Investigation of Conformational Control of Photoinduced Electron Transfer in Ruthenium Polypyridyl Dye-Sensitized Solar Cells

Karen Elizabeth Spettel

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Investigation of Conformational Control of
Photoinduced Electron Transfer in
Ruthenium Polypyridyl Dye-Sensitized Solar Cells

by

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Carleton College, 2010

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Investigation of Conformational Control of Photoinduced Electron Transfer in
Ruthenium Polypyridyl Dye-Sensitized Solar Cells

written by Karen E. Spettel

has been approved for the
Department of Chemistry and Biochemistry

by:

_____________________________________
Niels H. Damrauer

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Cortlandt G. Pierpont

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Date

The final copy of this thesis has been examined by the signatories, and we find that both
the content and the form meet acceptable presentation standards of the scholarly work in
the above mentioned discipline.
Abstract

To explore the impact of structure on photoinduced electron transfer processes, systematically tuned 4’-aryl-substituted terpyridyl ruthenium(II) complexes are synthesized and then studied in solution, film, and device settings. These complexes are introduced in the framework of dye-sensitized solar cells (DSSCs)—a low cost alternative to conventional silicon-based devices. A monolayer of ruthenium chromophores attached to a mesoporous TiO$_2$ semiconductor is designed to efficiently absorb photons and initiate the separation of charge across a dye/semiconductor interface. Acting as a working electrode in a complete cell, this construction of sensitized TiO$_2$ particles allows for the conversion of photons to current. In our work, structural tuning is performed within the aryl-terpyridine ligands, by systematically introducing methyl substituents at the ortho positions of the aryl moiety in order to explore dynamical electron transfer coupling at ruthenium/TiO$_2$ interfaces.

First, syntheses, electrochemical potentials, static emission, and temperature-dependent excited-state lifetimes of several 4’-aryl-substituted terpyridyl complexes of ruthenium(II) are presented. In these solution phase studies, the power of structural tuning manifests primarily with a 14-fold decrease in the excited-state lifetime of dimethylated species relative to unsubstituted aryl-terpyridine species. Next, an overview of the materials and procedures utilized to make complete DSSCs is presented. In an effort to determine the implications of structural tuning of these complexes within the
DSSCs, total solar power conversion efficiency measurements are performed. These are then deconstructed to better understand the fundamental processes and how they impact light-to-current conversion. Injection yields are identified as the primary factor limiting the efficiencies of these ruthenium terpyridyl DSSCs. The final chapter presents an investigation of the kinetics of charge recombination—an energy-wasting back electron transfer process at play in photoinduced charge-separated processes. Transient absorption spectroscopy is applied to sensitized TiO$_2$ films in an electrochemical setup simulating device conditions. The addition of methyl steric bulk is found to inhibit charge recombination, with measured recombination lifetimes increasing by over 12-fold across the series of structurally-tuned complexes. If injection yields can be improved, the structural tuning of recombination rate constants may be an important design rule for improving solar conversion efficiency in solar cells and water splitting devices.
Acknowledgements

My graduate career began like many others. As a bright student I was guided to continue learning, only to find that there is so much more to learn than is possible. What I know for certain is that I would not have gotten to where I am today without the help of several people along the way.

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List of Abbreviations

\( \alpha(\lambda) \)  
Absorptance

\( \Gamma \)  
Surface Coverage

\( \Delta A \)  
Change in absorption

\( \Delta E_a \)  
Activation energy

\( \Delta E_p \)  
Peak-to-peak separation

\( \Delta G^{\circ}_{\text{MLCT}, E_{\text{oo}}} \)  
Free energy in the lowest MLCT excited state

\( \Delta G_{\text{BET}} \)  
Driving force for back electron transfer

\( \Delta G_{\text{INJ}} \)  
Driving force for electron injection

\( \varepsilon(\lambda) \)  
Molar extinction coefficient

\( \eta \)  
Solar power conversion efficiency

\( \eta_{\text{COLL}} \)  
Collection efficiency

\( \eta_{\text{REG}} \)  
Regeneration efficiency

\( \sigma(\lambda) \)  
Absorption cross section

\( \tau \)  
Characteristic lifetime

\( \tau_{\text{obs}} \)  
Observed excited-state lifetime

\( \varphi_{\text{INJ}} \)  
Injection quantum yield

\( \phi_r \)  
Radiative quantum yield

\( \phi_{\text{sun}} \)  
Spectral intensity of solar emission, photon flux

\( 2D \)  
Two-dimensional

\( A(\lambda) \)  
Absorbance

\( \text{ADC} \)  
Analog-to-digital converter

\( \text{AM1.5} \)  
Air mass 1.5 sunlight
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<td>A₀</td>
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<td>APCE</td>
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<tr>
<td>BBO</td>
<td>β-Barium borate</td>
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<td>Fluorine-doped tin oxide</td>
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<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
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</tr>
<tr>
<td>H_{ab}</td>
<td>Electronic coupling matrix element</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest-occupied molecular orbital</td>
</tr>
<tr>
<td>\hbar\omega_{M}</td>
<td>Medium frequency acceptor mode</td>
</tr>
<tr>
<td>I_o</td>
<td>Incident photon flux</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon-to-current efficiency</td>
</tr>
<tr>
<td>IRF</td>
<td>Instrument response function</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium-doped tin oxide</td>
</tr>
<tr>
<td>J-V Curve</td>
<td>Current-voltage characteristic</td>
</tr>
<tr>
<td>J_{pp}</td>
<td>Photocurrent density at maximum power point</td>
</tr>
<tr>
<td>J_{sc}</td>
<td>Short-circuit photocurrent density</td>
</tr>
<tr>
<td>k_{BET}</td>
<td>Back electron transfer rate constant</td>
</tr>
<tr>
<td>k_{ET}</td>
<td>Forward electron transfer rate constant</td>
</tr>
<tr>
<td>k_{inj}</td>
<td>Electron injection rate constant</td>
</tr>
<tr>
<td>k_{int}</td>
<td>Charge interception rate constant (with electrolyte)</td>
</tr>
<tr>
<td>k_{nr}</td>
<td>Nonradiative rate constant</td>
</tr>
<tr>
<td>k_r</td>
<td>Radiative rate constant</td>
</tr>
<tr>
<td>k_{rec}</td>
<td>Charge recombination rate constant (with oxidized dye)</td>
</tr>
<tr>
<td>k_{reg}</td>
<td>Dye regeneration rate constant</td>
</tr>
<tr>
<td>k_{relax}</td>
<td>Excited-state relaxation rate constant</td>
</tr>
<tr>
<td>k_{trans}</td>
<td>Charge transport rate constant</td>
</tr>
<tr>
<td>KWW</td>
<td>Kohlrausch-Williams-Watts</td>
</tr>
<tr>
<td>LHE</td>
<td>Light harvesting efficiency</td>
</tr>
<tr>
<td>LP filter</td>
<td>Long-pass filter</td>
</tr>
</tbody>
</table>
LUMO  Lowest-unoccupied molecular orbital
MC      Metal-centered state
MLCT    Metal-to-ligand charge transfer state
N719    Bis-tetrabutylammonium
cis-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′dicarboxylato)-ruthenium(II)
NMR     Nuclear magnetic resonance
OTTLE   Optically transparent thin-layer electrode
PBE     Perdew-Burke-Ernzerhof exchange and correlation functional
PEDOT   Poly(3,4-ethylenedioxythiophene) polystylenesulfonate
P_max   Maximum power achieved by the device
P_o     Incident irradiance of sunlight
PMII    1-Propyl-3-methylimidazolium iodide
PMT     Photomultiplier tube
P_T     Maximum theoretical device power
Q_eq    Equilibrium internuclear distance
RE      Reference electrode
SCE     Saturated calomel electrode
S_M     Huang-Rhys factor
t-Bu    Tert-butyl
t_{1/2}  Half-life time
TA      Transient absorption
TAC     Time-to-amplitude converter
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>TBA</td>
<td>Tetrabutylammonium</td>
</tr>
<tr>
<td>TBP</td>
<td>Tert-butylpyridine</td>
</tr>
<tr>
<td>tbtpy</td>
<td>4,4′,4″-Tri-tert-butyl-2,2′:6′,2″-terpyridine</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conducting oxide</td>
</tr>
<tr>
<td>TCSPC</td>
<td>Time-correlated single photon counting</td>
</tr>
<tr>
<td>tpy</td>
<td>2,2′:6′,2″-Terpyridine</td>
</tr>
<tr>
<td>ttpy</td>
<td>4′-Tolyl-2,2′:6′,2″-terpyridine</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Ultraviolet-visible</td>
</tr>
<tr>
<td>Voc</td>
<td>Open-circuit photovoltage</td>
</tr>
<tr>
<td>Vpp</td>
<td>Photovoltage at the maximum power point</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
</tbody>
</table>
Chapter 1
Introduction and Motivation

1.1 Introductory Remarks

Climate change is not only rising sea levels, melting glaciers, and changing rainfall patterns: it is affecting our ecosystem.¹ The current prediction is that one in every six species* will be extinct by 2100 if we follow our trajectory for increasing global temperature.² The need for an inexpensive and environmentally safe energy source is increasing every day.³

The case has already been made that sunlight is an abundant, clean, and sustainable source of energy.⁴,⁵ However, finding an inexpensive means for harvesting it on a terawatt scale still poses a tremendous challenge. Reducing material costs for photovoltaics enough to make them an economically viable replacement for carbon-based energy sources is only the first step.⁶ The far more challenging hurdles are affordably manufacturing efficient photovoltaics and storing their generated energy, on the requisite massive scale.

The most reasonable manufacturing method to achieve this will likely involve roll-to-roll printing, such that photovoltaics modules could be printed as easily as newspaper.⁷ The low-cost materials and low-cost production processes of dye-sensitized solar cells (DSSCs) bring us closer to achieving these energy goals.⁸ However, the search

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* Climate change is already estimated to have affected the extinction of 1 in 12 species (7.9%).²
continues for a more efficient photovoltaic technology, with fundamentals suitable for mass production.

Our work takes a molecular approach to solar energy conversion. Based on the mechanisms of plant photosynthesis, systems are designed to use light absorption to initiate electron transfer for the conversion and storage of energy. At the heart of these mechanisms lie photoinduced excited states. Our work is focused on understanding the fundamental aspects of photoinduced electron transfer processes by studying systems of chromophores that are structurally modified to control the fate of excited states. Specifically, we aim to exploit dynamics useful for energy conversion while preventing those that lead to energy degradation pathways (see Figure 1.1). We design systems with relatively long-lived excited states that are capable of fast energy transfer to other useful systems, with little energy loss, while avoiding the pathway of charge recombination back to the ground state.

![Figure 1.1. Extracting excited-state energy from photoinduced processes.](image-url)
1.2 Ruthenium Polypyridyl Complexes

As alluded to above, photoinduced electron transfer systems are often modeled on the reaction centers of natural photosynthetic organisms. These models are referred to as donor-bridge-acceptor (DBA) systems. They consist of a donor chromophore that acts as an antenna, specialized to collect photons, and an acceptor that converts the excited electron into a useable electrochemical potential by charge separation. An additional bridge subunit is often included to provide a means to control the extent of electronic interaction between donor and acceptor species.

Coordination complexes are commonly used as donor chromophores due to their highly tunable absorption energies, their large extinction coefficients, and their photoredox activity. Historically, ruthenium(II) polypyridyl complexes have dominated in photochemical fields. They are highlighted for their use in photoinduced intramolecular, intermolecular, or interfacial electron transfer processes in the contexts of artificial photosynthesis, photocatalysis, dye-sensitized solar cells (DSSCs), and energy collection and/or storage of fuels.

The photochemistry of tris-2,2′-bipyridyl ruthenium(II): \([\text{Ru(bpy)}_3]^{2+}\) and hundreds of its derivatives has been extremely well studied, while the photochemistry of bis-2,2′:6′,2″-terpyridyl ruthenium(II): \([\text{Ru(tpy)}_2]^{2+}\) and its terpyridine derivatives is only slightly less prevalent in the literature. The structures of these Ru(II) polypyridine species are shown in Figure 1.2. As model compounds, the photophysics of these two complexes are frequently measured as standards and will be referenced often throughout this dissertation. Ru(II) terpyridyl-based systems are mainly
explored in this work due to the relative ease of modifying ligands without possible isomer complications.\textsuperscript{34}

Figure 1.2. Structure of [Ru(bpy)\textsubscript{3}]\textsuperscript{2+} and [Ru(tpy)\textsubscript{2}]\textsuperscript{2+}.

Ru(II) polypyridyl complexes are widely utilized in photochemistry due to a unique combination of factors that couple photon absorption to charge transfer. With a coordination number of six, these complexes are of pseudo-octahedral symmetry. As d\textsuperscript{π}\textsuperscript{6} coordination compounds, they exhibit highly allowed (large molar extinction coefficient) metal-to-ligand charge transfer (MLCT) transitions in the visible spectrum, which as the name suggests, involves promoting an electron from the Ru(II) metal to the \(\pi^*\) orbital of one of the polypyridine ligands. Ru(II) complexes can also easily undergo highly reversible redox reactions in both the ground state and the excited state.\textsuperscript{35} For most Ru(II) polypyridine complexes, the ground state is singlet in nature, with the lowest excited state as a triplet MLCT state.\textsuperscript{35} As a spin-forbidden process, the \(^3\text{MLCT}\) excited state undergoes relatively slow, radiative and nonradiative decay back down to the ground state, and thus exhibits long-lived phosphorescence.\textsuperscript{35} Again, a long-lived excited-state is ideal for energy conversion purposes (see Figure 1.1). While osmium(II) d\textsuperscript{π}\textsuperscript{6} coordination complexes are very similar to ruthenium(II), they have shorter excited-state lifetimes due to spin-orbit coupling, which allows for increased ground and excited state mixing.\textsuperscript{36}
Iron(II) complexes have even shorter MLCT excited-state lifetimes, due to lower lying metal-centered (MC) states, which contribute to much shorter degradation timescales.\(^{37}\)

In the end, Ru(II) polypyridyl complexes are chosen for their unique combination of strong and highly tunable light absorption bands, stable redox chemistry, and relatively long excited-state lifetimes.\(^{38}\)

Additionally, Ru(II) polypyridine donor chromophores can easily be appended with conformationally active aryl bridges before attaching to acceptor systems. Phenylene bridging subunits are investigated in this dissertation for several reasons. First, transition metal complexes with aryl-substituted polypyridine ligands have increased molar extinction coefficients\(^{39}\) and increased emission lifetimes.\(^{39-41}\) These increased lifetimes are essential for Ru(II) terpyridine systems, which have shorter excited-state lifetimes compared to bipyridine analogues\(^{†}\) and would otherwise be non-emissive at room temperature.\(^{15}\) This property of aryl-polypyridine ligands is due to their ability to facilitate delocalization of an excited electron across the entire ligand \(π\)-system by ring rotation.\(^{41}\) Ring rotation is defined as a change in the dihedral angle, \(Δθ\), between the aryl substituent and the polypyridine moiety (see Figure 1.3). It is the degree of ring rotation that we hope to exploit for electron transfer studies across a series of complexes.

\(^{†}\) The smaller N-Ru-N tridentate bite angles in terpyridine systems make for lower energy metal-centered excited states that allow for more rapid excited-state degradation processes.\(^{42}\)
Figure 1.3. Design scheme for conformational trapping of charge-separated equivalents in a bipyridyl DBA system. Ring rotation is performed at steps indicated by $\Delta \theta$. Both rate constants ($k_{\text{ET}}$ and $k_{\text{BET}}$) are modulated by ligand-based motion. The break in energy is intentional to show the amount of energy expended is small compared to the fraction absorbed.

The phenylene bridge is particularly amenable to torsional motions that facilitate electron transfer and inhibit energy-wasting back electron transfer due to changes in electronic coupling (vide infra). The idea that low frequency torsional motions have an impact on electron transfer rates is not a new one. Similar torsional motions have been utilized to control electron transfer, exchange-mediated energy transfer, and conduction in molecular systems for years. From these studies, one can conclude that an aryl-polypyridyl ligand is canted in its ground state, due to steric interactions between hydrogen atoms of the aryl spacer and the atoms of the bipyridyl ligand (see Figure 1.3). However, in its excited state, the aryl-bipyridyl ligand undergoes a nuclear rearrangement to assume a more coplanar geometry with a smaller dihedral angle, $\theta$. 
between aryl substituent and bipyridine moiety (see $\Delta \theta$ in Figure 1.3).\textsuperscript{41} Such ring rotational dynamics were found to occur within \(~2\) ps.\textsuperscript{49} These torsional effects are merely enhanced with methyl substituent functionalization, which provides greater steric hindrance, thereby decreasing electron delocalization due to a canted conformation (see Figure 1.3).\textsuperscript{41,45,47,50,51,56,57} The phenylene bridge will serve as our platform for conformational control of electron transfer across a series of complexes with increased steric hindrance.

Previous work in our group has involved the exploration of DBA systems juxtaposing chromophoric Ru(II) bipyridyl complexes with electroactive bipyridinium acceptor moieties via a conformationally active arylated bridge (see Figure 1.3).\textsuperscript{43,57} The design principle, explored both computationally and experimentally, has two interrelated components depicted in Figure 1.3. On the one hand, photoexcitation of the chromophore initiates planarization between a bipyridyl ligand and its aryl substituent, driven by delocalization of the electron directly involved in the MLCT transition. This predisposes the system for electron transfer to the acceptor, due primarily to increases in electronic coupling. On the other hand, following electron transfer to the acceptor, the conformation between the bipyridyl ligand and its aryl substituent returns to a more twisted form, driven by steric interactions between rings. Critically, such twisting between $\pi$-systems attenuates the electronic coupling, inhibiting energy-wasting back electron transfer. Work in our group has shown that a sterically encumbered aryl-substituted bipyridyl ligand produces a more than 8-fold increase in the back electron transfer lifetime of the photoproduct with a methylated bipyridinium moiety (see Figure 1.4).\textsuperscript{43}
Conformationally influenced electron transfer processes in DBA systems can be extended to a more practical setting by considering their roles in charge injection and recombination losses in the context of dye-sensitized-solar cells (DSSCs). Molecular systems for exploring this require a ruthenium donor chromophore, a conformationally active aryl bridging unit, and a carboxylic acid substituent to covalently attach to surface of mesoporous TiO$_2$ electrodes. Throughout this dissertation, this is investigated with the three metal complexes shown in Figure 1.5, referred to as the Steric Series. Structural modifications are made across the Steric Series by introducing methyl substituents at the ortho position on the phenylene bridge.
Figure 1.5. Synthesized ruthenium(II) terpyridyl complexes studied in this dissertation.

This molecular system is highly applicable to DSSCs because both ruthenium bipyridine- and terpyridine-based complexes make up the framework for the two most studied and most efficient DSSC sensitizers to date: \([\text{Ru(4-carboxy,}4′\text{-carboxylato-2,2′-bipyridine)}_2(\text{NCS})_2]^{2-}\) (N719 dye) and \([\text{Ru(4,4′,4″-tricarboxy-2,2′;6′,2″-terpyridine)}_2(\text{NCS})_3]^{3-}\) (Black dye, also known as N749 dye), shown in Figure 1.6.\(^{58}\) To fully explain how we intend to study the effects of photoinduced electron transfer across the Steric Series in DSSCs, we first review the fundamental processes involved in DSSC operation.
1.3 Fundamentals of Dye-Sensitized Solar Cells (DSSCs)

Dye-sensitized solar cells (DSSCs) are a low-cost, semi-transparent, color-tunable form of next-generation solar cells. A significant breakthrough in the quest for low-cost photovoltaics came in 1991 with the seminal paper by Brian O’Regan and Michael Grätzel of a DSSC based on the sensitization of mesoporous TiO₂ electrodes instead of planar electrodes. It is for this reason that DSSCs are also referred to as “Grätzel cells”.

The best solar conversion efficiencies of liquid electrolyte-based DSSCs to date is 11-12%. However, DSSCs perform better than all other photovoltaics under diffuse light conditions (i.e. indoor-light conditions) and at higher temperatures (above 25 °C). DSSCs are also highlighted for their reasonable price to performance ratios, especially when made out of completely flexible materials. Due to their low thicknesses, their semi-transparency has useful applications as windows. While generally it is always
desired to absorb as much of the solar spectrum as possible, the inclusion of differing sensitizers also allows for modifiable aesthetics with color-tunable properties. In general, the key features of DSSCs include the prospect of low-cost materials and fabrication. While state of the art flexible DSSCs have been made, research in this dissertation is focused solely on small-scale laboratory solar cells.

In this section, I present a broad overview of the basic operating principles of DSSCs, as shown in Figure 1.7. A DSSC typically consists of a wide-band gap semiconductor (such as a TiO$_2$ film) that is sensitized to visible light by the adsorption of dyes to its surface. Such films employ a nanocrystalline deposition with a greater surface area than a flat surface can provide. This large surface area allows for efficient light absorption with a single monolayer of adsorbed dye molecules. The nanocrystalline semiconductor is attached to a conducting glass slide of fluorine-doped tin oxide (FTO) to allow for the transfer of electrons to a load. A complete cell is typically made up of two FTO slides, one as the working electrode (with TiO$_2$ and dye) and another as the counter electrode, with a redox mediator species in a liquid electrolyte to transfer charge between the slides. The iodide/triiodide redox couple is the most commonly used electrolyte species.
Figure 1.7. Operating principles of a dye-sensitized solar cell. The sensitized TiO$_2$ film acts as a working electrode with platinum on FTO as the counter electrode. The transfer of electrons in a working cell is shown with green dots.

Exposure of a DSSC to light leads to a sequence of reactions that allow for the conversion of sunlight to electricity. The absorption of light by the sensitizer, S, leads to the formation of an electronically excited state, S* (equation 1.1). The sensitizer in its excited state is designed such that it can inject electrons into the conduction band of TiO$_2$ (equation 1.3) rather than decaying back to the ground state via various radiative or non-radiative processes (equation 1.2). Injected electrons can then travel through the mesoporous network of particles to reach the FTO surface (equation 1.4), while a redox mediator in solution is employed to regenerate the resulting ground state dye (equation 1.5). The reduction of the oxidized form of the redox mediator at the counter electrode completes the circuit (equation 1.10). However, it is also possible for injected electrons to instead recombine with the oxidized dye to reform the ground state dye (equation 1.13) or
to be intercepted by the oxidized form of the redox mediator in the electrolyte (equations 1.11 and 1.12), both of which break the cell cycle. All of these electron transfer processes are given in equations 1.1-1.13 and shown with rate constants in Figure 1.8.

Photoexcitation (hv):

\[ S + h\nu \rightarrow S^* \]  \hspace{1cm} (1.1)

Excited-State Relaxation \( (k_{\text{relax}} = k_r + k_{\text{nr}}) \):

\[ S^* \rightarrow S \]  \hspace{1cm} (1.2)

Electron Injection \( (k_{\text{inj}}) \):

\[ S^* + TiO_2 \rightarrow S^+ + TiO_2(e^-) \]  \hspace{1cm} (1.3)

Charge Transport \( (k_{\text{trans}}) \):

\[ TiO_2(e^-) \rightarrow FTO(e^-) \]  \hspace{1cm} (1.4)

Dye Regeneration \( (k_{\text{reg}})^{66} \):

Overall:  \( 2S^+ + 4I^- \rightarrow I_3^- + I^- + 2S \)  \hspace{1cm} (1.5)

1.  \( S^+ + I^- \rightarrow [S^+I^-] \)  \hspace{1cm} (1.6)

2.  \( [S^+I^-] + I^- \rightarrow S + I_2^- \)  \hspace{1cm} (1.7)

3.  \( 2I_2^- \rightarrow I_3^- + I^- \)  \hspace{1cm} (1.8)

Aside:  \( I^- + I_2 \rightarrow I_3^- \)  \hspace{1cm} (1.9)

\[ I_3^- + 2e^- \rightleftharpoons 3I^- \]  \hspace{1cm} (1.10)

Charge Interception \( (k_{\text{int}})^{67} \):

\[ I_3^- + TiO_2(e^-) \rightarrow I_2^- + I^- \]  \hspace{1cm} (1.11)

\[ I_3^- + FTO(e^-) \rightarrow I_2^- + I^- \]  \hspace{1cm} (1.12)

Charge Recombination \( (k_{\text{rec}}) \):

\[ S^+ + TiO_2(e^-) \rightarrow S + TiO_2 \]  \hspace{1cm} (1.13)
Figure 1.8. Electron transfer pathways in DSSCs. Photoexcitation of dye (hν), electron injection from the excited state of the dye to the conduction band of TiO₂ (k_{inj}), electron transport within the TiO₂ network to the FTO substrate (k_{trans}), and regeneration of ground state dye by iodide (k_{reg}) make up the forward electron transfer processes in green. Back electron transfer processes are shown in red for the decay of excited state dye to ground state (k_{relax}), interception of TiO₂ electrons by the triiodide redox mediator (k_{int}), and recombination of TiO₂ electrons with the oxidized dye (k_{rec}).

The performance of DSSCs is determined thermodynamically from the four redox potentials depicted in Figure 1.8: the ground state of the sensitizer (S⁺/S), the excited state of the sensitizer (S⁺/S*), the iodide/triiodide redox couple (I⁻/I³⁻), and the conduction band edge or quasi-Fermi level (E_F) of the TiO₂ film. The difference between the energy levels of S⁺/S and S⁺/S* determines what energy photon is absorbed thereby governing the possible the amount of photocurrent. For sufficiently high photocurrents, the S⁺/S* level must be more negative than the conduction band edge to efficiently inject electrons, and the S⁺/S level must be more positive than the I⁻/I³⁻ to efficiently accept...
electrons. The total open circuit photovoltage that can possibly be obtained, $V_{oc}$, is dictated by the difference between $E_F$ and the $I_3^-$/$I^-$. Of course, the kinetics of the electron transfer processes also play a role in device performance. In DSSCs, the photocurrent is mainly determined by the kinetics at the semiconductor/electrolyte interface\(^\dagger\) because this physical barrier separates the electrons from the holes.\(^64,68\) This is unlike conventional p-n junction solar cells, where the charge separation and subsequent electron transfer processes depend on a built-in electric field (i.e. a Schottky barrier).\(^64,68\)

The following sections review the main electron transfer processes in DSSCs that dictate the total photocurrent that can be obtained in working device. The timescales for these processes are typically monitored experimentally by time-resolved laser spectroscopy.\(^68\) In the following sections, an efficient process is defined as a path with a rate constant two orders of magnitude larger than all kinetically competitive processes.\(^69\)

1.3.1 Electron Injection

Interfacial electron injection typically occurs on a femtosecond to picosecond timescale.\(^38\) This is several of orders of magnitude faster than emission decay lifetimes, resulting in efficient charge separation for the majority of sensitizers.\(^70\) Electron injection is observed to be particularly fast due to sensitizers strong binding to the TiO$_2$ surface and the vast continuum of acceptor states available in the TiO$_2$ network.\(^71\)

Electron injection kinetics are non-exponential in nature.\(^70\) This is attributed to the surface heterogeneity of nanocrystalline TiO$_2$, the distribution of anchoring modes of sensitizer attachment, and multiple injection processes occurring from different excited

\(^\dagger\) Diffusion in the electrolyte and nanocrystalline media also plays a role.
Electron injection can occur from the vibrationally hot $^1$MLCT (i.e. Franck-Condon state), thermally relaxed $^1$MLCT, or thermally relaxed $^3$MLCT excited states. Typically, if injection is slow (>1 ps) compared to vibrational relaxation of the excited state, then it likely originates from the lowest energy excited state, whereas if injection is fast (<50 fs) compared to nuclear relaxation, then it must originate from the $^1$MLCT state.

For a wide range of sensitizers studied, the picosecond component of electron injection was found to be dependent on driving force and distance, in agreement with non-adiabatic Marcus theory. Following the framework of Marcus theory, or more accurately Marcus-Gerischer theory as applied to solid/liquid interfaces, the rate of electron injection depends on the semiconductor acceptor density of states and the electronic coupling between sensitizer and semiconductor. As such, the precise sensitizer, anchoring substituent, and conduction-band-determining ions present in a particular electron injection measurement may have a drastic effect on the timescale.

### 1.3.2 Excited-State Relaxation

The rate of excited-state relaxation for a sensitizer competes with the rate of electron injection in the sense that the excited state must be around long enough for injection to occur. Ruthenium polypyridine complexes have been highly optimized as sensitizers due to their relatively long excited-state lifetimes. For instance, N719 has an excited-state lifetime of 60 ns and black dye has an excited-state lifetime of 32 ns.

### 1.3.3 Charge Transport

After electron injection occurs, electron transport within the conduction band and trap sites of the TiO$_2$ film occurs by diffusion, on a millisecond timescale. The typical
carrier diffusion coefficients of trap-limited transport in nanocrystalline TiO$_2$ are several orders of magnitude lower than those of single crystal TiO$_2$ (10$^{-4}$ cm$^2$/s vs. 0.4 cm$^2$/s).$^{69,79}$ This typically leads to an approximate one millisecond average transit time for collection over a 12 µm thick TiO$_2$ film.$^{69}$ However, because trap states have an exponential distribution of energies, the electron transit time has been observed to decrease with increasing light intensity (due to a higher electron population).$^{69}$

1.3.4 Charge Interception

Competing with charge transport, it is possible for acceptor species present in the electrolyte solution to directly intercept electrons in TiO$_2$. The timescale for this charge interception is also referred to as the electron lifetime.$^{69}$ Lifetimes observed with the iodide/triiodide redox couple are very long—millisseconds to tens of milliseconds—compared with other redox couples used in DSSCs, in part explaining the success of iodide electrolytes.$^{69}$ The rate of charge interception increases (to the detriment of collection efficiency) with thicker TiO$_2$ films.$^{64}$

This process of charge interception manifests itself in DSSCs as the main source of unfavorable cathodic current that is observed in the dark.$^{70}$ Charge interception is reported to depend strongly on the distribution and occupancy of intra-bandgap states in the semiconductor, and therefore upon variations in light intensity, applied potential bias, and the nature and concentration of species adsorbed.$^{69}$ While there are several possible acceptor species within the iodide electrolyte such as I$_2$, I$_3^-$, I$_2^-$, or I$, the interception with triiodide is expected to dominate.$^{67}$
1.3.5 Dye Regeneration

The reduced form of the redox mediator must regenerate the sensitizer prior to its recombination with an electron in TiO$_2$. Iodide has been reported to reduce N719$^+$ dye with a half-life time of one microsecond.$^{66}$ Of course, the kinetics of regeneration are complicated by the fact that the iodide/triiodide system is a two electron redox couple (equation 1.10), which requires the reaction to proceed through one or more intermediate states.$^{65}$ While the mechanism of the reduction of the oxidized dye by iodide is still debated,$^{38,69}$ there is general consensus for the three reactions given in equations 1.6-1.8, where reaction step 2 (equation 1.7) is thought to be rate limiting.$^{67}$ While there is evidence that iodide binds to the thiocyanate ancillary ligands with dyes such as N719,$^{66}$ the structure of intermediate complexes for non-thiocyanate containing sensitizers is still unknown.$^{67}$ In general, the rate of regeneration of the sensitizer has been found to depend strongly on the nature and concentration of species present in the electrolyte as well as the ground state reduction potential of the sensitizer.$^{38,69}$

1.3.6 Charge Recombination

The kinetics for the recombination of electrons in the conduction band with the oxidized sensitizer follow a multi-exponential time law (i.e. stretched exponential), occurring on a timescale of tens to hundreds of microseconds depending on the cell conditions.$^{59,69}$ The precise recombination rate constant is strongly dependent on excitation intensity, electrolyte composition, and the application of electrical bias to the TiO$_2$ film.$^{80}$

This timescale raises the question of why the rate of back electron transfer (i.e. charge recombination) is observed to be up to 10 orders of magnitude slower than the rate
of forward electron transfer (i.e. electron injection) in DSSCs.\textsuperscript{69} This is explained by a multitude of factors, summarized below.

In contrast to electron injection into TiO\textsubscript{2} with a continuum of acceptor states, charge recombination occurs from a solid to the discrete electronic state of the oxidized dye.\textsuperscript{69} This significantly decreases the acceptor density of states that contributes to the rate of back electron transfer in the Marcus-Gerischer model.\textsuperscript{81-83}

Recombination rate constants for several ruthenium polypyridyl sensitizers have been found to depend on distance\textsuperscript{84,85} and driving force\textsuperscript{86} in accordance with Marcus-inverted-regime behavior,\textsuperscript{70} although there is much debate on the matter.\textsuperscript{38,59,87} This leads to decreased recombination rate constants with larger driving force.

Also, on a molecular level, there is a greater electronic coupling constant for electron injection because the lowest-unoccupied molecular orbital (LUMO) is prominent on the ligand that directly attaches to the semiconductor surface. However, the highest-occupied molecular orbital (HOMO) is localized away from the surface, with the positive charge stabilized by the metal, thereby reducing the electronic coupling constant for back electron transfer.\textsuperscript{69}

Finally, electrons in the conduction band can readily thermalize and become trapped in intraband states.\textsuperscript{69} The dynamics of trapping and detrapping as well as transport of carriers within the TiO\textsubscript{2} network are known to inhibit the overall reaction kinetics of recombination.\textsuperscript{69}

Despite the microsecond timescale for recombination with the oxidized dye, this electron transfer process is typically not that much slower than the ~1 microsecond timescale regeneration rates with optimized dyes.\textsuperscript{88} Therefore, charge recombination is
known to noticeably decrease efficiencies of DSSCs.\textsuperscript{89,90} For this reason, we focus our studies on inhibiting this particular process with conformational changes to the dye.

1.4 Research Plan

We incorporate methyl steric hindrance in arylterpyridyl ruthenium complexes into DSSCs in the hopes of decreasing recombination rate constants, thereby more effectively completing the cycle of dye regeneration in productive ways. We study the systematic introduction of steric hindrance across the Steric Series of chromophores to better elucidate the extent to which conformational changes are beneficial to photoinduced electron transfer processes.

In principle, excited state inter-ring conformational dynamics between the aryl substituent and one of the polypyridines of the chromophore in DSSCs would serve two functions analogous to their role in the DBA molecules. See Figure 1.9 for a schematic of the description that follows. First, in the forward direction, planarization driven by intraligand electron delocalization would facilitate forward electron transfer from the MLCT excited state manifold of the dye into the conduction band of the TiO\textsubscript{2}. Once the dye has been oxidized, inter-ring twisting would occur, driven by steric interactions. The more twisted conformation would then limit recombination of a conduction band electron to the oxidized dye. While there has been exploration into the impact of dye structure on DSSC function, studies that have focused, for example, on recombination rates, have largely focused on distance and driving force dependencies.\textsuperscript{82,85-87,91-93} To our knowledge, there have not been efforts to consider dynamical functionalities impacting electronic coupling.
Figure 1.9. Design scheme for conformational trapping of electrons in DSSCs. Ring rotation is performed at steps indicated by $\Delta \theta$. Both rate constants ($k_{\text{inj}}$ and $k_{\text{rec}}$) are expected to be modulated by ligand-based motion as seen in other DBA models. The break in energy is intentional to show the amount of energy expended is small compared to the fraction absorbed.

Chapter 2 of this dissertation serves as the foundation for the study of the structurally tuned aryl-substituted terpyridine ruthenium chromophores. This chapter includes the synthesis and electrochemical characterization for the Steric Series and relevant model Ru(II) terpyridine systems from which the Steric Series is derived. The photophysics of each of these Ru(II) complexes in solution are also explored and reported. The solution-based values for MLCT extinction coefficients, reduction potentials of ground state and excited states, amount of energy stored in the excited
states, and excited-state lifetimes are all subsequently used in device studies in Chapters 4 and 5.

Chapter 3 describes the materials and procedures needed for assembling complete DSSCs. The Ru(II) complexes of the Steric Series are incorporated into functioning DSSCs that include a sensitized mesoporous TiO$_2$ film on an FTO working electrode, a platinum-coated FTO counter electrode, and an optimized iodide/triiodide electrolyte solution. For comparison, DSSCs are also made with the champion dye, N719, under the same conditions as the Steric Series. This chapter also includes absorption characteristics for the dyes on film and in devices, and determines the parameters needed to consistently measure the efficiencies of complete devices in Chapter 4.

To determine the implications of incorporating aryl-substituted terpyridine complexes in DSSCs, efficiency measurements are performed as described in Chapter 4. First, a photovoltaic conversion background is provided to define the basic solar cell terms and conditions. Consistent efficiency measurements are made across several DSSCs of each sensitizer to assess trends. The total power conversion efficiency measurements are determined and then deconstructed into external and internal efficiency components with the help of additional wavelength-dependent photocurrent measurements. The deconstruction of underlying photoinduced electron transfer processes in this chapter allows us to further elucidate what aspects of the device are most greatly affected by the introduction of steric hindrance.

In Chapter 5, transient absorption kinetics are measured to determine the charge recombination timescales of sensitized TiO$_2$ films. This chapter concludes the work on the series of structurally tuned aryl-substituted terpyridine ruthenium complexes by
determining if the conformational changes of these chromophores are beneficial for DSSCs. While rates of charge recombination are observed to drastically increase across the Steric Series in concurrence with our original hypothesis, it will be necessary to obtain better injection yields in order to see the benefits in the context of DSSCs. Alternative applications of aryl-substituted polypyridyl ruthenium complexes are suggested for better implementations of these structurally tuned conformations.

This body of work describes a systematic approach to studying the role of structural modifications and structure-specific dynamics on photoinduced electron transfer processes in DSSCs. In preparing and characterizing the arylterpyridyl ruthenium complexes in solution, the power of structural conformational changes is shown with drastically different excited-state lifetimes. In application to DSSCs, these changes are more subtly seen in efficiency measurements, with benefits mainly seen in the lengthened energy-wasting back electron transfer pathway. More lucrative applications of these complexes are suggested in devices where charge recombination pathways are more detrimental.

1.5 References

(1) Dixson-Declève, S. Presentation of the IPCC Fifth Assessment Working Group II Report, 2014.


Chapter 2

2.1 Introductory Remarks

As outlined in Chapter 1, the characterization of structurally tuned aryl-terpyridine ruthenium(II) complexes reported in this chapter lays the groundwork for understanding future studies of these complexes on TiO₂ film and in complete DSSCs. In this chapter, the synthesis, and electrochemical and photophysical properties (static, time-resolved, and temperature-dependent) of a series of Ru(II) complexes are reported. All are based on a 2,2ʹ:6ʹ,2ʺ-terpyridine (tpy) ligand framework, modeled on Black dye, one of the champion dyes in DSSCs.²

As the foundation for studying the effects of structurally-tuned aryl-substituted terpyridine ruthenium complexes, nine complexes are explored (see Figure 2.1). Three of the complexes reported feature a carboxylic acid linker at the para-position of the aryl moiety for future studies in complete DSSCs (Chapters 4 and 5). For the simplicity of studying chromophore perturbations due to a single aryl substituent, we consider the dynamic arylated bridge at only the 4ʹ-position of the tpy. For the ancillary spectator ligand, the electron-rich 4,4ʹ,4ʺ-tert-buty1-2,2ʹ:6ʹ,2ʺ-terpyridine (tbtpy) is used, as opposed to thiocyanate ligands common to efficient sensitizers such as black dye and N719. This serves to avoid complications in the interpretation of initial photophysics due

§ All data reported in this chapter have previously been published.¹
to the presence of linkage isomers from the thiocyanate ligands. Any future efforts to optimize dyes of this nature are likely to require the thiocyanate ligands, due to superior dye properties in light harvesting, particularly in redder regions of the solar spectrum.

Figure 2.1. Synthesized Ru(II) complexes investigated in this chapter. The Heteroleptic Series (outlined in black) compares heteroleptic [Ru(tpy)(tbtpy)]^{2+} as derived from homoleptic [Ru(tpy)]^{2+} and [Ru(tbtpy)]^{2+}. The Ester/Acid Addition (outlined in dark red) compares para substitution on the aryl group from methyl in [Ru(tpy)(tbtpy)]^{2+} to methyl ester in [Ru(1')(tbtpy)]^{2+} to carboxylic acid in [Ru(1)(tbtpy)]^{2+}. The Steric Series compares the sequential addition of methyl steric bulk for both methyl ester complexes (outlined in dashed blue) and carboxylic acid complexes (outlined in solid blue).
The complexes described herein allow for three distinct comparisons to be made, as outlined in Figure 2.1. First, we review and supplement literature concerning the insertion of an aryl substituent at the 4′-terpyridine position. The photophysics of homoleptic model complexes [Ru(tpy)₂]^{2+} and [Ru(ttpy)₂]^{2+} where tpy = 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine provide a baseline from which subsequent arylterpyridyl Ru(II) trends can be noted. This is followed by a comparison (the Heteroleptic Series) between homoleptic and heteroleptic complexes involving both the electron rich tbtpy ligand and the simplest of the arylated ligands, tpy.

Property variations in heteroleptic complexes are then explored relative to changes at the para-position of the aryl substituent, primarily focusing on the introduction of carboxylic acid and methyl ester moieties (the Ester/Acid Addition).

The last comparison is among complexes of varying degrees of steric bulk across the arylterpyridine ligand, with the introduction of methyl substituents in the ortho-aryl position(s) (the Steric Series). The Steric Series is studied in two separate subgroups: carboxylic acid-containing complexes ([Ru(1)(tbtpy)]^{2+}, [Ru(2)(tbtpy)]^{2+}, and [Ru(3)(tbtpy)]^{2+}) and methyl ester-containing complexes ([Ru(1′)(tbtpy)]^{2+}, [Ru(2′)(tbtpy)]^{2+}, and [Ru(3′)(tbtpy)]^{2+}) (see Figure 2.1). In addition to providing the necessary foundation for future photophysical studies on TiO₂ films, these complexes reveal new insights into the excited-state properties of terpyridyl Ru(II) complexes. We show that through minor synthetic modifications, the activation barriers (from the ³MLCT states to the triplet metal-centered (³MC) states) are changed, leading to drastic impacts on excited-state lifetimes.
2.2 Experimental

2.2.1 General Information

All reagents and materials from commercial sources were used as received. Solvents and reagents for synthesis were purchased from Sigma-Aldrich unless otherwise noted. This includes the ligands 2,2′-bipyridine (bpy), 2,2′:6′,2″-terpyridine (tpy), and 4,4′,4″-tri-tert-butyl-2,2′:6′,2″-terpyridine (tbtpy). All deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc.

2.2.2 Synthesis

The ligand 4’-bromo-2,2′:6′,2″-terpyridine (brtpy) was purchased from TCI America. Ruthenium(III) chloride hydrate and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) were purchased from Strem Chemicals, Inc. The arylboronic acids used in Suzuki coupling, 4-formyl-2,6-dimethylphenylboronic acid and 4-formyl-2-methylphenylboronic acid, were purchased from Cuschem, Inc. The ligands 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine (ttpy) and 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (I) were synthesized according to published procedures (see schematic in Figure 2.2).³⁴ Precursor complexes Ru(tpy)Cl₃, Ru(ttpy)Cl₃, and Ru(tbtpy)Cl₃ and homoleptic target complexes [Ru(bpy)₃](PF₆)₂, [Ru(tpy)₂](PF₆)₂, [Ru(ttpy)₂](PF₆)₂, and [Ru(tbtpy)₂](PF₆)₂ were prepared in a similar manner to previously published procedures,⁵⁻⁷ using triethylamine as a reductant.¹H NMR and two-dimensional (2D) COSY NMR spectra were obtained on a Bruker Advance-III 300 MHz spectrometer. Accurate mass spectrometry analyses of metal complexes were obtained in-house from
the University of Colorado’s Central Analytical Laboratory. All $^1$H NMR spectra are reported in section A.1. of Appendix A.

![Figure 2.2](image)

Figure 2.2. Arylterpyridyl ligand syntheses.

The intermediate formyl-containing arylterpyridyl ligands (2a and 3a) were prepared by modifying a previously published procedure from our lab (see Figure 2.2). This utilized the Suzuki cross-coupling catalytic cycle, the mechanism of which is outlined in Figure 2.3.

One mmol of brtpy and 1.4 mmol of arylboronic acid were reacted in the presence of 2 mmol Na$_2$CO$_3$ and 2.5 mol% Pd(PPh$_3$)$_4$ in a 75 mL degassed solution of 1:1 water/acetonitrile at reflux under nitrogen for 72 hrs. The solvent was removed and the residual oil extracted in water and dichloromethane. The organic layer was again concentrated and the residue was purified on a silica column using chloroform with the
gradual addition of 1-20% methanol. The compounds (2a and 3a) were used in the next synthetic step without further purification.

(2a) yield: 94.8 mg (54%). $^1$H NMR (300 MHz, Chloroform-d) δ 10.06 (s, 1H), 8.73 – 8.67 (m, 4H), 8.48 (s, 2H), 7.91 (ddd, $J = 8.2$, 7.5, 1.6 Hz, 2H), 7.84 (dt, $J = 1.8$, 0.7 Hz, 1H), 7.80 (ddd, $J = 7.8$, 1.7, 0.6 Hz, 1H), 7.54 (d, $J = 7.7$ Hz, 1H), 7.37 (ddd, $J = 7.5$, 4.7, 1.3 Hz, 2H), 2.44 (s, 3H). ESI+MS: 352.1 [M+H$^+$].

(3a) yield: 167.3 mg (45%). $^1$H NMR (300 MHz, Chloroform-d) δ 10.00 (s, 1H), 8.71 (dt, $J = 8.0$, 1.1 Hz, 2H), 8.66 (ddd, $J = 4.8$, 1.8, 0.9 Hz, 2H), 8.31 (s, 2H), 7.88 (ddd, $J = 8.0$, 7.5, 1.8 Hz, 2H), 7.63 (s, 2H), 7.33 (ddd, $J = 7.5$, 4.8, 1.2 Hz, 2H), 2.17 (s, 6H). ESI+MS: 366.1 [M+H$^+$].

Figure 2.3. Suzuki cross-coupling catalytic cycle applied to aryl-substituted terpyridine ligands utilized in this work. Adapted from Gjiri, E. (2015).
Tollen’s oxidation was subsequently performed to turn aldehyde substituents into carboxylic acids by modifying a procedure\textsuperscript{12} to utilize formylarylterpyridines instead of formylterpyridines. Here, 0.5 mmol of formylarylterpyridine (2a or 3a) was mixed with 0.55 mmol AgNO\textsubscript{3} in 2.25 mL of 1M NaOH and stirred in 7.5 mL of ethanol for 16 hours until solid silver precipitated on the sides of the flask. The remaining black silver oxide was removed by filtration, rinsed with 1 M NaOH (~2 mL), and the solid was discarded. Approximately 10 mL of water was added to the collected filtrate and the ethanol was removed by rotary evaporation. The synthesized carboxylate form of the ligand was then protonated (pH = 3) using 1 M HCl, leading to a white flaky precipitate (2 or 3). The solid was collected on a Buchner funnel and rinsed with water. As carboxylic acids, ligands 1, 2, and 3 are insoluble in many common solvents. DMSO-\textit{d}_6 was found to be suitable for obtaining NMR spectra.

(2) yield: 47.5 mg (56%). \textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_6) \(\delta\) 8.89 – 8.84 (m, 2H), 8.83 (ddd, \(J = 5.1, 1.7, 0.8\) Hz, 2H), 8.54 (s, 2H), 8.25 (td, \(J = 7.9, 1.7\) Hz, 2H), 8.02 – 7.97 (m, 1H), 7.93 (ddd, \(J = 8.0, 1.8, 0.6\) Hz, 1H), 7.70 (ddd, \(J = 7.2, 5.0, 1.0\) Hz, 2H), 7.56 (d, \(J = 7.9\) Hz, 1H), 2.40 (s, 3H). ESI+MS: 368.1 [L+H\textsuperscript{+}].

(3) yield: 141.3 mg (77%). \textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_6) \(\delta\) 8.76 – 8.65 (m, 4H), 8.23 (s, 2H), 8.05 (ddd, \(J = 8.2, 7.5, 1.6\) Hz, 2H), 7.79 (s, 2H), 7.52 (ddd, \(J = 7.5, 4.7, 1.3\) Hz, 2H), 2.10 (s, 6H). ESI+MS: 382.1 [L+H\textsuperscript{+}].

For ease of purification of metal complexes, ligands were converted to their methyl ester forms via standard Fischer esterification.\textsuperscript{4,13,14} Here, 0.33 mmol of the carboxylic acid form of the ligand (1, 2, or 3) was heated in 12 mL methanol with a catalytic amount of concentrated H\textsubscript{2}SO\textsubscript{4} (3.3 mmol) for 24 hours or until the solution...
became clear. Approximately 10 mL of water was added, the methanol was removed by evaporation, and the remaining aqueous solution was neutralized with 1 M NaOH, causing a white precipitate to form. The solid was filtered over a Buchner funnel, dried overnight, and recrystallized in 1:1 methanol/dichloromethane to remove any off-white color from the precipitate due to iron-containing impurities. The recrystallized ligands (1', 2', and 3') were then used as such for subsequent metal complexation.

(1') yield: 191.6 mg (81%). $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 8.77 (s, 2H), 8.76 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 2H), 8.70 (dt, $J = 8.0, 1.1$ Hz, 2H), 8.22 – 8.14 (m, 2H), 8.02 – 7.95 (m, 2H), 7.92 (td, $J = 7.7, 1.8$ Hz, 2H), 7.39 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 2H), 3.97 (s, 3H). ESI+MS: 368.1 [L+H$^+$].

(2') yield: 96.1 mg (80%). $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 8.73 – 8.65 (m, 4H), 8.46 (s, 2H), 8.00 (dt, $J = 1.8, 0.6$ Hz, 1H), 7.97 – 7.86 (m, 3H), 7.43 (d, $J = 7.9$ Hz, 1H), 7.39 – 7.33 (m, 2H), 3.96 (s, 3H), 2.41 (s, 3H). ESI+MS: 382.1 [L+H$^+$].

(3') yield: 124.2 mg (93%). $^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 8.77 – 8.63 (m, 4H), 8.31 (s, 2H), 7.91 (td, $J = 7.7, 1.8$ Hz, 2H), 7.81 (s, 2H), 7.36 (ddd, $J = 7.6, 4.8, 1.2$ Hz, 2H), 3.94 (s, 3H), 2.15 (s, 6H). ESI+MS: 396.1 [L+H$^+$].

Several of the bis-heteroleptic metal complexes were synthesized in a manner similar to previously published procedures.$^{5,6}$ For [Ru(1')(tbtpy)]$^{2+}$, [Ru(2')(tbtpy)]$^{2+}$, [Ru(3')(tbtpy)]$^{2+}$, and [Ru(ttpy)(tbtpy)]$^{2+}$, one equivalent of Ru(tbtpy)Cl$_3$ was reacted with 1 eq. of the arylterpyridyl ligand (1', 2', 3', or ttpy) with a few drops of triethylamine in 20 mL of refluxing ethanol for 5 hours. A silica column was used for purification with 8:1:1 acetonitrile, water, and saturated potassium nitrate as the eluent. The metal complex was collected as the nitrate salt, concentrated, and a 10-fold excess of
aqueous $\text{NH}_4\text{PF}_6$ was then added. The red precipitate was collected in a medium frit, and washed with water and diethyl ether. Recrystallization was performed with slow diffusion of diethyl ether into concentrated acetonitrile solutions of the compound. To remove any excess nitrate or hexafluorophosphate salts, compounds were rewashed with water followed by a diethyl ether rinse. NMR coupling assignments of $[\text{Ru}(1')(\text{tbtpy})]^{2+}$, $[\text{Ru}(2')(\text{tbtpy})]^{2+}$, and $[\text{Ru}(3')(\text{tbtpy})]^{2+}$ are confirmed with 2D COSY spectra reported in section A.2. of Appendix A.

$[\text{Ru}(1')(\text{tbtpy})]^{2+}$ yield: 79.3 mg (71%). $^1\text{H}$ NMR (300 MHz, Acetonitrile-$d_3$) $\delta$ 9.01 (s, 2H), 8.78 (s, 2H), 8.64 (ddd, $J = 8.1$, 1.3, 0.8 Hz, 2H), 8.51 (dd, $J = 2.1$, 0.7 Hz, 2H), 8.39 – 8.27 (m, 4H), 7.95 (ddd, $J = 8.2$, 7.6, 1.5 Hz, 2H), 7.36 (ddd, $J = 5.6$, 1.5, 0.7 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.12 (dd, $J = 6.0$, 2.1 Hz, 2H), 3.99 (s, 3H), 1.75 (s, 9H), 1.31 (s, 18H). Acc. Mass: found 435.1604 [$\text{M}^{2+}$]; calcd. 435.1599.

$[\text{Ru}(2')(\text{tbtpy})]^{2+}$ yield: 113.2 mg (99%). $^1\text{H}$ NMR (300 MHz, Acetonitrile-$d_3$) $\delta$ 8.79 (s, 2H), 8.74 (s, 2H), 8.51 (ddd, $J = 4.3$, 1.4, 0.8 Hz, 4H), 8.18 (dt, $J = 1.8$, 0.6 Hz, 1H), 8.13 (ddd, $J = 8.0$, 1.8, 0.7 Hz, 1H), 7.91 (ddd, $J = 8.2$, 7.6, 1.5 Hz, 2H), 7.80 (d, $J = 7.9$ Hz, 1H), 7.36 (ddd, $J = 5.6$, 1.5, 0.7 Hz, 2H), 7.27 (dd, $J = 6.0$, 0.5 Hz, 2H), 7.19 (ddd, $J = 7.6$, 5.6, 1.3 Hz, 2H), 7.14 (dd, $J = 6.0$, 2.1 Hz, 2H), 3.97 (s, 3H), 2.70 (s, 3H), 1.74 (s, 9H), 1.31 (s, 18H). Acc. Mass: found 442.1678 [$\text{M}^{2+}$]; calcd. 442.1678.

$[\text{Ru}(3')(\text{tbtpy})]^{2+}$ yield: 95.1 mg (91%). $^1\text{H}$ NMR (300 MHz, Acetonitrile-$d_3$) $\delta$ 8.79 (s, 2H), 8.60 (s, 2H), 8.52 (dd, $J = 2.1$, 0.7 Hz, 2H), 8.44 (ddd, $J = 8.2$, 1.3, 0.8 Hz, 2H), 7.99 (s, 2H), 7.90 (ddd, $J = 8.2$, 7.6, 1.5 Hz, 2H), 7.36 (ddd, $J = 5.6$, 1.5, 0.7 Hz, 2H), 7.25 – 7.13 (m, 6H), 3.96 (s, 3H), 2.44 (s, 6H), 1.75 (s, 9H), 1.32 (s, 18H). Acc. Mass: found 449.1769 [$\text{M}^{2+}$]; calcd. 449.1756.
[Ru(ttpy)(tbtpy)]^{2+} yield: 107.7 mg (96%). \(^1\)H NMR (300 MHz, Acetonitrile-\(d_3\)) \(\delta\) 8.99 (s, 2H), 8.80 (s, 2H), 8.65 (ddd, \(J = 8.2, 1.3, 0.8\) Hz, 2H), 8.53 (dd, \(J = 2.1, 0.7\) Hz, 2H), 8.12 (d, \(J = 8.2\) Hz, 2H), 7.93 (ddd, \(J = 8.1, 7.7, 1.5\) Hz, 2H), 7.61 – 7.55 (m, 2H), 7.34 (ddd, \(J = 5.6, 1.5, 0.7\) Hz, 2H), 7.25 (dd, \(J = 6.0, 0.6\) Hz, 2H), 7.19 (ddd, \(J = 7.6, 5.6, 1.3\) Hz, 2H), 7.12 (dd, \(J = 6.0, 2.1\) Hz, 2H), 2.54 (s, 3H), 1.75 (s, 9H), 1.31 (s, 18H). Acc. Mass: found 410.1660 [M\(^{2+}\)]; calcd. 410.1660.

To obtain carboxylic acid-containing bis-heteroleptic species \([\text{Ru}(1')(tbtpy)]^{2+}\), \([\text{Ru}(2')(tbtpy)]^{2+}\), and \([\text{Ru}(3')(tbtpy)]^{2+}\), the respective methyl ester metal complexes \(([\text{Ru}(1')(tbtpy)]^{2+}, [\text{Ru}(2')(tbtpy)]^{2+}, \text{or} [\text{Ru}(3')(tbtpy)]^{2+})\) were first hydrolyzed in 33 \(\mu\)mol aliquots with 2.5 mL of 1 M NaOH in 20 mL of acetonitrile heated at reflux overnight. The solutions were concentrated and 20 mL of aqueous HPF\(_6\) was added to crash out the acidic product (pH = 2). The solid was filtered and rinsed with water and diethyl ether. Recrystallization was performed with slow diffusion of diethyl ether into concentrated acetonitrile solutions of the compound. In time, compounds were observed to become a darker red with a decreased solubility in acetonitrile. This has been noted by others and ascribed to a loss of HPF\(_6\) in the solid state.\(^4\) Therefore, prior to photophysical and electrochemical characterization, compounds were reacidified in aqueous HPF\(_6\), filtered, and washed with water and diethyl ether.

\([\text{Ru}(1')(tbtpy)]^{2+}\) yield: 35.4 mg (97%). \(^1\)H NMR (300 MHz, Acetonitrile-\(d_3\)) \(\delta\) 9.02 (s, 2H), 8.78 (s, 2H), 8.64 (dq, \(J = 8.1, 0.8\) Hz, 2H), 8.53 – 8.48 (m, 2H), 8.37 (d, \(J = 8.3\) Hz, 2H), 8.32 – 8.26 (m, 2H), 7.94 (td, \(J = 7.9, 1.6\) Hz, 2H), 7.36 (ddd, \(J = 5.5, 1.5, 0.7\) Hz, 2H), 7.26 – 7.17 (m, 4H), 7.12 (dd, \(J = 6.0, 2.1\) Hz, 2H), 1.75 (s, 9H), 1.31 (s, 18H). Acc. Mass: found 428.1524 [M\(^{2+}\)]; calcd. 428.1521
$[\text{Ru}(2)(\text{tbppy})]^2^+ \text{ yield: 34.4 mg (92.5%).}$ $^1\text{H NMR (300 MHz, Acetonitrile-$d_3$)} \delta$

8.79 (s, 2H), 8.77 (s, 2H), 8.56 – 8.50 (m, 4H), 8.22 (s, 1H), 8.17 (d, $J = 8.2$ Hz, 1H), 7.95 – 7.87 (m, 2H), 7.78 (d, $J = 7.9$ Hz, 1H), 7.36 (ddd, $J = 5.6$, 1.6, 0.7 Hz, 2H), 7.29 (dd, $J = 6.0$, 0.5 Hz, 2H), 7.23 – 7.17 (m, 2H), 7.16 (dd, $J = 6.0$, 2.1 Hz, 2H), 2.73 (s, 3H), 1.75 (s, 9H), 1.32 (s, 18H). Acc. Mass: found 435.1605 [M$^{2+}$]; calcd. 435.1599

$[\text{Ru}(3)(\text{tbppy})]^2^+ \text{ yield: 59.0 mg (99%).}$ $^1\text{H NMR (300 MHz, Acetonitrile-$d_3$)} \delta$

8.78 (s, 2H), 8.60 (s, 2H), 8.51 (dd, $J = 2.1$, 0.7 Hz, 2H), 8.49 – 8.39 (m, 4H), 7.99 (s, 2H), 7.89 (ddd, $J = 8.2$, 7.7, 1.5 Hz, 3H), 7.36 (ddd, $J = 5.4$, 1.5, 0.6 Hz, 2H), 7.25 – 7.13 (m, 6H), 2.44 (s, 6H), 1.75 (s, 9H), 1.32 (s, 18H). Acc. Mass: found 442.1678 [M$^{2+}$]; calcd. 442.1678

2.2.3 Absorption and Emission Spectra

Solutions of complexes for all photophysical measurements utilized Burdick and Jackson UV-grade acetonitrile. Steady-state electronic absorption spectra were recorded with a Hewlett-Packard diode array UV-vis spectrophotometer (HP8452A). Emission spectra, quantum yields, and room-temperature lifetimes were each determined in triplicate for samples at 23-24°C. Emission spectra were obtained at room temperature using a Photon Technology International spectrofluorometer (PTI-814) with an Ushio xenon short arc lamp (UXL-75XE) and a Hamamatsu PMT (R928P) operating at −1000 V, DC. Samples in 1 × 1 cm quartz cuvettes (NSG precision cells) were excited at 450 nm and the emission from 535 nm to 845 nm was recorded at 90° relative to the excitation. A 500 nm long pass filter (ThorLabs) was in place before detection to eliminate scatter at 3/2 $\lambda_{\text{ex}}$. Monochromator slit widths were kept at 1.05 mm / 1.05 mm excitation and 2 mm / 2 mm collection to ensure all samples were within the linear
regime of photon detection but with a reasonable ratio of signal to noise. All emission spectra were corrected for instrument response using a tungsten lamp provided by the manufacturer, which has been calibrated against a NIST standard tungsten lamp.

Radiative quantum yields ($\phi_r$) were measured for new compounds relative to deaerated $^{**}$ [Ru(bpy)$_3$](PF$_6$)$_2$ in acetonitrile ($\phi_{std} = 0.095$). Values are calculated according to equation 2.1,$^{16}$

$$\phi_{smp} = \phi_{std} \left( \frac{I_{smp}}{A_{smp}} \right) \left( \frac{A_{std}}{I_{std}} \right) \left( \frac{\eta_{smp}}{\eta_{std}} \right)^2 \quad (2.1)$$

where $\phi_{smp}$ is the radiative quantum yield of the sample, $\phi_{std}$ is the radiative quantum yield of the [Ru(bpy)$_3$]$^{2+}$ standard, $I_{smp}$ and $I_{std}$ are integrated emission intensities of the sample and the standard, respectively, $A_{smp} \sim 0.1$ and $A_{std} \sim 0.01$ are the absorbances of the sample and the standard, respectively, at the excitation wavelength (450 nm), and $\eta_{smp}$ and $\eta_{std}$ are the indexes of refraction of the samples and standard solutions. Because both measurements were taken in the same solvent, the last term is 1.

Corrected emission spectra (following solvent background count subtraction) were analyzed by a one-mode Franck-Condon fitting procedure described previously by Meyer and coworkers.$^{7,17}$ The spectra were fit to equation 2.2$^{17}$ with a best fit determined by visual inspection and minimization of the squared sum of the residuals.

$$I(\nu) = \sum_{\nu'' = 0}^{n} \left( \frac{E_0 - \nu'' \hbar \omega_M}{E_0} \right)^3 \left( S_{M \nu''} \right)^2 \times \exp \left[ -4 \ln 2 \left( \frac{\nu - E_0 + \nu'' \hbar \omega_M}{\Delta \nu_{0.1/2}} \right) \right] \quad (2.2)$$

$^{**}$ Teflon tubing was used to introduce a stream of argon into the solution for 30 min to remove oxygen. [Ru(bpy)$_3$]$^{2+}$ was found to be the only sample susceptible to oxygen quenching and thus is the only sample deaerated in the reported quantum yield measurements.
The spectral fitting procedure yielded the energy separation between the emissive $^3$MLCT state and the ground state ($E_0$), the quantum spacing for the medium frequency acceptor mode ($\hbar \omega_M$), the electron vibration coupling constant or Huang-Rhys factor ($S_M$), and the homogeneously broadened linewidth of the zeroth vibronic transition ($\Delta \nu_{0,1/2}$). A graphical depiction of these parameters is represented in Figure 2.4.

![Graphical depiction of parameters used in emission spectral fitting.](image)

Figure 2.4. Graphical depiction of parameters used in emission spectral fitting. The steady state emission spectrum is deconvoluted into four Gaussian vibrational components. Reprinted with permission from Murtaza, Z. et al. (1994). Copyright 1994 American Chemical Society.

It is noted that the value of $\hbar \omega_M$ was held constant at 1350 cm$^{-1}$ for bipyridyl-based complexes and at 1380 cm$^{-1}$ for terpyridyl-based complexes as the procedure leads to an over-parameterized fit. The values 1350 cm$^{-1}$ and 1380 cm$^{-1}$ were chosen because these are the reported values for $\hbar \omega_M$ for [Ru(bpy)$_3$]$^{2+}$ and [Ru(tpy)$_2$]$^{2+}$, respectively, in low temperature studies. This type of spectral fitting procedure (i.e., where the medium frequency acceptor mode value is held constant) has been applied to similar systems.
2.2.4 Time-Correlated Single Photon Counting (TCSPC).

TCSPC methods were employed to measure excited state lifetimes. Excitation laser pulses were derived from a mode-locked femtosecond Ti:sapphire oscillator (Tsunami, Spectra Physics) operating at 790 nm with a repetition rate of 82 MHz pumped by a continuous wave diode laser (Millennia Xs Pro, Spectra Physics). The pulses (laser pulse width ~100 fs) were passed through a pulse-picker (NEOS technologies) utilizing an acousto-optic modulator (Bragg cell) to change the repetition rate to 4.1 MHz. The deflected output beam was passed through a β-barium borate (BBO) crystal to generate the second harmonic of the fundamental centered at 395 nm. The output was filtered to remove any unconverted fundamental and passed through an acetonitrile solution of the sample in a 1 × 1 cm quartz cuvette with 25-60 µW of laser power (6-15 pJ/pulse). The emitted light was collected at 90° to the excitation, collimated and then focused, passed through a 10 nm bandpass filter (640 nm, Thorlabs), and detected using a water-cooled microchannel plate photomultiplier tube (R3809U-50 PMT, Hamamatsu) negatively biased at -2900 V. The photon counting procedure was initiated by signal detection at the PMT.

Figure 2.5. Schematic of TCSPC setup. The Millennia pump laser (in enclosure 1) of 532 nm light is directed into the Tsunami oscillator to generate a mode-locked 790 nm beam. The beam is brought down to 4” height by the periscope and then directed into a pulse picker (PP) to create the desired 4.1 MHz repetition rate. The beam is frequency doubled with a BBO crystal to generate 395 nm light. The sample is excited with 395 nm light and detected by the PMT at 90° (in enclosure 2). The red light that is not doubled by the BBO is used as a trigger for single photon counting experiments.
The signal from the PMT was fed into a preamplifier (HFAC-26, Becker & Hickl GmbH) and then to a constant fraction discriminator (CFD). The output from the CFD was used as the start pulse in a time-to-amplitude converter (TAC). The stop signal was obtained by diverting a small fraction of the laser output from the pulse picker onto a fast photodiode (Silicon Pin Detector, Newport). The output signal of the TAC was fed into the analog-to-digital converter (ADC), the contents of which were transferred to and stored in a computer with a single-photon counting card (SPC-630, Becker & Hickl GmbH).

A 15-minute scan (650 to 2500 counts depending on emission intensity) was collected and processed using programs of local origin. Linearity of the PMT signal was checked, with the signal intensity adjusted if necessary via attenuation of the excitation beam using neutral density filters. No differences in transient lifetimes were found upon magic angle detection of emission. The instrument response function was recorded with the use of a dilute scattering solution (CaCO$_3$ in water). The recorded fwhm for the response function was ~115 ps.

Temperature-dependent lifetime measurements were made for samples thermally jacketed in a sample holder whose temperature was varied (280 – 330 K) using a water-circulating bath. The precise temperature was measured with a thermocouple kept in direct contact with the sample cuvette.

2.2.5 Electrochemistry

Cyclic voltammograms were measured using a CH Instruments 601C electrochemical analyzer. A standard three-electrode setup was employed with a 1.6 mm diameter Pt working electrode, Pt wire counter electrode, and 0.01 M Ag/AgNO$_3$
reference electrode.†† Analyte solutions of approximately 2 mM were prepared in freshly made supporting electrolyte of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in anhydrous acetonitrile. All measurements were made after an approximate 2 minute argon purge and are referenced to ferrocene as an internal standard.

Figure 2.6. Picture of three-electrode cyclic voltammetry setup. The counter electrode (red) and working electrode (green) are placed in low-volume cell with the dye solution. The reference electrode (white) is put in an external solution of supporting electrolyte.

2.2.6 DFT Calculations

All complexes were studied without including explicit solvent molecules or solvent models, using the PBE0 functional. Optimized geometries were obtained without symmetry constraints. The 6-31g(d) basis set was used for all atoms except Ru for which the SDD effective core pseudopotential and associated basis set were used. Assignment of a triplet optimized geometry to either ³MC or ³MLCT character was accomplished through examination of the Ru center atomic Mulliken spin population

†† The reference electrode was assembled (immediately before use) by dissolving the appropriate mass of AgNO₃ with 0.1 M TBAPF₆ to make 0.01 M AgNO₃ solution in which the silver wire was placed.
value of approximately 2 or 1, respectively, corresponding to the number of unpaired elections present on the metal center. Ground state singlet and excited state triplet geometries were confirmed as stable through frequency calculations that return zero imaginary frequencies in all complexes except those containing a tolyl moiety (i.e. [Ru(tpy)₂]²⁺ and [Ru(tpy)(tbtpy)]²⁺) where imaginary frequencies correspond to methyl rotation that is assumed to be inconsequential to the overall energy. All calculations were performed with the Q-Chem 4.0.0.2 software package.²⁶

2.3 Results and Discussion

2.3.1 Homoleptic Complexes

While systematic trends in the photophysical and electrochemical properties of structurally varied heteroleptic arylterpyridyl-containing Ru(II) complexes serve as the main subject of this chapter, the behavior of related homoleptic species provides a useful basis for comparison. We first consider steady-state electronic absorption data for [Ru(tpy)₂]²⁺, [Ru(tbtpy)₂]²⁺, and [Ru(tpy)₂]²⁺, as shown in Figure 2.7 (top) and reported in Table 2.1.
Figure 2.7. (Top) Electronic absorption spectra for Ru(II) terpyridyl complexes in room temperature acetonitrile. (Bottom) Overlay of electronic absorption spectrum from [Ru(tpy)(tbtpy)]^{2+} (dark red) with one (dashed orange) that is the calculated average of the [Ru(tpy)_2]^{2+} and [Ru(tbtpy)_2]^{2+} spectra from the top panel.
Each of the Ru(II) compounds exhibits an intense visible $^1$MLCT band as the lowest energy electronic transition. These are red-shifted by approximately 30 nm relative to [Ru(bpy)$_3$]$^{2+}$ as a result of the more extended π-network within the terpyridine ligand (manifest also in a more positive ligand reduction potential, vide infra). The complex [Ru(tbtpy)$_2$]$^{2+}$ exhibits a slightly red-shifted $^1$MLCT band ($\lambda_{\text{max}} = 480$ nm) compared to [Ru(tpy)$_2$]$^{2+}$ ($\lambda_{\text{max}} = 476$ nm). For [Ru(ttpy)$_2$]$^{2+}$, the band is further red-shifted ($\lambda_{\text{max}} = 490$ nm) and grows in intensity (see Figure 2.7 top).

<table>
<thead>
<tr>
<th>Complex</th>
<th>MLCT $\lambda_{\text{max}}$/nm ($\varepsilon$)$^a$</th>
<th>$E_m$ $\lambda_{\text{max}}$/nm</th>
<th>$\phi_r$/10$^{-5}$</th>
<th>$\tau_{\text{obs}}$/ns</th>
<th>$b_kr$/10$^4$ s$^{-1}$</th>
<th>$c_knr$/10$^9$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>450 (16000)</td>
<td>619</td>
<td>9500</td>
<td>855$^d$</td>
<td>7.7$^d$</td>
<td>0.00048$^d$</td>
</tr>
<tr>
<td>[Ru(tpy)$_2$]$^{2+}$</td>
<td>476 (17000)</td>
<td>--</td>
<td>--</td>
<td>0.124$^e$</td>
<td>--</td>
<td>8.06$^e$</td>
</tr>
<tr>
<td>[Ru(ttpy)$_2$]$^{2+}$</td>
<td>490 (30000)</td>
<td>652</td>
<td>3 ± 1</td>
<td>0.74 ± 0.02$^f$</td>
<td>4 ± 2</td>
<td>1.4 ± 0.6</td>
</tr>
<tr>
<td>[Ru(tbtpy)$_2$]$^{2+}$</td>
<td>480 (20000)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>[Ru(tpy)(tbtpy)]$^{2+}$</td>
<td>486 (24000)</td>
<td>661</td>
<td>7 ± 3</td>
<td>1.88 ± 0.08</td>
<td>4 ± 2</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td>Carboxylic Acids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(1)(tbtpy)]$^{2+}$</td>
<td>488 (21000)</td>
<td>676</td>
<td>27 ± 9</td>
<td>8.2 ± 0.3</td>
<td>3 ± 1</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>[Ru(2)(tbtpy)]$^{2+}$</td>
<td>484 (18000)</td>
<td>656</td>
<td>5 ± 1</td>
<td>1.36 ± 0.05</td>
<td>4 ± 1</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>[Ru(3)(tbtpy)]$^{2+}$</td>
<td>480 (16000)</td>
<td>651</td>
<td>4 ± 1</td>
<td>0.59 ± 0.02</td>
<td>6 ± 2</td>
<td>1.7 ± 0.4</td>
</tr>
<tr>
<td>Methyl Esters</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(1')(tbtpy)]$^{2+}$</td>
<td>488 (22000)</td>
<td>677</td>
<td>25 ± 8</td>
<td>8.6 ± 0.3</td>
<td>3 ± 1</td>
<td>0.12 ± 0.04</td>
</tr>
<tr>
<td>[Ru(2')(tbtpy)]$^{2+}$</td>
<td>484 (18000)</td>
<td>657</td>
<td>6 ± 2</td>
<td>1.37 ± 0.04</td>
<td>4 ± 1</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>[Ru(3')(tbtpy)]$^{2+}$</td>
<td>480 (17000)</td>
<td>653</td>
<td>4 ± 1</td>
<td>0.60 ± 0.02</td>
<td>7 ± 1</td>
<td>1.7 ± 0.3</td>
</tr>
</tbody>
</table>

$^a$Units for molar absorptivity $\varepsilon$ are M$^{-1}$cm$^{-1}$. $^b k_r = \phi_r/\tau_{\text{obs}}, c_k_{nr} = (1-\phi_r)/\tau_{\text{obs}}$. $^c k_r$ and $k_{nr}$ data taken from literature. $^d$From transient absorption data. $^e$Half-wave potentials ($E_{1/2}$) and their corresponding peak-to-peak separations ($\Delta E_p$) are reported in Table 2.2. All waves are taken from literature. $^f$Data collected in our laboratory match literature.

Insight is gained into MLCT band positions using cyclic voltammetry to indicate one-electron reduction potentials (terpyridine based 2+/1+ couple) and oxidation potentials (metal center localized 3+/2+ couple). Half-wave potentials ($E_{1/2}$) and their corresponding peak-to-peak separations ($\Delta E_p$) are reported in Table 2.2.
chemically reversible, as evidenced by scan-rate independent $\Delta E_p$ and linear correlations between peak currents and the square root of the scan rate for $\nu = 100$-500 mV/s. The reported $\Delta E_{1/2}$ (corresponding to the subtraction of the 2+/1+ couple from the 3+/2+ couple) may be reasonably correlated with MLCT energies as has been extensively explored by Lever.$^{29,30}$ As can be inferred from Table 2.2, the MLCT red-shifting for $[\text{Ru(tbtpy)}_2]^{2+}$ relative to $[\text{Ru(tpy)}_2]^{2+}$, arises due to a corresponding decrease in the 3+/2+ couple. This is a manifestation of electronic induction to the metal center originating in the electron donating $t$-Bu substituents at the 4, 4′, and 4″-position.$^{31-33}$ The effect on the 3+/2+ couple slightly outweighs a similar impact on ligand reduction within the 2+/1+ couple (-1.38 V for $[\text{Ru(tbtpy)}_2]^{2+}$ versus -1.25 V for $[\text{Ru(tpy)}_2]^{2+}$). The further red-shifting of the MLCT for $[\text{Ru(ttpy)}_2]^{2+}$ versus $[\text{Ru(tbtpy)}_2]^{2+}$ can be ascribed to the more positive 2+/1+ potential (-1.24 V for $[\text{Ru(tppy)}_2]^{2+}$ versus -1.38 V for $[\text{Ru(tbtpy)}_2]^{2+}$). The 4′-tolyl substituent is slightly electron donating (see changes in the 3+/2+ couple for $[\text{Ru(tppy)}_2]^{2+}$ versus $[\text{Ru(tpy)}_2]^{2+}$) so this effect is understood to be a consequence of electron delocalization within the larger aromatic system of the ttpy ligand upon complex reduction.$^{27,34}$
### Table 2.2. Electrochemical Data Collected in Room Temperature Acetonitrile

<table>
<thead>
<tr>
<th>Complex</th>
<th>( E_{1/2} ) vs. SCE (( \Delta E_p / \text{mV} ))</th>
<th>( \Delta E_{1/2}/\text{V} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( 3+/2^+ )</td>
<td>( 2+/1^+ )</td>
</tr>
<tr>
<td>[Ru(bpy)](3^+)</td>
<td>1.29 (65)</td>
<td>-1.34 (56)</td>
</tr>
<tr>
<td>[Ru(tpy)](3^+)</td>
<td>1.30 (56)</td>
<td>-1.25 (65)</td>
</tr>
<tr>
<td>[Ru(tpy)](2^+)</td>
<td>1.24 (69)</td>
<td>-1.24 (66)</td>
</tr>
<tr>
<td>[Ru(tbpy)](2^+)</td>
<td>1.12 (75)</td>
<td>-1.38 (61)</td>
</tr>
<tr>
<td>[Ru(tpy)(tbpy)](2^+)</td>
<td>1.18 (67)</td>
<td>-1.28 (63)</td>
</tr>
<tr>
<td>Carboxylic Acids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(1)(tbpy)](2^+)</td>
<td>1.21 (67)</td>
<td>-1.29 (55)</td>
</tr>
<tr>
<td>[Ru(2)(tbpy)](2^+)</td>
<td>1.21 (68)</td>
<td>-1.31 (58)</td>
</tr>
<tr>
<td>[Ru(3)(tbpy)](2^+)</td>
<td>1.22 (75)</td>
<td>-1.31 (53)</td>
</tr>
<tr>
<td>Methyl Esters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(1')(tbpy)](2^+)</td>
<td>1.21 (72)</td>
<td>-1.21 (67)</td>
</tr>
<tr>
<td>[Ru(2')(tbpy)](2^+)</td>
<td>1.21 (73)</td>
<td>-1.26 (77)</td>
</tr>
<tr>
<td>[Ru(3')(tbpy)](2^+)</td>
<td>1.22 (86)</td>
<td>-1.27 (68)</td>
</tr>
</tbody>
</table>

\(aE_{1/2}\) potentials measured versus Fc\(^{70}\) with 0.40 V added to obtain values versus SCE. Conditions for cyclic voltammetry: electrolyte, 0.1 M TBAPF\(_6\) in acetonitrile; working electrode, Pt; counter electrode, Pt wire; scan rate, \(\nu = 100\ \text{mV/s}\); error, \(\pm 0.02\ \text{V}\). \(b\Delta E_p = E_{\text{peak anode}} - E_{\text{peak cathode}}\). \(c\Delta E_{1/2} = E(3+/2^+) - E(2+/1^+)\). \(d,e,f\) These data collected in our laboratory match literature. \(^6,34,35\)

Turning toward excited-state properties, it is well-known that the parent [Ru(tpy)]\(2^+\) is non-emissive in room-temperature solutions in stark contrast to [Ru(bpy)]\(3^+\). This can be understood as arising due to the weaker ligand field strength (vis-à-vis the bite angle) of terpyridine compared to its bidentate analog in [Ru(bpy)]\(3^+\). \(^36,37\) This leads to a lower energy triplet metal-centered state (\(^3\text{MC}\)) in [Ru(tpy)]\(2^+\), which in turn serves as a thermally accessible non-radiative pathway from the \(^3\text{MLCT}\) to the ground state. Temperature-dependent emission lifetime studies reveal the low barrier to the \(^3\text{MC}\) and computational studies confirm this basic picture. \(^38-40\) In DFT work by our group, the optimized \(^3\text{MC}\) and \(^3\text{MLCT}\) were identified and found to
have similar energies.\textsuperscript{41} Further, we have interpreted ultrafast transient absorption data as revealing an additional observable time scale due to the equilibration of $^3$MLCT population with the $^3$MC state.\textsuperscript{27}

The complex [Ru(tbtpy)$_2$]$^{2+}$ should have a slightly lower energy MLCT relative to [Ru(ppy)$_2$]$^{2+}$ (see Figure 2.7 (top) and Table 2.1) and at the same time we would expect a comparative increase in the $^3$MC energy given enhanced basicity of the tbtpy ligand due to the three electron donating t-Bu substituents. Nonetheless, the compound behaves similarly to [Ru(ppy)$_2$]$^{2+}$ inasmuch as it is also non-emissive at room temperature. This basic picture that is applicable to these two complexes, particularly the energetic proximity of the $^3$MC to the $^3$MLCT and the role of the former in non-radiative decay, serves as a baseline for understanding how structural perturbations manifest in physiochemical properties.

Relative to the parent [Ru(ppy)$_2$]$^{2+}$, the introduction of the $p$-tolyl moiety at the 4’-position within the complex [Ru(ttpy)$_2$]$^{2+}$, leads to a stabilization of the $^3$MLCT (see Figure 2.7 (top) and $\Delta E_{1/2}$ in Table 2.2). Low temperature emission studies indicate an energy stabilization of 1100 cm$^{-1}$ in this context\textsuperscript{20,28} At the same time, the $^3$MC should destabilize more for [Ru(ttpy)$_2$]$^{2+}$ than it does for [Ru(ppy)$_2$]$^{2+}$ because of increased basicity of the ttpy ligand relative to tpy. Finally, one might expect two effects that arise because of excited-state electron delocalization in the arylterpyridyl $\pi$-system within the $^3$MLCT of [Ru(ttpy)$_2$]$^{2+}$. The first is a smaller reorganization energy between the $^3$MLCT and the ground state while the second is a larger transition dipole moment coupling the two states. We anticipate all of this contributes to the observation that [Ru(ttpy)$_2$]$^{2+}$ is emissive at room temperature. On the basis of multiple probe wavelength transient
absorption data, we have previously assigned ground-state recovery in \([\text{Ru(ttpy)}_2]^{2+}\) as being rate-limited by thermal activation from the \(^3\text{MLCT}\) to the \(^3\text{MC}\).\(^{27,42}\)

2.3.2 Heteroleptic Series.

The properties of \([\text{Ru(ttpy)}(\text{tbtpy})]^{2+}\) can be understood in relation to the homoleptic complexes from which it is conceptually derived. As shown in Figure 2.7 (bottom), the absorption spectrum of \([\text{Ru(ttpy)}(\text{tbtpy})]^{2+}\) closely matches a superposition of features from \([\text{Ru(ttpy)}_2]^{2+}\) and \([\text{Ru(tbtpy)}_2]^{2+}\). This is entirely analogous to what has been previously shown in our laboratory for \([\text{Ru(tpy)}(\text{ttpy})]^{2+}\) compared to \([\text{Ru(tpy)}_2]^{2+}\) and \([\text{Ru(tppy)}_2]^{2+}\).\(^{27}\) Further, a comparison of ligand reduction potentials for the homoleptic complexes \([\text{Ru(ttpy)}_2]^{2+}\) and \([\text{Ru(tbtpy)}_2]^{2+}\), provides insight into assigning reductive half-wave potentials within \([\text{Ru(ttpy)}(\text{tbtpy})]^{2+}\) (Table 2.2). The first ligand reduction potential (2+/1+) more closely matches that of \([\text{Ru(ttpy)}_2]^{2+}\), while the second ligand reduction potential more closely matches that of \([\text{Ru(tbtpy)}_2]^{2+}\) (1+/0). These observations are to be expected given the greater electron density of the tbtpy ligand. The electrochemical data then suggest that the lowest energy \(^3\text{MLCT}\) of \([\text{Ru(ttpy)}(\text{tbtpy})]^{2+}\) is ttpy-localized. This phenomenon was kept in mind in the design of the seven new heteroleptic complexes reported herein (i.e., to allow for a unique comparison of MLCT excited states based on differing aryl-substituted terpyridine complexes with the same electron rich ancillary ligand).
Corrected emission spectra collected in acetonitrile at room temperature following 450 nm excitation. All spectra are taken with absorbance of 0.1 at 450 nm, thus indicating a relative quantum yield observed in integrated emission counts.

While the absorption spectrum of [Ru(ttpy)(tbtpy)]^{2+} mimics a superposition of data from the related homoleptic species as described above, there are noteworthy non-additive changes in the photophysical properties of [Ru(ttpy)(tbtpy)]^{2+} in relation to [Ru(ttpy)]^{2+} and [Ru(tbtpy)]^{2+}. For example, even as [Ru(tbtpy)]^{2+} is non-emissive, the introduction of a tbtpy ligand in [Ru(ttpy)(tbtpy)]^{2+} compared to [Ru(ttpy)]^{2+} leads to an approximately twofold increase in the emission quantum yield, $\phi_r$ (Table 2.1). The emission spectra ($^3_{\text{MLCT}} \rightarrow ^1\text{GS}$) from which $\phi_r$ is determined are shown in Figure 2.8 (the black spectrum corresponds to [Ru(ttpy)]^{2+} whereas the dark red spectrum corresponds to [Ru(ttpy)(tbtpy)]^{2+}). To explore this trend, we measured the observed lifetime ($\tau_{\text{obs}}$) of the emissive $^3_{\text{MLCT}}$ states by time-correlated single photon counting (TCSPC). Transient emission decay traces are shown in Figure 2.9 below. These data in
conjunction with $\phi_r$, provide access to $k_r$ and $k_{nr}$. As can be seen in Table 2.1, the increase in $\phi_r$ for $[\text{Ru(ttpy)(tbtpy)}]^2^+$ relative to $[\text{Ru(ttpy)}_2]^2^+$ is a manifestation of a more than twofold reduction in $k_{nr}$ upon appending a tbtpy ligand.

Figure 2.9. Two plots of time-resolved emission collected using TCSPC at 640 nm in acetonitrile at room temperature following 395 nm excitation. Single exponential fits are shown in black. Methyl ester complexes are shown in the lighter shade of the color used for the respective carboxylic acid complexes. The IRF shown in gray is $\sim$115 ps full width at half maximum as determined from the PMT, cables, and TCSPC electronics.
Following the energy gap law, a nonradiative decay rate constant, $k_{nr}$, will typically decrease exponentially with increasing energy separation. However, the trend described above in $k_{nr}$ cannot be explained with the energy gap law. The featureless emission spectra of the complexes in room temperature acetonitrile were fit using a standard one-mode Franck-Condon analysis as described in the Experimental Section 2.2.3. A summary of all Franck-Condon fitting parameters is given in Table 2.3.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_0$/cm$^{-1}$</th>
<th>$\Delta G^0_{3\text{MLCT}}$/cm$^{-1}$</th>
<th>$\Delta G^0_{\text{MLCT}}$/eV</th>
<th>$\hbar \omega_M$/cm$^{-1}$</th>
<th>$S_M$</th>
<th>$\Delta \nu_{0.1/2}$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(bpy)$_3$]$^{2+}$</td>
<td>16310 ± 70</td>
<td>17800 ± 80</td>
<td>2.21 ± 0.01</td>
<td>1350</td>
<td>0.91 ± 0.07</td>
<td>1840 ± 20</td>
</tr>
<tr>
<td>[Ru(tppy)$_2$]$^{2+}$</td>
<td>15350 ± 20</td>
<td>16600 ± 200</td>
<td>2.06 ± 0.02</td>
<td>1380</td>
<td>0.7 ± 0.2</td>
<td>1700 ± 100</td>
</tr>
<tr>
<td>[Ru(tppy)(tbtpy)]$^{2+}$</td>
<td>15070 ± 30</td>
<td>16240 ± 60</td>
<td>2.01 ± 0.01</td>
<td>1380</td>
<td>0.58 ± 0.03</td>
<td>1630 ± 20</td>
</tr>
<tr>
<td>Carboxylic Acids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(1)(tbtpy)]$^{2+}$</td>
<td>14780 ± 40</td>
<td>16000 ± 40</td>
<td>1.98 ± 0.01</td>
<td>1380</td>
<td>0.53 ± 0.02</td>
<td>1670 ± 10</td>
</tr>
<tr>
<td>[Ru(2)(tbtpy)]$^{2+}$</td>
<td>15200 ± 20</td>
<td>16480 ± 80</td>
<td>2.04 ± 0.01</td>
<td>1380</td>
<td>0.62 ± 0.09</td>
<td>1700 ± 60</td>
</tr>
<tr>
<td>[Ru(3)(tbtpy)]$^{2+}$</td>
<td>15330 ± 70</td>
<td>16600 ± 100</td>
<td>2.06 ± 0.01</td>
<td>1380</td>
<td>0.72 ± 0.04</td>
<td>1720 ± 60</td>
</tr>
<tr>
<td>Methyl Esters</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Ru(1')(tbtpy)]$^{2+}$</td>
<td>14780 ± 40</td>
<td>16000 ± 60</td>
<td>1.98 ± 0.01</td>
<td>1380</td>
<td>0.53 ± 0.01</td>
<td>1663 ± 8</td>
</tr>
<tr>
<td>[Ru(2')(tbtpy)]$^{2+}$</td>
<td>15240 ± 50</td>
<td>16460 ± 50</td>
<td>2.04 ± 0.01</td>
<td>1380</td>
<td>0.65 ± 0.04</td>
<td>1661 ± 2</td>
</tr>
<tr>
<td>[Ru(3')(tbtpy)]$^{2+}$</td>
<td>15380 ± 90</td>
<td>16610 ± 50</td>
<td>2.06 ± 0.01</td>
<td>1380</td>
<td>0.8 ± 0.2</td>
<td>1670 ± 60</td>
</tr>
</tbody>
</table>

The relative uncertainty for the parameters reported represent 2σ where σ is the standard deviation determined from three separate measurements and fittings of emission data for each sample.

With $E_0$ and $\Delta \nu_{0.1/2}$ values in hand, the free energy available in the $^3\text{MLCT}$ state, $\Delta G^0_{\text{MLCT}}$ (commonly written as $E_{00}$), can be calculated from equation 2.3 (see results in Table 2.4). The fitting results are consistent with the observed red-shift in the emission maximum on going from [Ru(tppy)$_2$]$^{2+}$ to [Ru(tppy)(tbtpy)]$^{2+}$ as shown in Figure 2.7 (top). Namely the stored energy in the $^3\text{MLCT}$ decreases by 0.05 eV. If the energy gap law were the only consideration of importance, we would expect an increase in $k_{nr}$ for the heteroleptic species relative to [Ru(tppy)$_2$]$^{2+}$.
The $\Delta G^\circ_{\text{MLCT}}$ data found from Franck-Condon fitting of emission spectra are separately confirmed using gas-phase DFT calculations employing the PBE0 functional. Data are reported in Table 2.4 under the heading $\Delta G^\circ_{\text{MLCT}}$ g.p. and correspond to the difference in the total energy of the optimized $^3\text{MLCT}$ geometry relative to the optimized $^1\text{GS}$ geometry. While these are gas-phase calculations, there is good agreement with experimental data from molecules studied in room temperature acetonitrile. This agreement is possible because of a cancelation of errors inherent in reporting the difference in $^3\text{MLCT}$ and $^1\text{GS}$ energies as has been noted by others.44

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta G^\circ_{\text{MLCT}}$/eV</th>
<th>$\Delta G^\circ_{\text{MLCT}}$ g.p. /eV</th>
<th>$A/10^{13}$ s$^{-1}$</th>
<th>$\Delta E_a$/eV</th>
<th>$\Delta E_a$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(tpy)$_2$]$^{2+}$</td>
<td>--</td>
<td>2.18</td>
<td>1.9$^c$</td>
<td>0.19$^c$</td>
<td>1500$^c$</td>
</tr>
<tr>
<td>[Ru(tpy)$_2$]$^{2+}$</td>
<td>2.06</td>
<td>2.06</td>
<td>0.9</td>
<td>0.23</td>
<td>1800</td>
</tr>
<tr>
<td>[Ru(tpy)(ttbpy)]$_2$$^{2+}$</td>
<td>2.01</td>
<td>2.00</td>
<td>2.7</td>
<td>0.28</td>
<td>2200</td>
</tr>
<tr>
<td>[Ru(1)(ttbpy)]$_2$$^{2+}$</td>
<td>1.98</td>
<td>2.00</td>
<td>11.7</td>
<td>0.35</td>
<td>2800</td>
</tr>
<tr>
<td>[Ru(2)(ttbpy)]$_2$$^{2+}$</td>
<td>2.04</td>
<td>2.02</td>
<td>1.0</td>
<td>0.25</td>
<td>2000</td>
</tr>
<tr>
<td>[Ru(3)(ttbpy)]$_2$$^{2+}$</td>
<td>2.06</td>
<td>2.07</td>
<td>0.5</td>
<td>0.21</td>
<td>1700</td>
</tr>
<tr>
<td><a href="ttbpy">Ru(1')</a>$_2$$^{2+}$</td>
<td>1.98</td>
<td>2.01</td>
<td>8.9</td>
<td>0.35</td>
<td>2800</td>
</tr>
<tr>
<td><a href="ttbpy">Ru(2')</a>$_2$$^{2+}$</td>
<td>2.04</td>
<td>2.02</td>
<td>2.1</td>
<td>0.26</td>
<td>2100</td>
</tr>
<tr>
<td><a href="ttbpy">Ru(3')</a>$_2$$^{2+}$</td>
<td>2.06</td>
<td>2.07</td>
<td>1.2</td>
<td>0.23</td>
<td>1800</td>
</tr>
</tbody>
</table>

$^a$Arrhenius activation energies were determined by fitting a single-exponential temperature-dependent lifetime data set to a linear Arrhenius model $\ln k_{\text{obs}} = \ln A - \Delta E_a/RT$. This effectively ignores a temperature-independent rate constant that would be explored at much lower temperatures. Temperature-dependent lifetimes were measured between $T = 280-330$ K. $^b$Gas-phase DFT with GS geometry $\Delta \text{SCF triplet calculation}$. $^c$Data are taken from literature.$^{36,38}$

As described above, we have previously explored [Ru(tpy)$_2$]$^{2+}$ using transient absorption (at multiple probe wavelengths) and understand its ground state recovery as
being rate limited by thermal activation from the $^3\text{MLCT}$ to the more highly displaced $^3\text{MC}$.\textsuperscript{27} In this context, it is noted that the addition of a strong $\sigma$-donor ligand (tbtpy) in $[\text{Ru(tpy)}(\text{tbtpy})]^{2+}$ is expected to increase the ligand-field splitting\textsuperscript{39} and result in an increase in the $^3\text{MLCT}$-$^3\text{MC}$ energy gap. To investigate this possibility, the temperature dependence of the observed emission lifetimes of $[\text{Ru(tpy)}_2]^{2+}$ and $[\text{Ru(tpy)}(\text{tbtpy})]^{2+}$ were studied over the range from $T = 280-330$ K.

Figure 2.10 (top) shows an Arrhenius plot of data for these two compounds with activation energies ($\Delta E_a$) and pre-exponential factors (A) listed in Table 2.4. The latter are on the order of $10^{13}$ s$^{-1}$, consistent with a transition between two states of like spin multiplicity.\textsuperscript{45} The fits suggest that $\Delta E_a$ due to the barrier from $^3\text{MLCT}$ to $^3\text{MC}$ increases by 0.05 eV (400 cm$^{-1}$) in going from $[\text{Ru(tpy)}_2]^{2+}$ (1800 cm$^{-1}$) to $[\text{Ru(tpy)}(\text{tbtpy})]^{2+}$ (2200 cm$^{-1}$). The combined lowering of the $^3\text{MLCT}$ and raising of the $^3\text{MC}$ contribute to the decrease in $k_{\text{obs}}$ (therein impacting $\phi_r$ and $\tau_{\text{obs}}$) via a decrease in $k_{\text{nr}}$. These trends are shown pictorially (with $\Delta G^{\circ}_{\text{MLCT}}$, $\Delta E_a$ and $\tau_{\text{obs}}$) in Figure 2.11 with the Heteroleptic Series among all other complexes studied in this chapter.
Figure 2.10. Temperature-dependent observed rate constants determined from TCSPC measurements of $^3$MLCT excited state lifetimes. (Top) Comparison between heteroleptic series and carboxylic acid or methyl ester appendages. (Bottom) Comparison between methyl ester and carboxylic acid steric series.
2.3.3 Ester/Acid Addition.

With an understanding of \([\text{Ru(ttpy)(tbtpy)}^2]^2+\) as a baseline, we turn to an exploration of the effects of appending a carboxylic acid or methyl ester substituent to the para-position of the arylated terpyridine. Steady-state electronic absorption shifts are minimal among the complexes \([\text{Ru(ttpy)(tbtpy)}^2]^2+, [\text{Ru(1)(tbtpy)}^2]^2+, \text{ and } [\text{Ru(1')}(tbtpy)]^2+\) (see Table 2.1 and Figure 2.12) and yet there is a 16 nm (15 nm) red-shift in the emission maximum (see Table 2.1 and Figure 2.8) upon introduction of the ester (acid) substituent. This trend is also reflected in the 0.03 eV decrease in \(\Delta G°_{\text{MLCT}}\) (see Table 2.4). This decrease in \(3\text{MLCT}\) energy is expected as a result of the impact of electron-withdrawing methyl esters (and carboxylic acids) in stabilizing the ligand \(\pi^*\) levels.\(^{46}\)
Figure 2.12. Electronic absorption spectra showing the effects of para substitution in the series of Ester/Acid Addition. Only minor changes are noted by comparing methyl, methyl ester, and carboxylic acid-containing complexes.

Along with red-shifting emission, the quantity $\phi_r$ increases a notable fourfold with the introduction of a carboxylic acid or a methyl ester substituent (Table 2.1). Similar to the trend described in the Heteroleptic Series, the increase in $\phi_r$ derives from a decrease in $k_{nr}$. These data, along with energy lowering of the $^3$MLCT as described above from static measurements, suggest a likely explanation for an increase in the energy barrier between the $^3$MLCT and the $^3$MC. Temperature-dependent emission lifetimes support this. As shown in the Arrhenius plots (Figure 2.10 (top)), $[\text{Ru}(1)(tbtpy)]^{2+}$ and $[\text{Ru}(1')(tbtpy)]^{2+}$ are nearly identical in their temperature-dependent transient behavior and both complexes exhibit an Arrhenius slope that is more negative than $[\text{Ru}(tppy)(tbtpy)]^{2+}$ corresponding to a $\Delta E_a$ increase of 0.07 eV ($600 \text{ cm}^{-1}$) upon
introduction of the acid or ester substituent (Table 2.4 and Figure 2.11). These data are consistent with those of Maestri and co-workers who have shown that π-accepting substituents serve to increase $\phi_r$ and $\tau_{obs}$ in Ru(II) terpyridyl complexes.\textsuperscript{47}

The combined lowering of the $^3$MLCT and raising of the $^3$MC that manifests in photophysical data as described above is supported by the electrochemical measurements in the case of the ester complex [Ru(1′)(tbtpy)]$^{2+}$. For this molecule, we observe the expected decrease in the $\Delta E_{1/2}$ compared to [Ru(tpy)(tbtpy)]$^{2+}$ (2.42 V versus 2.46 V), which is driven by the 0.07 V positive shift in the first ligand reduction potential that follows from the introduction of the electron-withdrawing ester substituent (-1.21 V versus -1.28 V). This positive shift in the first reduction potential is somewhat counterbalanced by a simultaneous 0.03 V shift in the 3+/2+ couple (1.21 V versus 1.18 V). This latter effect is also a consequence of the electron-withdrawing ester substituent, which, through an inductive effect, lessens electron density at the metal center thus requiring more potential for one-electron oxidation.\textsuperscript{‡‡} These observed shifts in electrochemical potentials follow what Maestri and co-workers have described.\textsuperscript{47} Namely, that π-accepting substituents stabilize the LUMO $\pi^*$ (approximated by the 2+/1+ couple) more effectively than the HOMO $t_{2g}$ set due to orbital overlap and physical proximity in the case of the former. The ester substituent would not be expected to impact the energy of the metal-based $e_g$ orbitals in any significant way. However, the stabilized $t_{2g}$ orbital (more positive 3+/2+ couple) and unchanged $e_g$ orbitals would nonetheless translate into a higher energy $^3$MC state vis-à-vis the larger ligand-field splitting.

\textsuperscript{‡‡} The overall shift is mitigated by the insertion of the phenylene spacer. Direct comparisons of carboxylic acid substituted terpyridine complexes with and without a phenylene spacer support this.
On the other hand, in the case of the carboxylic acid complex [Ru(1)(tbtpy)]^{2+}, the measured $\Delta E_{1/2}$ of 2.50 V (Table 2.2) is larger than that of [Ru(ttpy)(tbtpy)]^{2+} (2.46 V) in opposition to our expectation based on photophysical data. This appears to be a consequence of the 2+/1+ couple (formally ligand reduction). A more negative value is seen for each of the carboxylic acid complexes (with ligands 1, 2, and 3) compared to their respective ester derivatives (with ligands 1', 2', and 3'), while the respective 3+/2+ couples remain the same. Similar differences between ester and acid ligand reduction potentials have been seen by Hanan and co-workers\textsuperscript{48} as well as Potvin and co-workers.\textsuperscript{4} Deviations from the expected correlation between $\Delta E_{1/2}$ and $\Delta G^{\circ}_{\text{MLCT}}$ in polypyridyl Ru(II) species have been reported by Lever and co-workers for other H-bond donors.\textsuperscript{29} We suspect that the effect arises due to hydrogen bonding between the acidic form of the metal complex and the anions of the electrolyte that is present in large concentration in the electrochemical measurements. Cyclic voltammograms of the carboxylic acid-containing complexes are shown in figures alongside their respective methyl ester-containing complexes in section A.3 of Appendix A. We reiterate that this discrepancy between ester and acid-containing complexes is small and no distinctions were found between these complexes in photophysical data.
Figure 2.13. Electronic absorption spectra for the Steric Series of methyl ester and carboxylic acid arylterpyridyl Ru(II) complexes in room temperature acetonitrile. Acid-containing complexes are depicted in solid lines while ester-containing complexes are in dashed lines.

2.3.4 Steric Series

The series of carboxylic acid and methyl ester complexes is studied with the systematic introduction of steric bulk at ortho-positions of the aryl-substituted terpyridine ligand (see the Steric Series in Figure 2.1). Electronic absorption spectra are shown in Figure 2.13 and indicate near perfect overlap for respective carboxylic acid and ester pairs. For both series, there is a systematic blue-shift in absorption maxima as well as a decrease in molar absorptivity as steric bulk is added. We note that the drop in molar absorptivity is more pronounced with introduction of the first methyl substituent.
We see similar, albeit slightly more pronounced, trends in static emission ($^3\text{MLCT} \rightarrow ^1\text{GS}$) properties. For clarity, only the methyl ester steric series is discussed, although nearly identical quantities are seen for respective carboxylic acid complexes. The $[\text{Ru}(2')(\text{tbtppy})]^2^+$ emission maximum is blue-shifted 20 nm relative to $[\text{Ru}(1')(\text{tbtppy})]^2^+$ (Figure 2.8), resulting in a $\Delta G_{\text{MLCT}}^\circ$ that is 0.06 eV higher in energy (Table 2.4). Upon the addition of a second methyl substituent, a blue shift is observed but the effect is muted relative to the first case. Here, $[\text{Ru}(3')(\text{tbtppy})]^2^+$ exhibits a $\Delta G_{\text{MLCT}}^\circ$ that is 0.02 eV higher in energy relative to $[\text{Ru}(2')(\text{tbtppy})]^2^+$ (see Figure 2.11).

Concomitant with the 0.06 eV increase in $\Delta G_{\text{MLCT}}^\circ$ for $[\text{Ru}(2')(\text{tbtppy})]^2^+$ compared to $[\text{Ru}(1')(\text{tbtppy})]^2^+$, an approximate fourfold decrease in $\phi_r$ is observed (Table 2.1) for the more sterically encumbered species. This cannot be explained in reference to impacts of the energy gap law on $k_{nr}$ (as described above in the Heteroleptic Series) nor can it be explained by trends in $k_r$ given that this quantity is larger for $[\text{Ru}(2')(\text{tbtppy})]^2^+$ ($4\times10^4$ s$^{-1}$) than it is for $[\text{Ru}(1')(\text{tbtppy})]^2^+$ ($3\times10^4$ s$^{-1}$).§§ Rather, the observed changes in $k_{nr}$ must be invoked: $k_{nr} = 1.2\times10^8$ s$^{-1}$ for $[\text{Ru}(1')(\text{tbtppy})]^2^+$ versus $k_{nr} = 7\times10^8$ s$^{-1}$ for $[\text{Ru}(2')(\text{tbtppy})]^2^+$. In a similar fashion to the Heteroleptic Series and the Ester/Acid Addition, these $k_{nr}$ differences can be readily understood in the context of energy barriers between the $^3\text{MLCT}$ and the $^3\text{MC}$. As the $^3\text{MLCT}$ level is destabilized with additional steric bulk, the barrier to the $^3\text{MC}$ should decrease. Indeed, temperature-dependent lifetime studies (Figure 2.10 (bottom) and Table 2.4) indicate a 0.09 eV (~700 cm$^{-1}$)

§§ The trend in $k_r$ in the series from $[\text{Ru}(1')(\text{tbtppy})]^2^+$ to $[\text{Ru}(3')(\text{tbtppy})]^2^+$ is consistent with the expectation given the blue shift in emission maxima. It is noted, however, that it is opposite to other observations in literature where the quantity increases as excited state electron delocalization is permitted.
decrease in ΔEₐ for [Ru(2')(tbtpy)]²⁺ versus [Ru(1')(tbtpy)]²⁺. The addition of a second methyl substituent from [Ru(2')(tbtpy)]²⁺ to [Ru(3')(tbtpy)]²⁺ leads to an additional > twofold increase in kₙₑ, with another 0.02 eV increase in ΔG°ₘₗₗ₅ and a 0.03 eV (~ 250 cm⁻¹) decrease in ΔEₐ. See Figure 2.11 for a pictorial relationship of ΔG°ₘₗ₅ and ΔEₐ.

There are two interrelated explanations for an increase in ΔG°ₘₗ₅ as steric bulk is added. The first concerns the reduction in the degree of excited-state delocalization that is permitted for the electron that is charge-transferred to the ligand π* system. Delocalization may be expected to lower the excited-state energy in a general sense by decreasing the electron kinetic energy. Steric bulk opposes this by forcing larger dihedral angles between the aryl substituent and the terpyridine moiety. The second explanation is electrostatic in nature and simply reflects the notion that added methyl substituents are electron donating.

To assess delocalization, we have considered evidence from analysis of emission spectra in the context of the Huang-Rhys factor, Sₘ,²²,⁴⁹ which quantifies the degree of nuclear distortion of the emitting excited state relative to the ground state along a single coordinate whose frequency is the same as that used in the specification of ħωₘ. In these molecules, as stated in the Experimental Section 2.2.3, ħωₘ is on the order of 1300 cm⁻¹, reflecting distortion along ring-breathing coordinates owing to the occupancy of π* orbitals in the MLCT excited state manifold. When excited-state electron delocalization is permitted, the extent of such distortions is attenuated. Alternatively, it can be stated that as the steric bulk of the ligand increases, it hinders the peripheral aryl moiety from further excited-state delocalization by adopting configurations that are less coplanar relative to the terpyridyl fragment.²²,⁴⁹,⁵⁰ Our expectations of steric control of excited-
state electron delocalization are reflected in the Franck-Condon emission fitting data (see Table 2.3). Values of $S_M$ were found to increase with steric bulk (from $S_M = 0.53$ for $[\text{Ru}(1')(\text{tbtpy})]^2^+$, to $S_M = 0.65$ for $[\text{Ru}(2')(\text{tbtpy})]^2^+$, to $S_M = 0.8$ for $[\text{Ru}(3')(\text{tbtpy})]^2^+$) thus providing evidence for a cutoff in delocalization. We reiterate here that as steric bulk is added, for example in $[\text{Ru}(3')(\text{tbtpy})]^2^+$, the $^3\text{MLCT}$ is prevented from stabilizing via excited-state electron delocalization. The smaller relative $\Delta E_a$ to the $^3\text{MC}$ state (with increased $\Delta G^\circ_{\text{MLCT}}$), compared to for example $[\text{Ru}(1')(\text{tbtpy})]^2^+$, results in a shorter excited state lifetime, $\tau_{\text{obs}}$. We note that the trend of increasing $S_M$ may impact $\Delta E_a$ indirectly via the increase in nuclear distortion, $\Delta Q_{eq}$. However, it is hard to argue whether this would lead to a higher or lower barrier when examined in a generalized coordinate associated with low-frequency Ru-$\text{N}$ modes as opposed to one associated with ring-breathing modes relevant to the emission signal.

As stated above, there may also be an electrostatic component to the higher $^3\text{MLCT}$ energy of sterically encumbered molecules due to the electron donating character of the methyl substituents. This should be reflected in reduction potentials sensitive to the substituted arylerpyridine ligand, and indeed, we observe changes across both series of molecules. For example, we note a negative shift in the $2^+/1^+$ couple (Table 2.2) as steric bulk is added: -1.21 V for $[\text{Ru}(1')(\text{tbtpy})]^2^+$ versus -1.26 V for $[\text{Ru}(2')(\text{tbtpy})]^2^+$ versus -1.27 V for $[\text{Ru}(3')(\text{tbtpy})]^2^+$. However, the fact that the addition of the first methyl group plays a significantly larger role in the $E_{1/2}$ perturbation indicates that the electron ***

*** We note the possibility that ligands with additional methyl substituents (associated with the increased steric bulk) could serve as stronger bases, which would then increase the ligand-field splitting and increase the energy of the $^3\text{MC}$. However, this does not appear to be the case as confirmed by the $3^+/2^+$ couples, which are measured to be identical for all acid and ester-containing complexes ($1.21 \pm 0.02$ V).
donating properties of the added substituents are not the full explanation. Here again, electron delocalization very likely plays a role by impacting the energy of those orbitals to which chemical reduction takes place. We conclude that both the electron-donating character of steric bulk as well as its impact preventing delocalization play a role increasing $\Delta G^0_{\text{MLCT}}$, which leads to shorter $\tau_{\text{obs}}$. Methyl substitutions of bis-arylterpyridyl iridium complexes have shown similar trends with shorter observed photophysical lifetimes, also explained by both a steric barrier to obtaining delocalization and the possible electron-donating character of methyl steric bulk.$^{51}$

The steric series of complexes reported in this chapter is unique in its 14-fold increase in $k_{nr}$ from $[\text{Ru}(1')(tbtpy)]^{2+}$ to $[\text{Ru}(3')(tbtpy)]^{2+}$ (or from $[\text{Ru}(1)(tbtpy)]^{2+}$ to $[\text{Ru}(3)(tbtpy)]^{2+}$). As a comparison to other dimethylated steric species in Ru(II) bipyridyl systems, differences in $k_{nr}$ across a series have been reported with a twofold increase at max.$^{7,52,53}$ We suspect that this drastic change in $k_{nr}$ for our system is due to the tpy framework that results in a lower-lying $^3\text{MC}$ state and a greater susceptibility to changes in ligand architecture.

2.4 Concluding Remarks

In this chapter, we considered three comparative series involving a number of Ru(II) terpyridyl complexes. In the first, the Heteroleptic Series, the principal finding concerns the photophysical consequences of introducing a strong $\sigma$-donor tbtpy ligand opposite to an arylated terpyridine ttpy ligand. This was found to raise the $^3\text{MC}$ energy level relative to the $^3\text{MLCT}$, thereby imparting a larger barrier in this principal channel for non-radiative decay (see Figure 2.11 for summary). In this way, we found the excited
state lifetime of [Ru(ttpy)(tbtpy)]^{2+} to be more than double that of [Ru(ttpy)_{2}]^{2+} (1.9 ns for the former versus 0.74 ns for the latter).

In the second series, the Ester/Acid Addition, the introduction of a carboxylic acid or methyl ester moiety at the para-position of the aryl-terpyridyl ligand was found to lower the $^3\text{MLCT}$ state characterized by $\Delta G_{\text{MLCT}}^\circ$ while concurrently destabilizing the $^3\text{MC}$ energy level. This leads to a further increase in excited state lifetime, with these species reaching 8.2 ns (acid: [Ru(I)(tbtpy)]^{2+}) and 8.6 ns (ester: [Ru(I')(tbtpy)]^{2+}). Given that electron injection generally occurs within femtoseconds to picoseconds in DSSCs, the multi-nanosecond $^3\text{MLCT}$ lifetimes of these dyes suggests opportunities for high electron injection yields in complete devices.

In the third series, the Steric Series, methyl substituents to the aryl group are introduced to alter structure and electron injection and charge recombination dynamics in later studies of DSSCs (Chapters 4 and 5). Here, we report that steric bulk strongly impacts excited-state lifetimes. The 8.6 ns reported for the ester complex with no methyl substituents (i.e. for [Ru(I')(tbtpy)]^{2+}) drops to 1.4 ns with one methyl substituent ([Ru(2')(tbtpy)]^{2+}) and to 0.60 ns with two ([Ru(3')(tbtpy)]^{2+}). The explanation for these observations again lies in the $^3\text{MLCT}/^3\text{MC}$ barrier. As steric bulk is added, excited state electron delocalization is limited, leading to an increase in the energy of the $^3\text{MLCT}$ (an increase in $\Delta G_{\text{MLCT}}^\circ$). The Steric Series is unique in its 14-fold increase in $k_{\text{nr}}$ from [Ru(I')(tbtpy)]^{2+} to [Ru(3')(tbtpy)]^{2+}. As a comparison to other dimethylated steric species in Ru(II) bipyridyl systems, differences in $k_{\text{nr}}$ across a series have been reported with a twofold increase at most.$^{7,52,53}$ The significant susceptibility to changes in ligand
architecture in the cases discussed here is determined to be the result of the general energetic proximity of the $^3\text{MLCT}$ to the $^3\text{MC}$ due to the tpy framework.

The large increase in $k_{nr}$ with steric functionality must be considered when going forward with DSSCs, as it will negatively impact the quantum yield for electron injection. Further modifications to ligands may be warranted, such as including phenyl substituents at terpyridine 4 and 4'' sites,$^{34,38}$ or switching to an aryl-substituted bipyridine framework instead.$^8$ Either of these modifications would presumably increase opportunities for excited-state delocalization while at the same time facilitating the design principle of a diode-like switch for electron transfer through the portion of the ligand containing the carboxyl functionality and to the point of attachment to the wide-bandgap semiconductor.

2.5 References


3.1 Introductory Remarks

In this chapter, the basic components needed to make complete DSSCs are introduced and a detailed procedure is provided for making functional devices with ruthenium polypyridine sensitizers. In transitioning from studying photoinduced properties of dyes in solution to those in DSSCs, several essential device conditions are outlined. Specifically, materials are chosen and procedures are implemented to provide consistent measurements among all the DSSCs studied in this dissertation. Preliminary characterizations of complete DSSCs are also included, in preparation for the efficiency measurements presented in Chapter 4. This chapter is a combination of a literature review of DSSCs and experimental optimization in the Damrauer lab.

3.2 Materials for DSSCs

DSSCs have many components that must be optimized, both individually and as a part of an integrated device. These components include: transparent conducting oxide (TCO), semiconductor, sensitizer, electrolyte composition, and counter electrode. The working principle of a generic DSSC is shown schematically in Figure 3.1. This section provides a broad overview of what components are typically used and outlines which materials were chosen for the DSSCs presented in this dissertation.
Figure 3.1. DSSC components. A sensitizer (S) is attached to a wide-band gap semiconductor. A liquid-based electrolyte with a redox mediator (A/A') is sandwiched between the working electrode and counter electrodes of transparent conducting oxide (TCO) glass slides.

3.2.1 Transparent Conducting Oxide (TCO)

DSSCs can be made on several different types of substrates: glass, flexible polymer-based plastics, and thin metal foils.\(^1\) Glass is often used for its superior protection against penetration by oxygen and water molecules, which are known to decrease device performance in time.\(^1,2\) A transparent conducting oxide (TCO) on glass is the most common scaffolding layer upon which the mesoporous semiconducting network is built.\(^3\) Fluorine-doped tin oxide (FTO) and indium-doped tin oxide (ITO) are the most common TCOs used in DSSCs.\(^3\) These materials are ideal for DSSCs because: (1) they have a high transparency to solar radiation in the visible-IR region; (2) they can efficiently transfer electrons with a low sheet resistance; and (3) they are relatively inexpensive.\(^3\) Comparing the performance of two cells that differed by TCO only, it has
been shown that an FTO substrate is superior to ITO, owing to its generally lower sheet resistance of 8 to 15 ohm per square (Ω/sq.)††† and more temperature-stable resistivity. For these reasons, FTO was chosen as the TCO for all studies in this dissertation.

3.2.2 Semiconductor

In 1991, Brian O’Regan and Michael Grätzel revolutionized DSSCs with the implementation of a mesoporous TiO$_2$ electrode, which supplied a high internal surface area to support a monolayer of sensitizer with great light harvesting efficiency. Titanium dioxide (TiO$_2$) is still by far the most studied metal oxide electrode, but others, such as SnO$_2$ and ZnO, have been extensively studied as well.\(^3\)

![Figure 3.2. Energy levels of conduction band edge (E$_{CB}$) and valence band edge (E$_{VB}$) of semiconductors and the ground and excited state reduction potential for champion ruthenium dye, N719. Figure adapted from Fessenden et al. (1995).\(^7\) Band gap energies are determined from Xu et al. (2000).\(^8\)](image)

\[\text{††† Do not be confused by units of sheet resistance. It is the typical units of electrical resistance (Ωm) divided by sheet thickness (m). However, because the units of length cancel and Ω could be confused as bulk resistance, it is convention to write Ω/square to define the dimensions exclusive to sheet resistance.}\(^4\)
TiO$_2$ was selected for this work as a chemically stable, non-toxic oxide that is readily available in large quantities (inexpensive).\textsuperscript{3} Besides selecting a semiconductor that has a high transport mobility of charge carriers, one of the biggest considerations regarding semiconductor choice is where the conduction band edge falls, in energy or reduction potential. TiO$_2$ is commonly chosen due to its good band edge matching to ruthenium sensitizers as shown above in Figure 3.2.\textsuperscript{7} That is, the excited state reduction potential for ruthenium dyes typically lies at a higher energy than the conduction band edge of TiO$_2$, allowing for efficient electron injection into TiO$_2$.\textsuperscript{9} The naturally occurring anatase crystal form of TiO$_2$, in particular, has been used in most ruthenium DSSCs due to its larger band gap (3.2 eV compared to the 3.0 eV of rutile) and higher conduction band edge energy.\textsuperscript{3,10} Therefore for ideal energy level matching, anatase TiO$_2$ particles make up the semiconducting layer in our DSSCs.

3.2.3 Sensitizer

![N719 and Black Dye](image)

Figure 3.3. Structures of champion ruthenium sensitizers: N719 and Black Dye. TBA$^+$ stands for tetrabutylammonium cation.
The solar light harvesting abilities of ruthenium polypyridyl complexes have been studied for years.\textsuperscript{11-13} To date, two Ru(II) polypyridyl complexes, N719 dye and Black Dye shown in Figure 3.3 above (reproduced Figure 1.6 from Chapter 1), have achieved some of the highest efficiencies as sensitizers in liquid-electrolyte based DSSCs (each at \sim 11\% efficiency).\textsuperscript{9,14,15} These are effective sensitizers because they have: (1) strong light absorption in the visible region with intense metal-to-ligand charge transfer (MLCT) bands; (2) relatively long excited state lifetimes on a nanosecond timescale to efficiently permit electron injection; (3) the presence of carboxylic acid anchoring substituents to provide good coupling with the semiconductor surface; (4) high solubility in organic solvents for facile deposition from sensitizing solutions onto semiconductors; and (5) good chemical and thermal stability in DSSCs, with stable excited and oxidized states that lead to high cell turnover over many years of exposure to sunlight.\textsuperscript{1,9,16}

![Figure 3.4. Structures of the Steric Series of ruthenium sensitizers. Counter ions are PF$_{6}^{-}$.](image-url)
The standard N719 dye and the ruthenium polypyridine dyes that make up the Steric Series (shown in Figure 3.4, reproduced Figure 1.5 from Chapter 1) are made into the complete DSSCs studied throughout this dissertation. The main motivations for studying these ruthenium polypyridine dyes were discussed previously (Chapter 2). In particular, we note here that for purposes of comparison with N719, each dye in the Steric Series was synthesized with a carboxylic acid linker specifically for their inclusion in DSSCs.

A carboxylic acid linker is one of many functional groups that efficiently binds to TiO$_2$. Other viable alternative linkers include phosphonic acid, hydroxamate, catechol, and acetylacetonate.$^{17,18}$ While a carboxylic acid linker does not bind as strongly to the surface hydroxyl groups on TiO$_2$ as a phosphonic acid linker does, carboxylic acid linkers are most common with ruthenium DSSCs due to their relative stability and ease of synthesis.$^3$ A plethora of studies in pursuit of optimal dye surface coverage and strong semiconductor coupling reveal that the precise binding nature of carboxylic acid linkers is still debated.$^{19-21}$ Figure 3.5 shows the expected modes of a carboxylic acid linker binding to TiO$_2$. The bidentate bridging modes are known to predominate with most dyes, as evidenced by Fourier transform infrared spectroscopy (FTIR).$^{18,19}$ For this reason, we expect the Steric Series to adequately adsorb to TiO$_2$ films in this study, most likely by covalently attaching to the titania particles in a bidentate bridging mode.
Of course, many highly functional DSSCs utilize alternatives to ruthenium sensitizers. Promising alternatives include: porphyrins, squaraines, perylenes, cyanines, coumarins, and linear acenes. DSSCs utilizing ruthenium sensitizers have simply been around longer and thus have had the greatest time to optimize with other components to achieve higher device efficiencies. Organometal lead halide perovskites, although they are impractical in liquid-electrolyte based DSSCs, have recently demonstrated breakthrough efficiencies based on a solid-state DSSC framework.\textsuperscript{22,23}

3.2.4 Redox Mediator

The redox mediator in DSSCs is responsible for transporting charge carriers between the working and counter electrodes (see Figure 3.1). It accomplishes this by providing a reduced form to continuously regenerate the ground state dye, and an oxidized form to quickly diffuse to the counter electrode. By far the most studied redox mediator for liquid-electrolyte based DSSCs is the iodide/triiodide redox couple.\textsuperscript{1}
However, more recently, the use of cobalt coordination complexes as the redox mediators has led to breakthroughs in DSSC efficiencies (reaching 12%). While iodide was chosen as the redox mediator in our DSSCs because of its more common usage, the benefits and limitations of both iodide and cobalt species are discussed below.

The iodide/triiodide redox mediator has been widely used in literature because it has a favorably positive reduction potential (0.29 V vs. SCE), allowing it to achieve a reasonably high open-circuit photovoltage, $V_{oc}$, while still providing a sufficient driving force to reduce a wide range of oxidized dye molecules. It also has good solubility, high conductivity (with high diffusion coefficients), and it does not absorb too much visible light. However, what really distinguishes iodide from most redox mediators is its very slow rate of interception of electrons in TiO$_2$ by triiodide (equation 3.1).

\[
I^+_3 + TiO_2(e^-) \rightarrow I^-_2 + I^- \tag{3.1}
\]

\[
2I^-_2 \rightarrow I^-_5 + I^- \tag{3.2}
\]

\[
I^-_5 + 2e^- \rightleftharpoons 3I^- \tag{3.3}
\]

The drawbacks of iodide are seen when one considers the possibilities for improvement in DSSCs. Iodide has been shown to be the limiting factor for $V_{oc}$ (with the maximum $V_{oc} \approx 0.8$ V), due to the overpotential found when regenerating a typical sensitizer. Effective reduction of oxidized sensitizers has been found with an approximately 0.5 eV driving force, while at least 0.75 eV is typically provided for ruthenium based DSSCs utilizing iodide redox mediators. Another concern is that the oxidized electrolyte species (in equation 3.3), triiodide, clearly still absorbs part of the
solar spectrum as a visibly yellow/brown solution. This decreases light harvesting efficiency and therefore limits photocurrent values. The iodide/triiodide redox mediator has also been a major limiting factor for large-scale production of DSSCs in industry, because it is extremely corrosive to many sealing materials and metals such as Ag and Cu.

Even though iodide was chosen for our DSSCs, several arguments could be made for better alternatives. For instance, Cobalt(III/II) polypyridyl redox mediators are examples of promising one-electron redox couples utilized in record breaking DSSCs. They have more positive reduction potentials, and there is not a large overpotential required when reducing oxidized sensitizers. For this reason, DSSCs with cobalt electrolytes have obtained $V_{oc}$ values exceeding 1 V. Compared to iodide redox mediators, cobalt complexes have low visible light absorption and significant tunability of redox potentials to allow for better matching with sensitizer reduction potentials.

The biggest disadvantage of cobalt is observed with the rate of charge interception. Co(III) species will quickly convert to Co(II) in the presence of electrons at the surface of TiO$_2$ particles, and this is often exacerbated by an association of Co(III) with certain sensitizers. The inclusion of organic dyes with large steric bulk has been studied to prevent this. When there are additional bulky dyes (with substituents such as long-chain alkoxy groups) present at the TiO$_2$ surface, the Co(III) species is prevented from coming close enough to intercept electrons, thereby eliminating this concern. In fact, in 2011, a DSSC prepared with an organic sensitizer in conjunction with a cobalt polypyridine redox mediator surpassed the efficiency record of DSSCs containing iodide-based electrolytes. However, while $[\text{Co(bpy-pz)}]^{2+/3+}$ (with bpy-pz = 6-(1H-pyrazol-1-
yl)-2,2′-bipyridine) is perhaps the most promising new cobalt redox couple, with high regeneration yields and values of $V_{oc}$ reported greater than 1 V,\textsuperscript{31,34} to date, there is no single cobalt redox couple that is recommended for highest efficiencies in ruthenium-based DSSCs. For this reason, and due to the benefits of iodide explained above, we decided to use iodide as our redox mediator for all our DSSCs.

3.2.5 Electrolyte Composition

Choosing iodide as the redox mediator was the first of many decisions to make with regards to the electrolyte. The particular concentrations of species in the electrolyte, the solvent, any additives, and counter ions are of critical importance to the functionality of the electrolyte as a whole.

In solution, iodine will bind to iodide to form triiodide (equation 3.4) with a high equilibrium constant ($K = 10^7$ M\textsuperscript{-1}) in organic solvents such that only iodide and triiodide remain in appreciable concentrations.\textsuperscript{27} The two species react in a 3 to 1 stoichiometric ratio as the two-electron reduction given in equation 3.3.

\[
I_2 + I^- \rightleftharpoons I_3^-
\]  

In general, a high concentration of the iodide and triiodide is needed to maintain good charge transport and to efficiently regenerate the ground state sensitizer.\textsuperscript{35,36} However, the higher concentration of iodide/triiodide also increases the rate of charge interception with the electrolyte species.\textsuperscript{37,38} These effects are not surprising due to the fundamental rate laws for all of these processes needing to include the concentration of electrolyte species.\textsuperscript{36,39}
Of course, the exact ratio of iodide to triiodide has fundamental implications for the ability to act as a redox mediator as well.\(^3\)\(^5\) The redox potential of the electrolyte, \(E_{\text{redox}}\), is given by the Nernst equation (equation 3.5).

\[
E_{\text{redox}} = E^0 + \frac{RT}{2F} \ln \left( \frac{[I_3^-]}{[I^-]^3} \right) \tag{3.5}
\]

From equation 3.5, an increase in the iodine concentration (and subsequent triiodide concentration) will result in a positive shift of the redox potential, which is desirable for a greater value of \(V_{oc}\).\(^3\)\(^5\) However, given that the charge interception is expected to be mainly due to triiodide,\(^2\)\(^6\) the concentration of triiodide should be kept much lower than that of iodide. Also, given that triiodide is more strongly colored, it should also be kept in low concentrations to prevent as much light absorption interference as possible.\(^2\)\(^6\) For these reasons, we use concentrations of iodide greater than 10 times those of triiodide.

From optimized literature concentration studies,\(^3\)\(^5\),\(^4\)\(^0\) we chose concentrations of iodide at 0.7 M and iodine at 0.05 M.

In the end, the conductivity of a redox mediator is determined by the medium it is in. The ideal electrolyte solvent has very low viscosity, negligible vapor pressure, and high dielectric properties.\(^1\) The most common iodide/triiodide solvents are a mixture of acetonitrile/valeronitrile or methoxypropionitrile.\(^1\),\(^4\)\(^1\) As low viscosity solvents, they permit the use of low iodide/triiodide concentrations with fast diffusion.\(^1\) However, their relatively high vapor pressures in closed environments limit their usage when temperatures are above 80 °C. Their high vapor pressure have also lead to sealing problems and therefore decreased efficiencies.\(^1\) Ionic liquids such as dialkyl imidazolium iodides have been added in an attempt to avoid this problem.\(^1\),\(^4\)\(^1\) Ionic liquids have high thermal stability, negligible vapor pressure, non-flammability, and good environmental
compatibility. Their main drawback is their high viscosity. Mixing an ionic liquid such as 1-propyl-3-methylimidazolium iodide (PMII) in a low-viscosity solvent such as methoxypropionitrile is a common approach to fixing this problem, thus this is what we decided to use. We used 0.6M PMII as the main source of iodide in the electrolyte.

Additives or counter ions such as Li\(^+\), H\(^+\), and tert-butylpyridine (TBP) are commonly included in the electrolyte solution as well. These particular additives are known to shift the conduction band edge, \(E_{\text{CB}}\), of TiO\(_2\) as shown in Figure 3.6. Before explaining why these are added, we first review why the conduction band is expected to shift. The conduction band edge of TiO\(_2\) is dependent on the pH of the Ti\(^{4+/3+}\) couple. The value of \(E_{\text{CB}}\) is determined in part by the trap-based redox equilibrium of cation adsorption/desorption given in equation 3.6.

\[
\text{Ti}^{4+} \text{O}_2 + e^- + M^+ \rightleftharpoons \text{Ti}^{3+}(O)(OM)
\] (3.6)

The addition of electrons to the material stimulates the uptake of cations \((M^+)\) at near band edge trap sites. In the end, the addition of Li\(^+\) and H\(^+\) shifts \(E_{\text{CB}}\) to more positive potentials, while a basic additive such as TBP shifts it to more negative potentials, as shown in Figure 3.6.

![Figure 3.6. The effects of H\(^+\)/Li\(^+\) and tert-butylpyridine (TBP) in DSSCs.](image)
The presence of Li\(^+\) has been reported to improve short-circuit photocurrent, \(J_{sc}\), while slightly decreasing \(V_{oc}\).\(^{46}\) Both of these effects are attributed in large part to the positive shift in \(E_{CB}\) by the adsorption of lithium cations to TiO\(_2\). This shift increases the driving force for electron injection, thereby increasing \(J_{sc}\), while simultaneously decreasing the thermodynamic potential that dictates \(V_{oc}\).\(^{47}\)

However, \(J_{sc}\) has been reported to increase with Li\(^+\) even further due to a faster rate of charge transport through TiO\(_2\) and a faster rate of dye regeneration.\(^{27,48}\) The rate of charge transport in DSSCs is dependent on the rate of diffusion of electrons in TiO\(_2\). When lithium cations are present, diffusion is fastest mainly due to ambipolar interactions.\(^{27}\) Ambipolar diffusion is a process in which ions diffuse together to ensure electrical neutrality.\(^{27}\) Due to their small radius, lithium cations have the ability to intercalate into the mesoporous TiO\(_2\) network and form ambipolar Li\(^+\)-e\(^-\) interactions in the conduction band, which increases the transport speed of electrons and therefore enhances \(J_{sc}\).\(^{27,49}\) The presence of Li\(^+\) also increases the rate of regeneration by creating a higher concentration of iodide near the positively charged lithium cations coordinated TiO\(_2\) surface.\(^{3,40}\) The iodide concentration is then locally higher near the oxidized dye molecules that have yet to be reduced.\(^{3,40}\) In the end, to provide these benefits, we included an appreciable concentration of Li\(^+\) at 0.1 M.\(^{42,50}\) This was provided in the form of the counter ion of an additional source of iodide: LiI.

Tert-butylpyridine (TBP) has the opposite effect of Li\(^+\): it improves \(V_{oc}\) while suppressing \(J_{sc}\). To some extent, TBP accomplishes this by shifting \(E_{CB}\) negatively, likely by deprotonation or simply by reducing the amount of Li\(^+\) adsorbed.\(^{46}\) As a bulky
additive it is too big to intercalate into the TiO$_2$ network, but instead it adsorbs to the TiO$_2$ surface, thereby blocking sites where reduction could occur and/or preventing the approach of triiodide to the surface (shown in Figure 3.6).$^{27}$ The inclusion of TBP therefore suppresses the rate of charge interception with the iodide/triiodide species in the electrolyte. This back electron transfer process is thought to be the main source of the cathodic current responsible for low $V_{oc}$ values, so inhibiting this process is desirable. We have prepared our electrolyte solutions with 0.5 M TBP, a commonly reported concentration.$^{50,51}$

When champion ruthenium dyes of N719 and Black dye are employed, additives such as tetrabutylammonium iodide (TBAI) and guanidinium thiocyanate (GuSCN) are also typically included.$^1$ Both Gu$^+$ and TBA$^+$ are included for similar reasons to TBP, but possess the additional ability to act as counter ions to the labile NCS ancillary ligands and deprotonated carboxylic acid substituents in N719 and Black dye. These structures are not present in the Steric Series of dyes discussed in this dissertation, so the inclusion of these additives was deemed unnecessary. So as not to only benefit the N719 DSSCs, these additives were not used in any of the cells reported in this dissertation.

3.2.6 Counter Electrode

A catalytic amount of platinum on FTO was chosen as the counter electrode in our DSSCs. Platinum is known to have great chemical stability and a very low overpotential for the triiodide reduction reaction.$^1$ While typically quite expensive, small quantities of platinum deposited onto a TCO (a few µg/cm$^2$) have been shown to be sufficient in DSSCs.$^1$
DSSCs including counter electrode materials other than platinum are further investigated in the literature mainly due to cost or the desire for alternative substrates (i.e. flexible materials). Carbon alternatives such as graphite, carbon black, single or multiwalled carbon nanotubes (CNT), and poly(3,4-ethylenedioxythiophene) polystylenesulfonate (PEDOT) have been used with great success. However, for simplicity of fabrication and ease of comparison to other DSSCs, we chose to stick with a platinum counter electrode. The procedure for making platinum-coated FTO is described in Section 3.3.

3.2.7 Summary of Materials

Fluorine-doped tin-oxide (FTO) glass was used as the transparent conducting glass to collect current. Pre-cut 2.5 cm x 2.5 cm slides of FTO were purchased from Hartford Glass (TEC 15, sheet resistance of 15Ω/sq.). Hartford glass reports their FTO as a 400 nm thick layer on one side of glass. In general, a thicker layer gives a lower Ω/sq., but 15Ω/sq. is reported to be sufficient.1

A pre-made TiO₂ paste of particles ranging in size from 15 to 20 nm was purchased from Solaronix (Ti-Nanoxide T/SP). Titanium(IV) chloride was used to form a 1 nm thick layer of TiO₂ particles before and after the approximate 8 μm thick mesoporous layer of TiO₂ was spread (vide infra).

The synthesis of the Steric Series is reported in Chapter 2 and N719 was purchased from Solaronix. Titanium(IV) chloride (TiCl₄), 1-methyl-3-propylimidazolium iodide (PMII), lithium iodide, iodine, 4-tert-butylpyridine (TBP), and anhydrous tert-butanol were all purchased from Sigma Aldrich, while 3-methoxypropionitrile was purchased from TCI America. The electrolyte solution was comprised of 0.6 M PMII, 0.1
M LiI, 0.05 M I₂, and 0.5 M TBP in methoxypropionitrile. Chloroplatinic acid hexahydrate was purchased from Strem Chemicals as the source of platinum for the chosen counter electrode of platinum on FTO.

3.3 Preparation of DSSCs

In the following section, we report the experimental procedures utilized for the formation of complete cells. Methods were determined based on reported influences of different procedures on the photovoltaic performance of DSSCs and the ease of implementation in a research lab previously not set up for device construction.

The FTO glass slides were first cleaned with acetone, water and methanol for 30 min each in an ultrasonic bath. After air-drying, approximately 5 mm of the edge of one side of the FTO glass slides were protected for lead connectivity with high-heat tape (polyimide Kapton tape, Marian Chicago) to prepare for the TiCl₄ treatment discussed next.

Figure 3.7. Cleaned FTO glass slides protected with high-heat tape for TiCl₄ treatment.
TiCl₄ treatment is a chemical bath deposition, undertaken in order to form an ultrathin and compact blocking layer of TiO₂ particles (~1 nm) on the FTO slides to increase cell efficiencies.³,⁵⁷ This has become a standard procedure for making DSSCs ever since Nazeeruddin and co-workers first utilized it in 1993.⁵⁸ The resulting ultrathin layer of TiO₂ particles coating the FTO slides has been reported to reduce charge interception by the electrolyte ions at the FTO surface (reducing dark current)⁵⁹.

Following standard procedures,⁵⁶ a 2 M TiCl₄ solution was first prepared by adding TiCl₄ (l) into a bottle containing ice, which was cooled to -20 °C, and then the solution was further diluted to 40 mM with water. Taped FTO slides were placed in this solution at 70 °C for 30 min. Following this chemical bath deposition, the slides were removed from solution, washed with de-ionized water, and ethanol- and air-dried.

Within the literature, the bulk of nanocrystalline TiO₂ films for DSSCs are typically made either by screen-printing or doctor-blading TiO₂ paste onto the TCO glass slides.³ Without easy access to a screen printer, we decided to use a doctor-blading technique (vide infra). To ensure precise particle sizes, we purchased a pre-made Ti-Nanoxide T/SP paste of 15 to 20 nm sized TiO₂ particles from Solaronix. It is worth noting though that this TiO₂ paste can be made via standard sol-gel techniques by the hydrolysis of titanium(IV) tetraisopropoxide with excess water catalyzed by acid or base.⁶⁰ The TiO₂ suspension is typically mixed with various polymer additives before being deposited on a substrate.³ The Ti-Nanoxide T/SP paste from Solaronix, in particular, contains ethyl cellulose as the organic binder in a medium of terpineol.
A layer of nanocrystalline TiO$_2$ paste was coated on FTO glass slides by doctor-blading onto a masked area of Scotch tape with a razor blade. The doctor-blading technique is illustrated in the Figure 3.8. Paper masks of 6.4 mm x 11 mm were printed to scale and aligned below each glass slide to outline a precise active area of TiO$_2$ for the Scotch tape mask (area = 0.704 cm$^2$). Applying a single coating of paste onto a single layered mask of scotch tape was found to be ideal for uniform slides (multiple coatings and/or multiple layers of tape lead to cracking). After doctor-blading the TiO$_2$ active areas, the paste was allowed to dry overnight and then slides were heated at 450 °C for 30 min in a furnace (FB 1300, Barnstead/Thermolyne). This heating process is known as sintering, which results in the nanoparticles making electrical contact between themselves and to the FTO surface while the organic components of the paste are burned off.$^{61}$

After sintering, the slides were given a TiCl$_4$ post-treatment using the same procedure as described above (including the application of high-heat tape). The slides were then heated again to 450 °C before sensitization. This subsequent post-treatment on top of the 15 to 20 nm mesoporous layer of TiO$_2$ has been known to increase dye adsorption due to an increased TiO$_2$ roughness factor.$^{3,62}$ The roughness factor is increased despite decreasing the total TiO$_2$ surface area because the total TiO$_2$ weight increases. In the end, this TiCl$_4$-hydrolyzed TiO$_2$ layer provides better surface coverage because it is thought to remove only the hard to reach fraction of exposed TiO$_2$ surface area that is otherwise sterically inaccessible to dye molecules.$^{57}$ A cartoon of this effect is shown in Figure 3.9.
Figure 3.9. Overall effect of TiCl$_4$ treatment. An additional $\sim$1 nm thick layer of TiO$_2$ was coated on the surface of both the nanocrystalline TiO$_2$ film and the FTO surface. Adapted from Ito (2010).  

The active device area for laboratory cells discussed in literature is typically below 0.25 cm$^2$ due to the known decreases in efficiency with greater areas (due to resistance losses). We used an active area of 0.704 cm$^2$ as a compromise between the greater areas needed for reasonable UV-vis measurements in our lab and minimal doctor-blading area uncertainties, and the smaller areas necessary for uniform doctor-blading depositions and lower resistances (mentioned above).

Figure 3.10. Surface profilometry scan of (a) doctor-bladed TiO$_2$ film compared to (b) Dyesol purchased TiO$_2$ film. Parameters: profile (hills and valley), speed (45 sec), scan resolution (5.003 $\mu$A/s), and distance (9000 $\mu$m).

A surface profilometer (Dektak 3, Veeco) was used to determine the thickness and uniformity of each TiO$_2$ slide prepared. The doctor-bladed TiO$_2$ films were found to
be as uniform, if not more so, than commercially purchased TiO$_2$ films from Dyesol prepared via screen-printing. See Figure 3.10 for example profilometry scans of TiO$_2$ films. On average, our doctor-bladed TiO$_2$ films were $8 \pm 2$ µm thick. The greatest deviation in thickness is at the edges of the TiO$_2$ active area, due to a buildup of material around the tape from the doctor-blading technique.

The preferred thickness of TiO$_2$ films has been well optimized in previous DSSC studies. Increased thickness allows for a greater number of adsorbed dye molecules, however thicker films often have connectivity problems between particles and this can eventually lead to higher charge interception rates. Optimal TiO$_2$ thickness has been determined to be anywhere from 5 to 18 µm depending on the dye. However, most Ru(II) polypyridine studies report a value of ~10 µm as ideal for highest efficiency cells. This thickness should be decreased if laser studies (such as transient absorption) are expected to be performed. In TA spectroscopy, thinner TiO$_2$ films (ranging from 3.5 to 7 µm) are more desirable because they limit scatter while allowing enough light to pass through the slide. Therefore, an average thickness of 8 µm TiO$_2$ film was determined to be ideal for both efficiency and laser studies. A distribution of our doctor-bladed TiO$_2$ film thicknesses is reported in Figure 3.11 below.
Figure 3.11. Histogram of measured thickness of all TiO$_2$ films made by doctor-blading. The average films were 8 ± 2 µm based on two standard deviations.

TiO$_2$ slides were hand picked for each study, not to achieve the highest efficiency, but instead to produce the most consistent DSSCs among the selection of dyes being compared. For each efficiency measurement (Chapter 4), and each recombination lifetime measurement (Chapter 5), four similar thickness TiO$_2$ films (agreeing within 0.4 µm) were selected for each of the four dyes.

Dye sensitization was carried out immediately after heating (or reheating) the TiO$_2$ films at 450 °C to avoid physisorbed water on the TiO$_2$ surface. Slides were cooled to 85 °C and immersed in 0.5 mM dye solutions of 1:1 acetonitrile/tert-butanol for 24 hours. Sensitizing solutions were sonicated prior to film immersion to avoid the presence of dye aggregates. While 24 hours is a standard soaking time, a quick Langmuir adsorption isotherm was fit to absorption data obtained for [Ru(1)(tbpy)]$^{2+}$ on a TiO$_2$ film in elapsed time to confirm that saturation was reached on these slides (see...
Figure 3.12). After sensitization, the slides were thoroughly rinsed with acetonitrile to remove excess dye, air-dried, and immediately prepared into complete cells. A complication arose concerning additional equilibration times (discussed later in Section 3.4.1), but it is believed to be inconsequential to device performance.

![Figure 3.12. Sensitization of [Ru(1)(tbpy)]^{2+} onto TiO_2 film in time. Black line is a fit to a Langmuir adsorption isotherm in time. Saturation is reached after 20 hours.](image)

To prepare the platinum counter electrode, a single hole approximately 1 mm in diameter was drilled into a second FTO slide. To prevent cracking, this was done using a diamond tip drill bit and a waxed backing on the glass side of the FTO slide. Prior to platinum deposition, the drilled slides were washed with 1:1 toluene/hexane mixture, 0.1 M HCl, and water. The slides were then cleaned with acetone, water and methanol for 30 min each in an ultrasonic bath as done previously with the FTO slides prior to TiO_2 preparation. The platinum catalyst was deposited on top of the FTO by drop casting 5 mM chloroplatinic acid (H_2PtCl_6) in isopropanol.\textsuperscript{73,74} The process of drop casting involved dropping 15 µl of H_2PtCl_6 solution onto a masked area of Scotch tape (A = 2.4 cm\(^2\)) and quickly spreading the solution with a glass microscope slide before it
evaporated. The coated counter electrodes were then slowly heated to 380 °C and held at 380 °C for 20 min to allow for thermal decomposition; forming platinum islands.\textsuperscript{75}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure3.13}
\caption{Configuration of assembled dye-sensitized solar cells layer by layer. The red brick represents the sensitized doctor-bladed TiO\textsubscript{2} active area. The Surlyn spacer was cut to go around the TiO\textsubscript{2} active area, leaving extra space for the electrolyte solution. Figure is adapted from Ito (2010).\textsuperscript{63}}
\end{figure}

The previous paragraphs discuss the critical working components of the DSSCs: the sensitized TiO\textsubscript{2} working electrode and the platinum counter electrode. To put them together, complete DSSCs were assembled in a sandwich-type format shown in Figure 3.13 above, with the sensitized TiO\textsubscript{2} working electrode slide and platinum counter electrode slide. The sealant that holds the electrode slides together is a 25-μm thick thermoplastic film made of Surlyn (Meltonix 1170-25, Solaronix). This sealant thickness was determined from optimized literature values.\textsuperscript{76} This thickness dictates the distance
between the two electrode slides, thereby also determining the amount of the electrolyte solution in the cell. Surlyn sealing spacers were cut using an X-Acto knife to make rectangular gaskets 1.5 mm wide on all sides with an open window for the TiO$_2$ active area (2 mm wider on all sides than the dimensions of the active area). The thickness and empty window inside the gaskets thus made up the total volume of electrolyte solution. Binder clips were used to keep FTO slides in place while a heat gun was pointed at the cell until the glass reached 110 °C, as monitored by a thermocouple in direct contact with the glass slides. Applying a slight pressure to the slides between fingers allowed for the transformation of a shiny plastic (with a similar look and feel as Saran wrap) to become transparent; indicating a uniform seal without wrinkles or bubbles.

The electrolyte solution, comprised of 0.6 M PMII, 0.1 M LiI, 0.05 M I$_2$, and 0.5 M TBP in methoxypropionitrile, was injected into the predrilled hole on the platinum counter electrode side with a Vac’n’Fill Syringe (Solaronix). This involved pulling up the electrolyte solution with a syringe, releasing some of the solution to free it of air bubbles, attaching the syringe suction tip to hole on the slide, releasing the spring-loaded plunger to pull vacuum in the cell, and slowly injecting electrolyte solution into the evacuated cell volume. An additional square of Surlyn and a small cover slip was used to seal the drilled hole on the side, thus completing the cell. Again, a binder clip was used to hold the cover slip in place while a heat gun was applied with slight pressure on the cell to seal it completely. Each DSSC that was properly sealed was found to be stable by UV-vis spectrophotometry after several months of storage in the dark.
3.4 Preliminary Characterization of DSSCs

Before making efficiency measurements of these complete devices, preliminary absorption spectra and efficiency collection parameters for cell studies were characterized. Detailed efficiency measurements are reported in Chapter 4.

3.4.1 Absorption Spectra

Steady-state electronic absorption spectra were recorded with a Hewlett-Packard diode array UV-vis spectrophotometer (HP8452A). First, spectra of 0.5 mM sensitizing solutions in 1:1 acetonitrile/tert-butanol were collected in 1 mm quartz cuvettes prior to soaking TiO$_2$ slides (see Figure 3.15.a). Then, absorption spectra of sensitized TiO$_2$ films (see Figure 3.15.b) were collected immediately after rinsing the films with acetonitrile. The absorption spectra of un-sensitized TiO$_2$ slides, iodide electrolyte solution, and complete DSSCs were measured as well (see Figure 3.15.c).
Figure 3.15. Absorption spectra for measurement comparison. (a) Dyes in 1:1 acetonitrile/tert-butanol sensitizing solutions. (b) Dyes adsorbed to TiO$_2$ films. (c) Complete dye-sensitized solar cells and components of cells.
All sample slides were held by a filter holder (Thor Labs) in an attempt to maintain the same angle and interrogation area for each UV-vis measurement (see Figure 3.16). We note that measurements taken via an integrating sphere would have been preferred to differentiate absorption due to reflection and scattering of the TiO₂ slides. All plotted spectra that include a TiO₂ slide are reported from the average of three measurements.

![Image of UV-vis lamp light striking a sensitized TiO₂ film](image)

**Figure 3.16.** Incoming UV-vis lamp light striking a sensitized TiO₂ film.

Absorption spectra of sensitized TiO₂ films exhibited features that were blue-shifted a few nanometers compared to spectra of the dyes in 1:1 acetonitrile/tert-butanol sensitizing solution. The recorded shifts in maximum absorbance are reported in Table 3.1 with spectra given both in Figure 3.17 and Figure 3.15. While spectral shifts were minimal, they were nonetheless characteristic of each dye after adsorption. The blue-shifted absorbance maxima are attributed to deprotonation of the carboxylic acid linkers upon binding to TiO₂ films.¹⁵,⁷⁷,⁷⁸ The large spectral shift of 14 nm seen with [Ru(3)(tbtty)]²⁺ is due to an artificial maximum as a result of greater Rayleigh scattering at shorter wavelengths (dependence ~1/λ⁴).⁷⁹,⁸⁰ The effect of TiO₂ particles scattering light is reported to be greatest for low surface coverage because less light is initially absorbed.⁷⁹
Spectra in Figure 3.17 show an increase in background Rayleigh scattering with the sensitized TiO₂ slides compared to solution, which matches that seen on unsensitized TiO₂ slides. The scattering does not increase further in the complete cells even though there is an additional Pt-coated FTO slide. This is because the scattering effect from the TiO₂ and FTO glass slides is reduced by the presence of the electrolyte, whose refractive index matches that of the FTO glass better than the refractive index of air does.⁶⁴

Relative differences in peak absorption maxima between sensitizing solution and TiO₂ films reflect the larger surface coverage obtained for N719 dye, and the smaller surface coverage of [Ru(3)(tbtpy)]²⁺ (see relative changes from (a) to (b) in Figure 3.15). These data become useful when deconstructing wavelength dependent efficiencies of each dye (Chapter 4). The light harvesting efficiency and charge interception rates of DSSCs are noted for their likely dependence on surface coverage.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Sensitizing Solution λ_{max}</th>
<th>Sensitized TiO₂ film λ_{max}</th>
<th>Complete Cell λ_{max}</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(1)(tbtpy)]²⁺</td>
<td>488</td>
<td>486</td>
<td>492</td>
</tr>
<tr>
<td>[Ru(2)(tbtpy)]²⁺</td>
<td>484</td>
<td>482</td>
<td>487</td>
</tr>
<tr>
<td>[Ru(3)(tbtpy)]²⁺</td>
<td>480</td>
<td>466</td>
<td>484</td>
</tr>
<tr>
<td>N719</td>
<td>532</td>
<td>535</td>
<td>532</td>
</tr>
</tbody>
</table>

Table 3.1. Wavelengths of maximum absorbance
After TiO₂ films were made, several new experiments could be performed. When electrochemical studies were performed on sensitized TiO₂ slides (cyclic voltammetry in Chapter 4 and bulk electrolysis in Chapter 5), we noted that films sitting in nitrile solvents exhibited decreased absorption over time. This was seen in the absence of external bias. Because no spectral shifts were observed, this absorption decrease was attributed solely to dye desorption from the TiO₂ surface. An example of this desorption after soaking a [Ru(1)(tbtpy)]²⁺ TiO₂ slide in acetonitrile is shown in Figure 3.18. For each dye in the Steric Series, there was an approximate 30% decrease in the peak sensitized TiO₂ absorption maximum in the first hour of soaking in 5 mL of acetonitrile. After a few hours, the absorption spectra of sensitized films become constant. We note
that desorption was not observed for N719 films, likely due to the insolubility of N719 in pure acetonitrile. Instead, N719 films were found to blue shift in time, which is suggestive of deprotonation of the carboxylic acid substituents not involved in binding to TiO$_2$ in the presence of acetonitrile.$^{78}$

![Absorption spectra of [Ru(1)(tbtpy)]$^{2+}$ on TiO$_2$ slides signifying desorption from TiO$_2$ after equilibration in acetonitrile. All spectra are taken of sensitized TiO$_2$ slides in air. An un-sensitized (bare TiO$_2$) slide spectrum is shown for comparison.](image)

Figure 3.18. Absorption spectra of [Ru(1)(tbtpy)]$^{2+}$ on TiO$_2$ slides signifying desorption from TiO$_2$ after equilibration in acetonitrile. All spectra are taken of sensitized TiO$_2$ slides in air. An un-sensitized (bare TiO$_2$) slide spectrum is shown for comparison.

To ensure reliable absorbances for film studies, absorption spectra were measured before and after every measurement in this dissertation. Unfortunately, not every sensitized TiO$_2$ film was allowed to equilibrate in acetonitrile for 24 hours prior to measurements, because this observation was only noted in the last year of study. However, an additional set of complete cells was made with the additional procedural step of equilibration in acetonitrile for 24 hours. These cells had no observable change in efficiencies compared to those without the equilibration step. Therefore, we assumed the extent of desorption was minimal in the small amount of methoxypropionitrile electrolyte.
solution. However, desorption is noted as a possible reason for generally lower efficiencies among the Steric Series of DSSCs.

3.4.2 Efficiency Parameter Optimization

For total solar power conversion efficiency measurements, current-voltage characteristics (J-V curves) were taken on DSSCs of each dye as reported in Chapter 4. However, before these measurements could be made, collection parameters had to be determined and optimized.

The scan rate and step size were two parameters that were allowed to vary for the given potentiostat. Empirical tests revealed a scan rate of 100 mV/s at a step size of 10 mV provided the greatest efficiency. The starting photovoltage was set to a positive voltage to allow the measurement to proceed before an accurate short-circuit photocurrent, $J_{sc}$, was obtained at voltage = 0. The wait time before photocurrent was measured was set to 1 second, because fluctuating non-steady state values of current were obtained at anything shorter.

To ensure good electrical contact for connections to the potentiostat, studies suggest scraping the edge of the FTO slides (outside the cell active area) with sandpaper. This was found to significantly increase photocurrents, presumably by decreasing the contact resistance. Therefore, slides were always sanded before efficiency measurements and care was taken to connect the leads to the cells in a similar manner. However, exactly how well the leads were connected to the FTO slides was found to be the greatest source of error that remained after parameter optimization. Lead connectivity was therefore always measured with at least three trials and the best J-V curve measurement was used in the end.
Figure 3.19. J-V curves and the respective efficiencies of N719 DSSC measured each day for five days. Conversion efficiency increased over time.

To test for reproducibility under a reasonable set of parameters, a single DSSC was measured in time. N719 current-voltage characteristics were tested every day for five days with the same parameters. J-V curve results are shown in Figure 3.19 with the respective efficiencies calculated as well (see Chapter 4 for efficiency calculation explanation). As can be seen, conversion efficiency was found to increase considerably and then level out in time. Ito, Grätzel and co-workers have previously reported similar early fluctuations in efficiency measurements in time.\textsuperscript{64} They state that optimal cell testing conditions are achieved only after at least three days of aging the cell in the dark.\textsuperscript{64} We believe this is the result of better electrolyte equilibration after the first few days. Therefore, we also waited at least three days to make efficiency measurements, and then measured the same cells again after five days. There was no observable increase or decrease in efficiency from day three to day five (see Chapter 4).
This concludes the set of conditions determined for efficiency measurements of DSSCs. Empirically optimized conditions for the complete cell include: electrolyte equilibration time (at least three days), scan rate (100 mV/s), step size (10 mV), starting voltage (0.1 V), and current wait time (1 sec) based on experiment and literature. J-V measurements were taken on DSSCs of each dye on the same day, with three trials after adjustments to lead connectivity. The trial with lead connectivity leading to the greatest photocurrent (and subsequent efficiency) was reported in each case within Chapter 4.

3.5 Concluding Remarks

This chapter establishes reliable methods for making ruthenium polypyridyl DSSCs for future conversion efficiency testing. In terms of the working electrode component, transparent conducting oxides were thoroughly cleaned, TiO\textsubscript{2} films were deposited and sintered with uniform thickness, dyes were adsorbed from 0.5 mM sensitizing solutions, and slides were thoroughly washed and allowed to equilibrate with acetonitrile. These were then immediately sealed to freshly prepared platinum counter electrode slides, and then each construct was injected with iodide electrolyte to form the complete cell. Before efficiency measurements were made, all cells were sanded for optimal electrical contact and aged in the dark for at least three days to allow for optimal electrolyte equilibration. Electronic absorption spectra were also characterized for all dyes in complete cells. The parameters to be used for J-V characteristics measured in the next chapter were also determined.
3.6 References


(4) Honesberg, C.; Bowden, S. In PVEducation pveducation.org, 2015.


(58) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Miiller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. Conversion of Light to Electricity by Cis-


4.1 Introductory Remarks

Having formed complete solar cells in Chapter 3, device functionality may now be explored. In this chapter, the process by which a DSSC converts energy from sunlight into electricity by the photovoltaic effect is described. It is then quantified by the measurement of both current and voltage dependencies of a cell, which together govern the total power that a device generates. This measurement is accomplished by illuminating a cell with a known irradiance of light generated to simulate the solar spectrum, applying a known potential across the cell, and monitoring the resulting photocurrent. Given the power of sunlight that strikes the DSSCs and the power that the DSSCs generate, the efficiencies of the DSSCs may be calculated.

Note that from the start, researchers must be careful in defining efficiency measurements of photovoltaic devices. For the purposes of this work, we consider only the total light-to-power conversion efficiency of DSSCs, and not production efficiency, which would include costs associated with materials, maintenance, long-term storage, and transportation of extracted electricity. The solar conversion efficiency of photovoltaics is conventionally quoted solely in terms of power. Still, power conversion efficiency measurements can be deceiving unless terms are defined and used precisely. Such definitions and conditions are explained in Section 4.2, entitled Photovoltaic Conversion Background. For the work presented in this chapter, we by no means expect
to break or even match any efficiency records. Instead, we aim to understand trends in efficiencies as the dye is changed in devices prepared in the same manner.

In this chapter, we characterize the power conversion efficiency of DSSCs made up of the Steric Series: \([\text{Ru}(1)(\text{tbtpy})]^ {2+}\), \([\text{Ru}(2)(\text{tbtpy})]^ {2+}\), and \([\text{Ru}(3)(\text{tbtpy})]^ {2+}\), with structures provided in Figure 4.1. The widely used ruthenium bipyridyl dye, N719, will also be studied as a standard for comparison with the same cell components (see structure in Figure 4.1). Again, the complete DSSCs were formed following procedures reported in Chapter 3.

Figure 4.1. Structures of dyes used in DSSCs. Counter ions are tetrabutylammonium (TBA\(^+\)) and hexafluorophosphate (PF\(_6^-\)).

Within a working photovoltaic device, the photovoltaic effect can be broken down into several processes: photon absorption, electron-hole pair (carrier) generation, carrier separation, carrier transport, and carrier collection. In this chapter, we aim to separately identify the results of these processes as a means of understanding which photovoltaic processes are most greatly affected by the conformational changes associated with the introduction of steric hindrance. By doing this, we attempt to reveal fundamental conditions that could drive future improvements to overall efficiency.
4.2 Photovoltaic Conversion Background

To understand photovoltaic generation of power, one must first understand how a cell works. In DSSCs, the sensitized TiO$_2$ film forms the working electrode, and platinum-coated FTO forms the counter electrode, as depicted in Figure 4.2 (repeat of Figure 1.7 from Chapter 1). The absorption of sunlight by the dye excites electrons, which can then be injected into the working electrode, where they are collected for powering a load. After flowing through an external circuit, the electrons build up at the counter electrode and reduce the redox mediator. The reduced form of the redox mediator transports electrons back to the dye, and the circuit is complete.

Figure 4.2. Operating conditions of a dye-sensitized solar cell. The sensitized TiO$_2$ film acts as a working electrode with platinum on FTO as the counter electrode. The transfer of electrons in a working cell is shown with green dots.
A current-voltage characteristic (J-V curve) is the measurement typically used to determine the efficiency of a device. For most DSSCs, this J-V curve is generated with a potentiostat connected to the sensitized TiO₂/FTO (the photoanode) and the Pt/FTO (the photocathode). A fixed potential bias is held while monitoring the current that arises when sunlight strikes the device. A typical J-V curve for data collected in our group is shown in Figure 4.3 below. The power density available from the cell at any point along the J-V curve is expressed in watts per area and is calculated by multiplying the voltage by the current density (see power curve as well in Figure 4.3).

Figure 4.3. An example of J-V and power curves collected for a typical DSSC. The J-V curve in light is depicted with the orange solid line, while the dark J-V curve is the dashed orange line. \( P_{max} \) is the maximum power achieved by the device. \( P_T \) is the maximum theoretical power (\( Jsc \times Voc \)). FF is the ratio of the purple rectangular area (\( P_{max} \)) to the green rectangular area (\( P_T \)). \( Jpp \) and \( Vpp \) are the respective current and voltage at the maximum power point.
The universal shape of the J-V curve of a solar cell under illumination is the result of two opposing mechanisms: (1) light-induced charge separation and extraction, which allows anodic current to flow, and (2) the application of an external negative bias, leading to an accumulation of electrons within the photoanode, which allows cathodic current to flow. At a sufficiently high forward bias ($V < 0$), the magnitudes of the two currents cancel, corresponding to open-circuit conditions ($J_{sc} = 0$). Ultimately, a solar cell generates power when it produces current at a non-zero bias.

To better understand the potential-dependent photocurrents of J-V curves, dark J-V curves are often measured as well. This measurement reveals the effect of light-independent processes driven solely by a negative potential bias. These dark curves are driven by cathodic current (commonly referred to as dark current). Dark current is thought to arise mainly due to the flow of electrons out of the working electrode as they are intercepted by the oxidized form of redox mediators (typically I$_3^-$) in the electrolyte. Note that the curvature of dark current does not always match that of photocurrent because there are additional photoinduced pathways that also lead to cathodic current (such as charge recombination).

In the end, the three key parameters needed to determine the total power conversion efficiency, $\eta$, are obtained by analyzing the J-V curve. These parameters are short-circuit photocurrent density, $J_{sc}$, open-circuit photovoltage, $V_{oc}$, and fill factor, $FF$, all of which are explained below.

The first parameter, $J_{sc}$, is the maximum rate at which charge can flow through the circuit, for a given cell area. Specifically, this is the measured cell photocurrent density when there is zero photovoltage (see y-intercept in Figure 4.3). It turns out that a
multitude of factors within a particular device will drastically affect the $J_{sc}$, and as such, the origins of this measurement are analyzed further in Section 4.4.2.

The open-circuit photovoltage, $V_{oc}$, obtained for a one-electron process, is defined as the maximum Gibb’s free energy of a particular device. It is the measured photovoltage when there is zero current within the cell (see $x$-intercept in Figure 4.3). In the context of DSSCs, $V_{oc}$ originates as the thermodynamic potential difference between the quasi-Fermi level of the semiconductor, $E_F$, and the Nernst potential of the redox mediator in the electrolyte (shown in Figure 4.2). The quasi-Fermi level of a semiconductor in a DSSC is determined by the equilibrium electrochemical potential of the device. It is termed a quasi-Fermi level because the value changes depending on the extent of solar irradiance striking the device, as shown in Figure 4.4.

![Figure 4.4](image_url)  
Figure 4.4. Changing the quasi-Fermi level, $E_F$, with forward bias or under greater illumination.
The fill factor, $FF$, is the last defining parameter of the solar cell. The $FF$ is calculated as the ratio given in equation 4.1,\(^9\) and visualized as the ratio of rectangular areas in Figure 4.3.

$$FF = \frac{J_{pp}V_{pp}}{J_{sc}V_{oc}}$$  \hspace{1cm} (4.1)

This ratio specifies the “squareness” of a J-V curve as a percentage of how close the maximum power is to that of an ideal cell. The $J_{pp}$ and $V_{pp}$ are the photocurrent and photovoltage, respectively, at the power point—the greatest power achieved for a particular cell (see power curve in Figure 4.3). Essentially, the $FF$ is a measure of how well the components of a cell contribute to productive current and voltage. The rate at which electrons recombine with other species (both oxidized dye and redox mediator) as photovoltage increases dictates the expected $FF$. Typical optimized devices have values of $FF$ in the range of 0.5-0.75, due to inherent series and shunt resistances.\(^{10,11}\)

After bringing each of these parameters together, one can determine the efficiency of a photovoltaic device. The total light-to-electrical-power conversion efficiency, $\eta$ or PCE, is a unitless efficiency standard characterized by the maximum electrical power output, $P_{max}$, divided by the total solar power input, $P_{in}$, as given in equation 4.2.\(^1,9\)

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{sc}V_{oc}FF}{P_o}$$  \hspace{1cm} (4.2)

The power conversion efficiency, $\eta$, is typically reported with the incident irradiance of sunlight, $P_o$, in equation 4.2, fixed at 100 mW/cm\(^2\)—the approximate power of one sun at AM1.5 spectral distribution.\(^12\) Air mass 1.5 sunlight is simply the amount of sunlight passing through 1.5 atmospheres at a solar zenith angle of 48.2°—the average angle across the continental United States.\(^1,12\) Efficiency measurements are known to vary with
temperature, thus as a standard, $\eta$ is reported at room temperature, 25 °C. In general, the optimization of $J_{sc}$, $V_{oc}$, and $FF$ are what maximizes the $\eta$ of a particular device.

4.2.1 Incident-Photon-to-Current Efficiency (IPCE)

While current-voltage characteristics are undoubtedly useful tools for measuring efficiencies of devices, the resulting parameters often fail to lend insight into why particular devices might have particularly high or low values. As alluded to in the previous section, J-V curves often have subtle differences in curvature as a result of the complicated internal processes that drive them.

Given the variable nature of photon absorption in DSSCs, it is not surprising that $\eta$ often varies greatly with the wavelength of incident light. Thus to understand reasons behind high or low $\eta$ values, incident-photon-to-current efficiency (IPCE) is used as a wavelength-dependent efficiency standard (see Figure 4.5).
Figure 4.5. Hierarchy of efficiency measurements. The intention is to show how to deconstruct a macroscopic measurement into microscopic components. For instance, in order to understand $\eta$, we needed to measure wavelength-dependent IPCE. Arrows only represent the main relationships between components.
IPCE is frequently referred to as the external quantum efficiency (EQE) of a device. Often given as a percent, it is expressed as the number of electrons generated by the device divided by the number of incident photons that strike the device (equation 4.3). IPCE is typically collected under short circuit photocurrent (V = 0) conditions as a function of wavelength divided by the power density, as shown in equation 4.3.\(^1\)

\[
IPCE(\lambda) = \frac{\#\text{electrons}}{\#\text{incident photons}} = \frac{J_{sc}(\lambda)/q}{P(\lambda)/(hc/\lambda)} = \frac{1240 \cdot J_{sc}(\lambda)}{\lambda[\text{nm}] \cdot P(\lambda)} \tag{4.3}
\]

Here, \(J_{sc}(\lambda)\) is the photocurrent density at each wavelength (units of A/cm\(^2\)), \(P(\lambda)\) is the incident power density at each wavelength (units of W/cm\(^2\)), \(q\) is the charge of an electron, \(h\) is Planck’s constant, \(c\) is the speed of light, and in the final expression the value of 1240 encompasses \(hc/q\). Based on these parameters, in order to measure the IPCE of a particular device, one must have a variable monochromatic light source, a measurement of power for a given area of excitation, and a measurement of the short-circuit photocurrent generated by the device for a given area of excitation. This yields a photocurrent action spectrum, which is depicted as %IPCE plotted versus wavelength.

As a type of sanity check, integrating the wavelength-dependent photocurrent density over all wavelengths should generate the same total wavelength-independent short circuit photocurrent density, \(J_{sc}\), as generated by a J-V curve.\(^2\) For solar cells, the relevant wavelengths are those within the solar spectrum, so we derive \(J_{sc}\) by integrating the overlap of the IPCE(\(\lambda\)) with the spectral intensity of solar emission (\(\phi_{\text{sun}}\)) as shown in equation 4.4.\(^3\)

\[
J_{sc} = q \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} IPCE(\lambda)\phi_{\text{sun}}(\lambda)d\lambda \tag{4.4}
\]
The spectral intensity of solar emission is also called the monochromatic photon flux density of the AM1.5 global solar spectrum, or simply the photon flux (photons/m²s).\textsuperscript{17} With \( q \) as the charge of an electron and IPCE a unitless quantity, the overlap integral of this curve with spectral intensity yields units of photocurrent density. To get the value of \( \phi_{\text{sun}} \), one needs solar irradiance units of energy per unit \( \lambda \) for an interval of a given \( \lambda \) (Wm\(^{-2}\)nm\(^{-1}\)). We use the energy through an aperture of known area at a given wavelength (units of W/m\(^2\)) and convert to irradiance by taking into account data collected every 10 nm (Wm\(^{-2}\)10nm\(^{-1}\)). In this work, the total photocurrent density is approximated experimentally as the sum of \( J_{\text{sc}}(\lambda) \) measurements taken with a monochromator (at 10 nm bandpass) every 10 nm in the range of visible light (400 nm to 800 nm).

### 4.2.2 Light Harvesting Efficiency (LHE)

Incident-photon-to-current efficiency, as the external quantum efficiency of a device, must take into account how many photons are absorbed by the particular device in the first place (see Figure 4.5). This amount is dependent on the dye and is termed the light harvesting efficiency, LHE, calculated as given in equation 4.5.\textsuperscript{18} Note that LHE is wavelength dependent and also frequently referred to as the absorptance of a dye, \( \alpha(\lambda) \).

\[
LHE(\lambda) = \alpha(\lambda) = 1 - \frac{I(\lambda)}{I_o(\lambda)} = 1 - 10^{-A(\lambda)} \tag{4.5}
\]

Equation 4.5 is based on a standard electronic absorption experiment with \( I_o(\lambda) \) defined as the intensity of incoming incident light and \( I(\lambda) \) as the intensity of light transmitted through the sample.\textsuperscript{18} \( A(\lambda) \) can then be approximated as the optical absorbance of the dye adsorbed to TiO\(_2\).\textsuperscript{19}

For an understanding of LHE in the context of DSSCs, one can substitute for \( A(\lambda) \) in equation 4.5 as given in equation 4.6.\textsuperscript{20}
\[ A(\lambda) = \Gamma \sigma(\lambda) \]  

(4.6)

Here, the surface coverage, \( \Gamma \), is the concentration of dye molecules for a given thickness of film in units of mol/cm\(^2\). The absorption cross section, \( \sigma(\lambda) \) (in units of cm\(^2\)/mol), is 1000 times the molar extinction coefficient (in M\(^{-1}\)cm\(^{-1}\)). Typical surface coverages of ruthenium dyes on TiO\(_2\) are on the order of 10\(^{-8}\) to 10\(^{-7}\) mol/cm\(^2\),\(^{21}\) with an estimated flat monolayer of dye coverage at approximately 10\(^{-10}\) mol/cm\(^2\).\(^{20,22}\)

4.2.3 Internal Efficiency Components

IPCE data allow for wavelength-dependent efficiencies to be determined, but the addition of wavelength-dependent LHE data allows for the determination of how device efficiencies may change after taking into account dyes that are known to be better absorbers. That is, the standard characterization of dyes in solution will tell how well a dye absorbs sunlight, but knowing how well that dye transfers electrons throughout a device is equally important, if not more so.

By definition, dividing the IPCE by the LHE generates the absorbed photon-to-current efficiency (APCE), as given in equation 4.7.\(^{5}\) The APCE is therefore a measurement of the internal quantum efficiency, which measures device efficiency independent of how well it absorbs light.

\[ APCE(\lambda) = \frac{IPCE(\lambda)}{LHE(\lambda)} = \varphi_{INJ} \eta_{COLL} \eta_{REG} \]  

(4.7)

APCE can then be broken down further into each particular efficiency component of a device (see Figure 4.5). A typical breakdown of APCE in the context of DSSCs separates the injection quantum yield, \( \varphi_{INJ} \), collection efficiency, \( \eta_{COLL} \), and regeneration efficiency, \( \eta_{REG} \). Note that frequently the \( \eta_{REG} \) factor is excluded when it is assumed to have a value of one.\(^{23}\)
Each macroscopic efficiency measurement is therefore in some way or another related to the kinetics of the microscopic electron transfer mechanisms (see Figure 4.5). Greater total power conversion efficiencies are found in DSSCs with measurably faster favorable forward electron transfer kinetics and slower unfavorable back electron transfer kinetics. To understand the kinetics of DSSCs, which often are multi-exponential and/or follow differing higher order rate laws, half-life times are typically used to compare trends among competing pathways. Equations 4.8-4.10 break down the yield and efficiency components into the main forward and reverse half-life times responsible for each process (see Figure 4.5).

\[ \phi_{\text{INJ}} = \frac{k_{\text{inj}}}{k_{\text{inj}} + k_{\text{relax}}} = \frac{1}{1 + \left(\frac{t_{\text{inj}}}{t_{\text{relax}}}\right)} \]  

(4.8)

The injection yield, \( \phi_{\text{INJ}} \), is dependent upon the excited state half-life time of a dye (\( t_{\text{relax}} \)) and the half-life time for electron injection into TiO\(_2\) (\( t_{\text{inj}} \)) as given in equation 4.8. While electron injection is typically thought of as a fast process occurring on a femtosecond timescale, studies have suggested that slower injection from the thermally relaxed triplet state may dominate photocurrent generation. Of course, as an approximation, a half-life time should take both of these slow and fast injection time components into account.

\[ \eta_{\text{REG}} = \frac{1}{1 + \left(\frac{t_{\text{reg}}}{t_{\text{rec}}}\right)} \]  

(4.9)

The regeneration efficiency, \( \eta_{\text{REG}} \), gives the fraction of ground state dye molecules that are regenerated by the redox mediator (\( t_{\text{reg}} \)). As an unfavorable alternative,
it is possible for the electrons within the TiO$_2$ network to recombine with the oxidized dye molecules instead ($t_{\text{rec}}$).

$$\eta_{\text{COLL}} = \frac{1}{1 + \left(\frac{t_{\text{trans}}}{t_{\text{int}}}ight)}$$ (4.10)

The efficiency of electron collection from the TiO$_2$, $\eta_{\text{COLL}}$, is dependent on the competition between the transport of electrons to the FTO ($t_{\text{trans}}$) and charge interception with triiodide in the electrolyte ($t_{\text{int}}$). While technically the charge recombination with photogenerated oxidized dye molecules ($t_{\text{rec}}$) that have not been reduced by the electrolyte is another pathway in competition with electron collection, it is excluded from equation 4.10. This is due to the likelihood that $t_{\text{reg}}$ and $t_{\text{rec}}$ will both be significantly faster than $t_{\text{trans}}$. Again, the components of $\phi_{\text{INJ}}$, $\eta_{\text{REG}}$, and $\eta_{\text{COLL}}$ only compare pathways in direct competition. So, while $t_{\text{rec}}$ is a highly important competing pathway, it is only factored into $\eta_{\text{REG}}$ (equation 4.9).

Further knowledge of each of these efficiency components allows us to understand the reasons behind particularly high or low $\eta$ values for a device. Results presented in this chapter are aimed at determining which efficiency components are most likely to change across DSSCs composed of the Steric Series.

### 4.3 Experimental

#### 4.3.1 Current-Voltage Characteristics (J-V Curves)

Photovoltaic measurements were measured with a 100 W Xenon lamp (6257, Newport/Oriel) equipped with an AM1.5 global filter (AM1.5 G, Newport). The power of the simulated light was calibrated to 100 mWcm$^{-2}$ using a thermopile (PowerMax 500D,
Photovoltaic performance was tested using a black metal mask 1.5 mm wider on each side than the active area of TiO$_2$, as shown in Figure 4.6 (mask area = 1.316 cm$^2$). This mask, of greater aperture than that of the active area of TiO$_2$, was used in order to capture both direct and diffuse light while eliminating multiple reflections due to light piping. The cells were kept at $25 \pm 0.5$ °C over the course of the measurement, as measured by a thermocouple kept in direct contact with the illuminated cell. Temperature stability was achieved using a home-built water-cooled metal cell holder (that also acted as the mask) run by a refrigerated constant temperature circulator (VWR).

![](image1.png)

Figure 4.6. Pictures of metal cell holder. (a) A thick black fabric was placed over the holder during measurement to cover the sides where the leads are connected. (b) The black metal front face acts as a mask that is 1.5 mm wider than the active area on each side. (c) The thickness of the holder allows the cell to be water-cooled to 25 °C.

Current-voltage characteristics were measured with linear-sweep voltammograms using an electrochemical analyzer (601C, CH Instruments). A three-electrode setup was used.

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A smaller mask would not capture diffuse light and instead allow for covered active areas that would only contribute to dark current. The absence of a mask would artificially inflate efficiencies by multiple reflection and reabsorption.
employed, with the sensitized TiO$_2$/FTO slide acting as the working electrode and the 
Pt/FTO slide acting as both the counter electrode and the reference electrode. The 
potentiostat leads were connected to allow for positive anodic photocurrent in the light 
upon applying a negative cell potential. Care was taken to ensure the leads were 
connected in a similar fashion for each measurement, as this was deemed a high source of 
error in reproducibility. A known hysteresis with DSSCs required all scans to be run in 
both a forward scan direction towards negative potentials and a reverse scan direction 
towards positive potentials.$^{30}$ All results are reported as an average of forward and 
reverse scan directions.

Samples were allowed to equilibrate to 25 °C for 30 min. Parameters and 
conditions were optimized for constancy and efficiency; electrolyte equilibration time 
(three days), scan rate (100 mV/s), step size (10 mV), starting voltage (0.1 V), and 
current wait time (1 sec) were chosen based on experiment and literature (Chapter 3). J-V 
measurements were taken on DSSCs of each dye on the same day, with three trials after 
adjustments to lead connectivity. The trial with lead connectivity leading to the greatest 
photocurrent (and subsequent efficiency) was reported in each case.

4.3.2 IPCE Setup

Photocurrent measurements were made with the same source and potentiostat as 
those used for J-V characteristics. However, to increase total excitation intensity, a rear 
reflector (60005, Oriel) was added and the Xe light was set to 110 W. The complete IPCE 
setup is pictured in Figure 4.7. The light from the Xe source was passed through a 125 
mm focusing lens (F/3.7, Newport) into a monochromator (77250, Oriel) at 10 nm 
bandpass (entrance and exit slits 1.5 mm). A water-cooled metal cell holder held the
complete DSSC sample with a metal circle mask of known aperture (area = 0.1257 cm$^2$).

The cell temperature was set to 25 ± 0.5 °C, with no equilibration time needed.

Figure 4.7. IPCE setup. From right to left: xenon lamp source, focusing lens, square AM1.5 G filter, monochromator, yellow 420 nm long-pass (LP) filter, water-cooled metal cell holder, complete DSSC.

The excitation power was measured at the sample, directly after the mask, before and after each measurement. This was repeated with a FTO slide in place to account for power losses due to FTO absorption and reflection. Care was taken to ensure that the excitation between 400-700 nm remained in the linear power regime of at least 2.5 mW/cm$^2$. This value was determined from literature, with known concerns of non-linear photocurrents below a photon flux of $10^{17}$ cm$^{-2}$s$^{-1}$. Unfortunately, excitation dropped to between 0.7-2.5 mW/cm$^2$ from 700-800 nm.
Photocurrents were measured over time under short circuit conditions (potential = 0 V), with the lights off, over the course of 500 seconds (collected every 0.1 second). Experiment duration at each given wavelength was adjusted to ensure that steady-state values were reached before recording. Raw data were based on the average short circuit photocurrent readings after 50 seconds at the first wavelength (400 nm), and then for 10 seconds at each subsequent wavelength (~8 min scan for each DSSC). For the measurement of all wavelengths greater than 630 nm, a 420 nm long-pass filter (Newport) was needed to filter out the apparent intensity arising from higher order diffraction.

4.4 Results and Discussion

4.4.1 Current-Voltage Characteristics (J-V curves)

A plot of J-V curves for the Steric Series is given in Figure 4.8. The maximum current and voltage for N719 were found to lie considerably outside the range of the Steric Series. Therefore, N719 J-V curves are excluded from Figure 4.8 and are instead given in Figure 4.9.
Figure 4.8. J-V curves for the Steric Series measured under AM1.5 G solar irradiance (100 mW/cm$^2$) and in the dark (dashed lines) at 25 °C. All curves are an average of the forward and reverse scan directions. An insert is provided for the respective solar energy parameters obtained from each J-V curve. Ru(1)-Ru(3) are shorthand for [Ru(1)(tbpy)]$^{2+}$ through [Ru(3)(tbpy)]$^{2+}$. The colors in the table correspond to the respective J-V curves.

<table>
<thead>
<tr>
<th></th>
<th>%$\eta$</th>
<th>Jsc /mAcm$^{-2}$</th>
<th>Voc /V</th>
<th>FF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(1)</td>
<td>0.17</td>
<td>0.49</td>
<td>0.48</td>
<td>0.71</td>
</tr>
<tr>
<td>Ru(2)</td>
<td>0.10</td>
<td>0.32</td>
<td>0.42</td>
<td>0.72</td>
</tr>
<tr>
<td>Ru(3)</td>
<td>0.05</td>
<td>0.18</td>
<td>0.40</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Figure 4.9. J-V curves for N719 measured under AM1.5 G solar irradiance (100 mW/cm$^2$) and in the dark (dashed lines) at 25 °C. Each curve represents the average of the forward and reverse scan directions.

N719  4.91  13.3  0.76  0.49
The J-V curves for the Steric Series show several noteworthy features and trends (Figure 4.8). In this data set, there is a slight decrease in $FF$ and $Voc$ across the Steric Series with each addition of a methyl substituent. Both of these components are derived in large part from the curvature of the J-V curves (vide supra). As a means of understanding J-V curvature, dark currents were measured to assess the onset of unfavorable charge interception pathways. A close look at the dark currents in Figure 4.8 reveals a trend of slightly increasing dark currents across the Steric Series, in hand with the lower $FF$ and $Voc$. This is shown by a later onset of cathodic current with the less stericly encumbered species, $[\text{Ru}(1)(\text{tbtpy})]^{2+}$, compared to $[\text{Ru}(3)(\text{tbtpy})]^{2+}$ (Figure 4.8). We believe this is a result of a slightly lower surface coverage across the Steric Series with increasing steric bulk. While each device was made up with the same concentration of dye sensitizing solutions and soaked for the same amount of time, differing total surface coverages were nonetheless unavoidable. Lower surface coverages simply do not provide as many Ru dye molecules to block the TiO$_2$ surface and thus have been known to allow for better intercalation of electrolyte species. As a consequence, the rate of charge interception with the electrolyte increases, leading to an increase in dark current.

Approximations of surface coverage were determined from the peak absorptions of dyes on TiO$_2$ films (Chapter 3) and known peak molar absorptivities (Chapter 2) in accordance with equation 4.6 given in Section 4.2.2. These values support the trend in increasing dark current with lower surface coverage, with $[\text{Ru}(1)(\text{tbtpy})]^{2+}$ at $4.2 \times 10^{-8}$ mol/cm$^2$ versus $[\text{Ru}(3)(\text{tbtpy})]^{2+}$ at $3.4 \times 10^{-8}$ mol/cm$^2$. However, again, we note that this

$\text{§§§}$ It is perhaps dictated by the differing pKa’s of the carboxylic acid substituents on the arylerpyridyl ligands due to its differing affinities to bind to the TiO$_2$ surface.
only lead to small changes in $FF$ and $Voc$.

More drastically shown in Figure 4.8 is a large decrease in $J_{sc}$, evident in changes in the $y$-intercepts of the plots. This decrease in $J_{sc}$ is similar in magnitude to the large (approximately twofold) decrease in efficiencies across the Steric Series. This suggests that the drop in efficiency is dominated by the large decrease in $J_{sc}$.

To address issues with uncertainties arising due to surface coverage and appropriately assess the changes in photocurrent among dyes, we deemed it important to evaluate the degree of certainty to which we know the trends among dyes within $J-V$ curves. To do this, we evaluated all four dyes (including N719), three different times (with three DSSCs), with two separate measurements (on different days). Measurements were taken on days three and five after formation of complete cells as explained in Chapter 3. No trends were observed between data taken on day three versus day five, and each cell was therefore assumed to have reached dynamical equilibrium. Histograms are provided in Figure 4.10 for all photovoltaic parameters obtained with the Steric Series. All tabulated values, with standard deviation as the degree of uncertainty, are provided in Table 4.1.
Figure 4.10. Histograms of solar cell parameters measured under AM1.5 G solar irradiance (100 mW/cm²) at 25 °C. Three solar cells were made for each dye with complete measurements taken on day three and day five of equilibration with electrolyte after sealing.

Perhaps best seen in the histograms of Figure 4.10, there was a clear trend towards decreasing $\eta$, $J_{sc}$, and $V_{oc}$ with the more sterically encumbered species. The $FF$ was the only parameter with no obvious correlation across the Steric Series. This is not unreasonable, as $FF$ values are determined most from the cell components and inherent defects, which are common to all of these DSSCs.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\eta$</th>
<th>$J_{sc}$/ mAcm²</th>
<th>$V_{oc}$/ V</th>
<th>$FF$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(1)(tbtpy)]²⁺</td>
<td>0.19 ± 0.02</td>
<td>0.55 ± 0.07</td>
<td>0.49 ± 0.02</td>
<td>0.68 ± 0.03</td>
</tr>
<tr>
<td>[Ru(2)(tbtpy)]²⁺</td>
<td>0.12 ± 0.04</td>
<td>0.40 ± 0.10</td>
<td>0.44 ± 0.03</td>
<td>0.70 ± 0.01</td>
</tr>
<tr>
<td>[Ru(3)(tbtpy)]²⁺</td>
<td>0.05 ± 0.02</td>
<td>0.18 ± 0.06</td>
<td>0.40 ± 0.01</td>
<td>0.64 ± 0.06</td>
</tr>
<tr>
<td>N719</td>
<td>4.2 ± 0.7</td>
<td>13 ± 1</td>
<td>0.74 ± 0.02</td>
<td>0.42 ± 0.06</td>
</tr>
</tbody>
</table>
Because all DSSCs in this dissertation were prepared under the same conditions, we can attempt to understand the reasons behind these $\eta$ changes, both within the Steric Series and compared to N719. In general, given that dyes in the Steric Series do not absorb the lower energy photons of 650-800 nm, we are not surprised by the lower $\eta$ values found for the Steric Series compared to N719. In fact, similar DSSCs of the homoleptic from of ligand 1: $[\text{Ru(1)}_{2}](\text{PF}_{6})_{2}$ are reported with $\eta$ values (depending on the conditions) ranging from 0.05% to 0.77%. We acknowledge the lower $\eta$ values of thiocyanate-free dyes and move on to understanding the trends within the Steric Series.

In summary, we find that in the most sterically encumbered species, $[\text{Ru(3)}(\text{tbtpy})]^{2+}$, there is a fourfold reduction in $\eta$ compared to the complex with no methyl substituents, $[\text{Ru(1)}(\text{tbtpy})]^{2+}$ (see Table 4.1). This was found to be due primarily to $J_{sc}$ values (threefold reduction), but with a minor contribution from $V_{oc}$ values, which decrease modestly (see Table 4.1).

Figure 4.11. Picture of complete DSSCs studied in this dissertation. Shown from the left: N719, $[\text{Ru(1)}(\text{tbtpy})]^{2+}$, $[\text{Ru(2)}(\text{tbtpy})]^{2+}$, and $[\text{Ru(3)}(\text{tbtpy})]^{2+}$ solar cells.

We first attempt to understand these trends without performing further experiments. First, the large decrease in $J_{sc}$ could be the result of the less visibly red solar cell (see Figure 4.11 reproduced from Figure 3.14 in Chapter 3). Based on known lower peak molar absorptivities obtained in solution (Chapter 2), we expected that DSSCs of $[\text{Ru(3)}(\text{tbtpy})]^{2+}$ with more methyl substituents would adsorb less of the solar
spectrum. This is likely also slightly exacerbated by lower surface coverages (vide supra). However, these minor decreases are unlikely to account for the full threefold reduction in $J_{sc}$.

We hypothesized that $[\text{Ru(1)(tbpy)}]^2^+$ would have the highest photocurrent because it has the longest excited-state lifetime observed in solution (Chapter 2). As given in equation 4.8, this would allow for a greater probability of electron injection and thus lead to the greatest $\phi_{\text{INJ}}$ for $[\text{Ru(1)(tbpy)}]^2^+$. However, the more sterically encumbered dyes were synthesized to improve $\eta_{\text{REG}}$, so we would have expected to see a change in charge recombination as well. Without further information, it is unclear how much a decreasing trend in $\phi_{\text{INJ}}$ would play a role in decreasing $J_{sc}$ across the Steric Series.

It is perhaps unexpected that $V_{oc}$ values would decrease as well across the Steric Series, given that the same semiconductor and electrolyte concentration is used in each DSSC. However, it is well established that the quasi-Fermi level of TiO$_2$ is known to vary with electron concentration.$^{35,36}$ Thus, we would expect the quasi-Fermi level to become more positive if there are fewer injected electrons inherent in a DSSC (see Figure 4.4 for quasi-Fermi level shift).$^{36}$ As hypothesized above, because $J_{sc}$ decreases across the Steric Series, we believe there would be fewer injected electrons in the most sterically hindered complex. This modest decrease in $V_{oc}$ with each methyl substituent addition tells us that these DSSCs are in a semiconducting regime with a density of states that is sensitive to electron population (albeit with a minimal effect). With this in mind, we assume the slight decrease in $V_{oc}$ is mainly caused by the decrease in $J_{sc}$ across the Steric Series.
Do to the inability to fully explain the overall trends in $\eta$ across the Steric Series from J-V curves alone, we conducted additional measurements (see Figure 4.5). As a wavelength-dependent measurement of efficiency, incident photon-to-current conversion efficiency (IPCE) deconstructs the $\eta$-defining parameter of photocurrent into wavelengths of the solar spectrum where the dye actually absorbs. This allows for the assessment of trends across the Steric Series from a more microscopic standpoint of individual components affected in the DSSCs (see Figure 4.5).

4.4.2 IPCE results

Monochromatic %IPCE spectra were measured for each cell on the same days that J-V curves were measured (days three and five). Again, measurements of each dye were taken of three cells on both days. A plot of %IPCE spectra collected for a single data set is given in Figure 4.12. A %IPCE spectrum of N719 is provided in Figure 4.13, showing strong agreement with literature under similar cell conditions.$^{37}$
Figure 4.12. Monochromatic %IPCE spectra of the Steric Series. Spectra are corrected for the loss of light intensity due to absorption and reflection by FTO. Insert of electronic absorption spectra of dyes on TiO$_2$.

Figure 4.13. %IPCE and %APCE spectra for N719. Spectra are corrected for the loss of light intensity due to absorption and reflection by FTO.
The %IPCE spectra partially mirror the absorption properties of the sensitized TiO₂ film. Specifically, the %IPCE spectra reach their maxima at known peaked metal-to-ligand charge transfer (MLCT) absorption wavelengths for the respective dyes on TiO₂, while there is decline in %IPCE to the redder wavelengths due to a decrease in molar absorptivity in that region. Any slight differences between %IPCE spectra and electronic absorption spectra on film towards the bluer region are due to unwanted triiodide absorption within the complete cell. In general, higher peaked %IPCE and broader spectra correspond to higher \( J_{sc} \) (as reported in Table 4.1).

To ensure calibrated measurements, \( J_{sc} \) was calculated for each cell using the overlap integral in equation 4.4. The averaged values for both calculated photocurrent, \( J_{sc} \) (IPCE), and measured photocurrent, \( J_{sc} \) (J-V), as well as the peak %IPCE values obtained at MLCT maximum wavelengths are reported in Table 4.2.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( J_{sc} ) (J-V) /mAcm(^{-2})</th>
<th>( J_{sc} ) (IPCE) /mAcm(^{-2})</th>
<th>Peak %IPCE</th>
<th>Peak %APCE</th>
<th>Average %APCE(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(1)(tbtpt)]^{2+}</td>
<td>0.55 ± 0.07</td>
<td>0.7 ± 0.2</td>
<td>3.2 ± 0.5</td>
<td>5 ± 2</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td>[Ru(2)(tbtpt)]^{2+}</td>
<td>0.4 ± 0.1</td>
<td>0.45 ± 0.05</td>
<td>2.1 ± 0.3</td>
<td>3.2 ± 0.4</td>
<td>1.8 ± 0.7</td>
</tr>
<tr>
<td>[Ru(3)(tbtpt)]^{2+}</td>
<td>0.18 ± 0.06</td>
<td>0.18 ± 0.08</td>
<td>0.8 ± 0.3</td>
<td>1.4 ± 0.6</td>
<td>0.7 ± 0.3</td>
</tr>
<tr>
<td>N719</td>
<td>13 ± 1</td>
<td>33 ± 3</td>
<td>84 ± 5</td>
<td>90 ± 7</td>
<td>70 ± 10</td>
</tr>
</tbody>
</table>

\(^a\)Average %APCE are analyzed between 400 nm and 700 nm.

For the Steric Series, \( J_{sc} \) values determined by J-V characteristics agree well with those calculated from integrated IPCE measurements. However, we note there is a greater difference between calculated and measured \( J_{sc} \) in N719 DSSCs. We believe this might be linked to a greater uncertainty in current due to lead connectivity problems found mainly with high current measurements (such as those of N719 DSSCs). Literature
reports for similar comparisons with certified solar simulators are not always in perfect agreement either, with values in disagreement by 8-17%.\textsuperscript{37,39,40}

In general, we were surprised by the low peak %IPCE values obtained for the Steric Series, because the peak %IPCE value for a cell with the homoleptic version of ligand 1: \([\text{Ru}(1)_2]^{2+}\) was reported at 13.8\%,\textsuperscript{41} compared to our studies with \([\text{Ru}(1)(\text{tbtpy})]^{2+}\) at 3.2\% (see Table 4.2). We do not believe there is a measurement error, because the %IPCE spectrum for N719 dye is well matched to literature. As the following section will indicate, we believe that %IPCE values are dictated by different dye absorption properties, but this is likely not the entire explanation either, because excited-state lifetimes might be playing a role as well in the total photocurrent measured at a particular wavelength (vide infra).

Subtle differences in measured %IPCE spectra raise the question of whether those differences will remain in %APCE spectra once light harvesting efficiencies are accounted for. The absorption spectra of each dye on TiO\textsubscript{2} are subtracted for TiO\textsubscript{2} absorption and converted to LHE as given in equation 4.5. The LHE of each dye as a function of wavelength is provided in Figure 4.14.
Figure 4.14. Wavelength-dependant light harvesting efficiencies of each dye. Values are determined from equation 4.5 based on the absorption spectra of the sensitized TiO$_2$ film in air, subtracted for unsensitized TiO$_2$ absorption.

4.4.3 Internal Efficiency Components

The efficiency of the internal components of a DSSC is determined with the percent absorbed photon-to-current (%APCE) spectra (see Figure 4.5). %APCE spectra are obtained by dividing %IPCE spectra by the known absorbances of each sensitized TiO$_2$ film, %LHE (equation 4.7). %APCE spectra for the Steric Series are given in Figure 4.15 below. A %APCE spectrum of N719 is overlaid with its %IPCE spectrum in Figure 4.13. Given that both %IPCE spectra and LHE spectra approach zero to the red of 700 nm and are fraught with noise, %APCE values are only analyzed between 400 and 700 nm. Maximum %APCE values are reported in Table 4.2, along with an averaged %APCE.
Close examination of the trends in Table 4.2 reveals a total decrease in average %APCE of close to threefold across the Steric Series with the introduction of methyl substituents. This is in contrast to the approximate fourfold decrease seen previously in the peak %IPCE or $\eta$ across the Steric Series (Table 4.1 and Table 4.2). Therefore, while the LHE of each dye was playing a role in the decrease in total efficiency, absorption characteristics were not the primary cause of the fourfold decrease (given that a threefold decrease remains).

To better understand trends in values for %APCE, one must recall equations 4.7-4.10 and the internal processes that lead to efficient current generation. The three components to consider are $\phi_{INJ}$, $\eta_{COLL}$, and $\eta_{REG}$. As a whole, %APCE is composed of each of these three components, but we would like to determine which of these factors are playing a role in the %APCE trends.
We start the process by assessing why DSSCs composed of the Steric Series have \%APCE values that are generally much lower than those of N719. To begin with the $\varphi_{\text{INJ}}$ contribution, we need to have a sense of electron injection timescales. The rate constant for electron injection, $k_{\text{inj}}$, can be expressed within the framework of Marcus-Gerischer Theory as shown in equation 4.11.\textsuperscript{42-44}

$$k_{\text{inj}} = \frac{4\pi^3}{\hbar^2 k_B T} \int_{-\infty}^{\infty} H_{ab}^2 g(E)(1 - f(E, E_F)) \exp\left(\frac{-\Delta G_{\text{INJ}}(E) + \lambda}{4\lambda k_B T}\right) dE \quad (4.11)$$

In this equation, $H_{ab}$ is the electronic coupling matrix element between the excited state dye and each conduction band state of the electrode, $g(E)$ is the normalized density of states of the conduction band, $1 - f(E, E_F)$ is the number of unoccupied Fermi states, $\Delta G_{\text{INJ}}$ is the driving force for electron injection (dependent on energy), and $\lambda$ is the total reorganizational energy.

A decrease in the degree of $H_{ab}$ for the Steric Series would result in smaller $k_{\text{inj}}$, which would lead to lower $\varphi_{\text{INJ}}$ and could explain lower average \%APCE values. $H_{ab}$ is indeed smaller in the Steric Series, based on the electron transfer distance added by the phenylene spacer (which is absent in N719). Also, each dye in the Steric Series attaches via one carboxylic acid site, as opposed to N719, which is predicted to attach via two of them.\textsuperscript{45} In general, \%APCE values have been known to decrease with one site of carboxylic acid attachment compared to two sites, simply due to poorer overall coupling.\textsuperscript{46} With these factors in mind, the electronic coupling in the Steric Series is expected to be weaker than in N719, and therefore we expect it to play a role in lower \%APCE values for the Steric Series. However, these were effects that we were aware of prior to synthesis and are expected to be inconsequential to the overall trends assessed across the Steric Series.
Changes to $\Delta G_{\text{INJ}}$ would also affect $\varphi_{\text{INJ}}$ (equations 4.8 and 4.11). To assess these changes, a summary of the reduction potentials for sensitizers, TiO$_2$ conduction band edge, $E_{\text{CB}}$, and common electrolyte species are reported in Figure 4.16. Data from literature for the homoleptic form of ligand 1, [Ru(1)$_2$]$^{2+}$, are also included in Figure 4.16. An excited state reduction potential, Ru$^{2+/3+}$, is determined from equation 4.12, where the ground state reduction potential, Ru$^{3+/4+}$, is determined from the electrochemical potential vs. SCE measured in solution (Chapter 2), and the amount of energy stored in the thermally relaxed $^3\text{MLCT}$ excited state, $E_{oo}$, is determined from Franck-Condon fittings of emission spectra (Chapter 2).

$$Ru^{2+/3+} = Ru^{2+/3+} - E_{oo}$$ (4.12)

As shown by the difference between Ru$^{2+/3+}$ and $E_{CB}$, the $\Delta G_{\text{INJ}}$ drops from -0.34 eV with N719 to -0.14 eV at best for [Ru(3)(tbtpy)]$^{2+}$ (Figure 4.16). This suggests that the Steric Series might be in a very different kinetic regime for electron injection. This has also been suggested for [Ru(1)$_2$]$^{2+}$ dye, with $\Delta G_{\text{INJ}}$ at -0.05 eV. Widespread literature
reviews suggest that there needs to be at least a -0.2 eV driving force for optimal injection.\textsuperscript{51-53} Therefore, $\varphi_{\text{INJ}}$ will undoubtedly decrease for the Steric Series, due to smaller $k_{\text{inj}}$ without a large driving force.

Literature values support low $\varphi_{\text{INJ}}$ as the main reason for why $[\text{Ru}(\mathbf{I})_2]^{2+}$ \%APCE values are low compared to N719.\textsuperscript{41} Therefore, along the same lines, we believe the \%APCE among the Steric Series is low compared to N719 mainly due to lower values of $\varphi_{\text{INJ}}$. Nonetheless, we believe that $\varphi_{\text{INJ}}$ can be easily improved by changing ancillary ligands from 4,4',4''-tri-tert-butyl-2,2':6',2''-terpyridine (tbtpy) to thiocyanate groups that better absorb lower energy photons and allow for excited states with more negative reduction potentials to yield higher driving forces.\textsuperscript{54-56}

In the end, as our primary focus, we examine the trend in decreasing \%APCE across the Steric Series. We start by assessing electron collection efficiency. $\eta_{\text{COLL}}$ is dictated by the transport of electrons through TiO$_2$ by diffusion, and thus is not expected to be dye-dependent.\textsuperscript{26} However, it is possible for the interception of electrons in TiO$_2$ with the redox mediators in the electrolyte to be dependent on the dye, if increased coverage provides a barrier against intercalation of the redox mediators (vide supra). Given that there was a sufficient decrease in surface coverage across the Steric Series for dark currents to be measurably different, it is possible that $\eta_{\text{COLL}}$ plays a role in the \%APCE decreasing, although it is expected to be minimal.

The regeneration half-life time that dictates $\eta_{\text{REG}}$ is known to be dependent on the driving force between the redox mediator and the ground state dye.\textsuperscript{57} Since each dye in the Steric Series has essentially the same very positive Ru$^{2+/3+}$ reduction potential (see Figure 4.16), regeneration by iodide is expected to be similarly fast across the Steric
Series. However, the full evaluation of $\eta_{\text{REG}}$ brings up an interesting issue with these dyes. Our expectation is that the charge recombination half-life times would lengthen across the Steric Series (supporting the opposite trend in $\eta_{\text{REG}}$) due to decreased electronic coupling, $H_{ab}$. $H_{ab}$ is expected to decrease with methyl steric hindrance due to the prevention of electron delocalization which favors planar conformations of the aryl-terpyridine attaching ligand (as explained in Chapter 1). This will be examined further in Chapter 5, but nonetheless it is very likely that $\eta_{\text{REG}}$ does not contribute to the %APCE (or %IPCE or $\%\eta$) decreasing across the Steric Series.

To understand the contribution from injection, dictated by $\phi_{\text{INJ}}$, we start by assessing the $\Delta G_{\text{INJ}}$ values shown in Figure 4.16. The most stericly encumbered species $[\text{Ru(3)(tbtpy)}]^{2+}$ has the highest $\Delta G_{\text{INJ}}$, which suggests an increase in $k_{\text{inj}}$ across the Steric Series. This opposes the overall trend of decreasing %APCE values across the Steric Series. However, because we hypothesize that $H_{ab}$ will decrease across the steric series in recombination, the same is likely true for injection as well. This would counteract these driving force trends and in the end might cause $k_{\text{inj}}$ to decrease across the Steric Series after all. Trends in $k_{\text{inj}}$ across the Steric Series are hard to assess without further measurements of $k_{\text{inj}}$, but such measurements are beyond the scope of this dissertation.

Regardless, to fully assess $\phi_{\text{INJ}}$ values contributing to %APCE, we also need to consider changes in the competing excited state degradation pathways (equation 4.8). Data for the Steric Series in solution (Chapter 2) revealed excited state half-life times, $t_{\text{relax}}$, that were perhaps shorter than is ideal for Ru(II) polypyridyl complexes. Values of $t_{\text{relax}}$ decreased from 5.7 ns, to 0.94 ns, to 0.41 ns across the Steric Series with increasing steric hindrance (a 14-fold half-life time decrease overall). Unfortunately, the lifetimes of
the Steric Series are expected to be even shorter when adsorbed to a surface (such as insulating Al₂O₃ films).⁵⁹,⁶⁰ Even when there is considerable driving force (which is not available in the Steric Series; see Figure 4.16), upwards of 30 ns is thought to be ideal for electron injection from the thermally relaxed ″MLCT state.⁵⁵,⁶¹ Therefore, while a \( t_{\text{relax}} \) value of 0.41 ns might not have been has detrimental to \( \phi_{\text{INJ}} \) under a regime with greater driving force, it likely plays a large role in the low efficiencies for \([\text{Ru}(3)(\text{tbtpy})]^{2+}\) under the conditions studied. The 14-fold decrease in excited state lifetimes across the Steric Series very likely contributes *in some part* to the threefold decrease in average %APCE from low \( \phi_{\text{INJ}} \). Because changes in \( \eta_{\text{COLL}} \) and \( \eta_{\text{REG}} \) do not explain the threefold decrease in %APCE, we conclude that \( \phi_{\text{INJ}} \) is likely the main factor in decreasing efficiencies across the Steric Series.

### 4.5 Concluding Remarks

The Steric Series of ruthenium terpyridyl dyes \([\text{Ru}(1)(\text{tbtpy})]^{2+}\), \([\text{Ru}(2)(\text{tbtpy})]^{2+}\), and \([\text{Ru}(3)(\text{tbtpy})]^{2+}\) was studied in complete DSSCs and utilized for light-to-electrical energy conversion. Total power conversion efficiencies, \( \eta \), were low among these dyes, attributed mainly to low \( J_{\text{SC}} \) values as a result of low \( k_{\text{inj}} \) due to poor driving force for electron injection into TiO₂.

Trends towards decreasing efficiencies across the Steric Series with increasing steric hindrance revealed more subtle differences. %IPCE spectra were measured to better understand trends in \( J_{\text{SC}} \), and deconstructed into LHE and %APCE, revealing that the majority of the differences within the Steric Series were driven by the internal components of %APCE. Assessing the internal efficiency components, \( \phi_{\text{INJ}} \), \( \eta_{\text{COLL}} \), and
η_{REG}, suggested that ϕ_{INJ} was the main contributing factor to the threefold drop in %APCE across the Steric Series. Low ϕ_{INJ} values across the Steric Series were predicted to result from shorter excited state lifetimes and smaller electronic coupling constants. However, additional electron injection studies to determine k_{inj} would be needed in order to fully rationalize the threefold decrease in %APCE.

We suggest that simply substituting thiocyanate ancillary ligands in place of tbtpy in future studies would drastically improve total power conversion efficiencies for the Steric Series. Not only would this substitution allow for more panchromatic sensitizers (absorbing more of the solar spectrum), it would provide greater electron injection driving forces and increase excited-state lifetimes of the Steric Series. This is hypothesized from known trends among terpyridyl Ru(II) dyes containing electron-rich thiocyanate ligands. These ligands negatively shift the reduction potentials of the ground and excited states\textsuperscript{54,56} and raise the energy of deactivating metal-centered pathways, compared to purely polypyridine based systems.\textsuperscript{55}

Additionally, if implementation of thiocyanate ligands remains a concern (for instance with isomerization or solubility\textsuperscript{62}), then applying the same design principle for the aryl-terpyridyl Steric Series to aryl-bipyridyl systems would likely be beneficial. This would increase excited state lifetimes\textsuperscript{63} and thus allow for greater ϕ_{INJ} and photocurrent for the Steric Series of DSSCs.

Given that there are subtle changes in %APCE across the Steric Series that would not support a trend of decreasing efficiencies, these complexes are still deemed interesting systems to investigate. Further studies are needed to determine the full story of how the introduction of methyl steric hindrance on phenylene spacers affects the electron
transfer pathways in DSSCs. The next chapter looks into the most promising aspect of these complexes: increased regeneration efficiencies due to longer recombination timescales.

4.6 References


(34) Sepehrifard, A.; Stublla, A.; Haftchenary, S.; Chen, S.; Potvin, P. G.; Morin, S. Effects of Carboxyl and Ester Anchoring Groups on Solar Conversion


Chapter 5
Charge Recombination Kinetics: Transient Absorption Studies of Ruthenium Polypyridyl Sensitized TiO$_2$ Films

5.1 Introductory Remarks

Charge recombination between an injected electron and an oxidized dye molecule in dye-sensitized solar cells (DSSCs) has been studied extensively over the past 20 years.$^{1-8}$ Charge recombination is one of the key processes that govern the performance of DSSCs.$^9$ As a back electron transfer process, its rate must be slower than the forward rate of regeneration of the oxidized dye by the redox mediator in order to efficiently generate photocurrent in a device.

Longer recombination lifetimes are ever more important in the most efficient liquid electrolyte-based DSSCs to date, which utilize cobalt redox mediators. While some ruthenium dyes have been reported to have better regeneration yields with cobalt mediators rather than iodide,$^{10}$ this is generally not the case if there is sufficient driving force.$^{11-14}$ Depending on the structure of the cobalt mediator utilized, a wide range of driving forces are possible.$^{15}$ If a cobalt mediator with a more positive reduction potential (leading to a smaller driving force) is utilized, then the subsequent longer regeneration timescales would require elongated back electron transfer timescales. Specifically, half-life times for regeneration with typical cobalt mediators are reported on the order of 10 $\mu$s,$^{15}$ as opposed to 1 $\mu$s with iodide/triiodide.$^{16}$ Therefore, the regeneration efficiency, $\eta_{\text{REG}}$, expressed in equation 5.1 (repeat of equation 4.9 in Chapter 4), is often decreased
when switching from iodide to cobalt electrolytes, unless there is a comparable increase in recombination half-life times.

\[ \eta_{REG} = \frac{1}{1 + \left( \frac{t_{reg}}{t_{rec}} \right)} \]  

(5.1)

Similar implementations yielding slower charge recombination rates may find applications in settings beyond DSSCs, for example in solar water splitting cells. These are photoelectrochemical cells that absorb light with photon energies >1.23 eV and use this energy to form the chemical bonds of H\(_2\) and O\(_2\).\(^{17}\) Solar water splitting cells have been known to utilize frameworks similar to those of DSSCs, with added catalysts for water oxidation and reduction.\(^{18}\) A schematic of a solar water splitting photoanode is shown in Figure 5.1.

Figure 5.1. Solar water splitting photoanode depicting a ruthenium dye molecule linking a porous TiO\(_2\) surface to an iridium oxide hydrate oxygen evolving catalyst. The rate of back electron transfer (0.1-0.4 ms) is faster than the forward electron transfer (~2 ms), resulting in low quantum efficiency. The figure is reproduced from Lee, S. et al. 2012\(^{19}\) with permission from the Royal Society of Chemistry.
Currently, the low quantum yield of oxidative water splitting is attributed to the rapid back electron transfer from TiO$_2$ to the oxidized sensitizer, which is about an order of magnitude faster than the electron transfer from a water oxidation catalyst (such as IrO$_2$) to the oxidized sensitizer.$^{18-21}$ Therefore, it is increasingly important to better understand systems that are capable of elongated charge recombination timescales.

In this chapter, we describe the charge recombination dynamics in DSSCs based on nanocrystalline TiO$_2$ films that have been sensitized with the same series of aryl-terpyridyl ruthenium(II) complexes (see Figure 5.2) that were previously reported in complete DSSCs (see Figure 4.1 from Chapter 4). The complexes included in the Steric Series, [Ru(1)(tbtpy)]$^{2+}$, [Ru(2)(tbtpy)]$^{2+}$, and [Ru(3)(tbtpy)]$^{2+}$, are of interest because they are expected to provide systematic variations in electronic coupling within a structurally homologous series of transition metal-based photosensitizers. N719 is investigated as well, to provide a comparison to a commonly studied efficient ruthenium dye from literature.

![Figure 5.2. Structures of dyes used in DSSCs. Counter ions are tetrabutylammonium (TBA$^+$) and hexafluorophosphate (PF$_6^-$).](image)

Previous studies in our group involving synthetic modifications of dyes with
methyl steric bulk on phenylene spacers (just like in the Steric Series) have shown great promise for elongating lifetimes of charge separated excited states, as explained in Chapter 1.\textsuperscript{22,23} The Steric Series was synthesized in an attempt to apply this previously known conformational design concept to the more functional system of DSSCs. To reiterate the design outlined in Chapter 1, we expect the electronic coupling between a dye molecule and a surface TiO\textsubscript{2} nanoparticle to be greatest with the dye containing the non-methylated phenylene spacer (i.e. [Ru(1)(tbtpy)]\textsuperscript{2+}). This is a reasonable hypothesis because the aryl-terpyridyl ligand that links the photo-oxidized meter center to the TiO\textsubscript{2} surface would be in the most coplanar conformation, with electronic communication via the entire $\pi$-system. Across the Steric Series, methyl substituents are added to the phenylene spacer in an attempt to disrupt conjugation and prevent co-planarization, thereby decreasing the coupling. This would have the effect of lengthening recombination timescales. A systematic introduction of methyl substituents in the Steric Series is used to elucidate whether the conformational control of recombination is useful in the context of DSSCs.

At a fundamental level, we expect slower recombination timescales across the Steric Series to contribute to more efficient devices. These ideas have support in the review by Martinson, Hamann, Pellin and Hupp, who have evaluated DSSC kinetic timescales based on N719 dye at its maximum power point (i.e. under device conditions with the maximum product of current and voltage).\textsuperscript{16} Their review highlights that the kinetic processes in DSSCs are complex and do not always conform to simple rate laws.\textsuperscript{16} Therefore, half-life times are conventionally reported instead of rate constants, to allow for a more meaningful comparison between different processes.
Figure 5.3. Kinetic timescales of DSSCs processes near the maximum power point. Processes in kinetic competition are shown in similar colors. Processes include: electron injection at 150 ps\textsuperscript{24} and excited-state relaxation at 12 ns\textsuperscript{25} in green; charge transport at 100 µs\textsuperscript{26} and charge interception at 1 ms\textsuperscript{26} in blue; and dye regeneration at 1 µs\textsuperscript{27} and charge recombination at 3 µs\textsuperscript{28} in purple. The figure is reproduced from Martinson, A. et al. 2008\textsuperscript{16} with permission from John Wiley and Sons.

Based on the half-life times for charge recombination and regeneration reported from this review\textsuperscript{16} shown in Figure 5.3, we can make some rational predictions. As shown in Table 5.1, based on reported timescales, increasing the length of the recombination half-life time by merely a factor of two could increase the regeneration efficiency by as much as 14%.\textsuperscript{****}

Table 5.1. Projected improvements in $\eta_{\text{REG}}$ based on previously reported half-life times.

<table>
<thead>
<tr>
<th>Process</th>
<th>Hupp 2008 Review\textsuperscript{16}</th>
<th>Hagfeldt 2010 Review\textsuperscript{29}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regeneration ($t_{\text{reg}}$)</td>
<td>1 µs</td>
<td>100 ns</td>
</tr>
<tr>
<td>Recombination ($t_{\text{rec}}$)</td>
<td>3 µs</td>
<td>1 µs</td>
</tr>
<tr>
<td>$\eta_{\text{REGa}}$</td>
<td>0.750</td>
<td>0.909</td>
</tr>
<tr>
<td>$\eta_{\text{REG w/ } t_{\text{rec}} \times 2}$</td>
<td>0.857</td>
<td>0.952</td>
</tr>
<tr>
<td>Projected Improvement</td>
<td>14%</td>
<td>4.8%</td>
</tr>
</tbody>
</table>

\* $\eta_{\text{REG}}$ is determined from the data in the preceding rows following equation 5.1.

\**** Of course, this assumes that all other pathways would be unaffected and is only based on timescales of highly optimized N719 DSSCs.
Other factors remaining equal, this increase in $\eta_{\text{REG}}$ could subsequently generate a 14% increase to the total power conversion efficiency, due to an increase in overall photocurrent. While increases in photocurrent were not observed across the Steric Series (attributed mainly to factors affecting the electron injection yield, detailed in Chapter 4), we nonetheless see great value in studying the Steric Series to assess fundamental changes to electron transfer that may beneficial in slightly different systems.

To assess charge recombination lifetimes, we employed transient absorption (TA) spectroscopy on sensitized TiO$_2$ films in an inert and inactive electrolyte (vide infra) under electrochemical bias, as it is typically measured.$^{30,31}$ We note that early charge recombination timescales of DSSCs varied widely in the literature, even among studies on the same dye.$^{4,32-34}$ This was found to be due in large part to the different experimental conditions of excitation intensity, electrochemical bias, and electrolyte composition.$^{35}$ For this reason, we approached these studies with a degree of caution by always ensuring stability and reproducibility. We provide a detailed account of the optimized experimental conditions for TA spectroscopy on sensitized TiO$_2$ films in Section 5.2.6.

### 5.2 Experimental

#### 5.2.1 Materials

The Steric Series of molecules was used as-is from previously reported syntheses (Chapter 2). N719 dye was purchased from Solaronix. Anhydrous tert-butanol and electrochemical grade tetrabutylammonium hexafluorophosphate (TBAPF$_6$) were purchased from Sigma Aldrich. The same bottle of Burdick and Jackson UV-grade anhydrous acetonitrile was utilized for all experiments in this chapter.
5.2.2 Spectroelectrochemistry in Solution

Spectroelectrochemistry experiments were carried out with a home-built optically transparent thin-layer electrode (OTTLE) cell with a transparent platinum mesh working electrode, a coiled 0.25 mm platinum wire auxiliary electrode, and a 0.01 M Ag/AgNO₃ reference electrode constructed immediately before use. Spectra were recorded using a Hewlett-Packard diode array UV-Vis spectrophotometer (HP8452A). The electrodes were placed in a modified 2 mm path length glass cell fitted with a Teflon lid to maintain an oxygen-free environment for the duration of the experiment. All measurements were made using a freshly prepared solution of 0.1 M TBAPF₆ in anhydrous acetonitrile. The concentration of the ruthenium dye in this solution varied between 0.5 and 1.0 mM as needed to obtain good signal to noise with relevant peak absorbances of less than 2. All samples were purged with argon before an external voltage was applied. Measurements were performed with the working electrode held at a constant voltage for the duration of the experiment. Both the oxidative and the reductive spectroelectrochemistry experiments were observed to be chemically reversible, based on recovery of the initial sample absorption after a period of time following an applied null voltage vs. Ag/AgNO₃. Note that reductive spectroelectrochemistry is not discussed further.

5.2.3 Film Preparation

The sensitized TiO₂ films studied by transient absorption spectroscopy were made in a similar manner to those measured for efficiency in complete DSSCs (Chapter 3). A surface profilometer (Dektak 3, Veeco) was used to measure the thickness of the unsensitized TiO₂ films. The average thickness of the TiO₂ films used for recombination studies was 7.9 ± 0.9 µm. Mesoporous TiO₂ films that had already been sintered were
reheated to 450 °C for 30 minutes, allowed to cool to 80 °C, immersed in 0.5 mM dye solutions of 1:1 tert-butanol/acetonitrile for 24 hours and then allowed to equilibrate in pure acetonitrile for at least six hours until the time of measurement. This equilibration step has to do with desorption observed with freshly sensitized films, which was previously discussed (Chapter 3).

Despite following identical procedures of TiO₂ sensitization for all dyes, the magnitudes of TA signals were found to vary based on different molar extinction coefficients and surface coverages for each dye. To further ensure that transient dynamics were independent of the number of oxidized dye molecules in our studies, we also considered both [Ru(1)(tbtpy)]²⁺ and N719 sensitized TiO₂ films at lower surface coverage. This was achieved with shorter soaking times (~4 hrs instead of 24 hrs) in lower concentration sensitizing solutions (0.15 mM of [Ru(1)(tbtpy)]²⁺ or N719 in 1:1 tert-butanol/acetonitrile). This obtained lower absorbances at excitation and probe wavelengths for two films of comparison. However, for all studies, film absorbances were always kept below an absorbance of one at the MLCT peak and between 0.35 - 0.6 at the excitation wavelength of 532 nm.

5.2.4 Sample Setup

For all transient absorption experiments, an electrochemical sample setup was utilized to allow for an external bias to be applied to the sensitized TiO₂ film. The degree of external bias was measured with a potentiostat (601C CH Instruments) under a controlled potential coulometry setup (also known as bulk electrolysis). The sensitized TiO₂ film formed the working electrode in a three-electrode configuration in a glass cell (4 × 4 × 1 cm, NSG Precision Cells, Inc.) shown in Figure 5.4. The rest of the setup
consisted of a coiled Pt counter electrode and a freshly prepared non-aqueous 0.01 M Ag/Ag\(^+\) reference electrode in 5 mL of redox-inactive supporting electrolyte of 0.1 M TBAPF\(_6\) in anhydrous acetonitrile. All cells were internally referenced to ferrocene (Fc\(^+\)/Fc) at the end of each experiment. In order to report electrochemical values vs. SCE, a conversion constant of +380 mV from Fc\(^+\)/Fc was applied.\(^{36}\) Sensitized TiO\(_2\) films were positioned in the glass cell (with a Teflon stand) normal to the probe light (vide infra) and at a 25° angle to the pump light (see Figure 5.4).

![Figure 5.4. Schematic of three-electrode sample setup for transient absorption measurements. The three electrodes for external bias consisted of a sensitized TiO\(_2\) film as the working electrode (WE), a non-aqueous Ag/Ag\(^+\) reference electrode (RE), and a coiled Pt counter electrode (CE). The fitted Teflon base and cap are not shown. The probe was directed normal to the surface of the films, while the pump was at a 25° angle to the normal, both positioned to provide maximum overlap at the surface.](image)

5.2.5 Transient Absorption Spectroscopy

Nanosecond to millisecond transient absorption measurements utilized a 532 nm laser excitation (1 Hz; 3-5 ns pulse width; beam diameter ~3.2 mm) generated by a Q
Switched Nd:YAG Laser (Continuum Minilite II). A low fluence (3.7 mJ/cm²) was established in each experiment by reducing the pulse energy to 0.3 mJ/pulse, as measured with a thermopile power meter (PowerMax 500D, Moletron/Coherent).

A Xenon lamp (75 or 100 W, Oriel) served as a broadband probe source. A one inch diameter beam of probe light was focused into the sample using a plano-convex lens of 100 mm focal length (f/), achieving an approximate 1.5 mm diameter spot size at the sample. Prior to reaching the sample, the probe light was passed through a long pass filter with an onset at 420 nm (Thorlabs) to prevent TiO₂ band gap excitation. The samples were excited with pump light at a 25° angle to the normal of the sample (see Figure 5.4 for a diagram of the sample setup). Passing through normal to the sample, the probe beam was re-collimated and then focused via a plano-convex lens (f/ = 50 mm) into a monochromator (SLM instruments, entrance and exit slits 1 mm, 2 nm bandpass). A 530 nm notch filter (Edmund Optics) placed after the sample eliminated pump scatter.

Probe intensity was monitored with a negatively-biased PMT (Hamamatsu R-928) operating at –1000 V DC. The signal from the PMT was passed into a digital oscilloscope (LeCroy 9384L) interfaced with a computer. For long time window collection (>100 µs), a 1000 ohm external resistor was used to amplify signal voltages; otherwise, all resistances were kept at the oscilloscope’s internal coupling of 50 ohm. The instrument response time was measured to be ~10 ns.

Transient absorption kinetics at a particular wavelength were obtained by averaging 30 oscilloscope time-traces of probe intensity with the pump laser on, followed immediately by averaging 30 time-traces of probe intensity with the pump off. These pump-on and pump-off time traces were transferred to a personal computer and processed.
with Labview programs of local origin to determine a ΔA signal as a function of time. The whole collection process was repeated at least three times and an average ΔA kinetic trace was determined. Single-wavelength kinetic traces were measured at 480 nm and fit with a stretched exponential decay model of equation 5.2, often referred to as the Kohlrausch-Williams-Watts (KWW) function.\(^{38}\)

\[
\Delta A(t) = A_0 e^{-\frac{t}{\tau}}
\]  

(5.2)

Here, \(A_0\) is the initial change in absorption, \(\tau\) is a characteristic lifetime, and \(\beta\) is the degree of dispersion, which is inversely related to the width of the underlying Lévy distribution of rate constants, \(0 < \beta < 1\), with lower values of \(\beta\) being more dispersive.\(^{39}\)

For ruthenium dyes on TiO\(_2\), \(\beta\) values in charge recombination studies have been reported to range from 0.25 to 0.5 depending on the electrolyte employed.\(^{31}\) To have a sense of recombination kinetics independent of the chosen fitting parameters, the time required to observe 50% of the initial change in absorption (half-life time, \(t_{1/2}\)) was measured as well.

5.2.6 Additional Electrochemical Conditions

To ensure consistent recombination lifetimes were measured under transient absorption spectroscopy, experimental conditions were optimized for excitation intensity, electrolyte composition, electrochemical bias, and equilibration time as described below.

Previously published recombination studies state that the number of electrons generated per nanoparticle in a given experimental setup was found to be a key parameter for determining the recombination lifetime.\(^9,33\) The recombination lifetime was found to be consistent across studies only when the number of electrons generated per nanoparticle was less than or equal to 1.\(^5,40\) Such studies are only of geminate recombination, where the recombination of an electron occurs with the same dye molecule from which it was
injected (without interparticle hopping).\(^9\) To ensure that our recombination timescales are consistent, sufficiently low excitation densities are investigated to keep electron concentrations low and observe only geminate recombination.

Charge recombination studies on sensitized TiO\(_2\) films are designed to balance an ability to understand something meaningful while closely matching operating cell conditions. This required a simplification of the redox mediator because iodide introduces the added dynamics of charge interception and dye regeneration. Therefore, for the purposes of studying only charge recombination, our experimental setup included the sensitized TiO\(_2\) film immersed in a redox inactive electrolyte of TBAPF\(_6\). It is noted that Li\(^+\) and tert-butylpyridine (TBP) are not included in this electrolyte even though they were included in the electrolyte of the complete DSSCs. This elimination was justified by the fact that Li\(^+\) and TBP are known to shift the conduction band edge of TiO\(_2\) in opposite directions.\(^{41,42}\)

Because charge recombination dynamics are well known to be highly dependent on electrochemical bias,\(^{30,35}\) it is important to determine a reasonable external bias condition to study. From efficiency measurements reported in Chapter 4, typical J-V maximum power points for the DSSCs (see Figure 4.3 in Chapter 4) reported herein were measured at a photovoltage of approximately -0.45 V, referenced to the internal cell potential (i.e. versus the iodide/triiodide redox couple). In order to determine an appropriate external bias, this photovoltage must be converted to a standard reference electrode. We used the saturated calomel electrode (SCE) as a standard reference for non-aqueous solutions. In order to convert between the internal cell potential and SCE, the reduction potential of the iodide redox couple had to be assessed. We determined a
potential of 0.27 V vs. SCE for the iodide electrolyte used in these cells, based on the standard reduction potential of the iodide/triiodide couple (reported at 0.29 V vs. SCE) and a Nernstian correction for the respective concentrations in our electrolyte (0.7 M I and 0.05 M I₂). The average measured cell photovoltage at -0.45 V, corrected to SCE, yields a value of -0.18 V. We therefore chose the bias of -0.2 V vs. SCE for transient absorption experiments as the average measured operating voltage of each sensitized film in a functional device. However, an external bias of 0 V vs. SCE was also applied before and after the higher bias condition for two reasons; to ensure reversibility in all bias measurements, and to provide two different external bias conditions to determine if there was a bias dependence on measured lifetimes.

![Graph showing current under bias over time](image)

Figure 5.5. Typical current observed for a sample film under external bias. Steady-state currents were not achieved until ~180 s. After each lifetime measurement, the external bias was varied between 0.0 V and -0.2 V vs. SCE to ensure consistent lifetime measurements, complete reversibility of current measurements, and stability of samples in time.

Before turning to the results and discussion section, we note that preliminary recombination lifetime data under an external bias had to be optimized. At a particular
bias, recombination lifetimes were observed to decrease in time and then level out. In particular, stable dynamics were not observed until a freshly prepared film had equilibrated at an applied bias for at least 20 min. While the origin of this lifetime decrease is unclear, we nonetheless only trusted lifetimes that were reproducible and therefore only report those of samples that first have equilibrated for 20 min. Additionally, all transients were collected at 296 K after the current under bias had reached a steady-state value (typically after 3-5 min at each potential) as shown in Figure 5.5. The effects of applied bias were found to be reversible in all cases (see Figure 5.5) as shown by a return to the steady-state values in current after cycling between high and low biases (-0.2 V and 0 V vs. SCE, respectively). The absence of any change in steady-state absorption spectra after each hour-long experiment (based on comparison of before and after spectra) suggested that samples were stable for the duration of the experiment.

5.3 Results and Discussion

Figure 5.6. (left) Transient absorption spectrum of [Ru(3)(tbtpy)]^{2+} sensitized TiO_2 film under applied bias of -0.2V vs. SCE. (right) Spectroelectrochemical difference spectra obtained for oxidized species: [Ru(3)(tbtpy)]^{3+} in 0.1 M TBAPF_6/acetonitrile solution with a voltage of 1.4 V vs. SCE.
Initially, we needed to determine a reasonable wavelength at which to probe single-wavelength recombination kinetics of dye. To this end, a transient absorption spectrum of a $[\text{Ru}(3)\text{(tbtpy)})^{2+}$ sensitized TiO$_2$ film under applied bias was measured as an example dye in the Steric Series. This TA spectrum is shown above in Figure 5.6 (left), with $\Delta A$ values determined from the $A_0$ pre-exponential terms in a global fit to a stretched exponential of equation 5.2. Due to the $\sim$10 ns instrument response of the TA experiments and presumed fast injection kinetics, we assume that all excited state features endemic to the dye are generated within the time window of the instrument response. The transient absorption feature to the red of 600 nm is therefore assigned solely to the absorption of the oxidized Ru(III) species formed after electron injection into TiO$_2$. The transient bleach signal from 450 to 600 nm is negative due to the loss of MLCT ground state absorption. Oxidative spectroelectrochemical experiments with $[\text{Ru}(3)\text{(tbtpy)})^{2+}$ in solution replicate these spectral TA features with the difference spectrum shown in Figure 5.6 (right). To maximize the signal to noise ratio for all kinetic traces, charge recombination kinetics were collected at 480 nm, corresponding to the recovery of the bleach signal rather than from 600-800 nm as the decay of oxidized dye absorption. Data from similar TA studies of sensitized TiO$_2$ films in literature suggest that the kinetics probed at each of these features do correspond.$^{44-47}$
Figure 5.7. Log-linear transient absorption recombination lifetime data for each dye on TiO\textsubscript{2} film at 480 nm. Each film was excited with 0.3 mJ/pulse at 532 nm at a bias of -0.2 V vs. SCE in 0.1 M TBAPF\textsubscript{6} in acetonitrile. Fits to a stretched exponential are overlaid in dark grey with parameters reported in Table 5.2. Data out to 10\textsuperscript{-4} s are an average of 30 scans at 50 ohm, while long time data are an average of 3 scans at 1000 ohm.

Charge recombination kinetics were fit to stretched exponential models and plotted on a conventional log-linear scale\textsuperscript{30,48} shown in Figure 5.7. This plot shows charge recombination kinetics collected for all dyes at 480 nm as a measure of the loss of oxidized dye (or the formation of the ground state dye), corresponding to reduction by electrons in TiO\textsubscript{2}. The log-linear plot gives a sense of the longevity of these stretched exponentials from 0.1 µs to 0.1 seconds—a change of six orders of magnitude—before the ground state was fully recovered. While it may be difficult to see with the characteristic lifetimes in Figure 5.7, the recombination dynamics of the most sterically encumbered species, [Ru(3)(tbtpy)]\textsuperscript{2+}, are slowest because they reach zero ΔA at a later
timescale. A linear plot out to millisecond timescales is provided as well in Figure 5.8 as another visual guide to these kinetic data. The charge recombination timescales of interest that were obtained from this single set of measurements are reported in Table 5.2.

Figure 5.8. Kinetic traces of each dye in a linear millisecond timescale under external bias of -0.2 V vs. SCE. Overlaid in gray are the stretched exponential fits.

Control TA measurements of un-sensitized TiO$_2$ films were undertaken as well in order to determine the magnitude of signals arising from the excitation of intra-band states of the semiconductor.$^{49}$ Probing at 480 nm, the un-sensitized films exhibited negligible transient signals, as expected from literature.$^{49}$

<table>
<thead>
<tr>
<th>Complex</th>
<th>$t_{1/2}$ /µs</th>
<th>$\tau$ /µs</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ru(1)(tbpy)]$^{2+}$</td>
<td>7.1</td>
<td>23</td>
<td>0.31</td>
</tr>
<tr>
<td>[Ru(2)(tbpy)]$^{2+}$</td>
<td>35</td>
<td>87</td>
<td>0.41</td>
</tr>
<tr>
<td>[Ru(3)(tbpy)]$^{2+}$</td>
<td>75</td>
<td>268</td>
<td>0.29</td>
</tr>
<tr>
<td>N719</td>
<td>5.4</td>
<td>20</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 5.2. Charge recombination data at -0.2 V vs. SCE.
In summary, all ΔA transients were well fit to stretched exponential models with β values corresponding to reasonable degrees of dispersion\(^{6,7,30,48,50}\) between 0.28 and 0.41 (Table 5.2). The values for β were justified with a procedure that linearized these data to extract β as reported in Section C.1 of Appendix C. However, we note that early time data for the N719 transient probed at 480 nm deviated slightly from the stretched exponential fit in the first six data points (see Figure 5.7). We believe this arises because, at this wavelength and timescale, it is possible to see convoluted kinetics due to the slightly longer excited state half-life of this dye on TiO\(_2\) (~12 ns).\(^{16}\) All other dyes have short enough excited state half-life times (< 10 ns) such that they cannot be seen on the timescale of these transient absorption measurements.\(^{51}\) Nonetheless, stretched exponential fits to N719 are deemed reasonable, with measured timescales that agree well with those in literature.\(^{16,35}\)

As can be seen in Table 5.2, the characteristic recombination lifetime, \(\tau\), increases by a little over three-fold across the Steric Series with each addition of a methyl group. Similar increases are seen with half-life times as well, although with these values the first addition of a methyl substituent ([Ru(1)(tbtpy)]\(^{2+}\) to [Ru(2)(tbtpy)]\(^{2+}\); 7.1 to 35 µs) indicates a greater impact than the second addition ([Ru(2)(tbtpy)]\(^{2+}\) to [Ru(3)(tbtpy)]\(^{2+}\); 35 to 75 µs). However, before fully assessing overall trends across the Steric Series, we felt it to be important to be wary of the convoluted effects of changing β. Even though no direct correlation has been found between β and \(\tau\),\(^{48}\) the latter does tend to vary when β is manipulated.

To assess trends in \(\tau\) and \(t_{1/2}\), additional experiments were performed and then
analyzed with $\beta$ fixed at 0.3 (see Table 5.3). This $\beta$ was chosen as a moderate average (see Table 5.2) and a reasonable stretch parameter for the given electrolyte conditions based on literature.$^{6,7,30,48,50}$ Charge recombination data were collected for all dyes on at least two different films, each measured under what we would consider three independent experimental conditions.$^{††††}$ Averaged results are reported in Table 5.3, with uncertainties determined for each recombination timescale from the standard deviation of at least six trials.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$t_{1/2}$/µs</th>
<th>$\tau$/µs</th>
<th>$\beta$</th>
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<tbody>
<tr>
<td>[Ru(1)(tbtpy)]^{2+}</td>
<td>4 ± 1</td>
<td>12 ± 4</td>
<td>0.3</td>
</tr>
<tr>
<td>[Ru(2)(tbtpy)]^{2+}</td>
<td>11 ± 3</td>
<td>40 ± 10</td>
<td>0.3</td>
</tr>
<tr>
<td>[Ru(3)(tbtpy)]^{2+}</td>
<td>50 ± 20</td>
<td>160 ± 60</td>
<td>0.3</td>
</tr>
<tr>
<td>N719</td>
<td>10 ± 6</td>
<td>40 ± 20</td>
<td>0.3</td>
</tr>
</tbody>
</table>

After taking into account uncertainties, both lifetime and half-life time trends agree between analyses with fixed versus variable $\beta$ values. After repeating measurements and controlling for $\beta$, we still observe the same trend in characteristic lifetime: increasing by over three-fold with each addition of a methyl group (Table 5.3). However, close examination of the half-life times now show that the first addition of a methyl substituent ($[\text{Ru(1)(tbtpy)}]^{2+}$ to $[\text{Ru(2)(tbtpy)}]^{2+}$; 4 to 11 µs) has slightly smaller change than the second addition ($[\text{Ru(2)(tbtpy)}]^{2+}$ to $[\text{Ru(3)(tbtpy)}]^{2+}$; 11 to 50 µs). Given that this is the opposite trend from that seen when allowing $\beta$ to vary, we conclude

$^{††††}$ A sensitized TiO$_2$ film was immersed in the 5 mL electrolyte solution in the glass cell. Stable lifetime measurements were observed under applied bias as confirmed by 1 hr of repeated trials. The film was rinsed with acetonitrile, and an absorption spectrum was measured to ensure that no changes occurred. This entire process was repeated three times with the same electrolyte solution topped off to 5 mL with fresh acetonitrile to account for evaporation.
that each addition of a methyl substituent results in a similar elongation in recombination timescales.

In addition, all reported characteristic recombination lifetimes and half-life times were found to be within error for the two biasing conditions held (0 V and -0.2 V vs. SCE). Select recombination studies with ruthenium dyes on TiO2 in literature have also shown this insensitivity to bias at low external potentials (positive of -0.1 V vs. Ag/AgCl or -0.13 V vs. SCE).33,52 This is likely due to a small amount of electron density added to the nanocrystalline film at low enough potentials.28

Overall, the data of Table 5.3 show an approximate 12 to 13-fold increase in the recombination timescales from [Ru\((1)\)(tbtpy)]\(^{2+}\) to [Ru\((3)\)(tbtpy)]\(^{2+}\) with the introduction of two methyl substituents. This is an intriguing result. To ensure that this recombination increase was not due to the measurement of fewer dye molecules adsorbed to the TiO2 films across the Steric Series, two additional studies were performed.

First, recombination transients were measured for [Ru\((1)\)(tbtpy)]\(^{2+}\) as the excitation intensity was varied. Recombination kinetics were found to be independent of excitation intensity below 0.3 mJ/pulse (see Figure C.3 in Appendix C), suggesting that differences in electron concentrations dictated by excitation intensity do not play a role. Second, films of TiO2 sensitized with [Ru\((1)\)(tbtpy)]\(^{2+}\) were purposefully made with a lower surface coverage of dyes (using decreased sensitizing solution concentration and decreased soaking time as explained in the Experimental Section 5.2.3). These recombination kinetics were within error and if anything on the shorter side (\(\tau = 10 \mu s\)) of the short recombination timescales (\(\tau = 12 \pm 4 \mu s\)) of [Ru\((1)\)(tbtpy)]\(^{2+}\) reported in Table 5.3. These negative results suggest that the trend seen across the Steric Series is real.
To understand the implication of these trends in charge recombination kinetics across the Steric Series, we make use of parameters explained by Marcus-Gerischer electron transfer theory. Following the theoretical treatments of interfacial electron transfer between the semiconductor and the adsorbed dye molecule, the rate of recombination can be expressed by equation 5.3.\(^{53-55}\)

\[
k_{BET} = \frac{4\pi^3}{\hbar^2 \lambda k_B T} \int_{-\infty}^{\infty} H_{ab} g(E) f(E, E_F) \exp \left( \frac{-\Delta G_{BET}(E) + \lambda}{4 \lambda k_B T} \right) dE
\]  

(5.3)

This equation is essentially an extension of Marcus non-adiabatic electron transfer theory, with the incorporation of a continuum of electronic states in the semiconductor, where \(g(E)\) is the normalized density of states of the conduction band and \(f(E, E_F)\) is the Fermi occupation factor.\(^{54}\) In this equation, \(k_{BET}\) is the rate constant for back electron transfer (i.e. charge recombination), \(H_{ab}\) is the electron-transfer coupling matrix element between the oxidized dye and each conduction band state of the electrode, \(\Delta G_{BET}\) is the driving force for back electron transfer (dependent on energy), and \(\lambda\) is the total reorganizational energy for back electron transfer.

Applying Marcus-Gerischer theory to charge recombination, we assess how each of these parameters would change across the Steric Series. Previously reported electrochemical potentials for each ground state \(\text{Ru}^{2+/3+}\) couple (Chapters 2 and 4) revealed that \(\Delta G_{BET}\) is essentially the same across the Steric Series. Given that each film was measured under the same applied bias, we also expect \(g(E)\) and \(f(E, E_F)\) to be similar for each DSSC explored. There is also reason to believe the reorganizational energy, \(\lambda\), is essentially the same across the Steric Series, because this is largely dependent on similar Ru-N distances, which leads to similarities in back electron transfer distances and nearly
identical solvation. If we assume these parameters ($\Delta G_{\text{BET}}$, $g(E)$, $f(E,E_F)$ and $\lambda$) are the same for all dyes in the Steric Series, then given equation 5.3, the ratio of back electron transfer rate constants depends only on the value of $H_{\text{ab}}$ as shown in equation 5.4.

$$\frac{k_{\text{BET}1}}{k_{\text{BET}2}} = \left(\frac{H_{\text{ab}1}}{H_{\text{ab}2}}\right)^2 \approx \frac{t_{1/2}^{2}}{t_{1/2}^{1}}$$

(5.4)

Therefore, we were thrilled to find that longer recombination lifetimes were observed across the Steric Series, due to decreased electronic coupling with methyl steric hindrance introduced on phenylene spacers. Specifically, using $t_{1/2}$ data from Table 5.3 with equation 5.4, $H_{\text{ab}}$ systematically decreased by approximately twofold with each addition of a methyl substituent. While additional temperature-dependent transient absorption experiments would need to be performed in order to determine the magnitude of $H_{\text{ab}}$ in these systems, this twofold decrease across the Steric Series is deemed quite reasonable in the context of aryl-polypyridine ruthenium systems. A similar decrease in $H_{\text{ab}}$ has been measured for back electron transfer across a methyl steric series of aryl-bipyridyl ruthenium donor-bridge-acceptor systems previously studied in our group. $H_{\text{ab}}$ is suggested to have decreased in the most sterically encumbered species because it is in the most canted conformation between the phenylene spacer and terpyridyl moiety. This essentially inhibits the communication between electrons in TiO$_2$ particles and the hole on the oxidized Ru(III) metal center.

In the context of DSSCs, although we did not measure regeneration half-life times of these films in the presence of iodide, typical values for similar ruthenium polypyridyl systems have been measured at around 0.5 to 1 $\mu$s. From these predicted regeneration half-life times and those measured for recombination, we can calculate the overall increase to regeneration efficiency, $\eta_{\text{REG}}$ (equation 5.1). With a three-fold increase with
each methyl substituent, the increase in $\eta_{\text{REG}}$ alone would lead to an 8-15% improvement in photocurrent across each dye, or as much as 23% from $\text{[Ru(1)(tbtpy)]}^{2+}$ to $\text{[Ru(3)(tbtpy)]}^{2+}$. While this predicted efficiency improvement was not evident from the findings in the context of complete DSSCs (Chapter 4), we suggest that this potential could be realized with minimal alterations (vide infra).

As far as we know, applying methyl steric hindrance to induce conformational control of back electron transfer has the largest effect reported so far within this aryl-terpyridyl Ru(II) system on TiO$_2$ (at the ~12 to 13-fold increase from $\text{[Ru(1)(tbtpy)]}^{2+}$ to $\text{[Ru(3)(tbtpy)]}^{2+}$). This has profound implications for systems requiring slower recombination rates. Depending on the extent of elongation needed, a singly or doubly methyl-substituted phenylene spacer may be introduced, with increasing benefits for each.

5.4 Conclusion

This dissertation investigated the effects of conformational control on photoinduced electron transfer dynamics in DSSCs. First, the Steric Series: $\text{[Ru(1)(tbtpy)]}^{2+}$, $\text{[Ru(2)(tbtpy)]}^{2+}$, and $\text{[Ru(3)(tbtpy)]}^{2+}$, was introduced as the chromophoric system to implement conformational control by the addition of methyl steric hindrance to phenylene spacers. In Chapter 2, the Steric Series were synthesized and characterized both photophysically and electrochemically. Photophysics in solution revealed that the introduction of methyl steric hindrance to phenylene spacers in ruthenium terpyridyl systems lead to a 14-fold decrease in excited-state lifetimes.

However, electron transfer rates have been known to vary by as much as 80-fold in moving from entirely coplanar to completely orthogonal structures.
Once these ruthenium terpyridyl sensitizers were assembled in complete DSSCs in Chapter 3, current-voltage characteristics were measured (Chapter 4), revealing that the Steric Series had a systematic fourfold decrease in overall power conversion efficiency with added steric hindrance. To understand these effects across the Steric Series of DSSCs, external efficiency measurements were broken down into internal collection efficiency components. %APCE was found to systematically decrease threefold across the Steric Series. We believe this was mainly due to low injection yields, both from small injection rate constants and large excited-state relaxation rate constants. We note that creating these DSSCs in more acidic conditions, or with a greater concentration of lithium cations, would be expected to grant these sensitizers sufficient driving force to improve injection efficiencies, thus it is not unreasonable to examine differing device conditions that would make better use of the slower recombination timescales. Additionally, changing the ancillary ligands to more electron-rich thiocyanate groups would also allow for greater electron injection yields, due to shorter injection times and longer excited-state relaxation times. Alternatively, applying the Steric Series’ conformational design scheme to aryl-bipyridyl ruthenium systems would allow for longer excited-state lifetimes and therefore a higher injection yield as well.

To conclude this dissertation, work in this chapter revealed a series of molecules adsorbed to TiO₂ that yield recombination timescales that lengthen by over three-fold with each methyl addition (~12 to 13-fold in total), due to a conformational change leading to a systematic decrease in electron coupling. The use of these dyes likely greatly improved regeneration yields, even though this was not seen in the complete cells due to decreases in other factors. In the end, for dyes similar to the Steric Series to become
practical in conventional DSSCs, they would likely need larger forward electron transfer driving forces for electron injection, longer excited-state lifetimes, increased light harvesting efficiencies at longer wavelengths, and perhaps higher surface coverages. However, the introduction of methyl steric hindrance to dye molecules to decrease back electron transfer coupling constants might be useful in contexts other than conventional DSSCs.

As mentioned in the introduction to this chapter, chromophores such as these, with lengthened recombination timescales, are extremely useful in the context of photoelectrochemical water splitting devices. Currently, photoelectrochemical device optimization has focused on catalyst development for more efficient water oxidation. However, we would argue that conformational control of the sensitizer to hinder the back electron transfer pathways, as implemented in this dissertation, might be a promising route of exploration.

5.5 References


Appendix A
Supporting Information for Chapter 2

A.1 $^1$H NMR Spectra for New Ligands and Complexes

A.2 2D COSY NMR Spectra for the Methyl Ester Steric Series

A.3 Cyclic Voltammograms of New Complexes at Different Scan Rates

A.1 $^1$H NMR Spectra for New Ligands and Complexes

Figure A.1. $^1$H NMR of 1 in DMSO-$d_6$. 
Figure A.2. $^1$H NMR of 1' in CDCl$_3$.

Figure A.3. $^1$H NMR of 2a in CDCl$_3$. 
Figure A.4. $^1$H NMR of 3a in CDCl$_3$.

Figure A.5. $^1$H NMR of 2 in DMSO-$d_6$. 
Figure A.6. \[^1\text{H}\] NMR of 3 in DMSO-\(d_6\).

Figure A.7. \[^1\text{H}\] NMR of 2' in CDCl\(_3\).
Figure A.8. $^1$H NMR of 3' in CDCl$_3$.

Figure A.9. $^1$H NMR of [Ru(ttpy)(btpy)]$^{2+}$ in CD$_3$CN.
Figure A.10. $^1$H NMR of $[\text{Ru}(1)(\text{tbpy})]^{2+}$ in CD$_3$CN.

Figure A.11. $^1$H NMR of $[\text{Ru}(1')(\text{tbpy})]^{2+}$ in CD$_3$CN.
Figure A.12. $^1$H NMR of [Ru(2)(tbtpy)]$^{2+}$ in CD$_3$CN.

Figure A.13. $^1$H NMR of [Ru(2')(tbtpy)]$^{2+}$ in CD$_3$CN.
Figure A.14. $^1$H NMR of $[\text{Ru}(3)(\text{tbtpy})]^{{2}^+}$ in CD$_3$CN.

Figure A.15. $^1$H NMR of $[\text{Ru}(3')(\text{tbtpy})]^{{2}^+}$ in CD$_3$CN.
A.2 2D COSY NMR Spectra for the Methyl Ester Steric Series

Figure A.16. 2D COSY NMR of [Ru(1′)(tbpy)](PF$_6$)$_2$ in CD$_3$CN.
Figure A.17. 2D COSY NMR of [Ru(2')(tbpy)](PF$_6$)$_2$ in CD$_3$CN.
Figure A.18. 2D COSY NMR of [Ru(3')(tbtpy)](PF_6)_2 in CD_3CN.
A.3 Cyclic Voltammograms of New Complexes at Different Scan Rates

Figure A.19. Cyclic voltammograms of Heteroleptic Series. Ferrocene as an internal standard is shown at approximately 80 mV vs. Ag/Ag⁺.
Figure A.20. Cyclic voltammograms of Methyl Ester Steric Series. Ferrocene as an internal standard is shown at approximately 80 mV vs. Ag/Ag\(^+\).
Figure A.21. Cyclic voltammograms of Carboxylic Acid Steric Series. Ferrocene as an internal standard is shown at approximately 80 mV vs. Ag/Ag⁺.
Appendix B
Supporting Information for Chapter 4

B.1 Cyclic Voltammetry of Sensitized TiO₂ Films

B.1.1 Experimental

The experimental conditions for cyclic voltammetry of dyes in solution were described previously (Chapter 2). Cyclic voltammetry of the sensitized TiO₂ film was performed in a similar manner to solution studies, instead with the sensitized TiO₂ film deposited on FTO glass as the working electrode. The active area of the film (Area = 0.704 cm²) was fully submerged in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. CV experiments comparing solution and film were carried out immediately after one another, in the same solution, at 50 mV/s, and under an argon atmosphere. The extent of dye adsorption for films studies was not quantified.

B.1.2 Results

Cyclic voltammetry performed on a [Ru(I)(tbtpy)]²⁺ sensitized TiO₂ film showed that the reversible oxidation of the Ru(II) center (reported as E_{red}(3+/2+)) did not deviate from values obtained in fluid solution (see Figure B.1). This equivalence between E_{1/2} values of ruthenium dyes in solution and on TiO₂ is confirmed in literature.¹⁻³ The only differences were found in the magnitude of peak currents and peak-to-peak separation, both of which would be expected to vary under different concentrations not quantified.
Figure B.1. Cyclic voltammograms of [Ru(1)(tbtpy)]^{2+} measured in acetonitrile solution compared to measurements on TiO_2 film. Relative current values were normalized and subtracted for baseline. E_{1/2} values were observed at the same potential: E_{red(3+/2+)} = 0.91 V vs. Ag/Ag^+.

B.2 References


Appendix C
Supporting Information for Chapter 5

C.1 Beta Fitting Rationalization

To accurately determine the stretching parameter, $\beta$, for a given stretched exponential trace, a Log of the negative Log of normalized $\Delta A$ vs. Log time will linearize the data to yield a slope of $\beta$ as shown in Eq. C.1 – C.7.

$$\Delta A = e^{-(t/\tau)^\beta}$$  \hspace{1cm} (C.1)

$$Log(\Delta A) = Log\left(e^{-(t/\tau)^\beta}\right)$$  \hspace{1cm} (C.2)

$$Log(\Delta A) = \frac{ln\left(e^{-(t/\tau)^\beta}\right)}{ln10}$$  \hspace{1cm} (C.3)

$$Log(\Delta A) = \frac{-\left(t/\tau\right)^\beta}{ln10}$$  \hspace{1cm} (C.4)

$$Log(-Log(\Delta A)) = Log\left(\frac{(t/\tau)^\beta}{ln10}\right)$$  \hspace{1cm} (C.5)

$$Log(-Log(\Delta A)) = \beta Log(t/\tau) - Log(ln10)$$  \hspace{1cm} (C.6)

$$Log(-Log(\Delta A)) = \beta Log(t) - \beta Log(\tau) - Log(ln10)$$  \hspace{1cm} (C.7)

This is a typical process of justifying a stretched exponential fit and what $\beta$ values are reasonable for charge recombination traces.$^1$ Again, $\beta$ values typically range around 0.3-0.4 depending on the conditions of electron concentration, external bias, and electrolyte.$^1$
Figure C.1. Linearized stretched exponential data for kinetic traces of each dye at -0.2 V vs. SCE. Linear fits yield slopes corresponding to $\beta = 0.31$, $\beta = 0.41$, $\beta = 0.29$ and $\beta = 0.28$ for $[\text{Ru}(1)(tbtpy)]^{2+}$, $[\text{Ru}(2)(tbtpy)]^{2+}$, $[\text{Ru}(3)(tbtpy)]^{2+}$, and N719, respectively.

C.2 Power Dependence Study

Figure C.2. $[\text{Ru}(1)(tbtpy)]^{2+}$ recombination lifetimes with no excitation power dependence below 0.3 mJ/pulse. While lifetimes are known to increase at higher excitation power, studies below 0.3 mJ/pulse were independent of excitation power.
C.3 References

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