In addition to electrochemistry, electronic absorption and emission experiments were performed in order to aid in confirming the presence of the [(Me₂bpy)₂Ru(dpp)](PF₆)₂ complex. The [(Me₂bpy)₂Ru(dpp)](PF₆)₂ complex absorbs strongly in the visible region (Figure 2.10) with a MLCT max around 450 nm. Similar to other Ru polypyridyl complexes of this architecture, the visible region is dominated by MLCT transitions. The lowest energy transition is assigned as the Ru→dpp MLCT, with the Ru→Me₂bpy transition at slightly higher energy and LF transitions in the UV region. Additionally, there is an intense emission around 650 nm upon excitation at 450 nm (Figure 2.11), which is characteristic of tris-substituted Ru polypyridyl complexes. ⁵,³²

³⁵,³⁸,₈₂
Figure 2.10 Electronic absorption spectrum of [(Me₂bpy)₂Ru(dpp)](PF₆)₂ in DMF. The lowest energy transition is assigned to the Ru→dpp transition, which is overlapping with the Ru→bpy transition. Ligand field (LF) transitions dominate the UV region, with the lowest energy LF transition being the dpp π→π* transition.

Figure 2.11 Emission spectrum of the [(Me₂bpy)₂Ru(dpp)](PF₆)₂ complex in DMF upon excitation at 450 nm.
2.2.3.3 \([\{(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\}(\text{PF}_6)_5]\)

The electrochemistry and electronic absorption properties of the \([\{(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\}(\text{PF}_6)_5\) complex exhibit characteristics very similar to published Ru,Rh,Ru complexes of similar architecture. The cyclic voltammogram and square wave voltammograms (Figure 2.12 and Figure 2.13) show the first reversible oxidation, assigned as the two overlapping Ru (III/II) couples, consistent with the presence of two Ru centers. The first reduction is assigned to the irreversible Rh(III/II/I) reduction, the second reduction is assigned to the dpp 0/− reversible couple, followed by more one-electron ligand reductions. Based on the electrochemistry, the HOMO is assigned as Ru-based, with a Rh-based LUMO and a dpp LUMO+1.

The light absorption properties are also consistent with previously reported data (Figure 2.14), with MLCT Ru−>ligand transitions throughout the visible region of the spectrum. The lowest energy transition is again assigned to the Ru−>dpp MLCT \(\lambda_{\text{max}} = 510\) nm), with the Ru−>Me_2bpy transition at higher energy \(\lambda_{\text{max}} = 405\) nm. The UV region is predominantly LF transitions with the dpp π−>π* transition at \(\lambda_{\text{max}} = 350\) nm.

Steady-state emission spectroscopy was also performed on the complex at an excitation of 450 nm to determine if there was \([(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}\)](\text{PF}_6)_2\) complex remaining after the purification process. There is a weak emission associated with the \([(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}\]{2+ complex. Based on the results in Figure 2.5, it is likely this impurity could be separated more easily using LH20 chromatography as opposed to hot ethanol reprecipitation.
Figure 2.12 Cyclic voltammogram of the (Me₂bpy)₂Ru(dpp)RhBr₂(PF₆)₅ trimetallic complex. The CV was performed in CH₃CN with 0.1 M Bu₄NPF₆ electrolyte solution. The scan rate was 100 mV/s and the scan started at 0.2 V vs. NHE, scanned oxidatively to 1.8 V vs. NHE, with the final switching potential at −1.2 V vs. NHE before returning to 0.2 V vs. NHE. The first oxidation occurs at 1.5 V vs. NHE and is assigned to the reversible Ru(III/II) couple. The first reduction at −0.3 V vs. NHE is assigned to two overlapping, irreversible one-electron reductions of Rh(III/II/I). The first ligand reduction at −0.7 V vs. NHE is assigned to the dpp bridging ligand followed by subsequent reversible one-electron ligand reductions.

Figure 2.13 Square Wave voltammogram of the (Me₂bpy)₂Ru(dpp)RhBr₂(PF₆)₅ trimetallic complex. Performed in CH₃CN with 0.1 M Bu₄NPF₆ electrolyte solution at a scan rate of 100 mV/s.
Figure 2.14 Electronic absorbance of \[\{(\text{Me}_2\text{bpy})_2\text{Ru}(\text{dpp})_2\text{RhBr}_2\}(\text{PF}_6)_3\] in DMF.

### 2.3 References


(56) Molnar, S. M.; Nallas, G.; Bridgewater, J. S.; Brewer, K. J. Photoinitiated Electron Collection in a Mixed-Metal Trimetallic Complex of the Form 


Chapter 3. Incorporation of Supramolecular Photocatalysts in a Nafion® Membrane

3.1 Introduction

Nafion® is a cation-conducting, electrically insulating, perfluorosulfonated ionomer membrane that has a high affinity for large, hydrophobic, cationic compounds (Scheme 3.1). Since many catalysts and photosensitizers based on transition metals are often large cationic complexes bearing organic ligands, the inherent affinity of Nafion® for such complexes makes it an ideal substrate for the immobilization of these complexes. For example, ruthenium complexes have been widely used as photoactive species and catalysts in Nafion® membranes for a variety of applications, including platinum and TiO₂ catalyzed H₂ production, O₂ evolution, photocurrent generation in the presence of a semiconductor, photoinduced methyl viologen radical cation formation, and sulfide to sulfoxide oxidation using a Ru(bpy)₃²⁺ mediated lead ruthenate pyrochlore catalyst (solid lead and ruthenium oxide alloy). Manganese and iron catalysts have also shown enhanced electrocatalytic activity in Nafion®. These studies have demonstrated that the immobilization of photosensitizers in Nafion® can enhance photo-induced electron transfer processes by limiting intermolecular quenching and vibrational relaxation of photoexcited molecules. Moreover, Nafion® membranes may also prevent the decomposition of absorbed catalysts, resulting in enhanced catalytic performance and stability.
Nafion® is a random copolymer consisting of a tetrafluoroethylene backbone and sulfonate terminated perfluorovinylether side chains (Scheme 3.1). The ion exchange capacity of Nafion® membranes can be described in terms of the equivalent weight (EW), defined as the mass of the dry polymer per mole of sulfonate groups. For the H+-form of Nafion®, the equivalent weight is related to m as, $\text{EW} = 100m + 446$, and for an 1100 EW membrane, $m = 6.6$ (on average). Due to the phenomenon of ionic aggregation, Nafion® consists of at least two distinct morphological regions: a hydrophobic region encompassing the polytetrafluoroethylene (PTFE) backbone and a hydrophilic region containing the ionic side-chains. The semi-crystalline hydrophobic region of the ionomer provides the mechanical stability of the membrane while the hydrophilic domains contain ionic aggregates that impart the membrane with unique transport properties related to ion conductivity and permselectivity. There are numerous models for the ionic domains of Nafion®. These models are based upon results from small angle X-ray (SAXS) and neutron scattering (SANS), water uptake, water and ion transport, uniaxial strain, and NMR results.
An early model for Nafion® morphology is the cluster-network model proposed by Gierke and coworkers (Figure 3.1a). This model consists of spherical clusters, 4 nm in diameter, interconnected by 1 nm channels. The 1 nm channels are included in order to account for the continuous pathway for transport between clusters and high permselectivity (i.e. preferential transport of cations) observed for Nafion® membranes. The characteristic dimensions of the 4 nm clusters were rationalized from SAXS and water absorption measurements; however, there is no experimental evidence to account for the 1 nm channels between clusters.
Figure 3.1 a) The cluster-network model with 4 nm spheres connected with 1 nm channels b) Fibrillar ribbon model with ribbon-like fibrils consisting of the fluorocarbon backbone which bundle together to form aggregates 4-5 nm in diameter c) Cylindrical water channel model with 1.8-3.4 nm diameter parallel cylindrical aggregates. The red dots represent the terminal sulfonate groups on the perfluoroether side chains (black lines) of Nafion®.
3.2 Experimental

3.2.1 Materials

Nafion® 117 (DuPont) was cleaned by refluxing in 8 M nitric acid for 1-2 h, followed by a H₂O rinse and refluxing in H₂O for ~1 h. Films were dried in a vacuum oven at 90 °C for ~12 h. Neutralization to the Na⁺-form of Nafion® was achieved by allowing the Nafion® to equilibrate in a 1M NaOH solution for ~24 h, followed by a H₂O rinse and reflux in H₂O for ~1 h to remove excess NaOH. Spectrophotometric grade dimethylformamide (Alfa Aesar) and HPLC grade acetonitrile (Fisher) were used for all absorption/adsorption experiments. For the metal complex syntheses, cis-dichlorobis(2,2’-bipyridyl)ruthenium(II) dihydrate ((bpy)₂RuCl₂•2H₂O) from Strem Chemicals, rhodium(III) bromide hydrate (RhBr₃•H₂O) from Alfa Aesar and 2,3-bis(2-pyridyl)pyrazine (dpp) from Sigma Aldrich were used.

3.2.2 Comparison of H⁺-form and Na⁺-form of Nafion®

A solution of 1×10⁻² mM [{(Me₂bpy)₂Ru(dpp)}RhBr₂](PF₆)₅ in DMF was prepared and the electronic absorbance of the solution was measured. Equal volumes of the solution were divided between two vials. A piece of H⁺-Nafion® (approximately 2.5 cm × 2.5 cm) was added to one vial and a piece of similar size Na⁺-form Nafion® was added to the other. The solutions were stored in the dark and allowed to equilibrate for 48 h. To measure the electronic absorbance after equilibration the films were removed from the DMF solution, dried with a chemwipe and held in front of the window of a Hewlett-Packard 8452A diode array spectrophotometer (2 nm resolution). The concentration of [{(Me₂bpy)₂Ru(dpp)}RhBr₂](PF₆)₅...
in each of the films was adjusted through trial and error in order to achieve absorbance values in a range that followed Beer-Lambert Law behavior.

3.2.3 Analysis of Ion-exchange with Metal Complexes and Nafion®

3.2.3.1 Ion-exchange of monometallic, [(bpy)₂Ru(dpp)]²⁺, and trimetallic, [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺, complexes into Nafion®

Ion-exchange of the monometallic, [(bpy)₂Ru(dpp)](PF₆)₂, and trimetallic, [{(bpy)₂Ru(dpp)}₂RhBr₂](PF₆)₅, complexes into Nafion® from CH₃CN and dimethylformamide (DMF) solutions (2×10⁻⁴ M) was monitored over time by analyzing the supernatant spectrophotometrically. Based on the ionic exchange capacity of 1100 EW Na⁺-form Nafion®, precise masses of the ionomer membranes were added to the solutions in order to establish a 1:1 charge ratio of sulfonate anions from Nafion® to cationic charge from each of the metal complexes. To determine solution concentrations, electronic absorbance measurements were conducted every 20 minutes using an Ocean Optics USB 2000 spectrometer (Figure 3.2c) with adjustable path length fiber optic probes (Figure 3.2d-e), DH-2000-BAL UV-Vis-NIR light source (Figure 3.2b), and a MPM 2000 multiplexer (Figure 3.2a). The path lengths of the probes were adjusted to maximize the range of absorbance values in the region following the Beer-Lambert law for each complex, at initial concentrations of 2×10⁻⁴ M. Applying the Beer-Lambert law, the transient concentrations of the monometallic, [(bpy)₂Ru(dpp)]²⁺, and trimetallic, [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺, complexes were calculated using extinction coefficients of 6.9×10³ M⁻¹cm⁻¹ at 430 nm and 1.3×10⁴ M⁻¹cm⁻¹ at 510 nm, respectively. For all Nafion®
absorption experiments, solutions of the metal complexes were kept in the dark during the entire course of the experiments to avoid photoreduction.

3.2.3.2 Procedure for Preparation of Solutions for Measurement of Transient Concentrations by Absorption with Ocean Optics Probes

Stock solutions of known concentrations greater than $2 \times 10^{-4}$ M of the monometallic, [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$, and trimetallic, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$_{5+}$, complexes were prepared. Approximately 5-10 mg pieces of Nafion$^\circledR$ films were weighed on an analytical balance to obtain precise masses of the films. The pathlength of the probes were adjusted by adding the necessary spacers to the probe tips (Figure 3.2e), keeping in mind that the pathlength is twice the distance from the end of the transmission probe to the mirror embedded in the tip. Pathlengths were optimized to maximize the absorption region that follows the Beer-Lambert Law for each complex at equal concentrations.

The baseline of the absorbance spectra is dependent on the position of the fiber optic cables, therefore, in order to ease the data analysis process, it is important to maintain the position of the fiber optic cables throughout the entire experiment. Nafion$^\circledR$ films were added to the appropriate scintillation vials, wrapped in foil to ensure the solutions remained in the dark throughout the course of the experiment. Using the equivalent weight for Nafion117 membranes (1100 g/mol $-\text{SO}_3^-$) moles of $-\text{SO}_3^-$ groups in the films were determined. The moles of monometallic, [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$, and trimetallic, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$](PF$_6$)$_5$ complexes required were determined using the equivalent weight of Nafion$^\circledR$. Nafion$^\circledR$ films were placed in the vials with known volumes of DMF and CH$_3$CN. The fiber optic cables were positioned and clamped in place while the absorbance of solution blanks were measured. Following the
measurement of the blanks, concentrated solutions of monometallic, \([(\text{bpy})_2\text{Ru(dpp)}](\text{PF}_6)_2\), and trimetallic, \([(\text{bpy})_2\text{Ru(dpp)}_2\text{RhBr}_2](\text{PF}_6)_5\) complexes were carefully added, ensuring the probes remained in the same position.

3.2.3.3 Ocean Optics Setup

The Ocean Optics system was set up by connecting all of the components in Figure 3.2. The USB 2000 spectrometer (Figure 3.2c) was connected to the computer by a USB cable, and to the DH-2000-BAL UV-Vis-NIR light source (Figure 3.2b) by a fiber optic cable. The light source was, in turn connected to the MPM 2000 Multiplexor (Figure 3.2a) by another fiber optic cable. The fiber optic probes (Figure 3.2d) were attached to the multiplexor by a fiber optic cable that T-s into two separate cables for attachment to the multiplexor. It was determined that for each channel on the multiplexor that was open, the channel directly opposite of it in the circle was also open. For example, using Figure 3.3 as a reference, if channel 5 was open to the light source, then channel 13 was also open. Therefore, the probes were attached to the two channels that would be open simultaneously if one of the two channels were open.
Figure 3.2 Ocean Optics Setup a) MPM 2000 multiplexer b) DH-2000-BAL UV-Vis-NIR light source c) USB 2000 spectrometer d) fiber optic transmission probe e) path length adjustable tips for transmission probes. Image adapted from oceanoptics.com
Figure 3.3 MPM-2000 Multiplexor control window. The red dot indicates that channel 5 is on, meaning both channels 5 and 13 are on.

3.2.3.4 Software Manipulation for Data Collection Over Long Time Periods

The software for the Ocean Optics setup does not support experiments greater than 8 hours and some manipulation was required in order to collect the desired data. In order to avoid photolysis between measurements, a probe was selected as an “auxiliary” and was not submerged in a solution. Reference spectra of each solution were taken before the addition of complex. To initiate the absorbance experiment, first the appropriate probe was selected using the control window seen in Figure 3.3. In the Spectrasuite software, a new absorbance experiment was initiated by selecting File→New→Absorbance measurement from the window shown in Figure 3.4. A window popped up and it was ensured that the USB 2000 spectrometer was selected. In the next window, Figure 3.5, smoothing parameters and integration times for the acquisition were set. The scans to average was set to 5 and the boxcar width was set to 10. The integration time was set by pushing the “Set Automatically…” button and waiting for the
software to set an integration time. Pushing the “Set automatically…” button was repeated until the value in the “Last peak value” box was close to the value in the “Recommended peak value” box. This was indicated by a color change from pink to black by the numbers in the “Last peak value” box. The next window was Figure 3.6, to determine the reference spectrum. The light bulb was clicked until the spectrum in the window did not change. The next window was for the dark spectrum, Figure 3.7. The shutter was closed on the DH-2000-BAL UV-Vis-NIR light source and the dark light bulb was clicked until the spectrum in the window did not change. After clicking “Finish” a very noisy spectrum appeared in the sample window. That spectrum changed to a baseline once the shutter on the light source was opened. If the spectrum did not appear as a flat baseline near zero, the Absorption Experiment Set-up was repeated until it did. This setup was repeated for each probe that was used to measure changes in concentration of metal complexes. To ensure that every spectra was saved, the “Result” tab was right-clicked and the “Export Result…” was selected (Figure 3.8). In the “Export Result” window the “Save every scan” option was selected. A folder was created for each absorbance plot and at least 10 “padding digits” were created to ensure data would not cease to be recorded prematurely (Figure 3.9). The file format was the tab delimited format. It is important to select the tab delimited file with a header to ensure that there is a time stamp on the spectra in case the spectra are needed for data analysis later. The “pause until started by user” box was also checked. Once all of the probes were set up, the concentrated metal complex solution was added to each blank solution as quickly as possible in order to ensure the initial ion exchange times as close to each other as possible. Once the complex was added, the acquisition was paused by right clicking on the green
dots shown at the bottom right corner of the screen (Figure 3.11) and the time was noted. The green dots should turn yellow to indicate the acquisition was paused.

Figure 3.4 File→New→Absorbance Measurement was selected to start a new absorbance measurement with the Ocean Optics fiber optic probes.
Figure 3.5 Window for setting integration time and smoothing for an absorbance measurement. The value in the “Last peak value:” box is close to the value “Recommended peak value:” box, indicated by the black color of the numbers in the “Last peak value:” box.
**Figure 3.6** Window for reference spectrum determination. The yellow light bulb button was pressed until the spectrum in the “Reference Spectrum Preview” window did not change between acquisitions.
Figure 3.7 Window for dark spectrum determination. The dark light bulb button was pressed until the spectrum in the “Reference Spectrum Preview” window did not change between acquisitions.
Figure 3.8 To save the absorbance spectra the “Result” tab on the drop down menu highlighted with blue was right-clicked, followed by left clicking the “Export Result…” option.
Figure 3.9 To export the results, under “Save Options” the “Save every scan” option was selected and the “Pause until started by user” box was checked. Under “File Options” the Tab Delimited File Type was chosen, a location for the save was chosen from the “Save to Directory” box and the “Padding Digits” were selected as 10.

After the reference spectra for each probe was stored for blank solutions without metal complex, a strip chart was created for the desired wavelength of each plot. From the menu File→New→Strip chart was selected (Figure 3.10). In the window that pops up, Figure 3.11, “Single Trend from this Source” was selected, under “Range Selection,” “One Wavelength,” was selected and the desired wavelength to be monitored was entered in the box. On the left side of
the window, under the “Update Rate” tab, the “Update after every scan” option was selected and
the “Pause until started by user” box was checked. Under the “Auto-save” tab in Figure 3.12 the
directory in which the trend was to be saved was selected and the time desired time interval to be
saved was selected. The save does not have to be as frequent for the strip chart as the absorbance
plots since at every auto-save time point all of the available data points will be saved. After the
initial strip chart trend was created the window in Figure 3.13 appeared and the trends from each
probe and absorbance plot were added to the strip chart following the same procedure as just
described.
Figure 3.10 To start a new strip chart to measure transient concentrations by absorbance with the Ocean Optics fiber optic probes File→New→Strip chart was selected.
Figure 3.11 Window to set the parameters for the strip chart trend. The “Single Trends from this Source” option was selected. Under “Range Selection” the “One Wavelength” option was selected and the appropriate wavelength to be measured was entered in the box. Under the “Update Rate” tab “Update after every scan” was selected and the “Pause until started by user” box was checked.
Figure 3.12 Under the “Auto-Save” tab in the Strip Chart Trend Settings window, the “Enable Trend Auto Save” box was checked and an appropriate location was selected in the “Save to Directory” window.
Following setting up the first trend in and strip chart, other trends may be added by clicking the “Add trend…” button and repeating the set up process.

Once the absorbance plots and strip chart were set up, the script titled “multiplex-m1b.exe” was started and the prompts shown in Figure 3.14 were followed and the appropriate values were entered. Following the prompt in Figure 3.14d, the “Int time:” item from the drop down menu in Figure 3.15 corresponding to the correct probe was left-clicked. At this point, the script will cycle through the appropriate probes throughout the duration of the experiment. Upon initiation of these measurements, it is important that the windows on the screen stayed open and
remained the same size, as the script depends on pixel counts from the corner of the window. The sleep, screensaver and automatic update features on the computer were disabled. In some instances, the strip chart plots appeared noisy due to baseline shifts. In these cases, the full absorbance plots, in which several were saved per time point, were used to determine the necessary baseline corrections.

![Figure 3.14](image)

**Figure 3.14** Prompts that appear once the multiplex-m1b.exe script is started.
Figure 3.15 After being prompted to click the screen, the Int time highlighted in blue should be clicked for each trend in the strip chart.

3.2.3.5 Competitive Ion-exchange Analysis

Mixed DMF : CH$_3$CN solutions containing monometallic, [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$, and trimetallic, [{(bpy)$_2$Ru(dpp)}RhBr$_2$](PF$_6$)$_5$, complexes at a 1:1 ratio were used to evaluate solvent dependent competitive absorption into Nafion®. The solvent system was varied from 0.1 to 20% (v/v) DMF in CH$_3$CN. A Hewlett-Packard 8452A diode array spectrophotometer (2 nm resolution) was used to determine initial and final metal complex concentrations before and after absorption into Nafion®. Due to solvatochromic shifts in the absorption spectra between DMF
and CH$_3$CN, the absorbance of the monometallic, [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$, and trimetallic, [{(bpy)$_2$Ru(dpp)}RhBr$_2$](PF$_6$)$_5$, complexes at a wavelength of 480 nm was selected because the extinction coefficients were independent of solvent composition at this wavelength (Figure 3.16). The concentrations of the mixed complex solutions (1:1 monometallic complex, [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$ : trimetallic complex, [{(bpy)$_2$Ru(dpp)}RhBr$_2$](PF$_6$)$_5$) were adjusted to an absorbance value of 1 in a 0.2 cm cell at 480 nm in order to maximize the absorbance range that follows the Beer-Lambert Law. At 480 nm, the extinction coefficient, $\varepsilon_{480}$, for the monometallic complex, [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$, was found to be $1.0 \times 10^4$ M$^{-1}$cm$^{-1}$ and for the trimetallic complex, [{(bpy)$_2$Ru(dpp)}RhBr$_2$](PF$_6$)$_5$, $\varepsilon_{480} = 2.0 \times 10^4$ M$^{-1}$cm$^{-1}$. Precise masses of 1100 EW Na$^+$-form Nafion® 117, ensuring a 1:1 charge ratio, were added to the solutions and allowed to equilibrate until solution concentrations remained constant for $> 24$ h. In order to isolate the concentrations of the trimetallic complex, [{(bpy)$_2$Ru(dpp)}RhBr$_2$](PF$_6$)$_5$, in the mixed complex solutions, a wavelength of 650 nm was chosen because only the trimetallic complex, [{(bpy)$_2$Ru(dpp)}RhBr$_2$](PF$_6$)$_5$, absorbs at this wavelength ($\varepsilon = 2.5 \times 10^3$ M$^{-1}$cm$^{-1}$ in both CH$_3$CN and DMF). Since the extinction coefficient is roughly an order of magnitude smaller at 650 nm than at 480 nm, the absorbance of the solutions were measured in a 1.0 cm cell at 650 nm to maintain absorbance values in a range that follow the Beer-Lambert Law. The Beer-Lambert Law and the absorbance at 650 nm were used to determine the concentration of the trimetallic complex, [{(bpy)$_2$Ru(dpp)}RhBr$_2$](PF$_6$)$_5$. These concentrations of trimetallic complex, [{(bpy)$_2$Ru(dpp)}RhBr$_2$](PF$_6$)$_5$, were then used to determine the absorbance contribution of trimetallic complex, [{(bpy)$_2$Ru(dpp)}RhBr$_2$](PF$_6$)$_5$, at 480 nm, which was subsequently subtracted from the total absorbance at 480 nm of the mixed complex solutions.
The remaining absorbance after subtraction was attributed to absorbance from the monometallic complex, [(bpy)$_2$Ru(dpp)](PF$_6$)$_2$, and the concentration was calculated using the Beer-Lambert Law.

![Electronic absorbance of complexes](image)

**Figure 3.16** Electronic absorbance of [{Ru(bpy)$_2$(dpp)}$_2$RhBr$_2$(PF$_6$)$_5$ in CH$_3$CN (red) and DMF (blue) and [Ru(bpy)$_2$(dpp)](PF$_6$)$_2$ in CH$_3$CN (black) and DMF (orange). The arrows indicate where the absorbance was measured in the mixed [{Ru(bpy)$_2$(dpp)}$_2$RhBr$_2$(PF$_6$)$_5$[/Ru(bpy)$_2$(dpp)](PF$_6$)$_2$ complex and mixed solvent (CH$_3$CN and DMF) solutions in order to determine the concentrations in those mixed solvent systems.

3.2.3.6 Diffusion of Ru,Rh,Ru Complex in a Nafion® Membrane

To determine if diffusion of the trimetallic, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$, complex occurs in a Nafion® membrane, two different methods were considered. First, a solution of the
trimetallic, \[\{(bpy)_2Ru(dpp)\}_2RhBr_2\]^{5+}, in DMF was prepared in a scintillation vial with the solution filling a very small portion at the bottom of the vial. A piece of Na\(^+\)-form Nafion\(^\text{®}\) that had been swelled for \(\geq 24\) h in DMF was placed in the vial. The piece of Nafion\(^\text{®}\) was sufficiently large that only a small portion of the film was submerged in the trimetallic, \[\{(bpy)_2Ru(dpp)\}_2RhBr_2\]^{5+}, complex/DMF solution. The vial was sealed with a lid and kept in the dark. For the second method, a piece of Na\(^+\)-form Nafion\(^\text{®}\) that had been swelled for \(\geq 24\) h in DMF was placed in the vial. was placed at the bottom of a scintillation vial and a drop of trimetallic, \[\{(bpy)_2Ru(dpp)\}_2RhBr_2\]^{5+}, complex/DMF solution was placed on top of the film. The vial was stored in the dark, ensuring it was kept as level as possible. For both methods, the diffusion was monitored qualitatively by observing the highly colored trimetallic, \[\{(bpy)_2Ru(dpp)\}_2RhBr_2\]^{5+}, complex diffuse through the colorless membrane over long time periods (> 24 h).

### 3.2.3.7 Ion-exchange with Ru,Rh,Ru Trimetallic Complex with Ph\(_2\)phen Terminal Ligands

Ion-exchange of the Ru,Rh,Ru trimetallic complex with 4,7-diphenyl-1,10-phenanthroline (Ph\(_2\)phen) terminal ligands was monitored qualitatively by observation of a color changes in a colorless Na\(^+\)-form Nafion\(^\text{®}\) membrane upon submersion in a solution of the trimetallic, \[\{(Ph_2phen)_2Ru(dpp)\}_2RhBr_2\]^{5+}, complex in DMF.

Ion-exchange of the reduced trimetallic, \[\{(Ph_2phen)_2Ru(dpp)\}_2Rh\]^{5+}, was monitored by electronic absorbance with a Hewlett-Packard 8452A diode array spectrophotometer (2 nm resolution). A 0.1 M solution of tetrabutylammonium hexafluorophosphate (Bu\(_4\)NPF\(_6\)) in DMF was prepared and added to the cell/cuvette combination depicted in **Figure 3.17** with carbon.
fabric working electrode, Ag/AgCl reference electrode and a Pt mesh auxiliary electrode. Sufficient volume of the electrolyte solution was added to ensure the solution covered the connecting glass between each side of the electrolysis cell where the porous frit is contained. The solution was deaerated by purging with Ar for $\geq 20$ min. The $\mathrm{[(Ph_2phen)_2Ru(dpp)}_2\mathrm{RhBr_2]}^{5+}$ complex was added to the solution and the deaeration process was repeated. Electronic absorbance with a Hewlett-Packard 8452A diode array spectrophotometer (2 nm resolution) was used to verify the concentration of $\mathrm{[(Ph_2phen)_2Ru(dpp)}_2\mathrm{RhBr_2]}^{5+}$. The trimetallic, $\mathrm{[(Ph_2phen)_2Ru(dpp)}_2\mathrm{RhBr_2]}^{5+}$, complex was reduced by applying $-1.00$ V vs. NHE while still purging the cell with Ar until the current was stable for several minutes after an initial exponential decay with a three-electrode BASi Epsilon Potentiostat. After the $\mathrm{[(Ph_2phen)_2Ru(dpp)}_2\mathrm{RhBr_2]}^{5+}$ complex was reduced, a piece of Na$^+$-form Nafion® was added to the cell as quickly as possible to limit exposure to air. The complex was allowed to equilibrate with the Nafion® overnight, both while continuing to apply a potential and while purging with Ar to prevent re-oxidation without an added potential.
Figure 3.17 Diagram of the bulk electrolysis cell/cuvette setup. The electrolysis cell doubles as a 1-cm cuvette and can be placed directly into the sample holder of a UV-Vis instrument. The anode and cathode are separated by fritted glass. One side of the cell was purged with Ar gas. A Pt mesh working electrode, Ag/AgCl reference electrode and a carbon fabric auxiliary electrode were used in this experiment.

3.2.4 Nafion® Swelling

The length and width of dry rectangular Nafion® films were measured with calipers and the film thickness was measured in three different places with microcalipers. The dry volumes of the films were then calculated from these dimensions. These dry films were then immersed in either pure DMF or CH₃CN, or a mixture of the two solvents and stored at room temperature for 24 h. Following this treatment, the dimensions of solvent swollen membranes were measured in a manner identical to that of the dry membranes, to yield the wet, solvent swollen, volume. The degree of solvent swelling was determined by Equation 3.1.
\[ \text{Swelling Volume} = 100 \left( \frac{V_{\text{wet}} - V_{\text{dry}}}{V_{\text{dry}}} \right) \]  

Equation 3.1

3.2.5 Molecular Dimensions of the Complex

Prof. Diego Troya calculated the axial dimensions and volumes of the complexes from the structures generated in SCIGRESS using ab initio calculations at the B3LYP/STO-3G level of theory, employing the Gaussian 09 suite of programs.\textsuperscript{222} The average dimensions of the complexes were determined by direct examination of the model-generated coordinates.

3.2.6 Small Angle X-ray Scattering

SAXS experiments were performed using a Rigaku S-Max 3000 SAXS system, equipped with a focusing mirror, 3 pinholes and a rotating anode emitting X-rays with a wavelength of 0.154 nm (Cu K\textsubscript{α}). The sample-to-detector distance was 1603 mm, and the q-range was calibrated using a silver behenate standard. The SAXS data were corrected for sample thickness, sample transmission and background scattering. All the SAXS data were analyzed using the SAXSGUI software package to obtain radially integrated plots of SAXS intensity versus scattering vector q, where \( q = (4\pi/\lambda)\sin(\theta) \), \( \theta \) is one half of the scattering angle and \( \lambda \) is the X-ray wavelength. Since the SAXS experiments are performed under high vacuum, the solvent swollen SAXS were measured with a humidity controlled sample cell designed by Mingqiang Zhang.
3.3 Results and Discussion

3.3.1 Introduction of Ru,Rh,Ru Trimetallic Complexes with Nafion®

The trimetallic complex, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$, used in this study is of particular importance due to its ability to catalyze the light activated production of hydrogen from water. Each coordinated Ru moiety acts as a light absorber. In the presence of a sacrificial electron donor, electron transfer to the Rh center occurs via a photoinduced metal to ligand charge transfer (MLCT) transition to the dpp bridging ligand, followed by electron transfer to the Rh. Upon reduction, the Rh(III) complex undergoes a rearrangement from octahedral geometry to square planar geometry, accompanied by loss of the halide ligands. Consequently, water reduction catalysis occurs at the Rh center.

![Scheme 3.2](image)

**Scheme 3.2** a) [(bpy)$_2$Ru(dpp)]$^{2+}$ monometallic complex containing a Ru(II) center, two bpy ligands and a dpp ligand. b) [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$ trimetallic complex containing two terminal Ru(II) with bpy terminal ligands and a dpp bridging ligand to a central Rh(III) containing two coordinated bromides.
Ion-exchange of Ru polypyridyl complexes into Nafion® has been shown to be advantageous for photo-induced electron transfer processes.\textsuperscript{30,123,126-128} It is hypothesized that the catalytic performance of trimetallic complex, [(bpy)_2Ru(dpp)]_2RhBr_2\textsuperscript{5+}, will be improved when absorbed in Nafion®, due to a number of factors including restriction of molecular mobility (reduced intermolecular quenching and limited long range diffusion). In order to understand the effect that the ionomer has on catalytic performance, it is important to understand the specific interactions between the polymer and the metal complex that lead to a functionally advantageous spatial distribution of catalyst molecules within (absorbed) or on the surface of (adsorbed) the host polymer film.

### 3.3.2 Analysis of Na\textsuperscript{+}-form of Nafion® Compared to the H\textsuperscript{+}-form of Nafion® for Ru,Rh,Ru Trimetallic Ion-exchange

The as-received Nafion® film is in the H\textsuperscript{+}-form. The pH inside of a H\textsuperscript{+}-Nafion® film is < 0 and Nafion® is considered a superacid.\textsuperscript{223-225} Considering the reactive nature of the H\textsuperscript{+}-form of Nafion®, it is likely that the [(Me\textsubscript{2}bpy)_2Ru(dpp)]RhBr\textsubscript{2}\textsuperscript{5+} complex decomposes under these conditions. Through the use of electronic absorbance experiments, it was determined that the Na\textsuperscript{+}-form of Nafion® would be a better choice for uptake experiments than the H\textsuperscript{+}-form. In this experiment, the [(Me\textsubscript{2}bpy)_2Ru(dpp)]RhBr\textsubscript{2}(PF\textsubscript{6})\textsubscript{5} (\textbf{Scheme 3.3}) trimetallic was exchanged into both the H\textsuperscript{+}-form and Na\textsuperscript{+}-form of Nafion®. A comparison of the electronic absorbance of [(Me\textsubscript{2}bpy)_2Ru(dpp)]RhBr\textsubscript{2}\textsuperscript{5+} in a DMF solution and [(Me\textsubscript{2}bpy)_2Ru(dpp)]RhBr\textsubscript{2}\textsuperscript{5+} exchanged in DMF swollen H\textsuperscript{+}-form and Na\textsuperscript{+}-form Nafion® films can be seen in \textbf{Figure 3.18}. It is obvious that the electronic absorbance of [(Me\textsubscript{2}bpy)_2Ru(dpp)]RhBr\textsubscript{2}\textsuperscript{5+} in the Na\textsuperscript{+}-form of Nafion®
(Figure 3.18b) is more similar to \([\{(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}\}\text{RhBr}_2\}]^{5+}\) in DMF than \([\{(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}\}\text{RhBr}_2\}]^{5+}\) in the \(\text{H}^+\)-form of Nafion® (Figure 3.18a). Further experimentation is necessary in order to determine the cause of the changes in the electronic absorbance of \([\{(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}\}\text{RhBr}_2\}]^{5+}\) in the \(\text{H}^+\)-form of Nafion®. For the purpose of this study, this was sufficient cause to use the \(\text{Na}^+\)-form of Nafion® instead of the \(\text{H}^+\)-form for the remainder of the ion-exchange experiments.

![Diagram of \([\{(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}\}\text{RhBr}_2\}]^{5+}\) trimetallic complex containing two terminal Ru(II) with \(\text{Me}_2\text{bpy}\) terminal ligands and a dpp bridging ligand to a central Rh(III) containing two coordinated bromides.](image)

**Scheme 3.3** \([\{(\text{Me}_2\text{bpy})_2\text{Ru(dpp)}\}\_2\text{RhBr}_2\}]^{5+}\) trimetallic complex containing two terminal Ru(II) with \(\text{Me}_2\text{bpy}\) terminal ligands and a dpp bridging ligand to a central Rh(III) containing two coordinated bromides.
Figure 3.18 Electronic absorbance of the \([\{(\text{Me}_2\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RhBr}_2](\text{PF}_6)_5\) complex in a DMF solution compared to DMF swollen H\(^+\)-form (a) and Na\(^+\)-form (b) Nafion\(^\circledR\) films. The spectra were normalized at 410 nm for a clearer comparison between the solution state and solid state measurements.

3.3.3 Ion-exchange with Ru,Rh Mixed-metal complexes Nafion\(^\circledR\) Membranes

Excess colorless and transparent pieces of 1100 EW Na\(^+\)-form Nafion\(^\circledR\) 117 (180 \(\mu\)m thick) were added to separate solutions of the trimetallic, \([\{(\text{bpy})_2\text{Ru}(\text{dpp})\}_2\text{RhBr}_2](\text{PF}_6)_5\), and monometallic, \([(\text{bpy})_2\text{Ru}(\text{dpp})](\text{PF}_6)_2\) (Scheme 3.2), complexes in DMF. Upon swelling in DMF, the volume of the Nafion\(^\circledR\) films increased by 100\%, determined by Equation 3.1. The metal complex solutions containing the Nafion\(^\circledR\) films were kept in the dark at room temperature for > 48 h. Following this treatment, the resulting DMF solutions were colorless, while the originally
colorless ionomer membranes were highly colored (Figure 3.19) This essentially complete ion-exchange suggests that Nafion® has a very high affinity for both the monometallic, [(bpy)2Ru(dpp)]2+, and trimetallic, [{(bpy)2Ru(dpp)}2RhBr2]5+, complexes.

3.3.3.1 Molecular Size Comparison for Ion Exchange

The favorable ion-exchange of the trimetallic complex, [{(bpy)2Ru(dpp)}2RhBr2]5+, into Nafion® was an unexpected result considering the large size of this mixed metal complex in comparison to the size of the ionic aggregates in Nafion®. Volumes and dimensions of the monometallic, [(bpy)2Ru(dpp)]2+, and trimetallic, [{(bpy)2Ru(dpp)}2RhBr2]5+, complexes have been calculated in order to compare them to the size of Nafion® ionic aggregates. The trimetallic complex, [{(bpy)2Ru(dpp)}2RhBr2]5+, consists of a mixture of 18 total isomers. These isomers have a mixture of Δ and Λ configurations (optical isomers), which do not yield significant variations in the volume and dimensions of the complex.226 The range in sizes of the complexes is principally defined by three geometric isomers about the Rh, where the geometry of the dpp bridging ligand coordination to the central Rh can vary. The average volumes of these three structural isomers were calculated to be 1.2×10³ Å³, with respective dimensions (maximum length in the x, y and z directions) listed in Table 3.1. A 3D model schematic representation of the monometallic complex, [(bpy)2Ru(dpp)]2+, is compared to that of isomer 1 of the trimetallic complex, [{(bpy)2Ru(dpp)}2RhBr2]5+, as shown in Figure 3.20. These dimensions are compared to the dimensions of proposed models of Nafion® ionic aggregates.
Figure 3.19 a) [(bpy)$_2$Ru(dpp)]$^{2+}$ monometallic complex and b) [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$ trimetallic complex in a DMF solution (left) and a solution containing excess Na$^+$-Nafion$^\circledR$ after ion-exchange (right). Solutions started at equal concentrations, a colorless and transparent piece of Nafion$^\circledR$ was added to solutions on the right and was allowed to equilibrate for at least 48 h.

Table 3.1 The x, y and z dimensions (Å) of three main isomers of the trimetallic complex, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$.

<table>
<thead>
<tr>
<th>dimension</th>
<th>Isomer 1</th>
<th>Isomer 2</th>
<th>Isomer 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>10.8</td>
<td>18.0</td>
<td>12.0</td>
</tr>
<tr>
<td>y</td>
<td>23.6</td>
<td>18.9</td>
<td>23.1</td>
</tr>
<tr>
<td>z</td>
<td>13.3</td>
<td>13.7</td>
<td>11.4</td>
</tr>
</tbody>
</table>

In order to demonstrate the relative size of the complexes compared to proposed models of Nafion$^\circledR$ ionic aggregates, a space filling model of one of the isomers is superimposed (to scale) inside the original cluster-network model of Nafion$^\circledR$ membranes$^{171}$ (Figure 3.21a), the more recent fibrillar ribbon model$^{175,183}$ (Figure 3.21b) and the cylindrical water channel model$^{174}$ (Figure 3.21c). It has been determined through electronic absorbance experiments that 86 ± 2% of the sulfonate groups are counterbalanced by the overall charge of the trimetallic complex, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$, absorbed into the membrane. Similarly, 90 ± 2% of the sulfonate sites are counterbalanced by the overall charge of the monometallic complex,
[(bpy)$_2$Ru(dpp)]$^{2+}$. While these ionic exchange values are quite high, given the large size of the complexes, it is not surprising that the quantity of sulfonate groups participating in the ion exchange process is less than 100% because some of the sulfonate terminated side chains are likely to be inaccessible.$^{94,227}$

**Figure 3.20** Three-dimensional model of monometallic complex, [(bpy)$_2$Ru(dpp)]$^{2+}$, and trimetallic complex, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$, isomer 1. Images generated in SCIGRESS.
Figure 3.21 Space filling model of isomer 1 of [(bpy)$_2$Ru(dpp)]$_2$RhBr$_2$${}^{5+}$ trimetallic complex super-imposed to scale in the a) cluster-network model, the b) fibrillar ribbon model and c) cylindrical water channel model (3.4 nm diameter) of Nafion® ionic domains.
Considering the cluster-network model\(^\text{171}\) (Figure 3.21a), it is possible for the trimetallic complex, \([\{(bpy)_2Ru(dpp)}_{2}RhBr_2\] \(^{5+}\), to fit in the 4-nm cluster, however, the 1-nm channels are too small to allow access of the large complex without some complicated (and likely inhibiting) structural rearrangement during the ion-exchange process. Moreover this simple model is not likely to be an accurate description of the structure in the highly swollen state (DMF volume fraction of \(\Phi_{\text{DMF}} = 0.5\)). In contrast, superimposing the trimetallic complex, \([\{(bpy)_2Ru(dpp)}_{2}RhBr_2\] \(^{5+}\), into more the open rod/ribbon-like\(^\text{175,183}\) (Figure 3.21b) or cylindrical water channel\(^\text{174}\) models of Nafion® (Figure 3.21c) suggests that the large trimetallic complex, \([\{(bpy)_2Ru(dpp)}_{2}RhBr_2\] \(^{5+}\), may be more readily exchanged into the ionic aggregates of more accommodating morphologies as opposed to the inherently restricted cluster-network model.
Small angle X-ray scattering (SAXS) is commonly used to probe the dimensions of the ionic aggregates of Nafion®. SAXS profiles of Nafion® loaded with trimetallic, 
\[\{(bpy)_2Ru(dpp)\}_2RhBr_2\]^{5+}, and monometallic, \[(bpy)_2Ru(dpp)]^{2+}, complexes were compared to Na\(^+\) and Cs\(^+\)-forms of Nafion® (Figure 3.22). The monometallic, \[(bpy)_2Ru(dpp)]^{2+}, and trimetallic, \[\{(bpy)_2Ru(dpp)\}_2RhBr_2\]^{5+}, complexes were loaded into Na\(^+\)-form Nafion® membranes. In the Na\(^+\)-form of Nafion®, there is no observed ionic scattering peak due to
contrast variation. The scattering intensity in SAXS is dependent on differences in electron density between different regions in the polymer. The intensity of the peaks is dependent on the differences in electron density (contrast) between different regions of the polymer. Changing the counter-ion alters the electron density of the ionic region of Nafion®. These alterations in electron density can cause the disappearance of peaks in the scattering profile, due to contrast variation. The appearance of the ionic scattering peak (marked with a red line at q_{max} = 1.8 nm\(^{-1}\)) in the films that have been loaded with monometallic, [(bpy\(_2\))Ru(dpp)]\(^{2+}\), and trimetallic, [(bpy\(_2\))Ru(dpp)]\(_2\)RhBr\(_2\)]\(^{5+}\), complexes indicates that the electron density of the Nafion® ionic aggregates has changed. This observed increase in electron density is consistent with the complexes present within the Nafion® ionic aggregates due to ion-exchange. Surprisingly, the relative peak position of the ionic peak in comparison to the Cs\(^+\)-form of Nafion® is not appreciably altered, suggesting the dimensions of the ionic aggregates are not significantly changed upon the incorporation of these relatively large complexes.

### 3.3.3.2 Solvent Swelling Dependent Ion-exchange Kinetics

In addition to the significant ion-exchange of the large trimetallic complex, [(bpy\(_2\))Ru(dpp)]\(_2\)RhBr\(_2\)]\(^{5+}\), into Nafion®, time dependent absorption in DMF shows that the larger trimetallic complex, [(bpy\(_2\))Ru(dpp)]\(_2\)RhBr\(_2\)]\(^{5+}\), is exchanged considerably faster than the smaller monometallic complex, [(bpy\(_2\))Ru(dpp)]\(^{2+}\) (Figure 3.23a). The half-life of ion-exchange of the monometallic, [(bpy\(_2\))Ru(dpp)]\(^{2+}\), and trimetallic, [(bpy\(_2\))Ru(dpp)]\(_2\)RhBr\(_2\)]\(^{5+}\), with Na\(^+\) in Nafion® (t\(_{1/2}\)) is defined as the time at which the concentration of the DMF/metal complex solution is one half the initial concentration. Half-lives were determined with a 1:1 Nafion® : metal complex charge ratio (i.e., 1 mol [(bpy\(_2\))Ru(dpp)]\(_2\)RhBr\(_2\)]\(^{5+}\) : 5 mol –SO\(_3\)\(^-\) and 1 mol
\[(\text{bpy})_2\text{Ru}(\text{dpp})\]^{2+} \cdot 2 \text{ mol} -\text{SO}_3^-\), where \(t_{1/2} = 60 \text{ h}\) for the monometallic complex, 
\[(\text{bpy})_2\text{Ru}(\text{dpp})\]^{2+}, and \(t_{1/2} = 20 \text{ h}\) for the trimetallic complex, \[{(\text{bpy})_2\text{Ru}(\text{dpp})}_2\text{RhBr}_2\]^{5+}.

**Figure 3.23** Concentration vs. time profiles of monometallic complex, \[(\text{bpy})_2\text{Ru}(\text{dpp})\]^{2+}, (orange) and trimetallic complex, \[{(\text{bpy})_2\text{Ru}(\text{dpp})}_2\text{RhBr}_2\]^{5+}, (purple) in the presence of a 1:1 charge ratio of Na\(^+\) Nafion\(^{-}\) 117 in a DMF solution (a) and CH\(_3\)CN solution (b).
The difference in the ion-exchange half-lives may be attributed to the relative affinity of Nafion® for the two metal complexes. The affinity of Nafion® for the metal complexes can be expressed with partition coefficients ($K_x$), defined as the ratio of equilibrium concentrations of the metal complex in the Nafion® membrane to equilibrium concentrations of the metal complex in a DMF solution (Equation 3.2). Despite the larger size, Nafion® has a higher affinity for the large trimetallic complex, $[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^5^+$, ($K_{\text{tri}} = 5.7 \times 10^3$) compared to the smaller monometallic complex, $[(\text{bpy})_2\text{Ru(dpp)}]^2^+$, ($K_{\text{mono}} = 1.1 \times 10^3$). This behavior is typical for ion-exchange materials whereby ions with a higher charge are favored over less charged ions. In addition, the organic character of the ligands likely yields a hydrophobic contribution to the large partition coefficients. Based on the seminal work of Reichenberg, the kinetics of ion exchange was shown to be affected by the relative affinities of the ionic polymer for the exchanging ions. For a given extent of exchange, the rate of ion exchange was found to be greatest for the system with the higher affinity coefficient. Therefore, the shorter ion-exchange half-life of the large trimetallic complex, $[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^5^+$, relative to the smaller monometallic, $[(\text{bpy})_2\text{Ru(dpp)}]^2^+$, observed (Figure 3.23a) is in agreement with the calculated partition coefficients (relative affinities) of the two metal complexes.

\[
K_x = \frac{[\text{metal complex}]_{\text{Naf}}}{[\text{metal complex}]_{\text{DMF}}} \quad \text{Equation 3.2}
\]
Since the ionic complexes must be accommodated within the ionic domains of Nafion® (i.e., either of sufficient size or having the ability to structurally rearrange), it is reasonable to expect that the rate of the trimetallic complex, \( [{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2]^{5+} \), exchange would be dependent on the degree of solvent-induced swelling of the Nafion® membrane. With DMF, the Nafion membrane swells by 100% (doubles in volume), while with CH₃CN, the membrane swells by only 10%. For the highly swollen membranes in DMF, the ion-exchange of the trimetallic complex, \( [{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2]^{5+} \), is much faster than the exchange of the monometallic complex, \( [(bpy)_2\text{Ru(dpp)}]^2^+ \). In contrast, for the less swollen membranes in CH₃CN, there is still a rapid ion-exchange of the smaller monometallic complex, \( [(bpy)_2\text{Ru(dpp)}]^2^+ \), while essentially no measureable exchange of the larger trimetallic complex, \( [{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2]^{5+} \), is observed (Figure 3.23b). Based on this result, it is apparent that a size-dependent competitive ion-exchange of monometallic, \( [(bpy)_2\text{Ru(dpp)}]^2^+ \), and trimetallic, \( [{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2]^{5+} \), complexes is operable. Kreuer and coworkers used SAXS to correlate the degree of water swelling to the average dimensions of the water swollen ionic domains in Nafion®. Following this “expansion law” argument, it is easy to rationalize that the DMF swollen films (\( \Phi_{\text{DMF}} = 0.5 \)) would contain ionic domains with dimensions significantly larger than those in CH₃CN swollen films (\( \Phi_{\text{ACN}} = 0.09 \)). Thus, with limited solvent swelling, the ionic domains are less accommodating to the larger complexes.

It was hypothesized that by controlling the degree of swelling, preferential absorption of either the monometallic, \( [(bpy)_2\text{Ru(dpp)}]^2^+ \), or trimetallic, \( [{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2]^{5+} \), complexes could be obtained.
Table 3.2 shows that even with solvent ratios as low as 5% DMF in CH$_3$CN, the change in volume of the Nafion® film is significant. With as low as 2% DMF in CH$_3$CN, the Nafion® film swells twice as much as it does for CH$_3$CN alone. As seen in Figure 3.24 and Figure 3.25, under low swelling conditions (< 1 % v/v DMF in CH$_3$CN), there is negligible ion exchange of either the monometallic, [(bpy)$_2$Ru(dpp)]$^{2+}$, or trimetallic [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$, complexes. At higher swelling conditions, ion exchange was dominated by the trimetallic, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$, complex. The preferential exchange of the [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$ complex is consistent with the larger partition coefficient for the trimetallic, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$, complex. Although there was no measurable concentration change in the metal complex solution under low swelling conditions, the exchange of the monometallic, [(bpy)$_2$Ru(dpp)]$^{2+}$, into the membrane is affected by the presence of the trimetallic, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$, in the solution.

Table 3.2 Changing Swelling Volumes with Changing DMF:CH$_3$CN solvent ratios.

<table>
<thead>
<tr>
<th>V% DMF in CH$_3$CN</th>
<th>Swelling V% (100(V$<em>{wet}$ – V$</em>{dry}$)/V$_{dry}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 3.24 Electronic absorbance of mixed monometallic, [(bpy)$_2$Ru(dpp)]$^{2+}$, and trimetallic, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_3$]$^{5+}$, complex solutions after equilibration in the presence a Na$^+$-form Nafion$^\circledR$ film for at least 96 hours. The decrease in solution concentration is indicative of ion exchange into the Nafion$^\circledR$ films. With increasing DMF in the DMF/CH$_3$CN solvent mixture, the solution absorbance decreases, indicating exchange into the Nafion$^\circledR$ film. A 0.2 cm path length cell was used to measure the absorbance at 650 nm (inset), while a 1.0 cm path length cell was used to measure the absorbance at 480 nm.
Figure 3.25 Percentage of sulfonate groups in Na⁺-form Nafion® films that have undergone ion exchange with a solution of mixed monometallic, [(bpy)₂Ru(dpp)]²⁺, and trimetallic, [(bpy)₂Ru(dpp)₂RhBr₂]⁵⁺ complexes in solutions of varying %(v/v) of DMF in CH₃CN. Total exchange of both monometallic, [(bpy)₂Ru(dpp)]²⁺, and trimetallic, [(bpy)₂Ru(dpp)₂RhBr₂]⁵⁺ (■), exchange of monometallic, [(bpy)₂Ru(dpp)]²⁺ (●), exchange of trimetallic [(bpy)₂Ru(dpp)₂RhBr₂]⁵⁺ (♦).

To further probe this size-dependent competitive ion-exchange phenomenon, a Nafion® membrane was exposed to the large trimetallic, [(bpy)₂Ru(dpp)₂RhBr₂]⁵⁺, and small monometallic, [(bpy)₂Ru(dpp)]²⁺, complexes in a sequential fashion. A Na⁺ form Nafion® membrane was first added to a solution of trimetallic complex, [(bpy)₂Ru(dpp)₂RhBr₂](PF₆)₅, in CH₃CN and allowed to equilibrate (monitored with electronic absorbance), then rinsed with pure CH₃CN, followed by immersion in a solution of the monometallic complex, [(bpy)₂Ru(dpp)](PF₆)₂, in CH₃CN. Under this sequential exposure process, no measurable exchange of either complex into Nafion® was observed. Note that if the Na⁺-form Nafion® film
was exposed to the monometallic complex, 
\[(\text{bpy})_2\text{Ru(dpp)}](\text{PF}_6)_2\], without first equilibrating in
the trimetallic complex, \[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2](\text{PF}_6)_5/\text{CH}_3\text{CN} \text{ solution},
significant ion-exchange of the monometallic complex, 
\[(\text{bpy})_2\text{Ru(dpp)}](\text{PF}_6)_2\], was observed as shown in Figure 3.23b. Therefore, under
this sequential exposure process, it is proposed that, in low
solvent swelling conditions, the large trimetallic complex, 
\[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}, is
electrostatically attracted to the Nafion® film, but is restricted from entering the ionic domains
within the membrane. Consequently, the large trimetallic complex, 
\[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+},
is only able to exchange with ions on the surface of the Nafion® film, thereby “blocking the
pores” and thus preventing further ion-exchange of the monometallic complex,
\[(\text{bpy})_2\text{Ru(dpp)}\]^{2+}, into the interior ionic domains of Nafion®, as depicted in Figure 3.26.

With the recognition that the dimensions of the trimetallic complex,
\[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}, are comparable to the dimensions of the ionic domains in Nafion®,
and the accommodation of these ionic species into the membrane may involve at least two
different ion-exchange processes (surface vs. bulk exchange sites in Nafion®), further insight
into the uptake mechanism may be obtained through additional analysis of the time dependent
ion-exchange data in Figure 3.23. Using exponential fits of these data as shown in Figure 3.27,
it was determined that the trimetallic complex, \[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}, was exchanged via a
biexponential (Figure 3.27b) process, while the monometallic complex, \[(\text{bpy})_2\text{Ru(dpp)}\]^{2+}, was
exchanged through a monoexponential (Figure 3.27a) process.
Figure 3.26 Representation of the process that occurs between trimetallic, \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5+}\), and monometallic, \([(\text{bpy})_2\text{Ru(dpp)})]^{2+}\), complexes with Nafion® and a low swelling solvent. Where trimetallic complex, \([(\text{bpy})_3\text{Ru(dpp)})_3\text{RhBr}_2]^{5+}\), adsorbs to the surface of Nafion® ionic aggregates, preventing absorption of monometallic, \([(\text{bpy})_2\text{Ru(dpp)})]^{2+}\).
Figure 3.27 Experimental data and fitting result of trimetallic complex, [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$, (a) and monometallic complex, [{(bpy)$_2$Ru(dpp)}]$^{2+}$, (b) absorbed into Nafion® from a DMF solution and fit to Equations 1 and 2 where [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$=[tri] and [{(bpy)$_2$Ru(dpp)}]$^{2+}$=[mono].
\[ [\text{tri}]_{\text{Nafion}} = 0.77[\text{tri}]_i e^{-0.045t} + 0.23[\text{tri}]_i e^{-0.0061t} \] \hspace{1cm} \text{Equation 3.3}

\[ [\text{mono}]_{\text{Nafion}} = [\text{mono}]_i e^{-0.014t} \] \hspace{1cm} \text{Equation 3.4}

In agreement with the results of the sequential exposure analysis (above) and behavior common to other ion-exchange materials, the biexponential uptake of the trimetallic complex, \([\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^{5+}\), is attributed to a fast ion-exchange of the complex with the surface accessible sulfonate groups, followed by a somewhat slower diffusion of these complexes into the interior of the membrane (exchange with bulk sulfonates). In contrast, the smaller dimensions of the monometallic complex, \([(bpy)_2\text{Ru(dpp)}]^{2+}\), yield a lower diffusive barrier for exchange with bulk sulfonate sites and thus less contrast in time-dependence between the surface ion-exchange and internal ion-exchange processes.

Although essentially no uptake in the less swelling CH$_3$CN solution (Figure 3.23b) was observed for the trimetallic complex, \([\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^{5+}\), at a 1:1 charge ratio of trimetallic complex, \([(bpy)_2\text{Ru(dpp)}]^{2+}\), to $\text{SO}_3^-$ in Nafion®, it is important to note that the equilibrated films had a slight color change that could not be removed by rinsing with various solvents (Figure 3.28). Surface ion-exchange experiments were performed with a large excess of Nafion® (1:100 and 1:50 charge ratios of trimetallic complex, \([\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^{5+}\), to $\text{SO}_3^-$ groups) and analyzed by electronic absorbance. The rate of surface exchange of the complex under these conditions followed a monoexponential trend and was found to be dependent on the surface area of the Nafion® films. The trimetallic complex, \([\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^{5+}\), was exchanged at a faster rate with a higher surface area of
Nafion®. This evidence further supports our theory that the overall uptake of the large trimetallic complex, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\), is governed by ion-exchange onto the surface of the Nafion® film.

![Figure 3.28](image)

**Figure 3.28** Photo of Nafion® films after complete ion exchange with \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\) in CH₃CN (a) and DMF (b). Although the solution did not show an observable change in concentration at a starting concentration of 0.20 mM with electronic absorbance in (a), the color on the film indicates the some surface exchange has occurred. Additionally, the significantly more intense color in (b) compared to (a) indicates that the concentration of \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\) in (b) is higher than that of (a).

### 3.3.3 Ion-Exchange of \([(bpy)_2Ru(dpp)Rh(phen)Cl_2]^{3+}\) Bimetallic Complex

Time dependent ion-exchange experiments with the bimetallic, \([(bpy)_2Ru(dpp)Rh(phen)Cl_2]^{3+}\), complex were performed in order to confirm the apparent trend observed with the monometallic, \([(bpy)_2Ru(dpp)]^{2+}\), and trimetallic, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\), complexes with respect to ion-exchange thermodynamic and kinetics. The difference in the half-life of ion-exchange between the monometallic, \([(bpy)_2Ru(dpp)]^{2+}\), and trimetallic, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\), complexes with Nafion® is attributed to the affinity of the cationic metal complexes with the Nafion® membrane. As expected based on the concept that affinity should increase with charge, the affinity of Nafion® for the bimetallic, \([(bpy)_2Ru(dpp)Rh(phen)Cl_2]^{3+}\), \((K_{bi} = 3.1 \times 10^3)\) (Equation 3.2) lies between the affinities of the
monometallic, $[(\text{bpy})_2\text{Ru(dpp)}]^2^+ \ (K_{\text{mono}} = 1 \times 10^3)$ and trimetallic, $\{[(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2\}^{5^+} \ (K_{\text{tri}} = 5.7 \times 10^3)$ complexes. Thus, if the half-life of ion-exchange is dependent on the affinities of the metal complex with Nafion®, the half-life of ion-exchange for the bimetallic, $[(\text{bpy})_2\text{Ru(dpp)}\text{Rh(phen)Cl}_2]^{3^+}$, should lie between the half-lives of the monometallic, $[(\text{bpy})_2\text{Ru(dpp)}]^2^+$, and trimetallic, $\{[(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2\}^{5^+}$ complexes. This behavior is as expected and the trend is clearly demonstrated in Figure 3.29 and Table 3.3.

![Scheme 3.4](image)

**Scheme 3.4** Ru,Rh bimetallic complex with 2,2'-bipyridine (bpy) terminal ligands on the Ru, a bis(2-pyridyl)pyrazine (dpp) bridging ligand a 1,10-phenanthroline terminal ligand on the Rh and two Cl$^-$ non-chromophoric ligands on the Rh.
Table 3.3 Half-lives of ion-exchange with Na⁺-form Nafion® for monometallic, [(bpy)₂Ru(dpp)]²⁺, bimetallic, [(bpy)₂Ru(dpp)Rh(phen)Cl₂]³⁺, and trimetallic, [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺, complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>t₁/₂ (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(bpy)₂Ru(dpp)]²⁺</td>
<td>60</td>
</tr>
<tr>
<td>[(bpy)₂Ru(dpp)Rh(phen)Cl₂]³⁺</td>
<td>30</td>
</tr>
<tr>
<td>[{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 3.29 Concentration vs. time profiles of monometallic complex [(bpy)₂Ru(dpp)]²⁺, (orange diamonds), bimetallic complex, [(bpy)₂Ru(dpp)Rh(phen)Cl₂]³⁺ (blue triangles) and trimetallic complex, [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺, (purple circles) in the presence of a 1:1 charge ratio of Na⁺ Nafion® 117 in a DMF solution.
Based on the scattering intensity of the ionic scattering peak in SAXS (marked with a red line at $q_{\text{max}} = 1.8 \text{ nm}^{-1}$ in Figure 3.22), it can be confirmed that loading Nafion® with the bimetallic, $[(\text{bpy})_2\text{Ru(dpp)}\text{Rh(phen)Cl}_2]^{3+}$, complex follows the anticipated electron density trends (Figure 3.22). SAXS measures differences in electron density throughout a material and the change in intensity from the monometallic, $[(\text{bpy})_2\text{Ru(dpp)}]^{2+}$, to the bimetallic, $[(\text{bpy})_2\text{Ru(dpp)}\text{Rh(phen)Cl}_2]^{3+}$, to the trimetallic, $[(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2]^{5+}$, complexes tracks changes in electron density relative to the changing electron densities of the complexes. Additionally, the consistency in the ionic scattering peak position between the monometallic, $[(\text{bpy})_2\text{Ru(dpp)}]^{2+}$, bimetallic, $[(\text{bpy})_2\text{Ru(dpp)}\text{Rh(phen)Cl}_2]^{3+}$, and trimetallic, $[(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2]^{5+}$, complexes and the Cs$^+$-form of Nafion® further implies that the dimensions of the ionic aggregates are not significantly altered upon incorporation of each of the three metal complexes.

The addition of the bimetallic complex, $[(\text{bpy})_2\text{Ru(dpp)}\text{Rh(phen)Cl}_2]^{3+}$, confirms the expected trends based on the data observed with the monometallic complex, $[(\text{bpy})_2\text{Ru(dpp)}]^{2+}$, and trimetallic complex, $[(\text{bpy})_2\text{Ru(dpp)}]_2\text{RhBr}_2]^{5+}$. The interactions between the Nafion® membrane and any of the complexes is likely a combination of electrostatics and hydrophobic interactions. The difference in the rates of exchange follow the trend in charge ($5^+, 3^+, 2^+$), the complex with the highest charge having the fastest half-life of exchange. The rate of exchange also could be attributed to the hydrophobic effect, and the larger complex would have a stronger hydrophobic effect. Therefore, the same trend would be expected for the three complexes based on size. It would be interesting to study systems/complexes that have more control over these variables in order to better understand the roles of the different intermolecular forces.
involved in the ion-exchange process. Systematic variation of the terminal ligands on both bimetallic and trimetallic complexes could assist in determining the contributions of hydrophobic interactions, while controlling the coulombic interactions between the metal complexes and Nafion®.

3.3.3.4 Diffusion of trimetallic, \([{(bpy)_2Ru(dpp)}_2RhBr_2]^{5+}\), in Nafion®

Diffusion of ions within an ionomer membrane is likely to be significantly slower than diffusion in a solution. The large calculated affinity of the \([{(bpy)_2Ru(dpp)}_2RhBr_2]^{5+}\) complex for the Nafion® membrane, \(K_{\text{tr}} = 5.7 \times 10^3\) (Equation 3.2) demonstrates that there is a significant thermodynamic driving force for the \([{(bpy)_2Ru(dpp)}_2RhBr_2]^{5+}\) complex to be within the Nafion® membrane as opposed to in solution. However, it was unknown whether or not the large trimetallic, \([{(bpy)_2Ru(dpp)}_2RhBr_2]^{5+}\), cations would diffuse at all after the initial ion-exchange process into Nafion®, as there is likely not a thermodynamic difference between different exchange sites in the membrane. In order to verify whether or not diffusion of the trimetallic, \([{(bpy)_2Ru(dpp)}_2RhBr_2]^{5+}\), complex was occurring in Nafion® membranes, two different methods were used to test for the diffusion.

The first was a “drop method” where a drop of a solution of the trimetallic, \([{(bpy)_2Ru(dpp)}_2RhBr_2]^{5+}\), complex in DMF was placed on top of a DMF-swollen Nafion® film and allowed to equilibrate over time. The fact that the trimetallic, \([{(bpy)_2Ru(dpp)}_2RhBr_2]^{5+}\), complex is highly colored and the Nafion® film is colorless allowed for the diffusion process to be followed visually. Figure 3.30 clearly demonstrates the diffusion process occurring with time. The initial drop placed on the film is shown in Figure 3.30a, before the ion-exchange
process occurred. Figure 3.30b shows the film after it was allowed to equilibrate for 30 days. The complex diffused some but is clearly still localized in the area where the initial drop was located. This evidence suggests that the complex diffuses through the Nafion® relatively slowly after the initial ion-exchange process. This is likely due

Diffusion of the trimetallic, \([\{(bpy)_{2}Ru(dpp)\}_{2}RhBr_{2}\}]^{5+}\), complex through a Nafion® membrane was further demonstrated with a second method, by submerging a portion of a DMF-swollen Na⁺-form Nafion® in a small volume of trimetallic, \([\{(bpy)_{2}Ru(dpp)\}_{2}RhBr_{2}\}]^{5+}\), complex solution in DMF. Figure 3.31a depicts the initial exchange of the trimetallic, \([\{(bpy)_{2}Ru(dpp)\}_{2}RhBr_{2}\}]^{5+}\), complex in DMF with a colorless piece of Na⁺-form of Nafion® submerged in part of the solution, following 24 h of exchange. There are significant portions of the Nafion® film that remain colorless after the initial exchange process. After about 1.5 years (600 d), the Nafion® film has some color throughout the entire membrane. There is an observable gradient throughout the film in Figure 3.31b, where the portion that was submerged in the trimetallic, \([\{(bpy)_{2}Ru(dpp)\}_{2}RhBr_{2}\}]^{5+}\), solution has the darkest color, which progressively becomes lighter as the distance increases from the area where the initial ion-exchange occurred. The change in the intensity of the color is indicative of a concentration gradient of the trimetallic, \([\{(bpy)_{2}Ru(dpp)\}_{2}RhBr_{2}\}]^{5+}\), complex throughout the Nafion® film.
Figure 3.30 a) DMF swollen Na\textsuperscript{+}-form of Nafion\textsuperscript{®} with a drop of a trimetallic, [{(bpy)}\textsubscript{2}Ru(dpp)}\textsubscript{2}RhBr\textsubscript{2}\textsuperscript{5+}, complex solution in DMF placed on top of the film. b) after 30 d

The qualitative experiments presented in Figure 3.30 and Figure 3.31 demonstrate that the trimetallic, [{(bpy)}\textsubscript{2}Ru(dpp)}\textsubscript{2}RhBr\textsubscript{2}\textsuperscript{5+}, complex diffuses throughout the surface of a Nafion\textsuperscript{®} membrane with time. Although a diffusion constant is unknown, it can be determined that the diffusion process is very slow, taking years for the complexes to reach an equilibrium fully diffused state in the membrane. If diffusion of the trimetallic, [{(bpy)}\textsubscript{2}Ru(dpp)}\textsubscript{2}RhBr\textsubscript{2}\textsuperscript{5+}, complex is desirable, an external bias may need to be applied to promote migration of the complex on a reasonable time scale for practical applications.
Figure 3.31 a) initial trimetallic, \([\{\text{bpy}\}_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^{5+}\), complex solution in DMF with a portion of a piece of DMF swollen Na\(^{+}\)-form Nafion\(^{®}\) submerged in the solution. b) after 24 h c) after 600 d.

3.3.3.5 Ion-exchange with Ru(II),Rh(III),Ru(II) Complexes and Reduced Ru(II),Rh(I),Ru(II) complexes with \(\text{Ph}_2\text{phen}\) terminal ligands

The Ru(II),Rh(III),Ru(II) complexes are considered a “pre-catalyst” for the actual \(\text{H}_2\) production catalysis. The catalyst is activated via a two-electron photoreduction of the Rh(III) to Rh(I), inducing a geometry change from octahedral to square planar and loss of the labile halide ligands.\(^{29,81,85,87}\) Following halide loss, there are open coordination sites available for the oxidative addition of water. Upon labialization of the halide, it is unlikely that the halide re-coordinates to the Rh(III) following Rh oxidation to propagate the catalytic cycle. The species coordinating to the complex following reoxidation likely depends on the environment the complex is in. In aqueous environments the species coordinating to the Rh is likely \(\text{OH}^−\). Considering that the geometry change from octahedral to square planar likely creates a change in the dimensions of the complex, and the Nafion\(^{®}\) ionic aggregates could be constricting to this
change in dimensions, it was important to verify that the reduced metal complex could be encompassed inside of the Nafion® ionic aggregates after the geometry change.

The most efficient hydrogen production catalyst reported by the Brewer Group is the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex (Scheme 3.5). One possible reason for the superior performance of the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex is the steric protection provided by the bulky Ph₂phen terminal ligands on the Ru metals. These bulky ligands may also make the change in dimensions of the complex from octahedral to square planar upon reduction to, [{(Ph₂phen)₂Ru(dpp)}₂Rh]⁵⁺ (Scheme 3.6) more dramatic. Therefore, it is reasonable to assume that if the reduced form of the bulkiest trimetallic, Ru,Rh,Ru hydrogen production catalyst is able to fit inside of the Nafion® ionic aggregates, the other, less bulky catalysts should be an appropriate size for incorporation in the aggregates.

Since the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex with Ph₂phen terminal ligands is larger than the trimetallic, [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex with bpy terminal ligands, it was necessary to verify that the complex would undergo ion-exchange with the Nafion® membrane before relevant information involving the incorporation of the reduced complex could be assessed. The ion-exchange of the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex was verified by adding a colorless, transparent Nafion® film to a solution of the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex in DMF. The ion-exchange was verified by electronic absorbance and the observation that the colorless Nafion® membrane became highly colored upon ion-exchange with the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex (Figure 3.32).
Scheme 3.5 Chemical structure of the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex. With two Ru(II) chromophores containing 4,7-diphenyl-1,10 phenanthroline (Ph₂phen) terminal ligands and bis(2-pyridyl)pyrazine (dpp) bridging ligands which are coordinated to a central electron collecting Rh(III) center, which is also coordinated to two Br⁻ ligands.

Scheme 3.6 Chemical structure of the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂Rh]⁵⁺, complex following a two-electron reduction at the Rh center (Rh(III)→Rh(I)), resulting in a geometry change from octahedral to square planar and a loss of the halide ligands. Due to the loss of the negatively charged halides, the overall charge of the complex is not altered.
Figure 3.32 Na⁺-form Nafion® membrane after ion-exchange with the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex. Na⁺-form Nafion® is a colorless, transparent membrane and the intense purple color observed serves as verification for ion-exchange of the Na⁺ ion for the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, ion.

The ion-exchange of the reduced trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂Rh]⁵⁺, complex was examined by electrochemically reducing a solution of the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex in DMF at -1.00 V vs. NHE. The Na⁺-form Nafion® membrane was added to the electrochemically reduced solution of the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂Rh]⁵⁺, complex. After allowing the solution to equilibrate for 12 h with the applied potential, the concentration of the solution remained unchanged based on the electronic absorbance. Surprisingly, based on previous experiments (Figure 3.28), the Nafion® film did not have a color change associated with ion-exchange of SO₃⁻ sites available on the surface of the film.

Since the initial ion-exchange process is assumed to be initiated by an electrostatic attraction between the cationic Ru,Rh,Ru trimetallic complexes and the anionic Nafion® membrane, it was hypothesized that the applied negative potential from the electrode may have interfered with the ion-exchange process between the trimetallic, [{(Ph₂phen)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex and the Nafion® membrane. To verify this theory, the
experiment investigating the ion-exchange of the reduced trimetallic,
[\{(\text{Ph}_2\text{phen})_2\text{Ru(dpp)}\}_2\text{Rh}]^{5+}, complex was modified and repeated. Instead of applying -1.00 V vs. NHE during the exchange process, the potential was turned off and Ar gas was bubbled through the solution to prevent the complex from oxidizing. After allowing the solution to equilibrate for 12 h, there was a significant decrease in the electronic absorbance and a color change to the film was observed, consistent with exchange of the \[{(\text{Ph}_2\text{phen})_2\text{Ru(dpp)}}\]_2\text{Rh}]^{5+} complex into the Nafion® membrane. This confirmed that the applied potential interfered with the ion-exchange process. Additionally the experiment established that the reduced trimetallic, \[{(\text{Ph}_2\text{phen})_2\text{Ru(dpp)}}\]_2\text{RhBr}_2]^{5+}, complex was readily exchanged with the ionic aggregates of the Nafion® membrane.

The exchange of the \[{(\text{Ph}_2\text{phen})_2\text{Ru(dpp)}}\]_2\text{Rh}]^{5+} complex was inhibited by the addition of an applied negative potential. It is likely that the columbic attraction between the Nafion® and the \[{(\text{Ph}_2\text{phen})_2\text{Ru(dpp)}}\]_2\text{Rh}]^{5+} complex was overcome by the columbic attraction of the complex to the electrode surface, caused by the applied negative potential. This columbic attraction between the \[{(\text{Ph}_2\text{phen})_2\text{Ru(dpp)}}\]_2\text{Rh}]^{5+} complex and Nafion® could be explored further by varying the applied potential and measuring the degree of ion-exchange by electronic absorbance.

3.3.4 Effect of Solvent-swelling on Scattering Profiles of Nafion®

Since DMF swells Nafion® to 100% of the dry volume, it is rational to determine whether or not the ionic aggregates in Nafion® swell to the same degree as the bulk film (affine swelling). SAXS was used to deduce how solvent swelling affects the dimensions of the ionic aggregates in
Nafion®. DMF and CH₃CN swollen Na⁺-form Nafion® films were compared to films of dry Na⁺-form Nafion® and Nafion® that had undergone ion-exchange with monometallic, [(bpy)₂Ru(dpp)]²⁺, and trimetallic, [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺, complexes (Figure 3.33).

Bragg’s law was used to determine relative real-space dimensions of the ionic aggregates with Equation 3.5 for the DMF swollen Nafion® film. The qₘₐₓ for the DMF swollen Na⁺-form Nafion® membrane corresponds to a d value of 4.1 nm. Since the qₘₐₓ for the dry film corresponds to a d value of 3.5 nm (q = 1.8) (Figure 3.22), which corresponds to 17% swelling, and Nafion® membranes swell to 100% of the dry volume, it appears that Nafion® does not exhibit affine swelling when swollen with DMF.

\[ d = \frac{2\pi}{q} \]  

Equation 3.5
Figure 3.33 SAXS profile of Na⁺-form Nafion® film swollen with DMF, compared to the scattering profiles of dry Na⁺-form Nafion®, and Nafion® that has undergone ion-exchange with the monometallic, [(bpy)₂Ru(dpp)]²⁺, and trimetallic, [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺, complexes.

3.3.5 Ion-Exchange with PFCB/PVDF Blend

A blend of perfluorocyclobutane ionomer (PFCB)/polyvinylidene copolymer (PVDF) (Scheme 3.7) have, like Nafion®, been explored for applications in proton exchange membranes.²³⁶ Ion-exchange of the polymer blend with cationic Ru(II) polypyridyl complexes was explored to aid in the characterization of the morphology of the ionomer blend.²³⁶ The ionic aggregates of the PFCB/PVDF blend are suggested to be ~2.4 nm in diameter (Figure 3.34), as evidenced by SAXS analysis.²³⁶
Scheme 3.7 Structure of Perfluorocyclobutane Ionomer (PFCB)/Polyvinylidene copolymer (PVDF) blend.

Figure 3.34 Representation of possible PFCB/PVDF morphology. Image copied.236
The PFCB/PVDF ionomer blend was allowed to equilibrate with a solution of monometallic, \([(\text{bpy})_2\text{Ru(dpp)}]^2^+\), and a solution of trimetallic, \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5^+}\), complexes. Electronic absorbance was used to determine the final and initial concentrations of the metal complex solutions. The monometallic, \([(\text{bpy})_2\text{Ru(dpp)}]^2^+\), complex was completely absorbed into the PFCB/PVDF film. The colorless solution and a highly colored film can be seen in Figure 3.35a. For the trimetallic, \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5^+}\), complex there is no observable change in the metal complex concentration of the solution based on electronic absorbance. The film, however, has a slight color change (Figure 3.35c), indicating that some interaction with the metal complex is taking place. The trimetallic, \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5^+}\), solution retained the initial purple color, however the film appeared to have a different color, more similar the color of the monometallic, \([(\text{bpy})_2\text{Ru(dpp)}]^2^+\), complex, seen at the bottom of the vial in Figure 3.35b.

The observed difference in color between the PFCB/PVDF film and the starting trimetallic, \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5^+}\), solution is not irrefutable verification and further experimentation is required in order to determine the ion-exchange processes occurring between the trimetallic, \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5^+}\), and/or the monometallic, \([(\text{bpy})_2\text{Ru(dpp)}]^2^+\), complexes in the system. One possible explanation for the observed color change in the PFCB/PVDF film is that, similar to the trimetallic, \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5^+}\), complex and Nafion® in CH₃CN, the trimetallic, \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5^+}\), complex has undergone exchange with surface SO₃⁻ groups. Another hypothesis is that monometallic, \([(\text{bpy})_2\text{Ru(dpp)}]^2^+\), impurities from the synthesis of the trimetallic, \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5^+}\), complex undergo ion exchange with the PFCB/PVDF membrane, thus purifying the trimetallic.


\[ \{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^{5+} \], complex through a size exclusion process. These possibilities could be either confirmed or refuted by performing experiments with mixtures of monometallic, \[(\text{bpy})_2\text{Ru(dpp)}\]^{2+}, and trimetallic, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^{5+} \], complexes and measuring electronic absorbance at different wavelengths, as described on page 105.

These preliminary results with the PFCB/PVDF blend indicate that unlike Nafion®, the monometallic complex, \[(\text{bpy})_2\text{Ru(dpp)}\]^{2+}, is more readily exchanged into the blend than the larger trimetallic complex, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^{5+} \]. This behavior indicates that the ionic domains of the PFCB/PVDF blends are less accommodating to the trimetallic, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2]^{5+} \] complex, which is consistent with the smaller proposed dimensions of the ionic aggregates of the PFCB/PVDF blend (Figure 3.34) compared to the proposed ionic aggregate dimensions in Nafion® membranes (Figure 3.1). This study shows that it is feasible to use the ion-exchange of these trimetallic complexes to compare the dimensions of ionic aggregates.
Figure 3.35 Solution of monometallic, $[(bpy)_2Ru(dpp)]^{2+}$ a) and trimetallic, $[(bpy)_2Ru(dpp)\cdot 2RhBr]^{5+}$ b) in methanol after ion exchange with PFCB/PVDF 70:30 wt/wt blend. c) PFCB/PVDF 70:30 wt/wt blend film after exposure to a trimetallic $[(bpy)_2Ru(dpp)\cdot 2RhBr]^{5+}$ solution.

3.4 References


(125) Yao, G. J.; Onikubo, T.; Kaneko, M. Photoresponsive bilayer membranes composed of tris(2,2'-bipyridine)ruthenium(2+) and methylviologen-containing layers sandwiched between ITO electrodes. *Electrochim. Acta* 1993, 38, 1093-1096.


Chapter 4. Hydrogen Production and Electrochemistry with Ru,Rh,Ru Trimetallic Complexes and Nafion®

4.1 Introduction

Nafion® is perhaps best known as a proton exchange membrane for fuel cell applications. The ionomer has also been used as a separator membrane for cation transport in electrocatalytic cells. Additionally, and particularly relevant to this study, Ru(bpy)$_3^{2+}$ supported in Nafion® for polymer modified electrodes has been the subject of significant interest. These studies provide a basis for the study of electron transport properties in Nafion® membranes.

The electrochemistry in polymer-modified electrodes can be significantly altered compared to solution state properties. One significant difference between the electrochemistry of Ru(bpy)$_3^{2+}$ in a Nafion® polymer modified electrode in comparison to the solution state is the difference between the anodic and cathodic peak values for reversible couples ($\Delta E_p$). In a Nafion® film, $\Delta E_p$ for the reversible Ru(bpy)$_3^{2+}$/Ru(bpy)$_3^{3+}$ couple is 120-170 mV, opposed to a $\Delta E_p$ near 59 mV observed in the solution state. This large peak separation that deviates from the 59 mV separation (Equation 4.1) can be attributed to differences in the apparent diffusion of the Ru(bpy)$_3^{2+}$ vs. Ru(bpy)$_3^{3+}$. The apparent diffusion is attributed to a combination of the Ru(bpy)$_3^{2+}$/Ru(bpy)$_3^{3+}$ mass transport to the electrode surface through the Nafion® ionic aggregates, “electron hopping” electron transfer events, and counter ion migration. The apparent diffusion coefficients for the Ru(bpy)$_3^{2+}$ ($D_2$) and Ru(bpy)$_3^{3+}$ ($D_3$) are on the order of $10^{-9}$ cm$^2$/s, the exact rate of these coefficients varied between...
experiments and were accepted as an order of magnitude value, however, between experiments the ratio was consistent with $D_2/D_3 \approx 2.197$. The apparent diffusion is dependent on the oxidation state of the Ru(bpy)$_3^{2+}$/Ru(bpy)$_3^{3+}$ complex. This result suggests that the molecule diffuses through the anionic aggregates faster when it is in the $+2$-oxidation state as opposed to the $+3$-oxidation state.

$$\Delta E_p = \frac{0.059}{n} V$$  \hspace{1cm} \text{Equation 4.1}$$

The apparent diffusion is independent of the loading concentration and whether the complex was loaded prior to casting the film on an electrode, or loaded after the casting process.$^{108}$ This result is significant for the preparation of polymer modified electrodes considering there are significant advantages to loading the complex prior to the casting process. These advantages include more careful control over the concentration of complex : $\text{SO}_3^- \text{ ratio};$ and elimination of loading complications after casting, such as the need for a high swelling solvent.

Furthermore, it was found that the amount of electroactive species was increased in cases where the Nafion$\textsuperscript{®}$-modified electrode was used, compared to bare electrodes under the same conditions.$^{108}$ Therefore, for electrocatalytic purposes, the concentration of a catalyst at an electrode surface can be increased by loading the complex in a Nafion$\textsuperscript{®}$ membrane that is cast on an electrode surface. This knowledge has led to the application of Nafion$\textsuperscript{®}$ membranes for electrocatalysis.$^{204}$

Nafion$\textsuperscript{®}$/\{$(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\}^{5+}$ modified high surface area electrodes were developed in order to perform photocatalytic experiments without the added complication of a
molecular sacrificial electron donor. Linear sweep voltammetry, bulk electrolysis and bulk photoelectrolysis experiments over very long times were performed in order to better understand how the interactions between the trimetallic, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\]^{5+}\) and Nafion® membrane affected photocatalytic hydrogen production.

4.2 Experimental

4.2.2 Materials

Fluorine doped tin oxide (FTO) coated glass slides Resistivity (8 Ω/square), cut into \(\approx 2 \times 2\) cm squares, from Sigma Aldrich, hydrophilic polyethylene frits from Applied Separations Inc. Glassy carbon rods (6 mm) diameter were purchased from VWR International. Monosodium phosphate, disodium phosphate, tetrabutylammonium hexafluorophosphate, tetrabutyl ammonium hydroxide and sodium hydroxide from Sigma Aldrich. Isopropyl alcohol, methanol, ethanol and nitric acid from Fisher Scientific. Spectrophotometric DMF and CH$_2$CN from Alfa Aesar. Nafion® 117 from DuPont.

4.2.3 Metathesis to \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\]Br$_5$\)

The \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\](PF$_6$)$_5$ complex was metathesized to the water soluble \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\]Br$_5$ complex by dissolving 100 mg of the \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\](PF$_6$)$_5$ complex in a minimum amount of CH$_3$CN (\(\sim 5\) mL). The solution was added dropwise to \(\sim 100\) mL of a saturated aqueous solution of TBABr. The
precipitate was collected on a fritted glass funnel, rinsed with EtOH, followed by Et₂O then dried in an oven at 50 °C overnight.

4.2.4 Electrode Preparation

4.2.4.1 Nafion® “Solution”

Nafion® 117 (DuPont) was cleaned by refluxing in 8 M nitric acid for 1-2 h, followed by a H₂O rinse and refluxing in H₂O for ~1 h. Films were dried in a vacuum oven at 90 °C for ~12 h. Neutralization to the Na⁺-form or TBA⁺ (tetramethylammonium)-form of Nafion® was achieved by allowing the Nafion® to equilibrate in either a 1 M NaOH, or 1 M tetrabutylammonium hydroxide (Bu₄NOH) solution respectively for ~24 h, followed by a H₂O rinse and reflux in H₂O for ~1 h to remove excess NaOH or Bu₄NOH. Following the conversion, the films were dried overnight in a vacuum oven at 90 °C. Approximately 7 g of the dry Nafion® was added to 300 mL of solvent, 1:1 H₂O:EtOH for the Na⁺-form Nafion® and 4:3:3 H₂O:MeOH:IPA for the TBA⁺-form Nafion®. Nafion® suspensions were formed by heating in a Parr Bomb at 250 °C and 1100 PSI for 2 h. The suspensions were filtered through 6 millipore filter paper and the wt % was determined by drying three 1 mL aliquots of the suspension in a vacuum oven at 90 °C overnight and monitoring the change in mass before and after the drying process. The average film thickness of modified electrodes following casting was calculated from these values.

4.2.4.2 FTO/Nafion® Modified Electrodes

The FTO/Nafion® modified electrodes were prepared by first measuring the dimensions to ensure a consistent surface area for all of the electrodes. Teflon tape was wrapped around the
slide to separate an area for electrical contact. With the Teflon tape as a guide, a needle was used to apply a small line of silicone caulk to act as a barrier for the casting solution (Figure 4.1a). The caulk was allowed to dry for at least 12 h. The Teflon tape was removed once the caulk was dry. A mixture of TBA⁺-form and Na⁺-form Nafion® “solution” (4.5 wt %) was mixed at a 1:1 volume ratio with DMF. For electrodes containing metal complex, the complex was dissolved in DMF, with the concentration monitored by electronic absorbance prior to mixing with the Nafion® solution. If the [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺ complex is not dissolved in DMF prior to mixing with the Nafion® solutions, the complex will not dissolve in the Nafion® suspension. An aliquot of 1.00 mL of the solution was slowly and carefully added on top of the FTO coated glass slide, with the silicone caulk barrier, positioned in a foil tray on an isotherm hot plate. The temperature was slowly raised to 80 °C (over ~30 min). The temperature was then held at 80° C until it appeared as if most of the solution had evaporated. Then, the temperature was raised to 200 °C and held for ~ 10 min. The electrode was allowed to cool to room temperature slowly. The silicone caulk was peeled off immediately upon cooling to room temperature. A piece of polyethylene frit that was cut to the size of the Nafion® coating was attached to the FTO slide by tying it on with a monofilament polyamide cord.

(a) Silicone Caulk Teflon tape
(b) Bare FTO Nafion/complex

Figure 4.1 Representation of an FTO/Nafion® modified electrode a) preparation method to leave part of the electrode exposed for electrical contact b) final modified electrode.
4.2.4.3 Nafion® Modified Glassy Carbon Electrodes

Pieces of 6 mm diameter glassy carbon rods were cut to ~ 1 cm in length and sanded with 400 grit, then 600 grit, and finally 1200 grit sandpaper before polishing with alumina. Solutions containing varying ratios of TBA⁺-form or Na⁺-form Nafion® solution and [(bpy)₂Ru(dpp)]₂RhBr₂]⁵⁺ in DMF were prepared. The glassy carbon rods were placed vertically in an alumina block with holes drilled in it on a hot plate, 6 µL aliquots of the Nafion®/[{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺ mixtures were placed on the end of the glassy carbon rods (Figure 4.2). The temperature was increased slowly, over ~ 30 min to 80 °C, if most of the solution had not evaporated, the temperature was left at 80 °C until it appeared that most of the solution was gone. Finally, the temperature was increased to 200 °C for ~10 min. The glassy carbon piece was attached to a hollow glass tube with heat shrinkable Teflon and a drop of Hg was added for electrical contact. A Cu wire was added and the tube, which was sealed with a small septum. The glassy carbon pieces could be removed and recycled. The Nafion® was removed by delamination, caused by swelling the film in DMF, the polishing process was repeated before reuse.
Figure 4.2 Representation of the process for casting Nafion® on glassy carbon rods. The glassy carbon rod was secured in an aluminum block, the Nafion® “solution” was added to the top of the rod.

4.2.4.4 Stability of [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$_{5+}$ at Casting Temperatures

The stability of the [{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$_{5+}$ complex with Nafion® solutions at casting temperatures was examined by preparing two 10 mL solutions of equal concentrations and solvent composition (10:4:3:3 DMF:H$_2$O:MeOH:IPA). One solution contained a 2.5 wt% TBA$^+$ Nafion® suspension. The electronic absorbance and emission of the solutions was measured before and after the thermal treatment for casting was performed with the solutions. The screw caps on the scintillation vials were loosely attached to prevent pressure build up and to hinder solvent loss. Electronic Absorbance was measured with Hewlett-Packard 8452A diode array spectrophotometer (2 nm resolution). Emission was measured with Quanta Master Model QM-200-45E from Photon Technologies International Inc. The excitation source was a 150 W Xe-Arc lamp and the spectra were detected with a thermoelectrically cooled Hamamatsu 2650 photomultiplier tube. The detector is $90^\circ$ from the excitation source. All solutions were
absorbance matched at the excitation wavelength prior to the emission experiments, and the slit widths were not adjusted between measurements.

4.2.5 Electrochemistry

4.2.5.1 Hydrogen Detection

Hydrogen was detected quantitatively with a HY-OPTIMA™ 700 in-line solid state H₂ sensor. The sensor was calibrated by injecting known volumes of H₂ gas into a cell purged with Ar and containing the same volume of electrolyte solution used during the electrolysis experiment with stirring. A calibration was performed periodically by creating a calibration curve, plotting the injected H₂ volume against the % H₂ reading from the sensor (Figure 4.3). A USB serial port was used for communication between the sensor and the computer. Hydrogen production was confirmed qualitatively with a GOW-MAC 580 gas chromatograph equipped with 1/8 in × 6 ft column with 5 Å molecular sieves and a rhenium-tungsten thermal conductivity detector, with the current set to 100 mA. Ultra high purity Ar was used as the carrier gas at ~2 mL/min. The injector was set to 130 °C, the oven was set to 55 °C, the detector was set to 100 °C.
Figure 4.3 Representative calibration curve for the hydrogen sensor after injecting known volumes of H₂.

4.2.5.2 Bulk Electrolysis Cell

Thomas Wertalik built the electrolysis cell in the Virginia Tech Chemistry glass shop (Figure 4.4). The side of the cell designed to house the H₂ sensor was equipped with a ground glass lid in which the H₂ sensor, reference electrode and working electrode could fit. The ground glass lid was added so the large FTO electrode could fit inside the cell. Since Nafion® is an ion-conducting membrane and Nafion® has been used as a separator for electrolysis cells, it is unnecessary to include a fritted glass separator. The reference electrode housing was also built in the glass shop and designed to fit in a ground glass port in the lid of the electrolysis cell. The electrode housing was equipped with a vycor tip and filled with a 3M NaCl solution, a Ag wire was added to complete Ag/AgCl reference electrode.

The experiment was set up by first equipping the cell with the FTO working electrode and Pt mesh counter electrode. The reference electrode fitting was plugged with a ground glass stopper. The cell was purged with Ar for 20-30 minutes. Next, the H₂ sensor was turned on and
allowed to “warm up.” The indicator light on the sensor changed from orange to green when the sensor was ready. The baseline reading is typically very high at this point and it is necessary to activate the sensor to acquire a baseline reading. Next, the sensor was activated by injecting H₂ into the cell and allowing the sensor to equilibrate for 20-30 min. Afterwards, the cell was purged with Ar again until the baseline was sufficient, ideally below 1%. Next, the reference electrode was added to the cell, by turning up the Ar flow to impede air from entering the cell while the ground glass stopper was removed. Carefully and swiftly, to avoid pressure build up and to prevent air from entering the cell, the reference electrode was positioned in the fitting while turning the Ar flow down. The vent lines remained intact in order to prevent pressure build-up while the electrolysis solution was added. An Ar purged solution was added, by syringe-full to the electrolysis cell, while carefully monitoring the volume of solution added. At this point the experiment is ready to begin.

Figure 4.4 Bulk electrolysis cell schematic.
4.2.5.3 Potentiostats

A PAR (Princeton Applied Research) 2273 Potentiostat/galvanostat was used for all of the bulk electrolysis, linear sweep and cyclic voltammetry experiments with modified electrodes. Cyclic voltammetry and linear sweep voltammetry experiments were performed with the prepared FTO electrodes and glassy carbon electrodes, a Ag/AgCl reference electrode and a Pt wire counter electrodes. The electrolysis solutions were all purged with Ar and a background measurement of the electrolyte solution was taken with either a Pt disc, or Glassy carbon disk working electrode. The NaBr CV was performed with BASi Epsilon Potentiostat with a Pt disc working electrode, Ag/AgCl reference electrode and a Pt wire auxiliary electrode and 0.1 M Phosphate buffer in H$_2$O. All Nafion$^\circledR$ modified electrodes were allowed to equilibrate in the appropriate electrolyte solution for at least 24 h prior to the start of the experiment.

4.2.5.4 Spectroelectrochemistry

The spectroelectrochemistry of the Nafion$^\circledR$/[{(bpy)$_2$Ru(dpp)}$_2$RhBr$_2$]$^{5+}$ FTO modified electrode was monitored by reflectance spectroscopy of the electrode with a Hitachi 4100 UV-Vis-NIR. The electrode was periodically removed from the electrolysis solution, the reflectance was measured and the electrode was returned to the electrolysis solution to continue the electrolysis process. In the solution state, the cell shown in Figure 3.17 was used and electronic absorbance measurements were performed every minute with a Hewlett-Packard 8452A diode array spectrophotometer (2 nm resolution) until the bulk electrolysis was complete and the spectrum no longer changed.
4.3 Results and Discussion

4.3.1 Ru,Rh,Ru Stability at Casting Temperatures

Loading the large trimetallic, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\}^{5+}\), complex onto either glassy carbon or FTO electrodes after Nafion® had been cast on the electrode was not successful. The ion-exchange of the large trimetallic, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\}^{5+}\), complex requires a high-swelling solvent such as DMF. Since DMF swells the Nafion® film to 100% of the starting volume, the film swells to the point where it delaminates from the electrode before the ion-exchange process is completed.

Fortunately, it has been demonstrated that the electrochemical properties of Ru(bpy)_3^{2+} on Nafion® modified electrodes were not affected by whether or not the Ru(bpy)_3^{2+} was loaded on the electrode before or after the casting process. This evidence suggests that the electrochemical properties of Nafion® modified electrodes with the trimetallic, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\}^{5+}\), complex would not be significantly affected by performing the ion-exchange process prior to the casting process. A concern with using this method for fabricating Nafion®/\([\{(bpy)_2Ru(dpp)\}_2RhBr_2\}^{5+}\) modified electrodes was the necessity of thermal processing in order to form the semicrystalline backbone to maintain the insolubility and mechanical integrity of the Nafion® membrane.

The thermal stability of the trimetallic, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\}^{5+}\), complex was verified with and without the presence of Nafion®. Two solutions of the trimetallic, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\}^{5+}\), complex were prepared, one with suspended Nafion®, and one without. The thermal treatment performed during the casting process was performed on both of
the solutions and the emission and electronic absorbance of the solutions was monitored before and after the thermal treatment. The emission spectroscopy of the solutions before and after the thermal treatment are shown in Figure 4.5 and compared to the emission spectrum of the monometallic, [(bpy)$_2$Ru(dpp)]$^{2+}$, complex. There is a significant increase in the emission intensity of the monometallic complex in the solution that did not contain the Nafion$^\text{®}$ suspension, while the emission of the solution that did contain Nafion$^\text{®}$ had a very slight increase in the emission intensity that could be attributed to solvent loss following the thermal treatment. Furthermore, Figure 4.6a demonstrates a definite difference in the electronic absorbance of the solution without Nafion$^\text{®}$ following the thermal treatment. It can be seen in Figure 4.6b that the shape of the electronic absorbance following the thermal treatment in the presence of Nafion$^\text{®}$ is very similar to the absorbance prior to heating. The differences in the absorbance spectra can be attributed to scattering from the Nafion$^\text{®}$ solution since some solvent was lost during the thermal treatment.
Figure 4.5 Emission spectra of the monometallic, \( [(bpy)_2Ru(dpp)]^{2+} \), complex (●) compared to the emission of the \( [(bpy)_2Ru(dpp)]_2RhBr_2\)\(^{5+}\), complex (purple) before and after thermal treatment with (■) and without (●) the presence of a Nafion\(^*\) suspension. Excited at 450 nm in deaerated solutions.

Figure 4.6 Electronic absorbance of the trimetallic, \( [(bpy)_2Ru(dpp)]_2RhBr_2\)\(^{5+}\), complex a) without Nafion\(^*\) before (purple) and after the thermal treatment (red) b) with Nafion\(^*\) before (black) and after (green) the thermal treatment.
Thermogravimetric analysis (TGA) was used to further investigate the thermal stability of the trimetallic \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+} complex in solid Nafion® membranes. There was ~3% trimetallic, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}, by mass in the \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+} loaded Nafion® films. The thermal degradation of the Nafion® films are shown in Figure 4.7. The thermal degradation of the trimetallic, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}, loaded Nafion® membranes does not demonstrate a difference in degradation between the films loaded with trimetallic, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}, complex and the TBA⁺-form of Nafion®. There is a difference in the TGA of the cast films compared to the as-received films, however there is not a significant difference between the films containing the trimetallic complex, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}, compared to Nafton® with TBA⁺. Based on the TGA, it appears as if the trimetallic complex, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+} is thermally stable regardless of the presence of the Nafton® membrane. However, it is important to note that the decomposition of the trimetallic complex \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}, to form the monometallic complex, \[(bpy)\text{Ru(dpp)}\]^{2+}, would not result in a mass loss and would not be observed by TGA.

Regarding the emission and electronic absorbance experiments of the \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+} complex, it is apparent that the thermal degradation of the trimetallic complex, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}, to form the monometallic complex, \[(bpy)\text{Ru(dpp)}\]^{2+}, is hindered in the Nafion® membrane. In the Nafton® suspension, the ionic –SO₃⁻ groups likely form inverse micelle type clusters around the trimetallic, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}, complex (Figure 4.8), effectively protecting the complex from thermal degradation. This evidence demonstrates that it is reasonable to cast the trimetallic, \[\{(bpy)_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+},
complexes with the Nafion® membrane without significant thermal degradation of the Ru,Rh,Ru complex.

**Figure 4.7** Thermogravimetric analysis of the TBA⁺-form Nafion® (black), and the trimetallic, [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex (purple) and the trimetallic, [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺, complex in Nafion® after various loading processes including ion exchange with a TBA⁺-form Nafion® 117 membrane (orange), casting with from a Nafion® suspension following ion exchange (blue) and a cast Nafion® membrane following a bulk electrolysis experiment (green). The full thermal analysis (a), zoomed on the initial mass loss (b).
4.3.2 Linear Sweep of Cyclic Voltammetry of \([\{(bpy)\_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}/Nafion® Modified Electrodes

Glassy carbon electrodes with Nafion® film thicknesses varying from 5 µm to 30 µm were prepared with \([\{(bpy)\_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+} loaded in the Nafion® membranes at varying concentrations of \([\{(bpy)\_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}. The electrochemical analysis of the \([\{(bpy)\_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+} complex on glassy carbon electrodes proved to be particularly challenging. In low solvent swelling conditions (CH₃CN with 0.1 M Bu₄NPF₆), the electrochemistry of the \([\{(bpy)\_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+} loaded Nafion® modified electrodes appeared identical to the Na⁺-form Nafion® and TBA⁺-form Nafion® membranes. It is important to note that it was possible to qualitatively reproduce previously published results with Ru(bpy)₃²⁺ under these conditions.¹⁰⁶,¹⁰⁸ Although it is expected that there would be some differences in the apparent diffusion of the \([\{(bpy)\_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+} complex, similar to that of Ru(bpy)₃²⁺,¹⁰⁶,¹⁰⁸ it was anticipated that a CV in the Nafion® membrane would somewhat represent the CV obtained in the CH₃CN solution (Figure 4.9).
Figure 4.9 Cyclic voltammogram of \([\{(bpy)\_2Ru(dpp)\}_2RhBr_2\]^{5+}\) with 0.1 M Bu\(_4\)NPF\(_6\) in CH\(_3\)CN. Scan rate =100mV/s.

The absence of observable electrochemical features of the \([\{(bpy)\_2Ru(dpp)\}_2RhBr_2\]^{5+}\) on Nafion\(^\text{®}\) modified electrodes in CH\(_3\)CN electrolyte solutions could be attributed to the low degree of Nafion\(^\text{®}\) swelling with CH\(_3\)CN solutions. Considering the ion-exchange behavior of the \([\{(bpy)\_2Ru(dpp)\}_2RhBr_2\]^{5+}\) complex with CH\(_3\)CN that we reported,\(^{235}\) it is reasonable to assume the apparent diffusion and particularly mass transport of the \([\{(bpy)\_2Ru(dpp)\}_2RhBr_2\]^{5+}\) complex in Nafion\(^\text{®}\) would be hindered in low-swelling CH\(_3\)CN solvents. Unfortunately, high swelling solvents, such as DMF swell the Nafion\(^\text{®}\) membrane so much that the film delaminates from the electrode, rendering the film useless for electrochemical analysis. Therefore, in an attempt to find a solvent swollen “middle ground” between the CH\(_3\)CN and DMF solvent swelling extremes, where the film would swell enough to allow for mass transport, but not enough to cause delamination from the electrode, phosphate buffered water solutions were prepared. Water swells Nafion\(^\text{®}\) 30\%, while DMF wells Nafion\(^\text{®}\) 100\% and CH\(_3\)CN swells Nafion\(^\text{®}\) 10\% of the dry volume (Equation 4.2).
\[
\text{Solvent Swelling} \% = \frac{100(V_{\text{wet}} - V_{\text{dry}})}{V_{\text{dry}}}
\]  \hspace{1cm} \text{Equation 4.2}

Upon performing cyclic voltammetry on Nafion®-modified glassy carbon electrodes in 0.1 M phosphate buffered solutions (pH = 7.00), the Nafion® films did not immediately delaminate from the electrodes, however after about 30 cycles the films delaminated before the appearance of any electrochemical couples attributed to the \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5+}\) complex observed in Figure 4.9. Although the electrochemical couples of \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5+}\), were not observed, there was a significant current increase as the potential approached the solvent window for water with the Nafion®/\([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5+}\) modified electrodes that was not observed for electrodes without the \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5+}\) complex. This current increase was attributed to the electrocatalytic water reduction current. FTO-modified Nafion® electrodes were prepared in order to increase the available surface area of the electrode. Linear sweep voltammetry was performed on the FTO/Nafion® modified electrodes with the \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5+}\) complex in the dark and under irradiation with a 470 nm LED; and compared with the voltammagrams of a TBA⁺-form Nafion® modified FTO electrode trimetallic, \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]\text{Br}_5\), complex dissolved in the phosphate buffer solution (Figure 4.10). The results indicate the onset of catalytic current for the \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5+}\) complex in Nafion® occurs before the onset of catalytic current for the \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]\text{Br}_5\) complex in solution. Furthermore, the difference between the light and dark current for the \([(\text{bpy})_2\text{Ru(dpp)})_2\text{RhBr}_2]^{5+}\) complexes in Nafion® was reversible,
although it took ~ 24 h for the current to return to the original “dark” current. The current enhancement upon irradiation with light indicates that the complex is behaving as a photocatalyst. There is also a current enhancement without the presence of light, which indicates that the complex may also be behaving as an electrocatalyst in the dark. The fact that the complex is behaving as both photocatalyst and electrocatalyst could explain why it takes 24 h for the current upon irradiation to return to the dark current.

Figure 4.10 Linear sweep voltammetry of a Na+ -form Nafion® membrane (black) 0.37µmol of [{(bpy)$_2$Ru(dpp)$_2$RhBr$_2$}]$^{5+}$ in 0.2 M phosphate buffer (pH = 7.00) (blue), with a Nafion® membrane in the dark (red), and after irradiating the same membrane with a 470 nm LED for 1 h (purple). All Nafion® membranes were cast for the Na+ -form Nafion® solution on an FTO electrode with a 2.5 cm$^2$ surface area, with an average film thickness of 30 µm. The [{(bpy)$_2$Ru(dpp)$_2$RhBr$_2$}]$^{5+}$ complex without Nafion® was performed with a 2.5 cm$^2$ surface area FTO electrode.

Analysis of the linear sweep experiments was used to determine the parameters for bulk photoelectrolysis experiments. In order to access the photoelectrocatalytic performance of the [{(bpy)$_2$Ru(dpp)$_2$RhBr$_2$}]$^{5+}$ complex in a Nafion® membrane, it was desirable to choose a
potential where there would be little water/proton electrolysis, yet where there was a difference between the observed light and dark currents. Furthermore, the concentration of $\text{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2^{5+}$ in Nafion® for bulk electrolysis was assessed using LSV experiments. A range of six concentrations of $\text{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2^{5+}$ in a Nafion® suspension from 1.0 - 3.0 mM were prepared and cast on FTO electrodes. LSV experiments were performed with irradiation from a 470 nm LED. The observed current increased with concentration, until a maximum of 2.0 mM. The decrease in current after the 2.0 mM maximum is attributed to saturation of light absorption by the $\text{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2^{5+}$ complex. Based on these results, bulk photoelectrolysis experiments were performed with an applied potential of $-1.0$ V vs. NHE and the FTO electrodes were cast from 2.0 mM $\text{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2^{5+}$ solutions. The 2.0 mM solutions corresponded to 0.37 µmol of $\text{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2^{5+}$ on the FTO electrode following the casting procedure.

### 4.3.3 Bulk Photocatalysis

Initially, bulk photocatalysis experiments were performed under these conditions at short times ($\leq 5$ h). The hydrogen production with the $\text{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2^{5+}$ complex in Nafion® under irradiation with a 470 nm LED was indistinguishable from the hydrogen production of the blank and the dark controls at these times. However, hydrogen production from a FTO Nafion®/$\text{(bpy)}_2\text{Ru(dpp)}_2\text{RhBr}_2^{5+}$ modified electrode that was reused after the initial bulk electrolysis experiment consistently produced more H₂ than the other electrodes.

Hydrogen production over much longer times is shown in Figure 4.11, the H₂ production for the initial bulk photocatalysis experiment is within error of the blank and dark experiments.
until around 150 h. Furthermore, the \( \text{H}_2 \) production of the films that were used a second time consistently performed better than the fresh films. This result suggests that there is a change occurring in the \( \{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2 \)\(^{5+}\) complexes during the first photoelectrolysis experiment, that promotes enhanced catalysis during the second photoelectrolysis. The efficiency of these experiments, based on coulometry from the potentiostat (Equation 5.2) is between .05 and 0.1.

**Figure 4.11** Hydrogen production via bulk electrolysis and bulk photoelectrolysis with an applied potential of \(-1.0\) V vs. NHE, 0.37\( \mu \)mol of \( \{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2 \)\(^{5+}\) cast on a 2.5 cm\(^2\) surface area FTO electrode from TBA\(^{-}\)-form Nafion\(^{\circledast}\) with an average thickness of \(-30\) \(\mu\)m in a 0.2 M phosphate buffer/H\(_2\)O solution (pH = 7.00), in the dark (black), with continuous irradiation from a 470 nm LED (purple) and upon reusing a film that had undergone one bulk photoelectrolysis under the same conditions with a fresh buffer solution (green).

In order to elucidate the change occurring in the Nafion\(^{\circledast}\) membrane during the photoelectrolysis process, the reflectance of the Nafion\(^{\circledast}\)/\( \{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2 \)\(^{5+}\) complex was monitored during a bulk photoelectrolysis experiment (Figure 4.12). As shown in the solution state (Figure 4.13), the MLCT \( \lambda_{\text{max}} \) blueshifts upon reduction of the complex, which occurs in less than 30 min. The MLCT \( \lambda_{\text{max}} \) of the \( \{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2 \)\(^{5+}\) in Nafion\(^{\circledast}\) also
blue shifted until about 160 h of the bulk electrolysis. Considering the drastically different chemical environments of the complexes in the solution state compared to the Nafion® membrane, it is difficult to ascertain any meaningful information about the shape of the reduced film compared to the solution-state reduction. Furthermore, there was a slight variation in film thickness throughout the FTO electrode that affects the intensity of the reflectance spectra. Regardless, this experiment demonstrates that the reduction of \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\] superscript 5+ in Nafion® occurs around the same time the increase in hydrogen production occurs.

**Figure 4.12** a) Reflectance spectra of a \([\{(bpy)_2Ru(dpp)\}_2RhBr_2\] superscript 5+ complex on an FTO electrode during bulk photoelectrolysis, normalized at 400 nm for clarity. Plot of the observed MLCT \(\lambda_{\text{max}}\) blue shift with time.
It has been demonstrated that the presence of the halide in the photolysis of Ru,Rh,Ru trimetallic and Ru,Rh bimetallic complexes impairs the catalysis, evidenced by a significant decrease in H₂ production. ⁸⁶,⁹⁰ Considering the anionic character of the Nafion® membrane, it is feasible that upon reduction and halide loss, the Br⁻ ions would be excluded from the Nafion® membrane due to charge repulsion. While scanning the Nafion®/[{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺ modified glassy carbon electrodes, the only feature that appeared in the CV, prior to delamination appears at the same potential as the Br⁻ oxidation (Figure 4.14). Furthermore, upon the analysis of the electrolyte solution following the bulk electrolysis of a fresh film, there appears to be a halide couple. A halide couple is not observed in the bulk electrolysis solution following the second bulk photoelectrolysis experiment with the same film. The halide couple was also not observed after cycling a Nafion® modified glassy carbon electrode without the [{(bpy)₂Ru(dpp)}₂RhBr₂]⁵⁺ complex. It is important to mention that the Cl⁻ couple appears in the same position as the Br⁻ couple and a Ag/AgCl reference electrode was used in all of the experiments. However, the same reference electrode was used between each of the bulk
electrolysis and each of the CV experiments. This suggests that upon reduction of the \[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\] complex inside of Nafion\textsuperscript{®} membranes the Br\textsuperscript{-} is ejected from the membrane due to charge repulsion. Since it has been shown that the catalysis of trimetallic complexes is enhanced in the absence halide in solution,\textsuperscript{86} it is reasonable to suggest that the second photoelectrolysis experiment in the absence of the halide could promote enhanced catalysis.

![Cyclic voltammograms](image)

**Figure 4.14 a)** Cyclic voltammogram of the trimetallic, \[\{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]\textsuperscript{5+} in a Nafion\textsuperscript{®} modified glassy carbon electrode, 30 scans at 20 mV/s from 0.0 V to 1.6 V to -1.0 V vs. NHE in a 0.1 M phosphate buffered H\textsubscript{2}O solution (pH = 7.00) the film delaminated from the electrode during scan 30 **b)** Cyclic voltammogram of NaBr in 0.1 M phosphate buffer (100 mV/s).

### 4.4 References


Chapter 5. Electrospun Carbon Mats

5.1 Introduction

An ideal sacrificial electron donor would irreversibly donate an electron, and then diffuse away from the acceptor molecule, ceasing to perform further reactions they may be detrimental to the catalytic process. Unfortunately, the use of molecular sacrificial electron donors for catalysis frequently results in the formation of highly reactive free radical species that lead to side reactions, resulting in decreased catalytic function.\textsuperscript{48-50} Sacrificial electron donor materials can be considered the “Achilles heel” of catalytic reduction processes.

Additional limitations with sacrificial electron donors are realized when considering catalysis in an ionic membrane material, such as Nafion®. There is added complexity concerning the changing oxidation states of electron donors. Since Nafion® is an anionic membrane with a higher affinity for more positive materials and electron donation makes the donor more positive, electron donation of a sacrificial donor could result in the donor having a higher affinity for Nafion® after the donation process. This could make the cycling of electron donors to propagate catalysis even more limiting than it is in the solution state.

Carbon materials as electron donors have an advantage over molecular sacrificial electron donors in that any radicals formed are delocalized throughout the conjugated sp\textsuperscript{2}-carbon backbone. Carbon nanotubes have been demonstrated to behave as radical scavengers.\textsuperscript{205} Furthermore, a solid material in conjunction with an ionomer membrane could alleviate the limitation associated with an increase in the affinity of molecular donors for an anionic
membrane following the donation process. Nitrogen doped carbon nanotube and graphene quantum dot materials have demonstrated electron donor capabilities.\textsuperscript{206-210}

Polyacrylonitrile (PAN) has been proven to perform as a precursor for the formation of carbon $sp^2$-type materials, classically used for the formation of carbon fiber mats.\textsuperscript{211-213} Recently, the technique of electrospinning has been shown to produce long nanofibers through electrostatic force.\textsuperscript{214} Electrospun PAN solutions form nanofibrous PAN which can be converted to an $sp^2$ carbon structure by following the oxidation and carbonization process previously reported for the development of larger diameter carbon materials for carbon fiber fabric shown in and Scheme 5.1. The initial step in the process requires heating in the presence of air to oxidize the PAN to form nitrogen containing six-membered rings. The carbonization process is more elusive and the mechanism for the formation of the carbon fibers is not well established. The evolution of H$_2$, N$_2$, and HCN is observed at high temperatures (400-1300 °C) (Scheme 5.2), and the resulting carbonized structure consists of a mixture of 5 and 6-membered rings.\textsuperscript{215,216}

![Scheme 5.1 Representation of PAN oxidation](attachment:image.png)
Scheme 5.2 Scheme of the suggested carbonization processes for oxidized PAN at different temperatures.
5.2 Experimental

5.2.1 Electrospun Carbon Nanofiber Mats

Jeremy Beach and Kristen Felice prepared the electrospun carbon mats by electrospinning 12% w/w solutions of polyacrylonitrile (PAN) in DMF, operating under the parameters outlined in Table 5.1. Following the electrospinning process, the mats were oxidized in an oven with a temperature ramp from 25 °C – 260 °C at 5 °C/min, then from 260 °C – 380 °C at 1 °C/min. Carbonization was performed in a tube furnace under a N₂ atmosphere with a temperature ramp from 25 °C – 1000 °C at 1 °C/min, once the temperature reached 1000 °C, the furnace was allowed to cool to room temperature under N₂. Mats were stored in a desiccator under vacuum.

<table>
<thead>
<tr>
<th>Table 5.1 Electrospinning parameters</th>
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<tr>
<td><strong>Parameter</strong></td>
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<tr>
<td>Volume</td>
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<td>Distance to Collector</td>
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<td>% Relative Humidity</td>
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5.2.2 Electrode Assembly

Electrodes from the electrospun carbon mats were prepared by cutting a piece of the electrospun mat out with a hole punch. A rectangular piece of an Aclar 22A, a
polychlorotrifluoroethylene moisture barrier membrane, was folded in half and melted with a soldering iron across the carbon mat and on the open side of the folded ends to form an envelope with an open end on the top of the pocket. A piece of glass tubing was inserted in the open end of the Aclar 22A film and heat-shrink tubing was used to seal the Aclar 22A to the glass tube.

The mass of the carbon mat assembly was measured prior to coating with Nafion®. The carbon mats were modified with Nafion® or Nafion®/[{(bpy)$_2$Ru(dpp)$_2$RhBr$_2$}]$^{5+}$ by dipping the electrode assembly in a 2.25 wt% TBA$^+$ Nafion® suspension 10:4:3:3 CH$_3$CN:H$_2$O:MeOH:IPA with the [{(bpy)$_2$Ru(dpp)$_2$RhBr$_2$}]$^{5+}$ complex dissolved in CH$_3$CN prior to mixing the CH$_3$CN solution with the 4:3:3 H$_2$O:MeOH:IPA TBA$^+$-form Nafion® solution. The electrode assembly was suspended in a desiccator under vacuum for ~12 h. The electrode assembly was placed in a 200 °C oven for 10 minutes. The mass of the electrode assembly was measured again and the mass and initial [{(bpy)$_2$Ru(dpp)$_2$RhBr$_2$}]$^{5+}$:SO$_3^-$ ratio was used to determine the moles of [{(bpy)$_2$Ru(dpp)$_2$RhBr$_2$}]$^{5+}$ in the electrode assembly. Finally, Hg and a Cu wire were added to the electrode assembly for electrical contact and the glass tube was sealed with a septum. An image of the final electrode assembly is shown in Figure 5.1.
5.2.3 Electrochemistry

Bulk photoelectrolysis experiments and H₂ detection experiments were performed with the same cell and setup described in Chapter 4 (p. 162) with 0.2 M phosphate buffer (pH 7.00). All electrochemical measurements were performed with a PARSTAT 2273 potentiostat/galvanostat.

5.2.4 Scanning Electron Microscopy (SEM)

SEM images were taken with a JEOL NeoScope JCM-5000 Benchtop SEM. Son-Nam Nguyen measured the Histograms with Nikon Instruments NIS-Elements Basic Research microscope imaging software.
5.2.5 X-ray Photoelectron Spectroscopy (XPS)

Samples of carbon nanofiber mats were submitted to Andrew Giordani at the Institute for Critical Technology and Applied Science (ICTAS) Nanoscale Characterization and Fabrication Laboratory (NCFL) for XPS analysis on a PHI Quantera SXM, scanning photoelectron spectrometer microprobe equipped with a scanning monochromatic X-ray source with a highly focused beam (<9 microns).

5.2.6 Reflectance/Electronic Absorbance

Reflectance spectroscopy of the modified carbon nanofiber mats and electronic absorbance prior to mixing [{(bpy)$_2$Ru(dpp)$_2$RhBr$_2$}]$^{5+}$ solutions with Nafion® solutions were performed with Hitachi 4100 UV-Vis-NIR.

5.3 Results and Discussion

5.3.1 Nafion® on Carbon Nanofiber Mats

Based on the results with FTO electrodes discussed in Chapter 4 (p. 174), it was apparent that higher surface electrodes with thinner Nafion® films would likely improve the performance of these materials. Therefore, woven carbon fabric was coated with Nafion® for electrochemical experiments. Unfortunately, upon the thermal treatment with Nafion®, the carbon mats crumbled apart and were rendered useless for any practical purpose. Manufactured carbon mats are typically coated with an epoxy binder, which appears to be unstable at temperatures necessary for solution processing of Nafion®. 131,132,244-246

With these results, it was hypothesized that electrospun carbon nanofiber mats may prove to be promising electrode materials. The mats have a very high surface area, are conductive and
the processing does not include an epoxy that would be unstable at temperatures required for the thermal processing of Nafion®. SEM images of the electrospun mats compared to the woven carbon fabric are shown in Figure 5.2. It is obvious from the comparison of Figure 5.2b and Figure 5.2c that the fibers in electrospun mats are significantly smaller than the fibers in the woven fabric. A histogram representing the size distribution in the diameter of the carbon fibers is represented in Figure 5.3, with fiber diameters of 580 ± 50 nm.

![SEM images](image)

**Figure 5.2** SEM images of a) woven carbon mat at × 50 magnification and b) × 2000 magnification c) electrospun carbon mat at × 2000 magnification

![Histogram](image)

**Figure 5.3** Histogram representing fiber diameter of the electrospun carbon mats

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SEM imaging was used to refine the Nafion® coating process. It was desired to coat the carbon nanofibers with a thin film of Nafion®, while avoiding adding too much Nafion®, which would form a film on the mats. Figure 5.4 shows that by following the dip-coating procedure (p. 185) that it is possible to form thin Nafion® coatings on the nanofibers. Furthermore, a comparison between Figure 5.4a and Figure 5.4b provides a visual representation of the importance of the thermal treatment on the Nafion® films during the casting process. The Nafion® appears much less uniform prior to the thermal treatment, while after the thermal treatment the polymer is much smoother and more uniformly distributed on the carbon fibers.

(a)  
(b)  

Figure 5.4 Electrospun carbon mats coated with Nafion® a) before thermal treatment b) following thermal treatment at 200 °C

Reflectance spectroscopy was used to verify the presence of the \[ \{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2 \]^5+ complex on the Nafion® modified electrospun carbon mats. Figure 5.5 clearly represents the appearance of a MLCT transition associated with the \[ \{(\text{bpy})_2\text{Ru(dpp)}\}_2\text{RhBr}_2 \]^5+ complex. The reflectance spectra of the Nafion®/carbon mat drops below 0 at lower wavelengths and is attributed to light scattering of the nanofiber mat. The
obvious absence of reflectance around 520 nm where the MLCT $\lambda_{\text{max}}$ of $[{(bpy)_{2}}\text{Ru(dpp)}_{2}\text{RhBr}_{2}]^{5+}$ appears is sufficient evidence to conclude the $[{(bpy)_{2}}\text{Ru(dpp)}_{2}\text{RhBr}_{2}]^{5+}$ complex is present on the Nafion®/carbon mat composite.

![Absorbance spectrum](image)

**Figure 5.5** Reflectance spectrum of carbon nanofibers a) with Nafion®, b) with Nafion® and $[{(bpy)_{2}}\text{Ru(dpp)}_{2}\text{RhBr}_{2}]^{5+}$

### 5.3.2 Electrochemical Properties of Nafion® on Electrospun Carbon Mats

Additionally, the thin Nafion® coating on the high surface area carbon fiber mats made it possible to observe some electrochemical features of the $[{(bpy)_{2}}\text{Ru(dpp)}_{2}\text{RhBr}_{2}]^{5+}$ complex with a low swelling CH$_3$CN solvent. Cyclic voltammagrams of $[{(bpy)_{2}}\text{Ru(dpp)}_{2}\text{RhBr}_{2}]^{5+}$ on Nafion® modified electrospun carbon mats are shown in **Figure 5.6**. The Ru couple appears around 1.7 V, consistent with the results of $[{(bpy)_{2}}\text{Ru(dpp)}_{2}\text{RhBr}_{2}]^{5+}$ in the solution state. Furthermore, the large peak separation is consistent with results observed for Ru(bpy)$_3$$_{2}^{2+}$ in Nafion®. The reductive side of the CV in Nafion® is very convoluted and the separation of the peaks was not accomplished with slow scan rates (as low as 5 mV/s) or potential step methods. However, following several reductive scans, the appearance of a couple consistent
with a bromide couple is observed (Figure 5.7), supporting that there is Br\(^-\) loss following the reduction of \(\{(bpy)_2\text{Ru}(dpp)\}_2\text{RhBr}_2\)\(^{5+}\).

**Figure 5.6** Cyclic voltammograms of \(\{(bpy)_2\text{Ru}(dpp)\}_2\text{RhBr}_2\)\(^{5+}\) with 0.1 M Bu\(_4\)NPF\(_6\) in CH\(_3\)CN
a) in Nafion\textsuperscript{®} on electrospun carbon mats 20 mV/s on a fresh mat, scanning oxidative initially (20mV/s)  
b) Solution state at 100mV/s

**Figure 5.7** CV of \(\{(bpy)_2\text{Ru}(dpp)\}_2\text{RhBr}_2\)\(^{5+}\) in Nafion\textsuperscript{®} on an electrospun carbon mat in 0.1 M Bu\(_4\)NPF\(_6\) in CH\(_3\)CN, scanning 50 mV/s after initially cycling 0 to –1.2 V vs. NHE several times at varying scan rates.
5.3.3 Hydrogen Production with Electrospun Carbon Mats

Bulk photoelectrolysis experiments were performed with the Nafion®/[{(bpy)₂Ru(dpp)}₂RhBr₆]⁵⁺ modified electrospun carbon mats under similar conditions to that of the Nafion®/[{(bpy)₂Ru(dpp)}₂RhBr₆]⁵⁺ modified FTO electrodes. Since it is difficult to control the amount of complex loaded onto the electrospun carbon mats by dip coating, hydrogen production is compared to the results seen with the FTO electrode by comparing turnover numbers (TON) (Figure 5.8a). TON is defined in Equation 5.1 and the ratio of Nafion®/[{(bpy)₂Ru(dpp)}₂RhBr₆]⁵⁺ remained constant between the two experiments. As expected for the much thinner Nafion® films and the large surface area of the electrospun carbon mats, there is significant catalytic enhancement for the Nafion®/[{(bpy)₂Ru(dpp)}₂RhBr₆]⁵⁺ complex during the bulk photoelectrolysis. The amount of time that it takes for the H₂ production to begin is also significantly decreased with the electrospun carbon mats and can be attributed to the much thinner Nafion® film.

\[
TON = \frac{\text{mol } H_2}{\text{mol catalyst}} \quad \text{Equation 5.1}
\]

\[
\text{Efficiency} = \frac{\text{mol } H_2}{2 \text{ mol } e^-} \quad \text{Equation 5.2}
\]

The efficiency of the electrolysis was calculated using coulometry following Equation 5.2. Surprisingly, the apparent calculated “efficiency” based on the output from the potentiostat is much greater than 100% efficient (Figure 5.8b). Note that the calculated efficiency for the FTO electrodes was between 0.05 and 0.1. The impossible calculated “efficiency” of the Nafion®/[{(bpy)₂Ru(dpp)}₂RhBr₆]⁵⁺ modified carbon mats suggests that electrons must be
coming from somewhere other than the applied electrochemical potential. Considering that nitrogen doped carbon nanomaterials have been show to behave as electron donors, it is possible that the electrospun carbon nanofiber mats are behaving as electron donors.\textsuperscript{206-210}

\textbf{Figure 5.8} \textit{a)} TON for H\textsubscript{2} production of [{(bpy)}\textsubscript{2}Ru(dpp)}\textsubscript{2}RhBr\textsubscript{2}\textsuperscript{5+} on Nafion\textsuperscript{®} with a carbon electrospun mat (black) compared to the second reduction with Nafion\textsuperscript{®}/[{(bpy)}\textsubscript{2}Ru(dpp)}\textsubscript{2}RhBr\textsubscript{2}\textsuperscript{5+} on FTO (green) \textit{b)} Efficiency of the electrolysis (Equation 5.2) experiment in (a) on carbon mats. Both experiments were performed in aqueous 0.2 M phosphate buffer in H\textsubscript{2}O (pH = 7.00) with an applied potential of -1.00 V vs. NHE. The impossibly large efficiency suggests electrons are coming from a source other than the applied potential.

If the electrospun carbon mats were capable of behaving as electron donors due to nitrogen doping, there would be some nitrogen present in the materials and the elemental composition would change following the electron donation process. Elemental analysis of the electrospun carbon mats by XPS demonstrates that the nitrogen content of the fresh electrospun films is about 9\%. Furthermore, following the bulk electrolysis experiment, the total nitrogen percent decreases and the total oxygen percent increases, consistent with an oxidation of the electrospun fibers (Table 5.2).
Table 5.2 Elemental analysis of the electrospun carbon mats before and after the photoelectrolysis, determined by XPS.

<table>
<thead>
<tr>
<th>Elemental Analysis (%)</th>
<th>Before Photoelectrolysis</th>
<th>After Photoelectrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>86</td>
<td>65</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>9</td>
<td>5</td>
</tr>
</tbody>
</table>

Additionally, if the electrospun carbon mats were capable of behaving as electron donor materials for the \([(bpy)_2Ru(dpp)]_2RhBr_2\)^\(5^+\) complexes, hydrogen production should be observed without the addition of an applied potential. Photolysis experiments without any applied potential did not produce H\(_2\). However, considering there is a lag time before hydrogen production begins in the photoelectrolysis experiments, it was hypothesized that the applied potential may induce migration of the \([(bpy)_2Ru(dpp)]_2RhBr_2\)^\(5^+\) complex to the electrode surface, allowing for H\(_2\) production to occur. Upon applying a potential of -1.0 V for 24 h, while irradiating the sample with a 470 nm LED, hydrogen production is observed long after the applied potential was turned off (Figure 5.9). In a control experiment, there is no observed H\(_2\) production for Nafion\textsuperscript{®} modified electrospun carbon mats that did not contain \([(bpy)_2Ru(dpp)]_2RhBr_2\)^\(5^+\) after the potential was turned off. This result indicates that the electrospun carbon mats are behaving as electron donating materials for photocatalytic hydrogen production with \([(bpy)_2Ru(dpp)]_2RhBr_2\)^\(5^+\) complexes.
Figure 5.9 Photocatalytic hydrogen production of \( [(bpy)_2\text{Ru(dpp)}_2\text{RhBr}_2]^{5+} \) in Nafion\(^{\circ}\) on an electrospun carbon mat, irradiating with a 470 nm LED in aqueous 0.2 M phosphate buffer in \( \text{H}_2\text{O} \) (pH = 7.00) with an applied potential of -1.00 V vs. NHE for the first 24 h of the experiment.

5.4 References


(50) Navon, G.; Sutin, N. Mechanism of the quenching of the phosphorescence of tris(2,2'-bipyridine)ruthenium(II) by some cobalt(III) and ruthenium(III) complexes. Inorg. Chem. 1974, 13, 2159-2164.


Chapter 6. Conclusions

We have demonstrated that the large trimetallic complexes, \([\{\text{bpy}\}_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}\) and \([\{\text{Ph}_2\text{phen}\}_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}\) and reduced \([\{\text{Ph}_2\text{phen}\}_2\text{Ru(dpp)}\}_2\text{Rh}\]^{5+}\) readily absorb into Nafion® via ion-exchange under appropriate solvent swelling conditions. This facile exchange is remarkable due to the calculated size of the trimetallic complex, \([\{\text{bpy}\}_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}\), in comparison to proposed dimensions of Nafion® ionic aggregates. In order to accommodate these large molecules, it is reasonable to rationalize a more open channel morphology over the more confining morphology of the cluster-network model. It has been determined that up to 86 ± 2% of the −SO₃⁻ groups in Nafion® can be counterbalanced by the trimetallic complex, \([\{\text{bpy}\}_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}\), and the morphology of the ionomer is not significantly altered upon exchange of the metal complex. Furthermore, consistent with other ion exchange materials, Nafion® has a greater affinity for the ion with the higher charge: the trimetallic complex, \([\{\text{bpy}\}_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}\), over the monometallic complex, \([\text{bpy}\}_2\text{Ru(dpp)}\]^{2+}\). Due to this higher affinity for the trimetallic complex, \([\{\text{bpy}\}_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}\), the half-life of ion-exchange in more swollen films is observed to be faster than that of the monometallic complex, \([\text{bpy}\}_2\text{Ru(dpp)}\]^{2+}\). In less swollen films, exchange of the trimetallic complex, \([\{\text{bpy}\}_2\text{Ru(dpp)}\}_2\text{RhBr}_2\]^{5+}\), is not observed in a measurable quantity. Investigation of the time dependent ion-exchange behavior has led to the conclusion that absorption occurs via a fast exchange of surface sulfonate groups followed by a slow exchange (via diffusion) of ions in the interior domains of the ionomer. With a low swelling solvent,
exposure of Nafion® films to both the monometallic, \([(bpy)_2Ru(dpp)]^{2+}\), and trimetallic, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\), complexes, yielded negligible exchange of either species. Given the higher affinity of Nafion® for the trimetallic complex, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\), it is proposed that the large complex exchanges with ions on the surface of the film, thereby blocking access to the ionic aggregates and thus preventing subsequent exchange of the monometallic complex, \([(bpy)_2Ru(dpp)]^{2+}\). The large size of the trimetallic complex, \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\), in comparison to the ionic aggregates of Nafion® allows for solvent controlled ion-exchange of the metal complex.

On Nafion®/\([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\) modified FTO electrodes, the \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\) complexes are capable of producing H₂ via bulk photoelectrolysis. The onset of catalytic hydrogen production corresponds to the time at which the \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\) complexes is reduced in the Nafion® film. With a second electrolysis experiment using the same Nafion®/\([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\) FTO modified electrode, there is a significant enhancement of the H₂ production, which may be attributed to halide loss following the first bulk photoelectrolysis experiment.

Electrospun carbon fibers that contain nitrogen can behave as electron donor materials for \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\) complexes embedded in a Nafion® membrane. The hydrogen production with the electron donor materials is initiated upon the applying a potential to the carbon fiber/Nafion®/\([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\) material. The onset is likely dependent on electrostatic migration of the \([\{(bpy)_2Ru(dpp)\}_2RhBr_2]^{5+}\) complex to the electron donating carbon nanofiber material.
Chapter 7. Recommendations for Future Work

The work described in this dissertation is just the beginning of a multitude of studies and experiments that could be performed in order to understand the interactions between Ru,Rh,Ru supramolecular photocatalytic complexes and polymer membranes. There are two other PhD projects underway examining the interactions between Ru,Rh,Ru complexes and polymer and ionomer membranes. Theodore Canterbury is studying the effects of polyelectrolyte interactions with Ru,Rh and Ru,Rh,Ru photocatalytic complexes in the solution state. Kristen Felice is interested in studying the effects of covalent attachment of the Ru,Rh,Ru trimetallic and Ru,Rh bimetallic complexes to conductive polymer, or polymer electron donating materials for photocatalytic hydrogen production.

More specifically, there is still much to be learned about the interactions of Ru,Rh,Ru trimetallic complexes and Nafion® membranes, particularly with the catalysis studies. A large effort has been put into working out the nuances of the interactions between the \([\{(bpy)_2Ru(dpp)}_2RhBr_2\] complexes with Nafion® membranes in order to develop methods to study these interactions. Following the procedures developed here, particularly with the development of the modified electrodes, systematic variations could bring about some very interesting results.

Film thickness variation on the FTO electrodes would make it possible to study whether or not the onset of hydrogen production is related to the diffusion of the \([\{(bpy)_2Ru(dpp)}_2RhBr_2\] complex through the Nafion® membrane to the electrode surface.
Concentration variation of these electrode materials would also be interesting. There is likely an important balance between light absorption and electroactive species.

The high-surface area carbon fiber electrodes could be especially beneficial for future studies, for both the electron donating ability and the potential as an inert electrode material. Many of the challenges encountered in this project, including the thermal processing and solvent swelling dependence in Nafion\textsuperscript{®}/[{(bpy)}\textsubscript{2}Ru(dpp)]\textsubscript{2}RhBr\textsubscript{2}\textsuperscript{5+} materials were not as pronounced with the high surface area carbon fibers and thin Nafion\textsuperscript{®} films. Carbon fabric materials that do not include an epoxy binder could also be useful for the investigation of the interactions between Ru,Rh,Ru supramolecular complexes and Nafion\textsuperscript{®} membranes.

Furthermore, for the sake of variable control, the [{(bpy)}\textsubscript{2}Ru(dpp)]\textsubscript{2}RhBr\textsubscript{2}\textsuperscript{5+} complex was used in almost all of the studies in this work. There are a large variety of bimetallic and trimetallic complexes of similar architectures with varying degrees of catalytic activities. It could be very interesting to compare these complexes in a polymer membrane and assess whether the trends observed in the solution state follow the trends in the membrane. Systematic variation of the terminal ligands on these pentavalent cations could also be used to determine the degree in which hydrophobic interactions contribute to the overall affinity of the complexes in Nafion\textsuperscript{®}.

Additionally, there are several commercially available perfluorosulfonate ionomer membranes with varying equivalent weights that could explored in regard to their interactions with the mixed-metal photocatalysts and catalytic activity. The structure of two of these ionomer membranes compared to Nafion\textsuperscript{®} are shown in Figure 7.1. Variation of the side chains results in
a larger range of equivalent weights and could result in interesting interactions between the photocatalytic complexes and the perfluorosulfonated membranes.

Figure 7.1 Chemical structures of a) Nafion® b) Hyflon® and c) 3M perfluorosulfonated ionomer membranes
References


Yan, S. G.; Brunschwig, B. S.; Creutz, C.; Fujita, E.; Sutin, N. Reversible Formation of Bis(2,2'-bipyridine)rhodium(III) Dihydride from Bis(2,2'-bipyridine)rhodium(I) and Dihydrogen. Direct Transfer of Dihydrogen from Rhodium(III) Dihydride to Rhodium(I). J. Am. Chem. Soc. 1998, 120, 10553-10554.


Navon, G.; Sutin, N. Mechanism of the quenching of the phosphorescence of tris(2,2'-bipyridine)ruthenium(II) by some cobalt(III) and ruthenium(III) complexes. Inorg. Chem. 1974, 13, 2159-2164.


(56) Molnar, S. M.; Nallas, G.; Bridgewater, J. S.; Brewer, K. J. Photoinduced Electron Collection in a Mixed-Metal Trinuclear Complex of the Form 


(59) Milkevitch, M.; Brauns, E.; Brewer, K. J. Spectroscopic and Electrochemical Properties of a Series of Mixed-Metal d6,d8 Bimetallic Complexes of the Form \[(bpy)2M(BL)PtCl2\]2+ (bpy = 2,2'-Bipyridine; BL = dpq (2,3-Bis(2-pyridyl)quinoxaline) or dpb (2,3-Bis(2-pyridyl)benzoquinoloxaline); M = OsII or RuII). *Inorg. Chem.* **1996**, 35, 1737-1739.


(90) Rogers, H. M.; White, T. A.; Stone, B. N.; Arachchige, S. M.; Brewer, K. J. Nonchromophoric Halide Ligand Variation in Polyazine-Bridged Ru(II),Rh(III)


(110) Ghosh, P. K.; Bard, A. J. Polymer films on electrodes. Part XV. The incorporation of tris(2,2'-bipyridine)ruthenium(2+) into polymeric films generated by electrochemical polymerization of 2,2'-bipyrazine (bpz) and tris(2,2'-bipyrazine)ruthenium(2+). *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1984**, *169*, 113-128.


Kakuta, N.; Park, K. H.; Finlayson, M. F.; Ueno, A.; Bard, A. J.; Campion, A.; Fox, M. A.; Webber, S. E.; White, J. M. Photoassisted hydrogen production using visible light and


Andrieux, C. P.; Saveant, J. M. Heterogeneous (chemically modified electrodes, polymer electrodes) vs. homogeneous catalysis of electrochemical reactions. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 1978, 93, 163-168.


